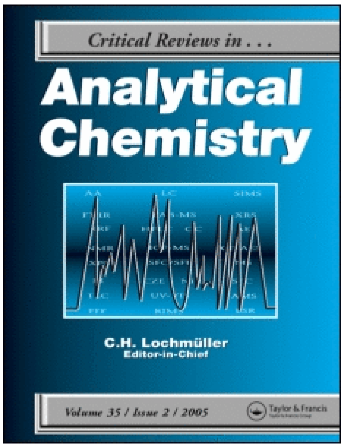

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ESTIMATION OF MEDIUM EFFECTS FOR SINGLE IONS IN NON-AQUEOUS SOLVENTS

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INTRODUCTION

Problem and Scope

The evaluation of single-ion solvation energies and of their changes with the solvent—the medium effects—remains one of the unresolved classical problems of solution chemistry, a challenging objective outside the realm of rigorous thermodynamics. For a long time progress in this field was at a standstill, discouraged by the prevailing opinion that quantities inaccessible to exact thermodynamics, such as activities, solvation energies, and medium effects of individual ions, were *ipso facto* devoid of physical significance and practical utility. Then, it was probably the successful formulation and the widespread use of one such "inexact" quantity—the aqueous pH—which contributed more than any other factor to the re-evaluation of this extreme position. Later, as operational pH measurements and, eventually, pH scales were extended to partially and totally non-aqueous solutions, it became necessary to interpret the meaning of pH values in these media and to correlate aqueous and non-aqueous pH scales. The possibility of a universal pH scale, independent of solvents, became a serious consideration. Other types of potentiometry as well as polarography were extended to non-aqueous solutions, giving rise to questions about the correlation of standard electrode potentials in different media and the evaluation of liquid-junction potentials at aqueous–non-aqueous phase boundaries. The idea of a universal, solvent-independent scale of standard potentials was born.

It was recognized that the key to universal scales of ion activities and electrode-potential series in any given solvent was the knowledge of the medium effect for any one single ion. The modern phase in the search for that key was initiated in 1947 when Pleskov proposed the rubidium electrode as the assumed solvent-independent reference point for a universal series of standard electrode potentials. Pleskov's initial step started a chain reaction, and the number of proposed extra-thermodynamic solutions to the title problem has multiplied rapidly. It is unfortunate that their proliferation has not yet produced the hoped-for convergence of results. There are examples where values of the medium effect for a given ion estimated by two methods differ not only in magnitude, but in sign as well. Today this area of research is more polarized and controversial than ever, and it suffers from a lack of sufficient critical evaluation and correlation of the already existing methods. From time to time the status of this field has been summarized and, to a limited extent, critically reviewed in chapters devoted to it in books[1-5] and in journal articles.[6-10] However, none of these were intended to be comprehensive reviews, and their treatment of the subject was understandably incomplete.

The objective of the present review is to take stock of what we already have in terms of methods for determining single-ion medium effects and to offer some opinions as to where we should be going. To accomplish this, the existing approaches will be grouped into meaningful categories and then critically evaluated both individually and through intercomparisons. The intention will be to weed out the obvious failures (to the extent that anything can be obvious in this field) and to focus attention on the strong points and the deficiencies of the more promising methods. The evolution of those approaches which appear to be most successful will be traced up to the present and projected into the future in terms of problems which are yet to be solved. Some subjective judgment will be unavoidable in this presentation, as I am actively engaged in this area of research myself. An effort will be made to cover all significant developments in the literature on medium effects for single ions through the first half of 1969. My hope is to contribute towards a better understanding of medium effects for single ions, to stimulate further progress in their estimation, and to pave the way for their eventual acceptance as legitimate properties of solutions. The number of papers devoted to this subject at the 1969 Fisher Award Symposium and the assignment to it of a session at the 1969 Eastern Analytical Symposium attest to the possibility that we may be progressing in that direction.

As the title problem has been attacked predominantly by electrochemists and acid-base chemists, it has been usually formulated in terms of the following interrelated objectives: 1) *The establishment of a single solvent-independent scale for the activities of individual ions, in particular for pH;* 2) *the formulation of a solvent-independent series for standard electrode potentials;* 3) *the evaluation of liquid-junction potentials at the interfaces of different solvents.* Many authors pursue only one of the above objectives, without necessarily relating it to the remaining two or invoking the concept of a medium effect. It is useful to realize, however, that all three of the above problems can be solved through the knowledge of medium effects for single ions in non-aqueous solvents. They represent merely three different aspects of the same problem.

Medium Effect

Definition and Fundamental Relationships

The activity of a solute i is usually referred to infinite dilution in the given solvent as its standard state. When the solution is non-aqueous, that activity is designated with an asterisk:

$$a_i^* = m_i \, {}_s\gamma_i \tag{1}$$

where m_i is molality and ${}_s\gamma_i$ is the salt-effect activity coefficient, which becomes unity at zero molality in the given solvent. The limitation of activity scales formulated in this manner is that they are specific for each solvent, due to their different standard states. If we wish to compare the activities of a solute in two or more solvents, it is necessary to refer them to the same standard state. Usually an infinitely dilute aqueous solution is chosen as the reference. When referred to the standard state in water, the activity of solute i in a non-aqueous solution is given by

$$a_i = m_i \, {}_w\gamma_i \tag{2}$$

The activity coefficient ${}_w\gamma_i$ becomes unity at infinite dilution only in water. As the solute molality approaches zero in any other solvent, ${}_w\gamma_i$ approaches the *medium effect*, ${}_m\gamma_i$. Of course, the medium effect can be formulated also on the molarity or the mole-fraction scale, but for the sake of consistency the molality scale is used exclusively in this review. As a rule, medium effects are significantly greater than salt effects, often by several orders of magnitude. Thus, an activity coefficient in a non-aqueous solvent when referred to the aqueous standard state is really a product of the salt and medium effects:

$${}_w\gamma_i = {}_s\gamma_i \, {}_m\gamma_i \tag{3}$$

As a corollary, the medium effect for a given solute can be viewed as a conversion factor from the non-aqueous to the aqueous activity scale:

$$a_i = a_i^* \, {}_m\gamma_i \tag{4}$$

For aqueous solutions, ${}_m\gamma_i$ is of course unity. Alternatively, the definition of a medium effect can be derived by considering the chemical potential or partial molal free energy, G_i, of the solute i in a non-aqueous solution. Again, we can choose the standard state either in the given non-aqueous solvent:

$$G_i = {}_sG_i^\circ + RT \ln a_i^* \tag{5}$$

or in water:

$$G_i = {}_wG_i^\circ + RT \ln a_i \tag{6}$$

where $[{}_wG_i^\circ]$ and $[{}_sG_i^\circ]$ are the standard free energies of solute i in water and in the non-aqueous solvent, respectively. By combining Equations 4, 5, and 6, we arrive at the most fundamental definition of a medium effect—as a measure of the difference between the standard free energy of a solute in water and in the given non-aqueous solvent:

$${}_sG_i^\circ - {}_wG_i = RT \ln {}_m\gamma_i$$

Thus, at a given temperature and pressure, the medium effect for a given solute is a constant dependent only on the nature of the solvent, but independent of concentration.

Frequently the medium effect is interpreted to be a measure of the standard free energy of *transfer* of a solute from water to the non-aqueous medium. The transfer process is represented by equations such as

$$\text{Solute } i\,(\mathrm{H_2O}, a=1) = \text{Solute } i\,(\text{non-aqueous solvent}, a^*=1) \quad (8)$$

While this interpretation has the merit of associating with a medium effect a physical process which is easily visualized and depicted in diagrams, it is not correct as a generalization. The concept of transfer is precisely applicable only to energy changes experienced by neutral molecules or by electrically neutral combinations of ions (sums of anions and cations or differences for pairs of ions of like charge). For individual ions, the standard free energy of transfer consists not only of the solvation-energy change given by Equation 7, but also of an additional energy step, ΨzF, originating from the transfer of the ionic charge z across the interface of the two solvents, where a potential difference Ψ exists. In the literature,[11-12] a distinction is drawn between so-called "real" and "chemical" solvation energies of single ions, depending on whether they include or neglect the energy step involved in transferring the ion across the vacuum-solution interface. Thus, "chemical" energies of solvation isolate the solvent-solute interactions only. For single ions, medium effects are determined by differences between the "chemical" energies of solvation and hydration and should not be identified with a transfer process. However, the work required to transfer a charge across a surface will differ in sign for anions and cations and will be zero for complete electrolytes and for other electrically neutral combinations of ions. For such combinations the distinction between "real" and "chemical" solvation energies disappears, and a transfer process becomes compatible with the definition of the medium effect. The physical significance of medium effects will be elucidated further in the next section, which is devoted to their applications.

While the most common literature term[1-4 6 13 14 20] for the parameter ${}_m\gamma_i$ is "medium effect" or "primary medium effect," other names have been used as well. Some of the better known examples are the "distribution coefficient," or "partition coefficient,"[15-17] the "degenerate activity coefficient,"[18-19] the "medium activity coefficient,"[6] and the "solvent activity coefficient."[7 8 20] In the case of the "solvent activity coefficients" of Alexander and Parker,[7 8] the reference medium for the solutes is not water, as in Equation 7, but methanol. In my opinion, the term "medium effect" is the most logical choice, by analogy with the "salt effect" or "concentration effect," all of which identify the causes for a solute's departure from ideal behavior as defined by a standard state. Owen[13] differentiated between a "primary medium effect" (our "medium effect") and a "secondary medium effect," the latter reflecting the difference between the salt effects in the two media at equal electrolyte concentrations. This nomenclature failed to gain acceptance, probably because salt effects are generally orders of magnitude smaller than solvent effects.

Referring to Equation 7, the reader might ask why we chose to focus our review on medium effects, rather than on solvation energies of individual ions, which are the more fundamental physicochemical properties of the two. The answer is that most researchers in this field determine the *differences* between $[{}_sG^\circ_i]$ and $[{}_wG^\circ_i]$ directly, bypassing their individual values. These differences are sufficient for solving the three interrelated problems outlined earlier. However, in some of the studies reviewed here, the hydration and solvation energies of individual ions were indeed determined separately and were subsequently combined into medium effects via Equation 7.

Applications

How would knowledge of medium effects for individual ions enable us to express ion activities and standard electrode potentials in a manner independent of the solvent and to evaluate liquid-junction potentials at the phase boundaries of different media?

We have pointed out earlier that the convention of referring solute activities to infinite dilution in any given solvent as the standard state produces as many activity scales as there are solvents or solvent combinations. Potentially, we are faced with an infinite number of thermodynamically unrelated activity scales for each solute. The practical disadvantages of this status are best illustrated by considering the problem of the correlation of pH scales in amphiprotic solvents.

In water and in some alcohol-water mixtures, pH values have been assigned[1] to reference standards on the basis of e.m.f. measurements on the hydrogen-silver chloride cell without transference:

$$\mathrm{Pt(s);\ H_2(g),\ HCl,\ AgCl(s);\ Ag(s)} \qquad (9)$$

If the standard potential of the above cell in a given non-aqueous solvent is ${}_sE^\circ$, values of $\mathrm{pa}_H^* \equiv -\log\,(m_H\ {}_s\gamma_H)$ in that solvent can be calculated from:

$$\mathrm{pa}_H^* = (E - {}_sE^\circ)\ /\ k + \log m_{Cl} + \log {}_s\gamma_{Cl} \qquad (10)$$

In Equation 10, E is the measured e.m.f., ${}_s\gamma_H$ and ${}_s\gamma_{Cl}$ are the salt-effect activity coefficients, m_H and m_{Cl} the molalities of hydrogen and chloride ions, respectively, and $k = (RT\ \ln\ 10)/F$. Unfortunately, the pa_H^* scales established in the above manner are different for each solvent composition, so that equal numerical values of pa_H^* in different media do not, as a rule, reflect equal acidities. For example, from such scales, it is impossible to tell whether a pa_H^* of 4 in ethanol represents a greater or a lesser acidity (proton activity) than a pa_H of 4 in water, etc. In order to express pH measurements in different media on a single scale, it is best to refer all of them to the aqueous standard state. According to Equation 4, the pa_H^* of a non-aqueous solution can be expressed on the (aqueous) pa_H scale with the aid of the medium effect for the proton, ${}_m\gamma_H$, characteristic of the solvent:

$$\mathrm{pa}_H = \mathrm{pa}_H^* - \log {}_m\gamma_H \qquad (11)$$

Alternatively, if in Equation 10 we use the aqueous standard potential for cell 9, ${}_wE^\circ$, the pa_H (aqueous standard state) can be calculated directly from the cell e.m.f., E, measured in the non-aqueous solvent, provided the medium effect for the chloride ion, ${}_m\gamma_{Cl}$, is known.[21]

$$\begin{aligned}\mathrm{pa}_H = {} & (E - {}_wE^\circ)\ /\ k + \log m_{Cl} \\ & + \log {}_s\gamma_{Cl} + \log {}_m\gamma_{Cl}\end{aligned} \qquad (12)$$

In either case, it is the medium effect for a single ion that enables us to correlate pH measurements in different solvents by translating them into a single scale referred to the aqueous standard state. Of course, the activity scales of any other single ion could be referred to their aqueous standard states in analogous manner.

The accepted convention for the formulation of e.m.f. series in different solvents generates a problem similar to that which limits the meaning of activity scales. In every solvent, standard electrode potentials are referred to the standard hydrogen electrode (SHE) in the same solvent. The latter is arbitrarily assigned the value of zero volts at all temperatures. Because the difference between the standard potentials of an electrode in two solvents is directly related to the difference between the corresponding solvation energies of the potential-determining ion,[11] the above convention would have physical meaning only if the solvation energies of the proton were equal in all solvents. Dismissing such a requirement as an absurdity, particularly with respect to the proton, which is expected to experience drastic energy changes in solvents of diverse basicities, we conclude that the conventional e.m.f. series in different media represent isolated, unrelated systems. Again, we can have as many thermodynamically unrelated e.m.f. series as there are solvents.

A single e.m.f. series, independent of solvent, can be formulated by referring the standard potentials in all solvents to a single arbitrary zero point—preferably that of the SHE in water. So long as our knowledge is restricted to potential differences (as opposed to single-electrode potentials), there seems to be no point in adopting a different arbitrary zero point. Given the medium effect for the proton characteristic of the solvent, the potential of the SHE in a non-aqueous medium SH on the single aqueous scale, ${}_wE^\circ$ (H, SH), can be calculated from:

$$\begin{aligned}{}_wE^\circ(\mathrm{H,\ SH}) = {} & (RT\ /\ F)\ \ln {}_m\gamma_H \\ & + {}_wE^\circ(\mathrm{H,\ H_2O})\end{aligned} \qquad (13)$$

where ${}_wE^\circ$ (H, $\mathrm{H_2O}$) is the potential of the SHE in water, assumed to be zero volts. As a rule, ${}_wE^\circ$ (H, SH) would then assume values other than zero. Subsequently, any conventional standard potential of an electrode reversible to species i in solvent SH, ${}_sE^\circ$ (i, SH), can be converted to its value on the aqueous scale, ${}_wE^\circ$ (i, SH), via:

$$ {}_wE^\circ(\text{i, SH}) = {}_sE^\circ(\text{i, SH}) + {}_wE^\circ(\text{H, SH}) \qquad (14) $$

The subscripts w and s denote aqueous and non-aqueous standard states, respectively, while the solvent in which the E° is measured is given in parentheses.

It should be emphasized that knowledge of medium effects for single ions does not lead to values of single-electrode potentials. The E°s expressed on the aqueous scale are still differences between two single-electrode potentials, one of which is always the SHE in water. However, their values in different solvents are now directly comparable, because in place of the infinite number of arbitrary zero points, we have settled for a single one— $[{}_wE^\circ(\text{H, H}_2\text{O}) = 0]$.

The third incentive for the estimation of medium effects for single ions lies in the possibility of using them to calculate liquid-junction potentials, E_j, at aqueous–non-aqueous interfaces. For example, from the potential E of the following galvanic cell with liquid junction:

$$ \text{H electrode} \mid a_H = 1 \mid a_H^* = 1 \mid \text{H electrode} \qquad \text{H}_2\text{O}|E_j|\text{SH} \qquad (15) $$

and a known log ${}_m\gamma_H$, it would be possible to evaluate the E_j at the above H_2O/SH boundary:

$$ E = {}_wE^\circ(\text{H, SH}) - {}_wE^\circ(\text{H, H}_2\text{O}) + E_j \qquad (16) $$

which in conjunction with Equation 13, leads to:

$$ E_j = E - (RT/F)\ln {}_m\gamma_H \qquad (17) $$

Knowledge of liquid-junction potentials at aqueous – non-aqueous boundaries would find practical application primarily in polarography and in conventional pH work. The majority of pH measurements are made with glass-calomel electrode pairs, connected by means of a salt bridge of aqueous potassium chloride and standardized against aqueous buffers. The resulting pH readings in any solvent deviate from pa_H by the residual liquid-junction potential, which expressed in pH units is $\Delta E_j/k$. The latter is the difference between the liquid-junction potentials at the interfaces of the bridge KCl solution with the aqueous standard buffer and with the unknown solution, respectively.

$$ \text{pH} - pa_H = \Delta E_j/k \qquad (18) $$

If the unknown is a non-aqueous solution, the ΔE_j cannot as a rule be minimized by interposition of a salt bridge[22] and the error introduced by it may well be comparable to the pH itself. Fortunately, there is evidence that the liquid-junction potentials between concentrated aqueous KCl of salt bridges and dilute buffers are approximately constant for a variety of non-aqueous solvents, depending primarily on the medium and not on the pH of the solution.[21] This constancy of ΔE_j is not only a necessary condition for the feasibility of determining relative hydrogen-ion activities in a variety of solvents, but also promises a more general applicability for such E_js as may be calculated eventually from known medium effects.

Determination of Medium Effects for Electrolytes

Medium effects for electrolytes and other electrically neutral combinations of ions as well as for neutral molecules are well-defined thermodynamic quantities, which can be calculated from experimental data without any assumptions. In the most generally applicable method, medium effects are determined from solubilities. The free energies of a solute i in its saturated solutions in water, $G(\text{i, H}_2\text{O})$, and in a non-aqueous solvent SH, $G(\text{i, SH})$, are equal, since each saturated solution is in equilibrium with the same solid phase (assuming, at the moment, no crystal solvates). Thus, the expressions

$$ G(\text{i, H}_2\text{O}) = {}_wG_i^\circ + RT\ln(a_i)_{\text{satd.}} \qquad (19) $$

and

$$ G(\text{i, SH}) = {}_sG_i^\circ + RT\ln(a_i^*)_{\text{satd.}} \qquad (20) $$

can be equated, leading to the relationship

$$\frac{{}_{s}G_i^\circ - {}_{w}G_i^\circ}{RT} = \ln \frac{(a_i)_{\text{satd.}}}{(a_i^*)_{\text{satd.}}} \qquad (21)$$

Recalling Equation 7, it follows that

$$ {}_{m}\gamma_i = \frac{(a_i)_{\text{satd.}}}{(a_i^*)_{\text{satd.}}} \qquad (22)$$

For an electrolyte, the ratio of activities in its saturated solutions is equivalent to the ratio of its solubility (ion-activity) products, K_{sp}, in water and in the solvent:

$$ {}_{m}\gamma_{\text{electrolyte}} = \frac{{}_{w}K_{\text{sp}}}{{}_{s}K_{\text{sp}}} \qquad (23)$$

In the special case where the solvent under study is immiscible with water, the medium effect turns out to be simply the distribution ratio of the solute between the aqueous and non-aqueous phases.

The above derivations are strictly valid only if both the aqueous and the non-aqueous saturated solutions are in equilibrium with the same solid phase. If a crystal solvate should form in either solvent or in both, the free energies of the solute in the two saturated solutions will be different. In the general case of solvate formation, Equations 19 and 20 must include the free-energy change accompanying the transfer of solvent *s* from the pure solvent to the solvate:

$$G = xRT \ln \left(\frac{P_s}{P_{\text{i}\cdot\text{x}\cdot\text{s}}}\right) \qquad (24)$$

where P_s and $P_{\text{i}\cdot\text{x}\cdot\text{s}}$ are the vapor pressures of the solvent and the solvate, respectively. When corrections via Equation 24 are introduced both for the solvate (i·x·SH) and for the hydrate (i·y·H_2O), Equation 21 will transform into:

$$\frac{{}_{s}G_i^\circ - {}_{w}G_i^\circ}{RT} = \ln \frac{(a_i)_{\text{satd.}}}{(a_i^*)_{\text{satd.}}} + \frac{y}{x} \ln \frac{P_{H_2O}\, P_{\text{i}\cdot\text{x}\cdot\text{SH}}}{P_{\text{SH}}\, P_{\text{i}\cdot\text{y}\cdot H_2O}} \qquad (25)$$

The medium effect of an electrolyte can also be calculated from the standard potentials of a galvanic cell reversible to its ions. For example, in the case of HCl, they are usually derived from the standard potentials of the hydrogen-silver chloride cell (Equation 9) in water, ${}_{w}E^\circ_{\text{AgCl}}$, and in the given solvent, ${}_{s}E^\circ_{\text{AgCl}}$:

$$\log {}_{m}\gamma_{\text{HCl}} = ({}_{w}E^\circ_{\text{AgCl}} - {}_{s}E^\circ_{\text{AgCl}}) \,/\, k \qquad (26)$$

The medium effect of a uni-univalent electrolyte is simply the sum of the two ionic medium effects (in logarithmic form). Thus, $\log {}_{m}\gamma_{\text{HCl}} = \log {}_{m}\gamma_{\text{H}} + \log {}_{m}\gamma_{\text{Cl}}$. Differences of ionic medium effects can be obtained from the conventional E°s of electrodes reversible to metal ions. For example, from the standard potentials of the potassium electrode in water, ${}_{w}E^\circ_{\text{K}}$, and in a solvent, ${}_{s}E^\circ_{\text{K}}$, follows the difference between the medium effects of the potassium ion and the proton:

$$\log {}_{m}\gamma_{\text{K}} - \log {}_{m}\gamma_{\text{H}} = ({}_{s}E^\circ_{\text{K}} - {}_{w}E^\circ_{\text{K}}) \,/\, k \qquad (27)$$

The above relationship is a consequence of the already much belabored point that a conventional E° is really a potential difference between the standard electrode of interest and the SHE in each solvent.

Accurate values of medium effects for electrically neutral combinations of ions are indispensable for a study of their single-ion counterparts. Some extrathermodynamic approaches start out with known values of medium effects for electrolytes and then split them into individual ionic components. Regardless of the approach, medium effects for electrically neutral combinations of ions are needed to test the internal consistency of their individual values.

Physical Significance

It follows clearly from the above section that medium effects for single ions cannot be determined by thermodynamic methods. We cannot prepare a saturated solution of a single ion, and it is equally impossible to distribute a given ion between two immiscible phases without dragging along an equivalent number of oppositely charged ions. At this time, no reliable methods exist for the determination of absolute single-electrode potentials. On the other hand, a comparison of identical electrodes in water and in a non-aqueous solvent yields a combination of the medium effect and the liquid-junction potential (Equation 17).

The inaccessibility of energic properties of single ions to exact thermodynamics has led some authorities to question the very "physical significance" of such properties.[23] Proponents of "single-ion thermodynamics" concede that such properties of individual ions as their activities, activity coefficients, solvation energies, and medium effects cannot be evaluated exactly. However, they argue in favor of estimating them on the grounds that they can provide valuable physicochemical information which cannot be obtained by other means. In Strehlow's view,[5] "single-ion thermodynamics" is a legitimate branch of physical chemistry, as it proved capable of giving correct predictions and correlations of experimental facts. A strong case for the reinstatement of the physical significance of single-ion activities in water was put forward by Frank.[24]

What is some of the experimental evidence to support the contention that energic properties of single ions do possess physical significance? The prime example of a thermodynamically inexact quantity which became an unqualified success is pH. Under favorable conditions in aqueous solutions, the pH values of standard buffers represent conventional pa_H with an accuracy of ± 0.005 unit.[25] These conventional pa_H values are believed to possess a definite meaning in terms of thermodynamic acid-base equilibria. It is striking that the accuracy of the above "ill-defined" quantity surpasses the precision of most experimental pH measurements. The wide acceptance of pH measurements under less ideal conditions shows how useful inexact quantities can be. For many physicochemical correlations, high precision and accuracy are not mandatory, and one should not reject a quantity for its lack of more significant figures than he can use.

No such accuracy as for pH in water can be claimed for the comparison of proton activities in different media. However, several examples given below attest to the physical meaning of such comparisons in a semi-quantitative manner. Consider dilute solutions of equal hydrogen-ion concentrations in the solvent series: acetic acid, water, ethylenediamine. It seems intuitively obvious that the proton activity should decrease in the indicated solvent order. Indeed, semi-quantitative support for this prediction comes from the "acidity potential ranges" for the above solvents as defined by van der Heijde.[26] The acidity potential range for a given solvent was arbitrarily defined as the height of a strong acid-strong base titration curve measured (in millivolts) for 0.01 *N* solutes using glass and calomel electrodes. If both protolysis and ion-pair dissociation were complete in each of the solvents, the acid limit of the potential range would represent the cell e.m.f. corresponding to 0.01 *N* SH_2^+. Granting that neither of these requirements is fulfilled (except in water) and that the measurements are distorted by superimposition of varying liquid-junction potentials, we nevertheless observe that the glass electrode reflects the expected order of proton activity. Thus, in the solvent series acetic acid, water, ethylenediamine, the acid limits of the acidity potential ranges (estimated from the diagrams) are roughly +800 mV, +350 mV, and −400 mV, respectively.

It has been known for some time [5] [27] that strong acids are more tightly solvated by liquid ammonia than by water, the difference of about 25 kcal/mole being largely independent of the anion. In contrast, alkali salts of these acids exhibit only small differences in solvation energy between the same pair of solvents.[27] [28] This circumstantial evidence invites the obvious explanation that the proton is more strongly solvated by ammonia than by water, while anions and cations which possess no pronounced acidic properties show little preference between the two solvents. Indeed, extrathermodynamic estimates of log $_m\gamma_H$ for liquid ammonia, which will be discussed later, attribute about 90% of the above solvation-energy change to the proton.

Many qualitative tests can be applied to determine whether a given set of individual ionic medium effects does reflect physical reality. Generally, correlations are sought with independent experimental evidence. Thus, we would expect reasonable estimates of log $_m\gamma_H$ to predict negative potentials for the SHE (referred to the aqueous $E_H^\circ = 0$) in strongly basic media, such as ammonia and hydrazine, and positive potentials in solvents less basic than water, such as formic acid or acetic acid. Similarly, negative standard potentials on the aqueous e.m.f. scale should be predicted for those electrodes whose ions form stable complexes with the molecules of the solvents in question. Examples are silver, copper, zinc, cadmium, lead, and mercury electrodes in ammonia and hydrazine. There is polarographic evidence that alkali metal ions are solvated more strongly by water than by several dipolar aprotic solvents.[20] In the case of the lithium ion in acetonitrile-water mixtures, this is corroborated by NMR and infrared studies.[20] To reflect this phenomenon, the corresponding values of log $_m\gamma$ for the alkali metal ions should be positive. Physically significant values of medium effects for single ions should also give correct predictions for the preferential solvation of ions in mixed solvents.[5] Transference measurements show that in acetonitrile-water mixtures, the silver ion is preferentially solvated by the acetonitrile, and the nitrate ion by water,[28] while in the case of $CaCl_2$ in methanol-water mixtures both ions are preferentially solvated by water.[29] These and similar data on mixed solvents can be used to test the validity of given ionic medium effects for that pair of solvents. Another possible test, specific for the medium effects of the proton, would be a correlation between values of log $_m\gamma_H$ and the rates of acid-catalyzed reactions in different solvents.

According to Alfenaar and DeLigny,[30] individual ionic medium effects proved to be of physical significance by providing reasonable interpretations for the effects of substituents in organic acids and bases on the interaction of their ions with the solvent.

MODELS AND ASSUMPTIONS FOR THE DETERMINATION OF MEDIUM EFFECTS FOR SINGLE IONS

Most extrathermodynamic methods for the estimation of medium effects for single ions can be placed in one of the following two broad categories: 1. Methods based on the assumption that liquid-junction potentials at aqueous–non-aqueous boundaries can be suppressed by interposition of a salt bridge. 2. Methods based on certain theoretical predictions about the relationship between the size of ions and molecules and their solvation energy. In principle, we could include here a third category—methods based on the evaluation of absolute single-electrode or Galvani potentials in water and in other media. However, the subject of Galvani potentials and of their constituent Volta and surface potentials[31] is a broad area of study in itself, which would merit an independent critical survey. It is beyond the scope of the present review.

Assumption of Negligible Liquid-Junction Potentials

If the liquid-junction potential E_j at the aqueous–non-aqueous boundary in cell 15 were reduced to a negligible value, medium effects for the proton could be calculated directly from Equation 17. Analogous potential measurements and calculations could be carried out for many other ions. This approach was adopted in the pioneering work of Bjerrum and Larsson.[15] For example, they derived values of log $_m\gamma_H$ for ethanol-water solvents from e.m.f. measurements on cells composed of a hydrogen electrode in a non-aqueous medium and a 3.5 *N* aqueous calomel reference electrode, connected with a bridge of aqueous 3.5 *N* KCl. Some of the medium effects calculated by Bjerrum and Larsson on the assumption of negligible E_j between concentrated aqueous KCl and the ethanol solutions employed are presented in Table 1. Of course, such "medium effects" are really algebraic sums of log $_m\gamma_H$ and E_j. Other errors inherent in the tabulated values stem from incomplete dissociation for some of the solutions, which was not corrected for, and from a dubious method of correcting for salt effects.

Similarly, Oiwa[32] determined values of log $_m\gamma_H$ for methanol-water mixtures from e.m.f. measurements on solutions of hydrochloric acid at 20, 25, and 30°C using a hydrogen electrode in the non-aqueous media *vs.* a saturated aqueous calomel electrode, connected with a bridge of saturated aqueous KCl. In this case, however, the E_j was not assumed to be negligible, but was estimated instead essentially from the Planck equation.[33] Oiwa's estimates of log ${}_m\gamma_H$ in methanol-water mixtures are compared with those of other workers in Table 8 towards the end of this review.

TABLE 1

Medium Effects of Ions in Absolute Ethanol at 25°C, According to Bjerrum and Larsson.[15]

Ion	$\log_m\gamma_i$	Ion	$\log_m\gamma_i$
H^+	2.5	NH_4^+	2.7
Li^+	2.8	$N(CH_3)_4^+$	3.0
Na^+	3.5	$N(C_2H_5)_4^+$	2.7
K^+	4.1	Cl^-	2.5
Rb^+	3.9	Br^-	1.8
Cs^+	4.0	I^-	1.4
Ag^+	2.1	ClO_4^-	0.7

Most recently, Parker and Alexander[8] considered the possibility of determining medium effects for the silver ion referred to its standard state in methanol from the measured e.m.f. of cells such as

$$\begin{array}{ccc} Ag(s), AgNO_3 & \| & AgNO_3, Ag(s) \\ 0.01\,M \text{ in } CH_3OH & E_j & 0.01\,M \text{ in solvent } S \end{array} \quad (28)$$

on the assumption that if the bridge solution is saturated tetraethylammonium picrate in methanol or in the solvent S, the E_j becomes negligible. This approach led to fair agreement with a few independent extrathermodynamic estimates of log ${}_m\gamma_{Ag}$ only if the solvent S was water or formamide, but not when a dipolar aprotic solvent was used. In the latter case the suggested remedy was to change from methanol to acetonitrile as the reference medium, but the whole approach received no strong endorsement in general.

Undoubtedly, methods in Category I were modelled after the relatively successful use of concentrated salt bridges to suppress liquid-junction potentials in all-aqueous cells. Added encouragement came from the availability of equations for an approximate calculation of E_j, such as Planck's or Henderson's.[33] The general expression for a liquid-junction potential E_j between solutions 1 and 2 is:

$$E_j = -k\int_1^2 \sum \frac{t_i}{z_i}\, d\log m_i\gamma_i \quad (29)$$

where t_i, z_i, m_i, and γ_i are the Hittorf transference numbers, the charges, the molalities, and the activity coefficients, respectively, of all ionic species i in the transition layers between phases 1 and 2. Both the Planck and the Henderson approximations evaluate only the "ideal" component of the above equation, which amounts to omitting all activity coefficients from the latter and using concentrations only. Unfortunately, when solutions 1 and 2 are in different solvents, their concentrations are no more acceptable as approximations for activities, because of the change in the standard states involved. Instead, equations for liquid-junction potentials at the phase boundaries of different solvents must deal explicitly with the difference in the free energy, ΔG_i, for each ion in the two solutions. This was done in a derivation by Alfenaar, DeLigny, and Remijnse,[22] the highlights of which, with some minor changes, follow below.

The liquid-junction potential due to transport of *ions* across an aqueous–non-aqueous boundary is given by:

$$E'_j = -k\sum \frac{t_i}{z_i}\Delta G_i \quad (30)$$

where, as an approximation, t_i was assumed to be independent of solvent and $\Delta G_i = {}_sG_i - {}_wG_i$. Applying Equations 19 and 20 (but without restricting them to saturated solutions), we obtain for each ion i:

$$\Delta G_i = {}_sG_i^\circ - {}_wG_i^\circ + RT\ln\frac{{}_sm_i}{{}_wm_i} + RT\ln\frac{{}_s\gamma_i}{{}_w\gamma_i} \quad (31)$$

From Equation 7, we recognize the first two terms on the right-hand side of Equation 31 as RT ln ${}_m\gamma_i$. Thus, the liquid-junction potential at an aqueous–non-aqueous boundary is a function of the medium effects for the single ions transported across it and, therefore, cannot be suppressed by means of a salt bridge. Furthermore, it becomes clear that the Planck and the Henderson approximations evaluate only the contribution of concentration differences to the potential-determining ΔG_i, corresponding to the third term on the right-hand side of Equation 31. The last term accounts for the difference between the salt effects in the two solutions.

In addition, the overall liquid-junction potential E_j contains a contribution from the transport of solvent molecules across the interfaces, $E_{j\,\text{solv.}}$. Consequently, $E_j = E'_j + E_{j\,\text{solv.}}$. The authors evaluated the $E_{j\,\text{solv.}}$ for methanol-water solvents from e.m.f. measurements on cells of the type:

$$\underset{H_2O}{\text{Ag(s), AgZ(s), MZ}}\,\underset{E_j}{|}\,\underset{CH_3OH\text{-}H_2O}{\text{MZ, AgZ(s), Ag(s)}} \qquad (32)$$

using very low and equal concentrations of alkali halides, MZ, in both half cells. This effectively eliminated the concentration and the salt-effect terms from Equation 31, leading to a simplified expression for the overall E_j via Equation 30:

$$E_j = \frac{-t_M}{F}\Delta G^\circ_M + \frac{t_Z}{F}\Delta G^\circ_Z + E_{j\,\text{solv.}} \qquad (33)$$

where $\Delta G^\circ_i = {}_sG^\circ_i - {}_wG^\circ_i$.

The e.m.f. E of cell 32 is then:

$$E = \frac{t_M}{F}\Delta G^\circ_{MZ} + E_{j\,\text{solv.}} \qquad (34)$$

Because ΔG°_{MZ} is the solvation-energy change for a complete electrolyte, the solvent contribution to the liquid-junction potential, $E_{j\,\text{solv.}}$, could be evaluated from experimental data. It was found that in methanol-water solvents the $E_{j\,\text{solv.}}$ is a function not only of the medium, but of the nature of the electrolyte as well. The latter dependence, however, seemed to be a second-order effect.

Whereas the $E_{j\,\text{solv.}}$ turned out to be a thermodynamically accessible quantity (at least as a consequence of its formulation by Alfenaar, DeLigny, and Remijnse[22]), a calculation of the overall E_j from Equation 33 requires knowledge of the solvation-energy changes, or medium effects, for the ions M^+ and Z^-. Such calculations were carried out by the authors cited, using the solvation-energy changes for individual ions estimated by Alfenaar and DeLigny.[34] According to their results, the $E_{j\,\text{solv.}}$ in general accounted for about 10-25% of the overall E_j, the remainder being the E'_j, due to the transport of ions. Of course, this particular split depends on numerical values for individual ionic medium effects which, at least at the moment, are by no means generally accepted.

In conclusion, methods belonging to Category I, which rely on salt bridges to "eliminate" the E_j between aqueous and non-aqueous solutions of electrolytes, appear to be fundamentally unsound. It is intriguing, however, that according to Equation 33, the E_j could be reduced to the (measurable!) $E_{j\,\text{solv.}}$ if both the transference numbers and the medium effects were equal for the two ions transported across the interfaces. Perhaps this requirement, reminiscent of the criteria for choosing potassium chloride as the optimum salt-bridge electrolyte in aqueous electrochemistry, offers some hope for this line of research in the future.

Assumptions and Models Based on the Size of Solutes

Simple Models for Solvation Energy

Electrostatic Energy

The simplest expression for the solvation energy of an ion is the Born equation:[35]

$$G^\circ = -\frac{z^2e^2}{2r}\left(1 - \frac{1}{D}\right) \qquad (35)$$

in which r is the radius of the ion, D is the dielectric constant of the solvent, and the other symbols have their usual meanings. In this model, G° is the difference between the electrostatic free energy required to impart charge ze to a sphere of radius r *in vacuo*, $(z^2e^2/2r)$, and the corresponding energy of charging in a continuum of uniform dielectric constant D, $(z^2e^2/2rD)$. From Equation 35, the difference between the solvation energies for one mole of single ions i in the non-aqueous solvent and in water becomes:

$$\Delta G_i^\circ \equiv {}_sG_i^\circ - {}_wG_i^\circ = \frac{Nz^2e^2}{2r}\left(\frac{1}{D_s} - \frac{1}{D_w}\right) \quad (36)$$

where D_s and D_w are the dielectric constants of the non-aqueous medium and of water, respectively. Combining Equations 7 and 36, we arrive at the Born version of the medium effect for a single ion:

$$\log {}_m\gamma_i = \frac{Nz^2e^2}{2RTr}\left(\frac{1}{D_s} - \frac{1}{D_w}\right) \quad (37a)$$

which upon substitution of appropriate numerical values for 25°C becomes[2]:

$$\log {}_m\gamma_i = \frac{121.6z^2}{r}\left(\frac{1}{D_s} - 0.0128\right) \quad (37b)$$

It should be noted that the work of transferring the ionic charge across the vacuum-solution interface was ignored in the formulation of the Born equation. Therefore, Equation 36 represents a difference between the "chemical" energies of solvation and hydration and is not the free energy for a transfer process[23] (*cf.* Introduction).

The parameters ordinarily introduced in the Born equation are the crystallographic radius of the ion and the bulk dielectric constant of the medium. Neither changes in ionic radius due to solvation nor dielectric saturation in the vicinity of the ion are recognized by the model. This in itself restricts the possible validity of the Born equation to large ions, where these effects are likely to be negligible.

Furthermore, the Born equation ignores the various short-range interactions between the ionic charge and the solvent molecules, which are predominant in the primary solvation layer. The more important solvation-energy components included here are associated with ion-dipole, ion- (induced dipole), ion-quadrupole, dipole-dipole, and dispersion forces.[36] The above energy terms are functions of r^{-2}, r^{-4}, r^{-3}, r^{-3}, and r^{-6}, in that order, where r is the corresponding interaction distance, which contains the ionic radius, but is not necessarily equal to it. These interactions are accounted for in the more comprehensive theories of solvation which have been reviewed.[12] An actual calculation of solvation energies from these theories requires knowledge of numerical values for such parameters as the radii of ions and solvents, the various interaction distances, the polarizabilities and multipole moments of the solvent molecules and the ions, the coordination numbers for the primary solvation shell, and various geometric factors. Even for aqueous solutions, our present knowledge of these parameters is too uncertain for reliable calculations of hydration energies. For non-aqueous systems such calculations are out of the question at the moment.

It must be emphasized that in the evaluation of medium effects we are computing a relatively small difference (sometimes of a few kcal or less) between two large solvation-energy values. Hydration energies are considered to be reliable to no more than 2 kcal/g-ion.[12, 37] If we assume a similar uncertainty in the corresponding (non-aqueous) solvation energy, the *error* in ΔG° can easily attain (or exceed) the magnitude of the ΔG° itself. Obviously, we need solvation energies of higher accuracy than presently attainable before they can be combined into meaningful medium effects.

For our purposes, one useful consequence of the more comprehensive formulations of solvation energy is the possibility of approximating the total electrostatic energy of ion-solvent interactions by a power series in r^{-1}. This general functional relationship forms the underlying basis for some of the approaches to single-ion medium effects which we discuss later.

Nonelectrostatic Energy

The Born equation excludes from consideration all nonelectrostatic contributions to the solvation energy of an ion. These may be specific solvent-solute interactions, such as acid-base or complexation reactions, or nonspecific energy terms. A particular problem child in the field of medium effects has been the nonspecific "neutral" component of the solvation energy of an ion. Ideally, it is thought to be equal to the solvation energy of a neutral molecule of the same size and structure as the ion. In practice, such analogs are not always easy to realize. Because of orientation of solvent dipoles in the electric field of an ion (dielectric saturation), the solvent structure around an ion is expected to be different from that around its neutral analog. Exceptions to it may be *very large* ions whose electric fields are expected to be weak enough so that absence of appreciable dielectric saturation at their surfaces may be assumed.[34] Thus, for very large ions, the neutral component of solvation energy is equal to the solvation energy of its uncharged analog and is additive with the electrostatic component. The latter can be calculated from the Born equation. For solvation-energy changes (and for medium effects), the additivity of electrostatic and neutral parts can be associated with the following sequence of imagined processes: 1) The ion is discharged in water; 2) the discharged ion is transferred from water to the non-aqueous medium; and 3) the ion is recharged in the non-aqueous medium. In Equation 38, steps 1 and 3 are represented by $\Delta G°(\mathrm{el})$, and step 2 by $\Delta G°(\mathrm{neut})$:

$$\Delta G° = \Delta G°(\mathrm{el}) + \Delta G°(\mathrm{neut}) \qquad (38)$$

Similarly, for the medium effect (*cf.* Equation 7):

$$\log {}_m\gamma = \log {}_m\gamma(\mathrm{el}) + \log {}_m\gamma(\mathrm{neut}) \qquad (39)$$

The ion size at which this requirement is likely to be fulfilled is identified with the distance at which dielectric saturation ceases to be appreciable. Alfenaar and DeLigny[34] calculated from Buckingham's theory[38] that dielectric saturation will be less than 1% at the surface of ions with $r > 5$ Å in water and with $r > 15$ Å in methanol. For $\Delta G°$s between methanol and water, the additivity of $\Delta G°(\mathrm{el})$ and $\Delta G°(\mathrm{neut})$ and the applicability of the Born equation to the former will be fulfilled for ions with $r > 10$ Å.[39] In other models, dielectric saturation in water is neglected for $r > 4$ Å,[40] or even for $r > 3$ Å.[12]

The following arguments have been advanced to support the assumption that the neutral part of an ion-solvent interaction can be identified with the solvation of a nonpolar solute. The solvation energy of a nonpolar molecule has been formulated[41] as a composite of energy terms associated with a) creation of a cavity for the solute in the solvent, b) solvent-solute dispersion interactions, and c) change in standard state from gas to solution. The last component vanishes for comparisons between two solvents. Alfenaar and DeLigny[34] feel that the energy necessary to create a hole in a given solvent is the same for a large ion as for a neutral molecule of the same radius r, and that for large solutes this energy will be proportional to r^2. (In the literature,[12] however, there is no unanimity on how to estimate the energy of hole formation in water). Similarly, they argue that for large ions and molecules of equal size the dispersion interactions will be equal and only slightly dependent on the radius. Indeed, Alfenaar and DeLigny[34] found that the free energy of transfer of noble gases and other nonpolar molecules from water to methanol, $\Delta G°$, was a linear function of r^2 through most of the range. From such functions they interpolated values of $\Delta G°$ corresponding to the crystallographic radii of alkali-metal and halide ions, adopting them as approximations for the neutral parts of the solvation-energy changes for these ions.

In a different approach, proposed a long time ago by Bjerrum and Larsson[15] and recently applied by Haugen and Friedman,[42] the neutral part of $\Delta G°$ of ions is identified with the corresponding $\Delta G°$ for isoelectronic noble gases. In this model, He, Ne, Ar, Kr, and Xe are the neutral analogs for Li^+, Na^+, K^+, Rb^+, and Cs^+, respectively.[42] Needless to say, the results obtained by this method differ significantly from those interpolated from a $\Delta G°$ *vs.* r^2 relationship.

The use of solvation energies of inert gases to evaluate the neutral component of the solvation energy of an ion is known as the "inert-gas assumption." It is by no means generally accepted.[6 12 37] A convenient alternative is the "zero-energy assumption," according to which the energy change for the transfer of a neutral molecule from its gaseous to its solution standard state is attributed merely to the accompanying change in volume. For comparisons of solvation energies in two solvents, the "zero-energy assumption" amounts to omission of the neutral component from consideration.

At present none of the above methods for estimating $\Delta G°$ (neut) seems reliable, and the sizeable discrepancies among them do not inspire confidence. In view of the relatively large $\Delta G°$s exhibited by inert gases and other nonpolar solutes, it is difficult to imagine the "zero-energy assumption" as anything more than a convention devoid of physical reality. The fact that certain empirical relationships for solvation energy do better without a correction via the "inert-gas assumption"[20] [37] should not be interpreted as support for the "zero-energy assumption." The application of inert gases as neutral analogs for monatomic ions is hampered by the fact that the radii of the ions involved are much too small to fulfill the requirement of negligible dielectric saturation at their surfaces. For small ions the neutral interaction does differ from that of a noble-gas molecule of the same size. Still, Alfenaar and DeLigny contend[34] that the above difference can be corrected for by empirical terms proportional to r^{-2}, r^{-3}, etc.

In the case of large polyatomic solutes we have much more convincing ion-molecule analogs at our disposal. Good examples are the ferricinium-ferrocene pair and tetraphenylmethane as the neutral counterpart of tetraphylphosphonium, tetraphenylarsonium, and tetraphenylborate ions. Very encouraging in this respect is the finding that solvation-energy changes, $\Delta G°$, experienced by tetraphenylphosphonium tetraphenylborate in dioxane-water mixtures correspond to the sum of $2\Delta G°$ for tetraphenylmethane and the $\Delta G°$ (el) calculated for the electrolyte from the simple Born equation.[43] Here, the additivity of the Born energy term and of the neutral energy derived from a reasonable analog was confirmed experimentally. Investigation of such additivities in other solvent systems and for other ion-molecule counterparts represents one of the most promising methods of studying single-ion solvation today.

Calculations Based on Modified Born Equations

It follows from the preceding section that the Born equation in its original form may be a valid quantitative expression if restricted to the *electrostatic* part of the solvation energy of a *large* ion. For ions of average size the Born equation overestimates the absolute values of free energies. Therefore, its modifications consist of decreasing the dielectric constant or of increasing the ionic radius (or both), until agreement is obtained between experimental and calculated energies for electrically neutral combinations of ions. These modifications are theoretically justified ostensibly because they account for such expected phenomena as the decrease of the dielectric constant in the vicinity of ions and the increase in ionic radii due to solvation and to other changes resulting from the transfer to a noncrystalline environment. Actually, the adjustments of the dielectric constant and of the radius may also account empirically for any number of interactions ignored by the model.

Hepler[40] modified the Born equation by expressing the dielectric constant as a function of the distance from the center of the ion r. In his model the region of dielectric saturation in water ($D_{\text{sat.}} = 5$) exists for $r < 1.5$ Å, the macroscopic dielectric constant is assumed at $r \geq 4$ Å, and the dielectric constant is expressed as a linear function of r in the intermediate region. The electrostatic free energy for one mole of univalent ions is given by:

$$G°(\text{el}) = \frac{\text{Ne}^2}{2} \int_{r_s}^{1.5} \frac{dr}{D_{\text{sat.}} r} + \int_{1.5}^{4.0} \frac{dr}{(Xr - Y)r^2} + \int_{4.0}^{\infty} \frac{dr}{D_0 r^2} \qquad (40)$$

where r_s is the radius of the ion, D_0 is the macroscopic dielectric constant of the solvent, $X = 0.4\,(D_0 - D_{\text{sat.}})$, and $Y = (1.5X - D_{\text{sat.}})$. Equation 40 is used in its complete form only for ions with $r_s < 1.5$ Å. For ions having $1.5 < r_s < 4.0$, the first integral is zero and the lower limit of the second integral becomes r_s, instead of 1.5. For an ion having a radius of 4 Å or greater, only the last term of Equation 40, which is identical with the simple Born equation, applies.

Woodhead, Paabo, Robinson, and Bates[44] used the Hepler model to calculate the electrostatic component of the free-energy change for the following transfer reaction between water and 50 wt. % aqueous methanol:

$$\mathrm{RNH^+(s) + H^+(w) + RN(w) \rightarrow RNH^+(w) + H^+(s) + RN(s)} \quad (41)$$

where RN is tris (hydroxymethyl) aminomethane, and the letters *s* and *w* designate the non-aqueous solvent and water, respectively. Equation 41 represents the difference between the dissociation equilibria of RNH$^+$ in 50% methanol and in water, for which $[\mathrm{p}({}_sK) - \mathrm{p}({}_wK)] = -0.254$, corresponding to $\Delta G° = -1.45$ kjoules/mole for the transfer process. Using $r_s = 4.0$ Å for the RNH$^+$ ion and $r_s = 2.8$ Å for the H$^+$ ion in Equation 40, the electrostatic part of this transfer energy is found to be 0.48 kjoules/mole. The difference between the total and the electrostatic energy of transfer, which amounts to -2 kjoules/mole, was termed the "basicity effect," $\Delta G_b°$. $[\Delta G_b° = \Delta G° - \Delta G°(\mathrm{el})]$.* Paabo, Bates, and Robinson[45] extended the above calculation to the energetics of the transfer process represented by Equation 41 for the ammonium ion. Again, the difference between the observed $\Delta G°$ of transfer from water to 50% methanol (-3.18 kjoules/mole) and the calculated $\Delta G°$(el) (1.35 kjoules/mole) was equal to the same "basicity effect" of -2.kjoules/mole. Similar calculations based on the Δp*K*s of ammonium ion for other methanol-water mixtures have shown that the "basicity effect" increases with methanol content up to 60 wt. % methanol and then drops off. This apparently reflects the behavior of the medium effect for the proton, $\log {}_m\gamma_{\mathrm{H}}$, in methanol-water mixtures. On the assumption that the $\Delta G_b°$ resides entirely in the corresponding $\log {}_m\gamma_{\mathrm{H}}$, I calculated values for the latter from the data in Ref. (45). In Table 8 these are compared with other literature estimates of $\log {}_m\gamma_{\mathrm{H}}$ for the methanol-water solvents.

A modification of the Born equation similar to the Hepler[40] model has been developed by Stokes[47] for the hydration energy of ions with noble-gas structure. It takes into account both the dielectric saturation and the increase in ionic radius from its crystallographic to its hydrated size. Dill, Itzkowitz, and Popovych[48] calculated the standard free energy of potassium ions, $G_{\mathrm{K}}°$, in water and in ethanol-water mixtures from the Stokes model:

$$G° \text{ (kcal/mole)} = 166\left[\frac{2.8}{9r_c(r_c + 2.8)} + \frac{D^{-1}}{r_c + 2.8}\right] \quad (42)$$

In Equation 42 the crystallographic radius of the potassium ion, $r_c = 1.33$ Å, D is the macroscopic dielectric constant of the medium, but its effective value in the hydration layer is 9. The increase in ionic radius due to hydration is assumed to be 2.8 Å. From the values of ${}_sG_{\mathrm{K}}°$ calculated via Equation 42, medium effects for the potassium ion, $\log {}_m\gamma_{\mathrm{K}}$, were obtained for ethanol-water mixtures. Using the standard potentials of potassium electrodes in ethanol-water solvents, determined in the same study, it was possible to calculate values of $(\log {}_m\gamma_{\mathrm{K}} - \log {}_m\gamma_{\mathrm{H}})$ via Equation 27. Finally, values of $\log {}_m\gamma_{\mathrm{H}}$ were obtained by difference.

As shown in Table 2, the calculated medium effect for the potassium ion is always positive and increases steadily with increasing ethanol content, as would be predicted qualitatively on the basis of the decreasing dielectric constant of the medium. In contrast, the medium effect for the proton is negative throughout the ethanol-water range and decreases with increasing ethanol content. This behavior is contrary to what would be

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*In a sequel to this study Schindler, Robinson, and Bates, *J. Res. Nat. Bur. Stand.*, 72A, 141, (1968), concluded that the energy term identified here as the "basicity effect" could be accounted for reasonably well by the free energy of transfer $\Delta G°$ for the uncharged base tris(hydroxymethyl)aminomethane, which was not considered explicitly in the earlier,[44] strictly electrostatic, treatment. (They determined values for $\Delta G°$ of RN in methanol-water solvents from solubility measurements). The above conclusion, however, is at variance with the following considerations. For conjugate acid-base species having radii as large as 4 Å, the $\Delta G°$ for the base RN should very nearly cancel the neutral component of $\Delta G°$ for its conjugate acid RNH$^+$ (*cf.* Equations 38, 52 and 53). Thus, the net contribution of the RN-RNH$^+$ pair to the transfer process (Equation 41) should be determined essentially by the *electrostatic* component of $\Delta G°$ for the RNH$^+$ ion, independent of the magnitude of $\Delta G°$ for the base RN. According to this reasoning, the calculations of the "basicity effects" from electrostatic considerations alone,[44] i.e., with the omission of $\Delta G°$ for the base RN, would appear to be *effectively correct as far as the energetics of the* RN-RNH$^+$ *pair is concerned.*

TABLE 2

Calculated Single-Ion Medium Effects for Potassium And The Proton in Ethanol-Water Solvents at 25°C (According to Dill, Itzkowitz, and Popovych[48])

Wt % ethanol	$(\text{Log}\,_m\gamma_K - \log\,_m\gamma_H)$	$\text{Log}\,_m\gamma_K$ (Calculated from Stokes[47] Model)	$\text{Log}\,_m\gamma_H$ (by difference)
92.3	2.803	0.711	−2.902
80.3	2.099	0.525	−1.574
60.2	1.574	0.305	−1.269
50.0	1.22[a]	0.225	−1.00
40.0	0.918	0.160	−0.758
30.0	0.625[a]	0.106	−0.519
20.3	0.353	0.0651	−0.288
15.0	0.159	0.0456	−0.113

[a] Interpolated

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predicted from electrostatic models, but it parallels the "basicity effects" in methanol-water mixtures[45] described earlier. Moreover, the unexpected values of log $_m\gamma_H$ in ethanol-water mixtures find corroboration in the Hammett acidity function, H_0, as shown in Figure 1. The acidity function is plotted as $(-H_0 - C_{HCl})$, where $C_{HCl} = 0.1\ M$, because in that form it represents an approximation of log $_m\gamma_H$ for those solutions where $H_0 = pa_H$. The two independent estimates of log $_m\gamma_H$ show good coincidence up to 50 wt. % ethanol, but then diverge. The discrepancies in the high-ethanol region are probably due to the failure of the Stokes model, which presumes hydration throughout the solvent range. If hydration is replaced by partial or complete alcoholation, the saturation values of the dielectric constant and the solvated radii will no longer be the same as in water, and the hydration model is bound to give erroneous results. Until we know more about dielectric saturation and other ion-solvent interactions in non-aqueous media, calculations from models such as Stokes'[47] and Hepler's[40] must be confined to water-rich solvents.

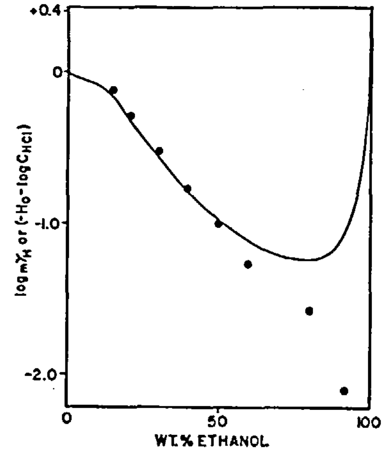
Because little is known about dielectric saturation except in aqueous solutions, the modified form of the Born equation which has found wide applicability in non-aqueous solvents is one in which the ionic radii, rather than the dielectric constant of the solvent, are adjusted. This modification was originated by Latimer, Pitzer and Slanski,[49] who were able to reproduce experimental values of hydration energies of alkali halides to ± 1−2 kcal by adding the empirical corrections $R_+ = 0.85$ Å to the crystallographic radii of the cation, r_+, and the anion, r_-, respectively:

$$-G^\circ_\pm = \frac{Ne^2z^2}{2}\left(1-\frac{1}{\mathrm{D}}\right)\left(\frac{1}{r_+ + R_+} + \frac{1}{r_- + R_-}\right) \tag{43}$$

The hydration energy of a cation was then assumed to be identifiable with $\left[\frac{-Ne^2z^2}{2}\left(1-\frac{1}{D}\right)\left(\frac{1}{r_+ + R_+}\right)\right]$ and that of the anion with $\left[\frac{-Ne^2z^2}{2}\left(1-\frac{1}{D}\right)\left(\frac{1}{r_- + R_-}\right)\right]$.

If solvation energies of alkali halides are known in a given non-aqueous solvent, Equation 43 can be fitted to them with different values of R_+ and R_-. The difference between the solvation and the hydration energy of a

FIGURE 1



Comparison of calculated medium effects for the proton with the $-H_0$ acidity function in ethanol-water solvents. The solid curve represents $(-H_0 - C_{HCl})$ from the data of Braude and Stern.[46] Circles are values of $\log_m\gamma_H$ estimated by Dill, Itzkowitz, and Popovych.[48] (Reprinted from *J. Phys. Chem.*, 72, 4586, December 1968. Copyright (1968) by the American Chemical Society. Reprinted by permission of the copyright owner.)

single ion (which is needed to calculate its medium effect via Equation 7) is then given (e.g., for cations) by:

$$-\Delta G^\circ_+ \equiv ({}_sG_+ - {}_wG^\circ_+)$$

$$= \frac{N e^2 z^2}{2}\left[\left(\frac{1-\frac{1}{D_s}}{r_+ + R_+\,(\mathrm{s})}\right)-\left(\frac{1-\frac{1}{D_w}}{r_+ + R_+\,(\mathrm{w})}\right)\right] \quad (44)$$

where $R_+(\mathrm{s})$ and $R_+(\mathrm{w})$ are the empirical radius corrections specific to the non-aqueous solvent and to water, respectively. In this manner, Keopp, Wendt and Strehlow[50] calculated the values of ΔG° of the rubidium ion (less rigorously termed the free energies of transfer of Rb^+ from water to the solvent) for several non-aqueous media. The solvation energies for the alkali halides, ${}_sG^\circ_\pm$, were estimated from the known values of their hydration energies, ${}_wG^\circ_\pm$, and a comparison of their solubilities in water and in the solvents of interest. An expression analogous to Equation 21 was used for the above estimation, except that the activities in saturated solutions were approximated by the solubilities. Compared to its aqueous value of -71.0 kcal/mole, ${}_sG^\circ_{\mathrm{Rb}}$ showed practically no change in methanol and in formamide but shifted negatively in acetonitrile (to -73.5 kcal/mole) and in formic acid (to -72.3 kcal/mole). It was argued by Coetzee and Campion[51] that the above shift for acetonitrile contradicted polarographic and other evidence to the effect that alkali metal ions are solvated more strongly by water than by acetonitrile. A possible reason for it was thought to be[51] the poor agreement of the radius corrections among the different salts in acetonitrile, and I am sure that equating solubilities to mean ionic activities did not improve matters either.

In subsequent studies,[5,20,51] it was realized that better correspondence between calculated and observed solvation energies can be obtained by adapting Equation 43 to differences between the solvation energies of pairs of cations, thereby excluding anions from consideration altogether. Further improvement in the precision of determining $R_+(\mathrm{s})$ and in the accuracy of the calculations is achieved by comparing the *changes* which such energy differences experience upon "transfer" from water to the non-aqueous solvent. Usually, each alkali metal, M, is subjected to a double comparison with either cesium or rubidium:

$$\Delta\Delta G^\circ_{(\mathrm{M-Rb})} \equiv {}_s(G^\circ_{\mathrm{M}} - G^\circ_{\mathrm{Rb}}) - {}_w(G^\circ_{\mathrm{M}} - G^\circ_{\mathrm{Rb}}) \quad (45a)$$

$$= \Delta G^\circ_{\mathrm{M}} - \Delta G^\circ_{\mathrm{Rb}} \quad (45b)$$

Each of the ΔG°s in Equation 45b is then expressed by the right-hand side of Equation 44, and the radius correction is fitted directly into the difference between such expressions for the two cations. So far, the choice of numerical values for $R_+\,(\mathrm{w})$ has been between the original[49] 0.85 Å, the Noyes' value[37] of 0.72 Å, and Simon's[52] newest estimate of 0.64 Å. However, the value that is significant in achieving a satisfactory fit for transfer energies is that of $\Delta R_+ \equiv R_+\,(\mathrm{s}) - R_+\,(\mathrm{w})$, rather than the individual values of R_+ in the two solvents. The uncertainty in the best reported values of ΔR_+ is ± 0.01 Å, corresponding to an error in $\log {}_m\gamma$ of $\pm 0.3-0.4$.[53] Once a value of $R_+\,(\mathrm{s})$ is determined for a given solvent by the above procedure, solvation-energy changes, ΔG°, for individual cations are evaluated as before from Equation 44.

Strehlow[5] obtained values of $\Delta R_+ = -0.043$ Å and $\Delta R_- = +0.12$ Å in methanol (assuming $R_+\,(\mathrm{w}) = 0.85$ Å and $R_-\,(\mathrm{w}) = 0.25$ Å) from the observed $\Delta\Delta G^\circ$s for the transfer of pairs of alkali-metal ions and pairs of halide ions from water to methanol. The $\Delta\Delta G^\circ$s for ions of like charge were calculated from distribution equilibria of alkali metals between an amalgam and the alkali-halide solutions in water and in methanol.[54] These were split into ΔG°s of individual ions, which are presented in the form of medium effects, $\log {}_m\gamma$, in Table 10. Unfortunately, all of Strehlow's ΔG°s for the alkali-metal ions in methanol turned out to have absolute values below 0.5 kcal/mole, which is about equal to the most optimistic estimates of error in such calculations.

Coetzee and his co-workers[20,51-53] used the above procedure to determine differences between the solvation energies of alkali-metal ions in water and in several dipolar aprotic solvents. Values of $\Delta\Delta G^\circ$ (M − Rb) (Equation 45a), from which the splits into individual ionic components were obtained, were estimated from the polarographic half-wave potentials of the alkali-metal ions in water, $E_{1/2}$ (M, H_2O), and in the non-aqueous solvents, $E_{1/2}$ (M, S).[55] First, the half-wave potential of each ion was referred to that of rubidium in the same solvent: $\Delta E_{1/2}$ (M, S) $\equiv E_{1/2}$ (M, S) $- E_{1/2}$ (Rb, S). Then, these differences in the non-aqueous solvent and in water were compared for each ion: $\Delta\Delta E_{1/2}$ (M) $= \Delta E_{1/2}$ (M, S) $- \Delta E_{1/2}$ (M, H_2O). On the assumption that $\Delta\Delta E_{1/2}$ (M) $\cong \Delta\Delta E^\circ$ (M), the former was used to calculate the $\Delta\Delta G^\circ$ (M $-$ Rb). Half-wave potentials differ from standard potentials by the free energies of amalgamation and by the effects of a supporting electrolyte and a liquid-junction potential in the polarographic cell. However, the proponents of this method feel that the assumption of $\Delta\Delta E_{1/2}$ (M) $\cong \Delta\Delta E^\circ$ (M) is justified, as the above effects should largely cancel in the double comparisons employed. Coetzee and his co-workers[20 52] express the medium effects for alkali metal ions as differences between the standard potentials of the alkali metals in the dipolar aprotic solvents and in water, $\Delta E^\circ = {}_wE^\circ$ (M, S) $- {}_wE^\circ$ (M, H_2O), where both E°s are expressed on the water scale, *i.e.*, referred to the aqueous SHE. The corresponding values of log ${}_m\gamma_M$ are simply $\Delta E^\circ/(2.3RT/F)$ (*cf.* Equation 13). In Table 3, their results are compiled in both forms. The medium effects for acetonitrile do not agree with other literature estimates, as shown in Table 14.

There is no question that the modified Born equation with empirically adjustable radii accounts satisfactorily for the observed differences between the free energies of transfer of pairs of alkali-metal ions. However, the assignment of individual ionic "transfer" energies, or medium effects, on this basis requires, as always, faith in the model. The basic assumption underlying all Born models is that the interaction of the ions (alkali metal ions in this case) with both water and the given non-aqueous solvent is predominantly electrostatic. The neutral part of solvation energy of an ion is ignored by all forms of the Born equation, including the Hepler[40] and the Stokes[47] models discussed earlier. This omission is frequently justified by invoking the "zero-energy assumption" or the equivalent assumption that the neutral components for

TABLE 3

Standard Potentials on the Water Scale and Medium Effects of Single Ions in Dipolar Aprotic Solvents
(According to Coetzee and his co-workers.[20 52])

	Acetonitrile		Propionitrile		Isobutyronitrile		Benzonitrile	
Ion	ΔE°	log ${}_m\gamma$	ΔE°	log ${}_m\gamma$	ΔE°	log ${}_m\gamma$	ΔE°	log ${}_m\gamma$
Li^+	0.40	6.76	0.37	6.25	—	—	0.46	7.78
Na^+	0.29	4.90	0.26	4.40	0.28	4.73	0.33	5.58
K^+	0.20	3.38	—	—	0.21	3.55	—	—
Rb^+	0.17	2.87	0.16	2.70	0.18	3.04	0.20	3.38
Cs^+	0.15	2.54	—	—	—	—	—	—

	Acetone		Nitromethane		Sulfolane	
Ion	ΔE°	log ${}_m\gamma$	ΔE°	log ${}_m\gamma$	ΔE°	log ${}_m\gamma$
Li^+	—	—	0.80	13.52	0.31	5.24
Na^+	0.17	2.87	0.55	9.30	0.21	3.55
K^+	0.12	2.03	0.38	6.42	0.13	2.20
Rb^+	0.11	1.86	0.33	5.58	0.11	1.86
Ca^+	—	—	—	—	0.09	1.52

$\Delta E^\circ = {}_wE^\circ$ (i, SH) $- {}_wE^\circ$ (i, H_2O), both referred to ${}_wE^\circ$ (H, H_2O) $= 0$ (in volts). From the ΔE° data we calculated log ${}_m\gamma = \Delta E^\circ/0.05916$ at 25°C.

pairs of alkali metal ions are similar and tend to cancel in the energy differences. However, no such similarities or cancellations are observed when the values of ΔG° (neut) for the "transfer" of alkali metal ions from water to methanol are estimated with the aid of the "inert-gas assumption."[34] On the contrary, these neutral components comprise the major part not only of the ΔG°s of individual ions, but also of their differences relative to one ion *(cf.* Table 7). Of course, the "inert-gas assumption" does not deserve an *a priori* acceptance, but neither does the "zero-energy assumption." The empirical corrections to ionic radii in the Born equation have the formidable task of accounting for all of the ion-solvent interactions which are ignored by the simple Born model. It was always accepted that these include the various short-range interactions, which are functions of higher powers of r^{-1}, and the dielectric saturation, but it is also possible that the radius correction may allow for the neutral component as well[53] (in spite of the latter's "wrong" functional form$-f(r^2)$). Nevertheless, the area of ΔG° (neut) is one in which proponents of the modified Born equation must come up with some more convincing answers.

In some respects it is unfortunate that the application of the modified Born equation has been largely restricted to differences between very similar cations. One consequence of such restriction may be the necessity of dealing with vanishingly small differences between ΔG°s, as in the case of Strehlow's[5] data for alkali metal ions in the methanol-water comparison. It seems that the model in its present form is not well suited to the determination of solvation-energy differences between similar solvents. A more dangerous consequence would result if some energy component which is not accounted for by the radius correction would tend to cancel in the energy difference between two cations. In such a case the model could still reproduce experimental data by accounting correctly for the difference between the residual (uncancelled) energy components of the two ions, but the individual ionic energies derived from such differences would be incorrect. Perhaps some of these questions could be resolved by extending the modified Born equation to pairs of cations other than alkali metal ions and to comparisons among dissimilar cations in general. If internal consistency were obtained for individual ionic ΔG°s derived from such diverse comparisons, faith in this model might be easier to come by.

Extrapolation Methods

On the basis of existing theories of solvation, Izmaylov[56,57] adopted the model in which all significant components of the solvation energy of an ion are functions of $1/r^n$, where r is the crystallographic radius of the ion and n can assume the values 1, 2, 3, 4, and 6. In this model the solvation energy of an infinitely large ion is zero. In order to determine the solvation energy of the proton, G°_{H}, in a given solvent, Izmaylov plotted the electrically neutral combinations $(G^\circ_{\mathrm{M}} - G^\circ_{\mathrm{H}})$ for a series of metal ions M as a function of $1/r_{\mathrm{M}}$. Similarly, the combinations $-(G^\circ_{\mathrm{H}} + G^\circ_{\mathrm{X}})$[*]; where x is a halide ion, were plotted *vs.* $1/r_{\mathrm{X}}$. Both functions should extrapolate to the same value of $-G^\circ_{\mathrm{H}}$ at $(1/r)=0$. The location of the intercept was improved by plotting the average of these two functions: $\left[-G^\circ_{\mathrm{H}} + \left(\frac{G^\circ_{\mathrm{M}} - G^\circ_{\mathrm{X}}}{2}\right)\right]$ *vs.* $1/r_{\mathrm{avg}}$, where $1/r_{\mathrm{avg}} = \frac{1}{2}(1/r_{\mathrm{M}} + 1/r_{\mathrm{X}})$. Analogous extrapolations were carried out to determine the solvation energies of Li^+ and Ag^+ ions. Typical plots are reproduced in Figure 2. Of course, once the G° of any single ion has been estimated, the G°s of all other ions in the same solvent become accessible through their electrically neutral combinations.

In a later modification of his method, Izmaylov[58] interpreted solvation of ions as a process of complex formation in which the solvent molecules act as donors of unshared electron pairs and the ions, having vacant orbitals, as their acceptors. Solvation energies of both cations and anions can be expressed as a single function of $(1/n^2)$, where n is the principal quantum number of the lowest vacant orbital of the ion. It was assumed that for isoelectronic pairs of alkali

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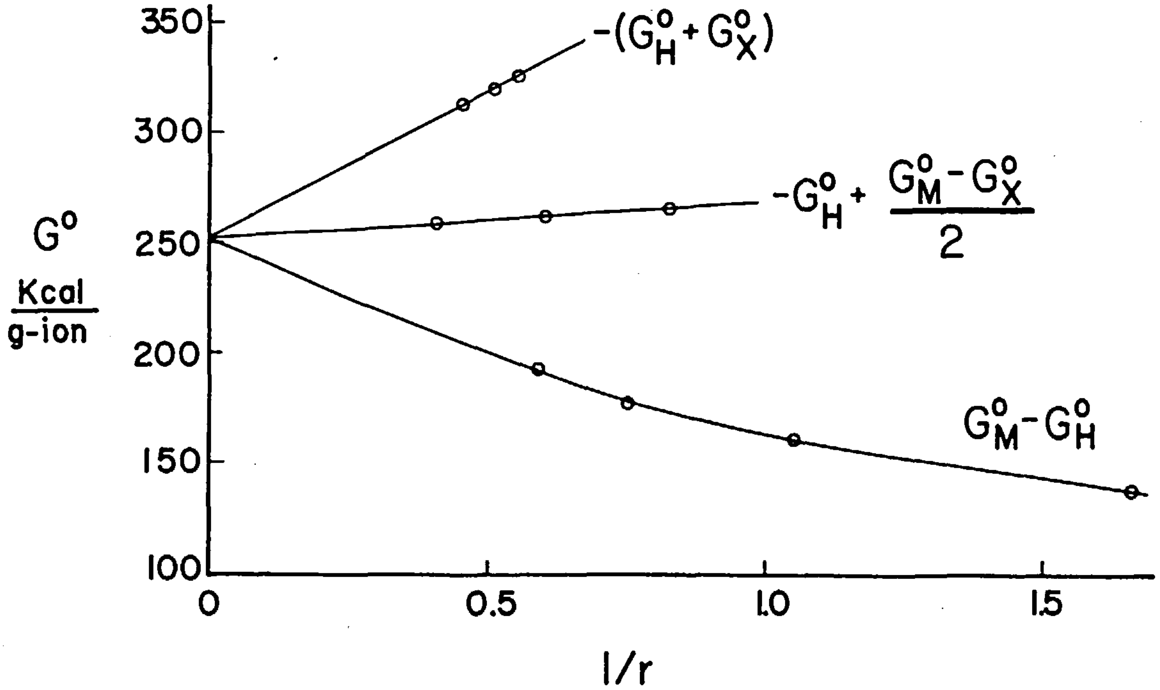
[*] In some reviews[2,5] Izmaylov's G°s are reported incorrectly with the opposite sign. This oversight was probably caused by the difference in terminology; Izmaylov reports his "solvation energies" in terms of the chemical affinity of a reaction, A, where $A = -G^\circ$.

(M) and halide *(X)* ions, the solvation-energy differences $(G_M^\circ - G_X^\circ)$ would approach zero with decreasing $(1/n^2)$. Therefore, the new procedure for the determination of the solvation energies of H^+, Li^+ and Ag^+ ions, $-G_i^\circ$, consisted of plotting the function $\left[-G_i^\circ + \left(\frac{G_M^\circ - G_X^\circ}{2}\right)\right]_{n=3,4,5,6}$ *vs.* $(1/n^2)$ and extrapolating to $(1/n^2) = 0$. Examples of such extrapolations are shown in Figure 3. For the isoelectronic pairs (Na^+, F^-), (K^+, Cl^-), (Rb^+, Br^-), and (Cs^+, I^-), the values of n are 3, 4, 5, and 6, respectively. The solvation energies obtained by the $(1/n^2)$ extrapolation were, on the average, 1.0 – 1.5 kcal/mole lower in absolute values for cations and higher by the same amount for anions when compared with their counterparts from the $(1/r)$ extrapolation. Izmaylov considered the $(1/n^2)$ extrapolation more reliable, because solvation energies of both cations and anions can be expressed as a single function of $(1/n^2)$, but not of $(1/r)$. Unless otherwise stated, the results from Izmaylov's studies tabulated in this review are those derived from $(1/n^2)$ extrapolations.

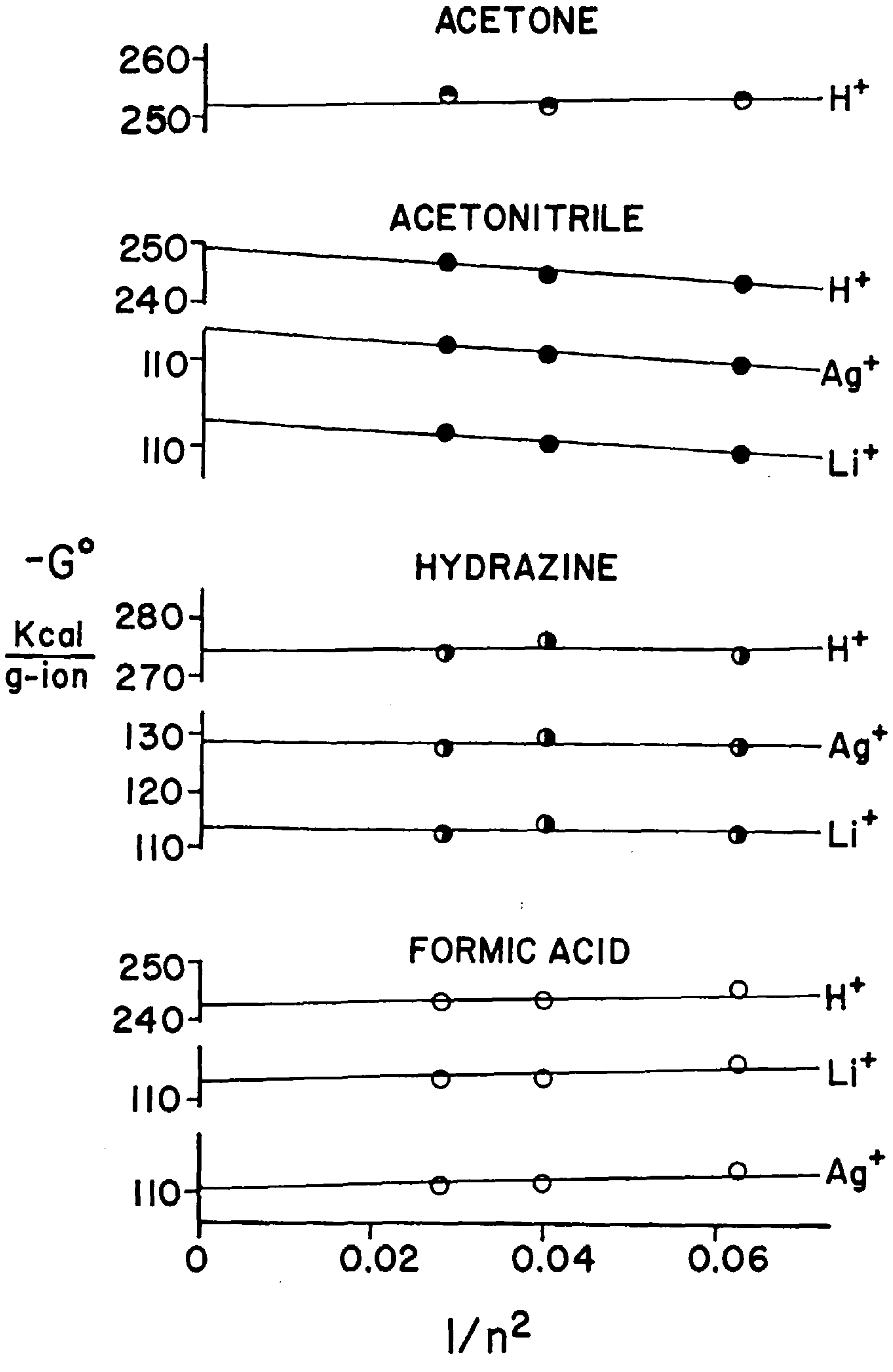
Using the above method, Izmaylov[59] estimated the solvation energies and then calculated the medium effects for several ions in ten solvents. In Table 4 are shown the medium effects and the energies of hydration, from which the corresponding solvation energies in any of the non-aqueous solvents can be calculated back, if desired. In order to carry out his extrapolations, Izmaylov[56, 57] first had to evaluate for each solvent the solvation energies for the required electrically neutral combinations of ions by a Born-Haber cyclic process. The sums $-(G_H^\circ + G_X^\circ)$ were derived starting from the E°s of the silver–silver halide electrodes, and the differences $(G_M^\circ - G_H^\circ)$ from the E°s of the corresponding metal electrodes. In some solvents the solubilities of alkali halides were used as the starting values in the determination of $-(G_M^\circ + G_X^\circ)$. Furthermore, this calculation required knowledge of the dissociation energy of molecular hydrogen, the sublimation energies of the metals, the ionization energies of the metals and of atomic hydrogen in the gas phase, and the crystal lattice energies of silver halides. Clearly, such calculations are subject to large

FIGURE 2



Determination of the solvation energy of the proton in methanol by extrapolation as a function of $1/r$. (After Ismaylov[56]).

FIGURE 3



Determination of the solvation energies of individual ions by extrapolation as a function of $1/n^2$. (After Izmaylov.[58])

errors. The subsequent extrapolations are long and non-linear, and in the $(1/n^2)$ method are often based on only three points. Consequently, Izmaylov's[59] estimate of error as being ±0.5 kcal/mole seems a bit optimistic. For example, in the case of hydration energies of individual ions evaluated by a vaguely similar extrapolation procedure, Noyes[60] hopes for an uncertainty of 2 kcal/mole for univalent ions. If a similar error exists in the solvation of a given ion in a non-aqueous solvent, the error in the energy difference will be, of course, even greater. Unfortunately, for the majority of univalent ions, the differences between solvation energies in water and in the other solvents studied by Izmaylov are only a few kcal/mole or less. Thus, we are again confronted by the impasse where the values of ΔG° required for the calculation of medium effects are of the same order of magnitude as the errors in the individual values of G°.

There are some examples, however, of large energy differences in Table 4, which demonstrate that Izmaylov's method does produce results of physical significance when applied to analytically favorable situations. For example, the expected tighter solvation of H^+, Ag^+, Zn^{++}, and Cd^{++} ions by ammonia and hydrazine, as compared to water, is reflected by the large negative medium effects (${}_sG^\circ$

TABLE 4

Medium Effects, $\log_m\gamma$, and Hydration Energies of Single Ions (According to Izmaylov.[59])

Ion	NH_3	N_2H_4	CH_3OH	C_2H_5OH	n-C_4H_9OH	iso-$C_5H_{11}OH$	CH_3COCH_3	CH_3CN	HCOOH	$-{}_wG^0$ kcal/g-ion
H^+	−15.8	−13.2	3.1	3.9	4.2	4.2	3.3	5.5	10.0	256.5
Cl^-	4.8	0.7	1.0	1.2	2.0	3.0	3.3	8.0	−3.3	74.5
Br^-	3.7	1.4	1.0	1.2	0.7	3.0	3.3	5.0	−1.3	69.0
I^-	0.6	0.7	0.0	0.8	1.4	1.1	2.6	2.3	−0.9	60.5
Li^+	−2.9	2.6	1.6	2.9	1.8	--	--	1.8	2.4	117.0
Na^+	−1.8	1.4	1.8	4.2	4.0	6.0	10.3	2.5	1.8	94.0
K^+	0.0	1.4	2.0	4.0	6.2	5.5	6.6	1.4	3.0	77.0
Rb^+	1.0	1.8	2.8	4.6	9.0	5.5	7.7	1.6	1.9	72.5
Cs^+	0.0	--	2.7	3.8	4.4	4.4	4.4	1.1	1.4	63.0
Ag^+	−15.6	−13.2	3.5	3.7	2.5	2.5	--	−3.0	−0.7	110.5
Ca^{++}	5.6	6.0	--	--	--	--	--	7.8	5.2	371.0
Zn^{++}	−13.8	−6.0	5.4	7.7	--	--	--	7.7	7.2	492.5
Cd^{++}	−10.9	−6.8	5.0	7.6	--	--	--	6.2	5.6	428.0

$< {}_{w}G^\circ$). The known preferential solvation of Ag^+ by acetonitrile[28] is predicted here by its negative medium effect, while the antagonism of the same solvent towards the halide ions[6] shows up in the large positive values of their $\log {}_{m}\gamma$. In general, cations are more favored by the basic solvents (small or negative medium effects), while anions are more favored by acidic solvents (here exemplified by formic acid). The comparatively high positive values of medium effects for acetone, *n*-butanol, and isopentyl alcohol are probably not very reliable, as they were derived largely from solubility data uncorrected for activity coefficients and ion-pair formation.

In formulating his method Izmaylov[56] considered the effect of a neutral part of solvation energy of an ion, but chose to ignore it on the grounds that, in his opinion, it would play a major role only for ions having radii of the order of 10 Å. For ions of average size the neutral components would comprise (according to Izmaylov) no more than 1-2% of the total solvation energy, which would furthermore tend to cancel in the combinations of G°s used in the extrapolations. We have stated earlier that G° (neut) is considered to be proportional to r^2 and would therefore approach infinity at $1/r = 0$. Should Izmaylov's evaluation of the relative importance of G° (neut) be inaccurate, his extrapolations may be seriously in error. The previously mentioned estimates of ΔG° (neut) via the inert-gas assumption[34] *(cf.* Table 7) attest to the existence of such a danger.

Feakins and Watson[61] modified Izmaylov's method of extrapolation as a function of $1/r$ in two respects. 1) Instead of evaluating G° for individual ions separately in water and in a non-aqueous solvent, they extrapolated directly to their values of ΔG° by plotting the energies of *transfer* of electrically neutral combinations of ions *vs.* the reciprocal radii of the varying ions. 2) They assumed a linear releationship between ΔG° and $1/r$. As always, the transfer process is defined as occurring from water to a given non-aqueous solvent and the corresponding $\Delta G^\circ = {}_{s}G^\circ - {}_{w}G^\circ$. Their data for the ions of HCl, HBr, and HI, derived from e.m.f. measurements *(cf.* Equation 26), were fitted to the equation

$$(\Delta G^\circ_{\mathrm{H}} + \Delta G^\circ_{\mathrm{X}}) = \Delta G^\circ_{\mathrm{H}} + a\ (r_{\mathrm{X}})^{-1} \qquad (46)$$

where X is a halide ion, and the $\Delta G^\circ_{\mathrm{H}}$ was evaluated at $(1/r_{\mathrm{X}}) = 0$. Similarly, data for LiCl, NaCl, and KCl were expressed by the function

$$(\Delta G^\circ_{\mathrm{Cl}} + \Delta G^\circ_{\mathrm{M}}) = \Delta G^\circ_{\mathrm{Cl}} + b\ (r_{\mathrm{M}})^{-1} \qquad (47)$$

where M is an alkali metal ion, and the $\Delta G^\circ_{\mathrm{M}}$ was obtained at $(1/r_{\mathrm{M}}) = 0$.

Originally[61] this method was applied in a limited number of methanol-water solvents, but later it was extended to the entire methanol-water range[62, 63] and to a few dioxane-water and acetic acid-water mixtures[64] as well. The results for the last two sets of media are compiled in Table 5. Medium effects for the proton in methanol-water solvents calculated from the values of $\Delta G^\circ_{\mathrm{H}}$ reported by Feakins and his co-workers are compared with other estimates of $\log {}_{m}\gamma_{\mathrm{H}}$ in Table 8. A similar comparison for alkali and halide ions is presented in Table 9.

TABLE 5

Medium Effects, $\log {}_{m}\gamma$, for the Proton and for the Chloride Ion in Acetic Acid-Water and Dioxane-Water Solvents (Calculated from the data of Bennetto, Feakins, and Turner.[64])

Wt. % Organic Solvent	$\log {}_{m}\gamma_{\mathrm{H}}$	$\log {}_{m}\gamma_{\mathrm{Cl}}$
	Acetic Acid-Water	
10	−0.14	0.32
20	−0.19	0.60
40	−0.09	1.08
60	0.15	1.70
	Dioxane-Water	
20	−1.76	2.05
45	−4.18	5.13

In view of what we know about theories of solvation and judging from the shapes of Izmaylov's extrapolations (Figure 2), the assumption of a linear dependence of ΔG° on r^{-1} for ions of average size would appear to be an oversimplification. The simple Born equation is not adhered to here, because the slopes of the lines represented by Equations 46 and 47 are not equal to the Born slopes and differ from each other even in sign. The extent to which the linear function is an approximation is not readily apparent from the data of Feakins and Watson[61], where only three points were available for each of the two extrapolations. However, when values for RbCl and CsCl are included in the plot of Equation 47, the assumption of linearity is shown to be very poor indeed.[34] Furthermore, values of $\Delta G°$ for the same ion derived alternately from Equation 46 and 47 may differ by up to 1.5 kcal/g-ion.[63] These must be the more important reasons why the results of Feakins and his co-workers differ drastically from those of Izmaylov (Table 4) even though the methods employed are fundamentally very similar. Thus, for anhydrous methanol, Feakins and his co-workers obtain positive values of log $_m\gamma$ for the halide anions, but negative values for the alkali metal cations and for the proton. Izmaylov's values of log $_m\gamma$ are positive for all these ions.

A major innovation in the extrapolation methods was introduced by DeLigny and Alfenaar.[34 39] In their formulation the $\Delta G°$ of an ion is the sum of an electrostatic part, $\Delta G°$ (el), and a neutral part, $\Delta G°$ (neut) *(cf.* Equation 38). A detailed discussion of this formulation was already given in Part II B (see page 84). For very large ions, $\Delta G°$ (el) is given by the Born equation (Equation 36) and is expected to vanish at $(1/r)=0$. On the other hand, $\Delta G°$ (neut) is thought to be a function of r^2 and would approach infinity as $1/r$ approaches zero. Consequently, extrapolations of measurable combinations of values of $\Delta G°$ to $(1/r)=0$ should be carried out only after subtraction of the $\Delta G°$ (neut).

We mentioned earlier that for the transfer of electrolytes from water to methanol, DeLigny and Alfenaar[39] assumed the Born equation to be a valid approximation of $\Delta G°$(el) for ions with $r > 10$ Å. Consequently, in the interval between $(1/r)=0$ and $(1/r)=0.1$, their extrapolations must be straight lines with the Born slope.

The authors estimated $\Delta G°$(neut) for alkali and halide ions in methanol from the measured values of $\Delta G°$ for the transfer of inert gases and other nonpolar solutes from water to methanol (Table 6) (*cf.* also Part II B (see page 84). Over wide ranges of methanol-water composition, the values of $\Delta G°$ for the inert solutes were linear functions of the mole fraction of methanol and could be interpolated for any solvent composition. The electrically neutral combinations of the values of ionic $\Delta G°$ were derived from the standard potentials of silver–silver halide electrodes and from those of the alkali-amalgam electrodes.

TABLE 6

Values of $\Delta G°$ for the Transfer of Some Nonpolar Solutes From Water to Methanol at 25°C (Cal/mole) (According to Alfenaar and DeLigny.[34])

Solute	$\Delta G°$
He	930 ± 20
Ne	1019 ± 20
Ar	1314 ± 20
Kr	1473 ± 70
Rn	2075 ± 70
CH_4	1667 ± 50
CCl_4	3912 ± 34
$Fe(C_5H_5)_2$	4360 ± 150
$Sn(CH_3)_4$	5380 ± 80
$Sn(C_2H_5)_4$	6803 ± 166

(Reprinted from *Rec. Trav. Chim.*, 86, 937, 1967, by permission of the Koninklijke Nederlandse Chemische Vereniging).

According to Alfenaar and DeLigny,[34] the $\Delta G°$ for a small ion *i* can be expressed as:

$$\Delta G_i^\circ = \Delta G_i^\circ(\text{neut}) + \frac{a}{r_i} + \frac{b}{r_i^2} + \frac{c}{r_i^3} + \ldots \qquad (48)$$

where ΔG_i°(neut) is set equal to the $\Delta G°$ of an uncharged solute of the same dimensions as the ion, r_i is the crystallographic radius of the ion, *a* is given by the Born equation, while *b, c,* etc. are empirical coefficients. The terms proportional to higher powers of $(1/r)$ are supposed to account both for the short-range ion-solvent interactions and for the expected difference between the neutral solvent-solute interaction of a small ion and a nonpolar molecule of the same size. On the basis of the above model, the solvation-energy change for the proton, ΔG_H°, was evaluated with the aid of the following two equations:

$$\Delta G_H^\circ + \Delta G_A^\circ - \Delta G_A^\circ\ (\text{neut}) = \Delta G_H^\circ + \frac{a}{r_A} + \frac{b}{r_A^2} + \frac{c}{r_A^3} + \ldots \qquad (49)$$

$$\Delta G^{\circ}_{\mathrm{H}} - \Delta G^{\circ}_{\mathrm{M}} + \Delta G^{\circ}_{\mathrm{M}}\,(\text{neut}) = \Delta G^{\circ}_{\mathrm{H}} - \frac{a}{r_{\mathrm{M}}} + \frac{d}{r^{2}_{\mathrm{M}}} + \frac{e}{r^{3}_{\mathrm{M}}} + \ldots \qquad (50)$$

where A is a halide ion and M is an alkali metal ion. The left-hand sides of Equations 49 and 50 can be calculated from experimental data if one accepts the "inert-gas assumption" for the estimation of the neutral components. On the right-hand sides, only a is known from the Born equation, whereas the other terms, including the sought quantity $\Delta G^{\circ}_{\mathrm{H}}$, are evaluated by the method of least squares. The extrapolations, which are reproduced in Figure 4, are long, nonlinear, and in some cases determined by too few points. Nevertheless, the highest uncertainty reported by the authors for the values of ΔG° is only about ±0.38 kcal/mole, corresponding to an uncertainty of ± 0.3 in $\log {}_{m}\gamma$.

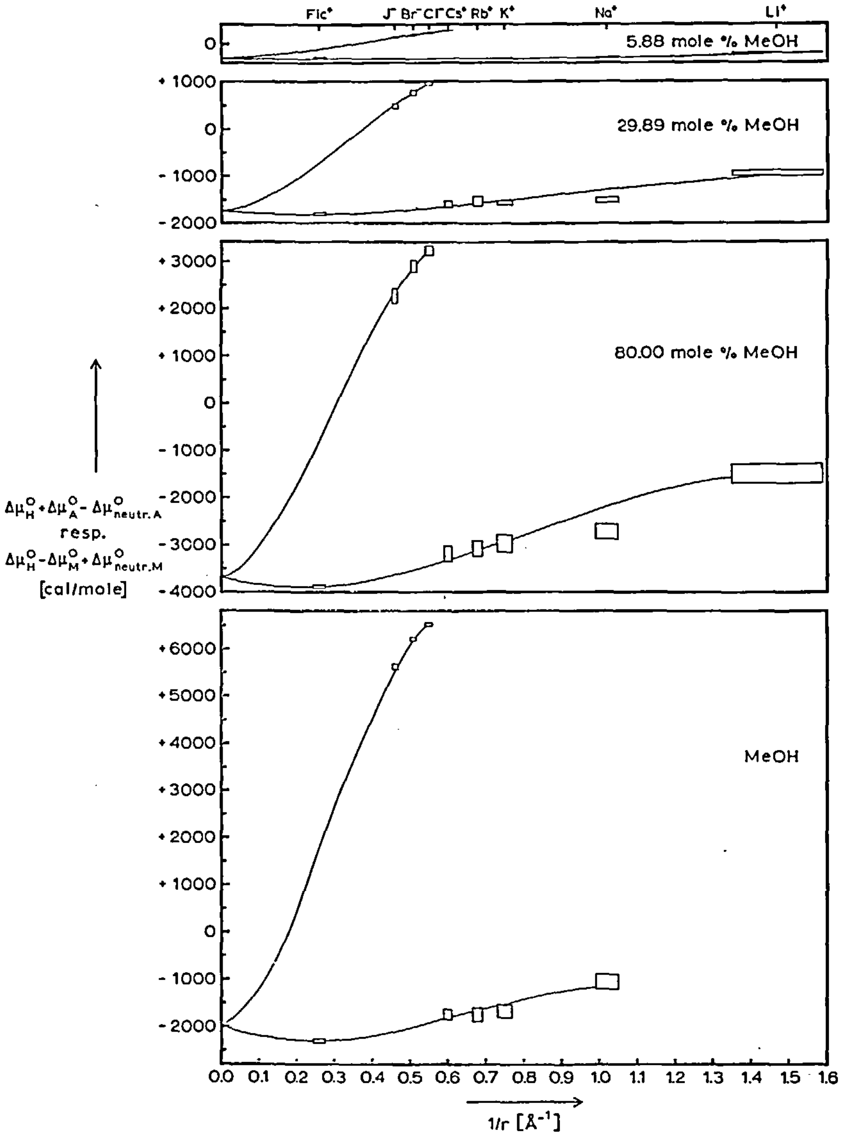
Values of $\log {}_{m}\gamma$ for individual ions and for their assumed neutral parts, $\log {}_{m}\gamma(\text{neut})$, were calculated from the corresponding values of ΔG° reported by the authors and are shown in Table 7. It is obvious that the neutral components of solvation-energy changes for ions are very significant and by no means amount to a minor correction. Therefore, the reliability of the model of DeLigny and Alfenaar depends primarily on the reliability of the "inert-gas assumption." The latter has not yet been proved.

Figure 5 reproduces the original plot of ΔG° *vs.* mole % methanol in water reported by Alfenaar and DeLigny.[34] We can see from Tables 8 and 9 that their results are in semiquantitative agreement with those of Feakins and his co-workers[62 63] to the extent that the medium effects obtained in both studies are negative for the alkali metal ions and for the proton and positive for the halide ions throughout the entire methanol-water range. Most other methods yield positive values for the medium effects of the above cations as well as anions in methanol (Table 11). Not many comparisons are available for methanol-water mixtures.

Thus, according to the medium effects reported by both Feakins et al. and by Alfenaar and DeLigny, the cations exist in a preferred (lower) energy state in all methanol-water solvents, as compared to water (${}_{s}G^{\circ}_{+} < {}_{w}G^{\circ}_{+}$), and the reverse is true for the anions. The preferential stabilization of cations in methanol-water solvents has been interpreted[61 65] as resulting from the inductive effect of the methyl group. The latter is believed to increase the electron density not only on the oxygen of the methanol molecule, but also on the oxygens of water molecules to which the methanol is hydrogen bonded. Solvation of cations is viewed here as being determined by the effectiveness of solvent oxygens as electron-pair donors. Presumably the same inductive effect destabilizes the solvation of anions by reducing the hydrogen-bonding ability of the solvent.

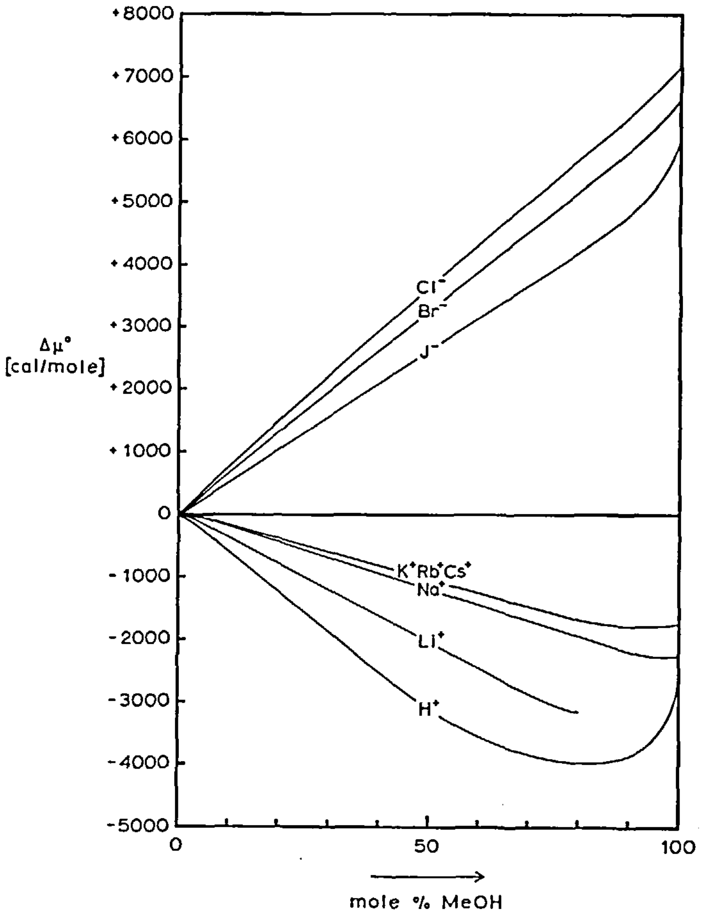
Another way of stating the above results is that all methanol-water solvents, including anhydrous methanol, are more basic than water—a conclusion which follows most directly from the negative values of $\log {}_{m}\gamma_{H}$ over the entire solvent range. The behavior of the medium effect for the proton in methanol-water solvents is of special interest to us because of its role in the interpretation of pH scales and acid-base equilibria in these solvents and because of its relation to the apparently unresolved controversy concerning the relative basicities of methanol and water. In Table 8 we show also the values of $\log {}_{m}\gamma_{H}$ estimated by Oiwa[32] from e.m.f. of cells with aqueous—non-aqueous liquid junctions and those calculated by us, somewhat arbitrarily, from the previously discussed data of Paabo, Bates, and Robinson.[45] In both sets of results $\log {}_{m}\gamma_{H}$ has small negative values in the water-rich regions, which decrease with increasing alcohol content to a minimum at about the mid-point of solvent composition in weight per cent and then rise to positive values in the alcohol-rich region. From analysis of the ΔpKs of weak acids of all types in methanol-water solvents, Bates and Robinson[66] concluded that addition of methanol to water does increase the basicity of the medium until a basicity maximum is reached at about 80 wt. % methanol. At higher methanol contents the basicity decreases sharply, thus confirming (in the opinion of Bates and Robinson[66]) previous literature claims that the methanol molecule is a weaker base than the water molecule. It is significant in this connection that the values of ΔpK of anilinium acids

FIGURE 4



Determination of the standard free energy of "transfer" of the proton, ΔG°_H, from water to methanol-water solvents by the extrapolation method of Alfenaar and De Ligny[34] (molal scale). (Reprinted from *Rec. Trav. Chim.*, 86, 945, 1967, by permission of the Koninklijke Nederlandse Chemische Vereniging).

FIGURE 5



Standard free energies of "transfer," $\Delta G°$, of individual ions from water to methanol-water solvents (mole-fraction scale). (Reprinted from Alfenaar and DeLigny,[34] *Rec. Trav. Chim.*, 86, 946, 1967, by permission of the Koninklijke Nederlandse Chemische Vereniging).

TABLE 7

Medium Effects for Single Ions ($\log {}_m\gamma_i$) and for their Neutral Components ($\log {}_m\gamma$(neut)) Estimated by the Inert-Gas Assumption at 25°C (According to Alfenaar and DeLigny[34])

	10.00 Wt % Methanol		43.12 Wt % Methanol		87.68 Wt % Methanol		100% Methanol	
Ion	$\log {}_m\gamma_i$	$\log {}_m\gamma$(neut)	$\log {}_m\gamma_i$	$\log {}_m\gamma$(neut)	$\log {}_m\gamma_i$	$\log {}_m\gamma$(neut)	$\log {}_m\gamma_i$	$\log {}_m\gamma$(neut)
Cl^-	+0.366	−0.049	+1.74	−0.25	+4.38	−0.67	+5.69	−0.84
Br^-	+0.290	−0.059	+1.55	−0.30	+4.03	−0.80	+5.31	−1.00
I^-	+0.240	−0.077	+1.23	−0.39	+3.30	−1.04	+4.56	−1.30
H^+	−0.214	–	−1.28	–	−2.70	–	−1.45	–
Li^+	−0.114	−0.037	−0.78	−0.19	−2.10	−0.51	–	–
Na^+	−0.020	−0.038	−0.38	−0.19	−1.22	−0.52	−1.34	−0.65
K^+	−0.021	−0.040	−0.35	−0.20	−1.06	−0.55	−0.90	−0.68
Rb^+	–	–	−0.38	−0.21	−1.00	−0.57	−0.89	−0.72
Cs^+	–	–	−0.35	−0.23	−0.96	−0.61	−0.94	−0.77

TABLE 8

Medium Effects for the Proton in Methanol-Water Solvents at 25°C

$\log {}_m\gamma_H$

Wt. % Methanol	Aleksandrov and Izmaylov[70]	Paabo, Bates, and Robinson[45]*	Oiwa[32]	Alfenaar and DeLigny[34]	Feakins, Tomkins, and Co-workers**	
10.0		+0.038		−0.21	−0.38[62]	−0.32[61]
20.0	+0.14	−0.068	−0.0205			
20.22					−0.69[62]	
30.0	+0.22					
33.4		−0.10			−1.44[62]	
40.0	+0.32		−0.105			
43.12				−1.28	−2.08[62]	−1.61[61]
50.0	+0.43	−0.11			−2.41[62]	
60.0	+0.52	−0.086	−0.179		−2.42[61]	
68.33					−3.44[62]	
70.0	+0.74	+0.053				
80.0	+0.95		−0.0306			
87.68				−2.70		
90.0	+1.45		+0.350		−4.00[62]	−4.18[61]
100.	+3.21			−1.45	−2.25[63]	−1.83[61]

*Calculated from their data on the assumption that $\Delta G^\circ_H = \Delta G^\circ_H(\text{el}) + \Delta G^\circ_b$.

**Converted to molal scale.

[($\Delta pK = p({}_sK) - p({}_wK)$)] become increasingly negative upon addition of methanol to water, reach a minimum close to 80 wt. % methanol, and then rise steeply to positive values in the anhydrous alcohol.[66] On the basis of their own as well as literature data, Alfenaar and Bates[67] confirmed this pattern specifically for the *p*-nitroanilinium ion (here the minimum in Δp*K* came at about 60-70 wt. % methanol), reporting at the same time that no such minimum was observed for methanol-propylene glycol solvents. Similarly, the Hammett acidity function $-H_0$ passes through a minimum in mixtures of water with methanol, ethanol, acetone, dioxane, and tetrahydrofuran[66] (*cf.* Figure 1). In all these mixtures the function $-H_0$ attains its minimum value (maximum solvent basicity) at approximately equimolar solvent composition and then rises steeply in the region of the anhydrous solvents. Again, no such minima are observed for mixtures of two organic solvents.[46] The following interpretation of this phenomenon was originated by Braude and Stern.[46] The effective basicity of highly structured liquid water is relatively low due to strong intermolecular hydrogen bonding. Addition of organic solvent to water brings about a gradual destruction of the water structure, thus exposing an increasing number of basic sites on the water molecules for bonding with protons. The effective basicity of the solvent reaches its maximum when the higher aqueous solvates $H^+(H_2O)_n$ are broken up and replaced by the H_3O^+ ions. This presumably corresponds to the minima in the $-H_0$ curves. In the region approaching the anhydrous non-aqueous solvent, the H_3O^+ ions are gradually replaced by the organic oxonium ions, which in the case of ROH_2^+ seem to be more acidic than H_3O^+ (or the medium is less basic than water). The overall conclusion by Braude and Stern[46] was that water is more basic in mixtures with other solvents than it is in the pure liquid state.

By now we have enough evidence to suspect that the characteristic behavior in alcohol-water solvents (*cf.* Figure 1 and discussion for the ethanol-water system) of 1) the "basicity effects" calculated by Paabo, Bates, and Robinson,[45] 2) the Δp*K*s of anilinium and ammonium acids, and 3) the $-H_0$ functions

TABLE 9
Medium Effects for Alkali and Halide Ions
In Methanol-Water Mixtures at 25°C
$\log_m\gamma_i$

Wt. % methanol	Li^+	Na^+	K^+
10	−0.26, −0.11[34]	−0.16, −0.020[34]	−0.16, −0.021[34]
20.22	−0.44	−0.26	−0.22
33.4	−1.07	−0.81	−0.73
43.12	−1.49, −0.78[34]	−1.06, −0.38[34]	−0.91, −0.35[34]
50	−1.70	−1.24	−1.08
68.33	−2.48	−1.81	−1.39
87.68	−2.10[34]	−1.22[34]	−1.06[34]
90	−3.10	−2.10	−1.23

Wt. % methanol	Cl^-	Br^-	I^-
10	0.49, 0.37[34]	0.45, 0.29[34]	0.40, 0.24[34]
20.22	0.91	0.82	0.76
33.4	1.79	1.64	1.41
43.12	2.54, 1.74[34]	2.32, 1.55[34]	2.02, 1.23[34]
50	2.94	2.70	2.36
68.33	4.29	3.99	3.48
87.68	4.38[34]	4.03[34]	3.30[34]
90	5.82	5.29	6.92

[34] Alfenaar and DeLigny.
The remaining data were taken from Ref. 62 and corrected to molal scale.

must be determined for all three phenomena by some single dominating property of the solutions. It was suggested earlier in this review that the determining property is almost certainly the medium effect for the proton, $\log {}_m\gamma_H$. The general relationship between $\log {}_m\gamma_H$ and the H_0 for a non-aqueous solution of acid HA at an analytical molality m_{HA} and with a degree of ionic dissociation α is

$$\log {}_m\gamma_H = -H_0 - \log m_{HA} - \log \alpha - \log {}_s\gamma_H + \log \frac{{}_s\gamma_{BH^+}}{{}_s\gamma_B} + \log \frac{{}_m\gamma_{BH^+}}{{}_m\gamma_B} \quad (51)$$

where ${}_s\gamma$ are the salt-effect activity coefficients and BH^+ and B are the acid and the base forms of the uncharged Hammett indicator. In any amphiprotic solvent the H_0 becomes equal to pa_H if the ratios of the salt effects and the medium effects for the indicator species become unity (when the last two terms on the right-hand side of Equation 51 become zero). If we have reason to believe that such a condition is *approximated* in a given solvent, we can at least estimate the magnitude of $\log {}_m\gamma_H$ (values for α and for ${}_s\gamma_H$ being generally unavailable or uncertain) in the form $(-H_0 - \log m_{HA})$. The salt-effect ratio $\frac{{}_s\gamma_{BH^+}}{{}_s\gamma_B}$ is usually assumed to deviate little from unity. Also, for a bulky organic conjugate acid-base pair, such as the indicators BH^+ and B, the neutral component of the medium effect for the BH^+ ion is expected to cancel approximately with $\log {}_m\gamma_B$.[5, 30] The electrostatic component of $\log {}_m\gamma_{BH^+}$ in methanol when calculated from the simple Born equation for an ion size of 2 Å is about unity, and it is practically zero when the modified Born equation with Strehlow's corrections to ionic radii is used. Thus, for alcohol-water solvents, the acidity function H_0 appears to be a reasonable approximation of pa_H to within an order of magnitude. Then, according to Equation 51, the term $(-H_0 - \log m_{HA})$ should represent a similar approximation of $\log {}_m\gamma_H$, although the true value of the latter would usually be more positive, because the terms $-\log \alpha$, $-\log {}_s\gamma_H$ and $\log {}_m\gamma_{BH^+}$(el) are all positive. Moreover, they should be increasingly more positive with increasing content of the organic solvent, and the corresponding deviations of $(-H_0 - \log m_{HA})$ from $\log {}_m\gamma_H$ should be increasingly more negative. This trend was indeed observed for ethanol-water solution in studies to be discussed later (Figure 6).

The relationship between $\log {}_m\gamma_H$ and the ΔpK of anilinium or ammonium acids is even simpler:

$$\Delta pK = \log {}_m\gamma_H - \log \frac{{}_m\gamma_{BH^+}}{{}_m\gamma_B} \qquad (52)$$

Since we are dealing here with the same acids which define the H_0 function, our previous conclusion about the cancellation of $\log {}_m\gamma_B$ with $\log {}_m\gamma_{BH^+}$(neut) still applies:

$$\Delta pK \cong \log {}_m\gamma_H - \log {}_m\gamma_{BH^+}(\mathrm{el}) \qquad (53)$$

In a compilation by Bell,[69] the ΔpKs of 13 ammonium and anilinium acids in methanol range from 0.8 to 1.6 with a mean of 1.2. Recalling that our estimates of $\log {}_m\gamma_{BH^+}$(el) for methanol were 0 and 1, respectively, we conclude that the medium effect for the proton in methanol should be somewhere between 1.2 and 2.2, a safe guess being the midpoint, $\log {}_m\gamma_H \cong 1.7$. In my opinion, this type of calculation based on the ΔpKs of anilinium and ammonium acids may represent a general method for estimating the *order of magnitude* of $\log {}_m\gamma_H$ in alcohol-water solvents and possibly also in other amphiprotic media of not too low dielectric constants. That knowing even the order of magnitude for $\log {}_m\gamma_H$ would be desirable is evident from Table 8, where the extreme estimates of $\log {}_m\gamma_H$ in methanol differ by almost 5.5 log units. If our conclusions about the relationship between $\log {}_m\gamma_H$ and the ΔpK of cationic acids are correct to within an order of magnitude, then the estimates according to which $\log {}_m\gamma_H$ in anhydrous methanol is negative (Table 8) are unreasonable, as they would require the electrostatic component of the medium effect for a sizeable ion, $\log {}_m\gamma_{BH^+}$(el), to assume large negative values. Also improbable is the value $\log {}_m\gamma_H = 3.21$, reported by Aleksandrov and Izmaylov.[70] In general, their estimates of the medium effect for the proton failed to reflect the basicity maximum characteristic of methanol-water solvents.

The original approach by which Aleksandrov and Izmaylov[70, 71] estimated the values of $\log {}_m\gamma_H$ over the entire range of methanol-water and ethanol-water solvents has a direct bearing on the already mentioned controversy concerning the relative basicities of water and of the alcohols. Their approach was based on the assumption that the classical methods of evaluating the relative basicities of water and other solvents by means of the so-called "proton-transfer constants," K_r, were indeed valid. K_r represents the equilibrium constant for the proton exchange between water and the alcohol, ROH:

$$\mathrm{ROH_2^+ + H_2O \rightleftarrows ROH + H_3O^+} \qquad (54)$$

(sometimes also written as the reverse of reaction 54). The constant K_r is derived from the changes in e.m.f., conductance, indicator, and catalytic measurements which result from addition of small amounts of water to a non-aqueous solution of a strong acid. Several comprehensive summaries of the results of these studies are available.[2, 13, 16] According to them, $K_r \simeq 100$ for methanol and ~ 250 for ethanol, indicating that water is more basic than the alcohols.

Izmaylov[70-72] formulated a medium effect for the ions of an acid as a composite of an electrostatic and a basic term:

$$(\log {}_m\gamma_H + \log {}_m\gamma_A) = 2\,(\log {}_m\gamma_{\mathrm{Basic}} + \log {}_m\gamma\,(\mathrm{el})) \qquad (55)$$

The basic component represents a difference between the proton affinity of an alcohol molecule and a water molecule, which ideally should be expressed in terms of the constant K_r for reaction 54 *in vacuo*. For practical reasons, however, Izmaylov assumed that the proton-transfer constant K_r determined in the corresponding mixed solvent could serve as a good approximation for the K_r *in vacuo*. Thus, the basic component was evaluated from the expression

$$\log {}_m\gamma_{\text{Basic}} \cong \tfrac{1}{2}\left(\log K_r + \log \frac{a^*_{H_2O}}{a^*_{ROH}}\right) \quad (56)$$

where the activities $a^*_{H_2O}$ and a^*_{ROH} are referred to an infinitely dilute solution of water in ROH and to the pure solvent ROH, respectively. Furthermore, the electrostatic term was assumed to be equally divisible between the proton and the anion. Consequently

$$\log {}_m\gamma_H = 2 \log {}_m\gamma_{\text{Basic}} + \log {}_m\gamma(\text{el}) \quad (57)$$

Several objections can be raised to this method. There is no *a priori* reason why the electrostatic term should be equal for the two ions, and there must be an error due to omission of the neutral terms as well. Also, it is difficult to agree that a K_r determined in a mixed solvent, where water is present in dilute solution and the alcohol as an almost pure liquid, could represent the relative proton affinities of the molecules of the two solvents. In their comprehensive review devoted to properties of alcohol-water solvents, Franks and Ives[65] categorically reject the use of K_r as an acceptable measure of relative proton affinities. In a polymerized, hydrogen-bonded liquid system, they contend, it may be neither possible nor meaningful to assign relative proton affinities to molecules of the two solvents which exist under each other's strong influence. Instead, the interaction of protons with the solvent should be considered in terms of the formation of complexes such as $[H_3O\ (ROH)_n]^+$. Franks and Ives also point out that conclusions opposite to those suggested by the values of K_r (*i.e.*, that alcohols are more basic than water) can be reached if one focuses on the decrease in the pK values of cationic acids upon addition of alcohol to water. Other studies where similar conclusions are drawn were cited by Bates.[2] From our previous discussion of the behavior of ΔpKs of cationic acids, the H_0 acidity functions, and the medium effects for the proton in alcohol-water solvents, we know that addition of alcohol to water does increase solvent basicity—up to the maximum—and that addition of water to alcohol accomplishes the same effect. However, it is incorrect to extrapolate from these observations to the proton affinities of the pure solvents. Moreover, we may have to draw a distinction between the relative proton affinities of the individual *molecules* of the two solvents and the relative basicities of the corresponding liquids. From two mass-spectrometric studies, the reverse of reaction 54 in the gas phase was reported to be exothermic by 14 kcal/mole[73] and 11 kcal/mole,[74] respectively. These enthalpy values were interpreted to represent the difference between the proton affinities of water and methanol *molecules in the gas phase*, with methanol being more basic. In the second of these studies,[74] however, it was further demonstrated that the preference for methanol on the part of the proton decreases with increasing number of the solvent molecules in a cluster, and that in marcroclusters, including liquid solutions, water is more basic than methanol. It follows from the above mass-spectrometric evidence that the proton-transfer constants K_r, derived from measurements in mixed solvents, do not express the true relative proton affinities of water and alcohol *molecules*. Izmaylov's[70-72] method for the determination of $\log {}_m\gamma_H$, which is based on the reverse assumption, is therefore unsound.

The considerable discrepancies among the results of the three extrapolation methods, which include many examples of disagreement in sign, do not inspire confidence. Nevertheless, it seems that the approaches of Izmaylov and of DeLigny and Alfenaar might be potentially sound, provided the dilemma of the neutral part of solvation energy is satisfactorily resolved. As it stands, the first approach ignores the neutral part altogether, and the second probably overestimates it. But even with that obstacle out of the way, the extrapolation methods will always face the analytically unfavorable task of evaluating a small difference between two uncertain solvation-energy values. It may be that their reliability will always be limited to comparisons between large solvation-energy differences, such as those encountered for strongly interacting ions in dissimilar solvents.

Empirical Assumptions for Reference Solutes

Assumption of Negligible Medium Effects

The difference between the standard potentials of an electrode in two solvents is determined by the corresponding difference between the solvation energies of the electrode components. Pleskov[11] reasoned that the rubidium ion, with its large radius, low charge and polarizability, and minimal tendency towards specific solvation, should have small solvation energies in all solvents and that their differences between pairs of solvents should be negligible. In our terminology, the medium effect for the rubidium ion would therefore approach zero in all solvents. On this basis, Pleskov assumed that the standard potential of the rubidium electrode could serve as a solvent-independent reference point for e.m.f. series in different media. Of course the rubidium ion is not nearly large enough (1.48 Å) to justify the above assumption, so that Strehlow and his co-workers[5 27 50] undertook to "correct" the rubidium model using the modified Born equation with adjustable ionic radii. The "corrections" turned out to be small (Table 10), which led Strehlow[5] to endorse the Pleskov assumption as a surprisingly good first approximation. This endorsement, however, depends implicitly on the acceptance of the modified Born equation. Qualitatively, the universal e.m.f. series based on rubidium as the reference does reflect the expected gross chemical effects, such as the considerable negative shifts of the hydrogen and the heavy-metal electrodes in basic media. Nevertheless, the contention that any solute could experience negligible changes in solvation energy upon transfer from water to a variety of solvents seems implausible as a generalization. In exceptional cases, however, such as for comparisons between pairs of very similar solvents, the assumption of negligible solvation-energy change cannot be ruled out. The recently proposed[8] "SN-transition state assumption" may represent such an exception.

Today, the significance of the rubidium method is largely historical, as it was the first bold step in the evolution of empirical approaches based on large solutes.

Assumption of Equal Medium Effects for Ion-Molecule Structural Analogs

In their search for improvements over the rubidium electrode as the solvent-independent reference point for e.m.f. series, Koepp, Wendt, and Strehlow[50] examined 18 metal-organic complexes in which the metal could exist in two adjacent oxidation states. Only the ferrocene-ferricinium and the cobaltocene-cobalticinium couples met the stringent requirements for a redox system whose potential could be reasonably expected to remain nearly independent of the solvent. Both complexes are large (for ferrocene $r = 3.8$ Å[34]), with the metal buried in the center of a spherical molecule. Their surface-charge densities are expected to be low, and specific interactions with solvents are expected to be at a minimum. The complexes do not change in structure in the course of the oxidation-reduction process. Moreover, the $0/+1$ charge type of these redox couples offers the advantage of relatively small changes in the electrostatic free energy of solvation. In contrast, for a redox couple of the $+2/+3$ charge type having the same radius, the Born equation predicts an electrostatic free-energy change greater by a factor of five. Any uncertainty in the electrostatic correction is likely to be multiplied too. Consequently, reference electrodes based on ion complexes of phenanthrolines (ferroins), which have found some limited application in the estimation of liquid-junction potentials [75 76] and of medium effects,[77] would seem to be disadvantageous on the basis of electrostatic considerations alone. Furthermore, it has been pointed out [51] that the open structure of the iron(II) and iron(III) complexes is conducive to specific interactions with the solvent.

The superiority of the ferrocene electrode (its cobaltocene analog is less popular because of instability in solution) over the rubidium electrode derives not only and not primarily from the larger size of the ferricinium ion. More important is the participation in solvation and transfer equilibria of the reduced form, the ferrocene molecule, which, being an excellent neutral analog of the ferricinium ion, provides a built-in counterbalance to the neutral part of the solvation-energy changes experienced by the ion. In an expression for the "transfer" of the redox couple ($Ox^+ + e = Red$) from water to a non-aqueous solvent, the medium effect for ferrocene, $\log {}_m\gamma_{Red}$, is opposite in sign with respect to the medium effect for the ferricinium ion $\log {}_m\gamma_{Ox}{}^+$ and is expected to cancel with the latter's neutral component, $\log {}_m\gamma_{Ox}{}^+$ (neut). The residual electrostatic component for the ion, $\log {}_m\gamma_{Ox}{}^+$ (el), should be small and subject to estimation. Thus, the solvent-independence of the potential of the ferrocene electrode is really based on the assumptions that $\log {}_m\gamma_{Red} = \log {}_m\gamma_{Ox}{}^+$ (neut) and that $\log {}_m\gamma_{Ox}{}^+ (el) = 0$. It is obvious that if the reduced form were not participating in the solvation processes (e.g., if it were to form an amalgam), the large size of the ferricinium ion alone would mislead us into completely erroneous conclusions about the magnitude of changes in its solvation energy and its electrode potential with the solvent.

On the assumption that the $E^\circ_{\text{ferrocene}}$ is indeed the same in water as in the non-aqueous solvent of interest, it is possible to refer the potential of the standard hydrogen electrode in that solvent to the aqueous scale from the measured e.m.f. of cell 58 in water, $E(H_2O)$, and in the solvent, $E(SH)$:

$$\text{Pt(s); } H_2 \text{ (g, 1 atm.), } H^+ \text{ (a = 1), ferrocene, ferricinium (1:1); Pt(s)} \qquad (58)$$

If $a_H = 1$ in both media:

$$E(H_2O) - E(SH) = {}_wE^\circ(H, SH) - {}_wE^\circ(H, H_2O) \qquad (59)$$

In Equation 59, ${}_wE^\circ(H, SH)$ is the potential of the SHE in the non-aqueous solvent SH, but referred to the SHE in water. The right-hand side of Equation 59 is a measure of the medium effect for the proton (*cf.* Equation 13). In Table 10 we list values of $\log {}_m\gamma_H$ calculated from the corresponding standard potentials ${}_wE^\circ(H, SH)$ reported by Strehlow.[5]

On the basis of e.m.f. measurements of cell 58, Strehlow and his co-workers[5] [78] defined an acidity "redox function," $R_0(H)$, where the subscript "0" refers to the charge on the ferrocene molecule, by analogy with the Hammett H_0 notation, and

$$R_0(H) = \frac{F}{2.303\,RT}\Big[E(x) - E(1)\Big] \qquad (60)$$

In Equation 60, $E(1)$ is the e.m.f. of an all-aqueous cell 58 containing a solution of unit hydrogen-ion activity, and $E(x)$ is the e.m.f. of the corresponding cell containing an unknown concentration of hydrogen ions in any solvent. If the unknown solution is non-aqueous, $R_0(H) = -\log a_H^* - \log {}_m\gamma_H$. The function $R_0(H)$ was shown to run parallel to the H_0 acidity function in $H_2SO_4 - H_2O$ mixtures, but the two did not coincide.[78] An R_0 function was similarly defined and used for the silver ion.[5]

It has been claimed[51] that both ferrocene and ferricinium ion may be involved in specific interactions with water, but the evidence offered to support this contention was not convincing. One argument was based on calculations of the free energy difference for the ferricinium ion in water and in acetonitrile using the modified Born equation with adjustable radii (the radius corrections used for the ferricinium ion were those of the alkali metal ions). However, it is an open question whether the modified Born equation is more reliable than the ferrocene assumption in the first place. The second argument, based on the discrepancy between the calculated shift in the ferrocene potential and the ratio of solubilities of ferrocene in water and acetonitrile, seems to be irrelevant since, as we pointed out above, the ferrocene assumption is based on the *cancellation* of $\log {}_m\gamma_{Ox}{}^+$ (neut) with $\log {}_m\gamma_{Red}$, the latter being determined by such a ratio of solubilities. The weak points of the ferrocene electrode lie elsewhere. Because of the low solubility of ferrocene in water and the instability of the ferricinium ion, the standard potentials of the ferrocene electrode are invariably approximated by the corresponding polarographic half-wave potentials. Those differ from the true standard potentials because of the presence of a supporting electrolyte in the polarographic cell and, at least theoretically, because the diffusion constants of ferrocene and ferricinium ions may be unequal. A more important drawback in the ferrocene electrode may be the residual electrostatic component of the ion. The ferricinium ion is not quite large enough (3.8 Å) to escape the problems of dielectric saturation even in water, so that the form of the Born equation to be used for its electrostatic-energy part is somewhat uncertain.

A long time before the introduction of the ferrocene electrode, the assumption that the medium effect for an uncharged molecule would cancel the neutral component of the medium effect for a structurally analogous ion was implicit in the formulation of the Hammett acidity functions. Although the *H* functions were not intended for the determination of medium effects of single ions, we have shown before (Equation 51 and discussion) that in those media where H_0 approximates pa_H it also represents a fair measure of log $_m\gamma_H$. According to Strehlow,[5] this is not true of the H_- function. The required cancellation here is between the medium effect for an uncharged acid HA and the neutral component of the medium effect of its conjugate base A^-, which leaves the residual log $_m\gamma_A$(el). The latter, however, turns out to be quite appreciable, in contrast to the vanishingly small values of log $_m\gamma_{BH^+}$ (el), which we discussed in connection with methanol-water solvents. According to Strehlow,[5] log $_m\gamma_A$(el) in ethanol is about 4.4. Thus, while the H_0 function may be useful as an approximate measure of log $_m\gamma_H$ in alcohol-water solvents, the H_- function seems to be far from it. Of course, all Hammett indicators are susceptible to greater specific interactions with solvents than the well-shielded ferrocene-ferricinium pair and should therefore be inherently less reliable than the ferrocene electrode.

The most recent addition to the arsenal of ion-molecule pairs of assumed equal medium effects is the iodine-triiodide couple proposed by Parker and Alexander.[8] Although the proponents of this method concede that differences in both specific solvation and in size are involved in the $I_2 - I_3^-$ pair, they stress that it is easy to use in a variety of solvents.

Assumption of Equal Medium Effects for Ions of a Reference Electrolyte

The next logical step in the evolution of methods based on large solutes was to eliminate even the small residual electrostatic component of the medium effect, which contributed to the uncertainty inherent in the ferrocene and the Hammett assumptions. Instead of "transferring" one large ion and its molecular analog from water to a nonaqueous solvent, the improvement consists of transferring an electrolyte composed of large symmetrical ions as similar in size and structure as are available. The assumption is that for such a "reference electrolyte,"[9] if properly selected, the medium effects could be apportioned equally between the anion and the cation. The criteria for choosing such reference ions are very similar to those used for the selection of reference redox couples. Preferably, the ions should be very large and effectively spherical, with the central atom and the charge shielded by large organic groups. This should minimize both surface

TABLE 10
Medium Effects for the Proton Based on the Assumptions of Pleskov, Strehlow, and Hammett
log $_m\gamma_H$ *

	Pleskov[11]		Strehlow[5]		Hammett
Assumption	Rubidium	Modified Born eq.	Ferrocene	Cobaltocene	H_0 function[27]
Methanol	0.3	0.07	−0.3	−0.3	0.3
Acetonitrile	4.2	2.3	2.4	2.6	1.8, 4.0[5], 5.0[5]
Formic acid	9.0	8.1	—	—	4.8
Formamide	–	1.2	−2.5	−2.4	0.7

*Converted to molal scale.

charge density and specific interactions with solvents. Moreover, the solvent structure around ions of this type would be very nearly the same as around a neutral molecule of equal dimensions. The effect of dielectric saturation should be small, and the various short-range solvent-solute interactions, including those which differentiate between smaller anions and cations of equal size, should be negligible. In fact, the medium effects for ions of this type are expected to be determined overwhelmingly by the neutral components, while there are reasons to believe that the electrostatic components may be calculable from the simple Born equation.

The first such "reference electrolyte," employed in a study[43] of solvation-energy changes in dioxane-water mixtures, was tetraphenylphosphonium tetraphenylborate ($Ph_4P\ BPh_4$). Later, I proposed tri*iso*amyl-*n*-butylammonium tetraphenylborate (TAB BPh_4),[9] based on the demonstrated equality of its Stokes radii in methanol,[79] water,[80] and, eventually, acetonitrile.[81] Most recently, Alexander and Parker[7] chose tetraphenylarsonium tetraphenylborate ($Ph_4As\ BPH_4$). Presently, the application of all three of these "reference electrolytes" is being studied in our laboratory. It appears that the ions chosen do conform to the criteria set down for them. Moreover, the slight solubilities of these electrolytes in alcohol-water solvents facilitate determination of their effects from solubility measurements (Equations 22, 23) without any major uncertainties in the correction for activity coefficients. Unfortunately, in dipolar aprotic solvents their solubilities are higher, which means that the determination of the ion-activity products of the "reference electrolytes" might become a task more formidable than most researchers would care to undertake.

Objections to the estimation of single-ion medium effects with the aid of the reference-electrolyte assumption focus on the following weaknesses: 1) there is insufficient evidence for the equality of the radii of the counterions, and the Stokes radii are not ideal indices of ion sizes;[51] 2) formation of crystal solvates is possible;[8] 3) methods based on splitting the medium effects of an electrolyte equally between its counterions may be inapplicable in dipolar aprotic solvents, which solvate anions much more poorly than cations;[51] and 4) there may be NMR[53] and other[82] evidence for specific interactions of the reference ions with solvents. There is no denying that our knowledge of the sizes of these reference ions is inadequate. Grunwald, Baugham, and Kohnstam[43] assign an average radius of 4.2 Å to the Ph_4P^+ and BPh_4^- ions and one of 4.05 Å to their "neutral analog," the tetraphenylmethane molecule. On the other hand, Coetzee and Cunningham[61] estimated from models an effective radius of 4.8 Å for the BPh_4^- ion. Finally, if one interpolates from a figure in a publication by Friedman,[82] the radii of both the BPh_4^- and the Ph_4As^+ ion are around 5.5 Å. Clearly, we need more direct experimental determinations of the sizes of the large tetraalkyl and tetraaryl ions. In the absence of such data, the equality of Stokes radii was used in the selection of TAB BPh_4[9] as an approximate guide to equal sizes and solvation numbers. The constancy of the Stokes radii for these ions in several solvents[81] seems to speak against major differences in their relative solvation. An encouraging finding in support of some of our choices of the reference ions is the fact that, within experimental error, $\log {}_m\gamma_{Ph_4As} = \log {}_m\gamma_{Ph_4P}$ for ethanol-water solvents as well as for acetontrile.[83] This suggests that the solvent-solute interactions for these ions may be determined primarily by the four phenyl groups (*i.e.*, by their neutral components) and that neither the small difference in size expected to accompany the change from phosphorus to arsenic, nor any specific solvent interactions with the central atom, plays a perceptible role here. This apparent independence of the medium effect of the nature of the central atom raises our confidence in the validity of at least two reference-electrolyte assumptions, namely, that $\log {}_m\gamma_{Ph_4As} = \log {}_m\gamma_{BPh_4}$ and that $\log {}_m\gamma_{Ph_4P} = \log {}_m\gamma_{BPh_4}$. Furthermore, it could mean that tetraphenylmethane represents an acceptable neutral analog for all three tetraphenyl ions, an idea which has received support in the past.[7 8 43] The formation of crystal solvates on the part of the reference electrolytes seems improbable in the media where their solubility is very low, and it is hard to see how it could represent an appreciable component of a solvation-energy change dominated by the neutral interaction. Nevertheless, such danger cannot be ruled out, especially for the more soluble systems, and experimental evidence must be sought to resolve this problem. If necessary, corrections for the formation of crystal solvates may have to be incorporated in the calculation of the medium effects from solubility products (Equation 25). The argument of differentiation between anions and cations on the part of dipolar aprotic solvents is based on the behavior of small ions. Whether or not it is applicable to the large organic reference ions, whose interaction with solvents seems to approach that of structurally similar uncharged molecules, is not known at this time. My guess is that the differentiation cannot be appreciable. I am not familiar with the nature of the NMR evidence for specific solute-solvent interactions on the part of the reference ions. Interpretation of NMR shifts in terms of solvation-energy changes is no simple matter, but there is no question that comprehensive NMR studies of the solutes of reference ions should be high on the agenda in this field.

Medium effects for single ions in methanol were determined by Popovych[9] with the TAB BPh_4 assumption and by Alexander and Parker[7] with the Ph_4As BPh_4 assumption. Both sets of results are compared with other literature data in Table 11. The agreement between the results obtained by the two reference-electrolyte methods is predictably good, although it is not definitive because Alexander and Parker used formal (concentration) solubility products rather than thermodynamic ion-activity products. Omission of the degree of ion pairing and of activity coefficients in the calculation of K_{sp}s in non-aqueous solvents may have had some justification in the work of Alexander and Parker, who were interested primarily in comparisons among similar organic solvents and used methanol, rather than water, as the reference medium for their "solvent activity coefficients." However, when comparisons of solubility products are made between water and organic solvents, the expedient of equating formal solubilities to mean ionic activities can easily lead to errors of several tenths of a unit in log $_m\gamma$, and we have encountered cases where this discrepancy approached an order of magnitude.[84] Izmaylov's results in methanol agree reasonably well with those obtained by the reference-electrolyte methods for some ions but disagree seriously for others. This is due to internal inconsistencies within Izmaylov's results, which we demonstrated elsewhere.[9] The individual ionic medium effects from the TAB BPh_4 assumption are internally consistent because their electrically neutral combination yield numerical values which are observed experimentally. Otherwise, Table 11 illustrates perfectly the state of controversy characteristic of the field today.

Medium effects for ions in acetonitrile were estimated by the Ph_4As BPh_4 assumption both by Alexander and Parker[7] and by Popovych[83] (Table 12). In the latter study, the Ph_4P BPh_4 assumption was also applied, and the results based on the two electrolytes agreed to 0.01 log units. Again, the use of formal concentration products by Alexander and Parker undoubtedly underlies some of the disagreements between the two studies. Errors due to omission of activity corrections must be especially serious for the potassium ion, where the pK_{sp} of KCl both in water and in methanol enters the calculation. For acetonitrile solutions, activity coefficients were estimated by us[83] from the Debye-Hückel equation with ion-size parameters.

A comprehensive study of medium effects in ethanol-water solvents was carried out by Popovych and Dill.[10] For electrolytes, the medium effects were calculated from ion-activity (solubility) products[84] and from literature values of standard potentials of the silver–silver chloride electrodes (*cf.* Equation 26). For individual ions, they were derived by the following sequence of calculations:

$$\log {}_m\gamma_{TAB} = \log {}_m\gamma_{BPh_4} = \tfrac{1}{2} \log {}_m\gamma_{TAB\ BPh_4}$$

(the "TAB BPh_4 assumption") (61a)

$$\log {}_m\gamma_{K} = \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{BPh_4} \qquad (61b)$$

$$\log {}_m\gamma_{Cl} = \log {}_m\gamma_{KCl} - \log {}_m\gamma_{K} \qquad (61c)$$

$$\log {}_m\gamma_{H} = \log {}_m\gamma_{HCl} - \log {}_m\gamma_{Cl} \qquad (61d)$$

TABLE 11

Medium Effects, log $_m\gamma$, in Methanol at 25°C

Method	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+
				log $_m\gamma$			
Pleskov, Rb electrode[11]	0.3	–	–	–	0.0	–	−0.3
Strehlow, modified Born eq.[5]*	0.07	–	−0.40	−0.12	−0.06	0.01	–
Izmaylov, $1/_n{}^2$ extrapol.[59]	3.1	1.6	1.8	2.0	2.8	2.7	3.5
Popovych, TAB BPh_4 assumption[9]	1.85	–	–	1.80	0.89	–	0.78
Alexander and Parker, Ph_4As BPh_4 assumption[7]*	–		–	1.7	–	1.4, 1.3	1.2
Alfenaar and DeLigny[34]	−1.45	–	−1.34	−0.90	−0.89	−0.94	–
Andrews et al.[63] (method of Feakins and Watson[61])*	−2.25	−2.89	−2.23	−1.57	–	–	–

Method	Cl^-	Br^-	I^-	Pi^-	TAB^+	BPh_4^-
Pleskov, Rb electrode[11]	3.7	–	–	–	–	–
Strehlow, modified Born eq.[5]*	4.00	3.53	2.96	–	–	–
Izmaylov, $1/_n{}^2$ extrapol.[59]	1.0	1.0	0.0	–	–	–
Popovych, TAB BPh^4 assumption[9]	2.08	–	–	0.95	−4.30	−4.30
Alexander and Parker, Ph_4As BPh_4 assumption[7]*	1.9	1.5	0.3,0,9	−1.2	–	−4.2
Alfenaar and DeLigny[34]	5.69	5.31	4.56	–	–	–
Andrews et al.[63] (method of Feakins and Watson[61])*	6.18	5.80	5.04	–	–	–

*Corrected to Molal Scale

$TAB^+ = C_{19}H_{42}N^+$ $BPh_4^- = (C_6H_5)_4B^-$ Pi^- = Picrate

TABLE 12

Medium Effects, log $_m\gamma$, in Acetonitrile at 25 °C

	Izmaylov[59]	Coetzee et al. Ref. (6)	Coetzee et al. Ref. (20)	Alexander and Parker[7a]	Popovych[83]	Kolthoff and Thomas[77]
H^+	5.5					5.1
Li^+	1.8		6.76			
Na^+	2.5		4.90			
K^+	1.4	3.2	3.38	3.4	0.7	
Rb^+	1.6		2.87			
Cs^+	1.1		2.54	2.7		
Ag^+	−3.0			$-4.2^{b,c}$		−6.7
Cl^-	8.0	5.6		8.3	7.4	
Br^-	5.0	3.7		5.8	5.5	
I^-	2.3	1.4		3.4	3.2	
NO_3^-		1.8				
SCN^-		0.8		3.3		
ClO_4^-		−1.4				
(Picrate)$^-$		−2.6		−1.1	−0.8	
$Ph_4As^+ = BPh_4^-$				−5.8	−5.5	

[a] Converted to molal scale [b] I_3^- - I_2 assumption [c] log $\gamma_{SN} = 0$ assumption

Medium effects are properties at infinite dilution and can therefore be added and subtracted (in logarithmic form) in the same manner that is used for limiting equivalent conductances.

Values of log ${}_m\gamma$ in ethanol-water solvents for all ions except the proton are shown in Table 13. In Table 14, literature values from the more extensive studies in anhydrous ethanol are intercompared. A positive log ${}_m\gamma$ indicates that the ion exists in a higher energy state in the non-aqueous solvent than in water (${}_sG^\circ > {}_wG^\circ$). In ethanol-water solvents the monatomic ions K^+ and Cl^- experience a continuous rise in log ${}_m\gamma$ (as a result of a rise in ${}_sG^\circ$) with increasing ethanol content, as would be predicted qualitatively from the Born equation on the basis of the decreasing dielectric constant of the medium. In fact, up to 60 wt % ethanol, the values of log ${}_m\gamma_K$ estimated by the TAB BPh_4 assumption agree fairly well with those calculated by us earlier[48] from a modified Born equation (Table 2). The opposite trend with changing solvent composition is observed for the large organic reference ions. Their solvation energy decreases continuously with increasing ethanol content, reflecting the dominating contribution of the neutral component to the overall free-energy changes. For example, for the transfer of an electrolyte composed of ions 4 Å in size from water to ethanol, the simple Born equation predicts a medium effect of +1.7 (log units). The observed medium effect for TAB BPh_4 in ethanol is −7.6. Evidently, log ${}_m\gamma$ (neut) for the electrolyte could amount to −9.3, which supports our earlier contention that the interaction of the reference ions with solvents is predominantly nonelectrostatic in nature.

TABLE 13

Medium Effects for Single Ions in Ethanol—Water Solvents at 25 °C (According to Popovych and Dill.[10])

log ${}_{\bar{m}}\gamma$

Wt % ethanol in water	TAB^+ $= BPh_4$	$(Picrate)^-$	K^+	Cl^-
100.0	−3.80	−0.16	2.84	3.28
90.0	−3.69	−0.24	2.00	2.72
80.0	−3.48	−0.30	1.31	2.31
70.0	−3.26	−0.27	0.83	2.12
60.0	−2.96	−0.22	0.44	1.93
50.0	−2.50	−0.18	0.20	1.65
40.0	−2.00	0.00	0.10	1.29
30.0	−1.30	0.10	0.11	0.87
20.0	−0.69	0.17	0.09	0.51
10.0	−0.30	0.10	0.08	0.19

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Values for the medium effects of the proton, log ${}_m\gamma_H$, estimated by the TAB BPh_4 assumption over the entire ethanol-water range, are shown in Table 15 and in Figure 6. They are negative in ethanol-water mixtures containing 10 to 98 wt % ethanol and pass through a

TABLE 14

Medium Effects, log ${}_m\gamma$, in Ethanol at 25° C

Assumption or Method	Bjerrum and Larsson[15] $E_j = 0$	Izmaylov[59] $1/n^2$ extrapolation	Popovych and Dill[10] $TAB^+ = BPh_4^-$
H^+	2.5	3.9	1.85
Li^+	2.8	2.9	–
Na^+	3.5	4.2	–
K^+	4.1	4.0	2.84
Rb^+	3.9	4.6	–
Cs^+	4.0	3.8	–
Ag^+	2.1	3.7	–
Cl^-	2.5	1.2	3.28
Br^-	1.8	1.2	–
I^-	1.4	0.8	–
$TAB^+ = BPh_4^-$	–	–	−3.80

$TAB^+ = C_{19}H_{42}N^+$ $BPh_4^- = (C_6H_5)_4B^-$

TABLE 15
Medium Effects for the Proton, $\log_{m}\gamma_{H}$, in
Ethanol—Water Solvents at 25°C

Wt. % ethanol in water	Popovych and Dill[10]	Gutbezahl and Grunwald[19]*	Aleksandrov and Izmaylov[70]
10.0	−0.06	—	0.090
20.0	−0.26	−0.006	0.175
30.0	−0.50	—	—
35.0	—	0.017	—
40.0	−0.82	—	—
50.0	−1.03	0.211	—
60.0	−1.14	—	—
65.0	—	0.485	—
70.0	−1.00	—	—
72.0	—	—	0.873
80.0	−0.74	1.077	—
88.5	—	—	1.50
90.0	−0.51	—	—
93.5	—	—	1.86
95.8	—	—	2.14
98.0	~+0.2	—	2.45
100.0	+1.85	4.603	4.05

*Converted to molal scale

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minimum at 60 wt %. Between 98 and 100%, log $_{m}\gamma_{H}$ experiences a steep rise of about 1.6 log units. Thus, ethanol-water mixtures in the 10-98 wt % range are more basic than either of the pure solvents (negative values of log $_{m}\gamma_{H}$) and exhibit a basicity maximum at 60 wt % ethanol. This parallels very closely the behavior of log $_{m}\gamma_{H}$ and of the related functions, such as H_0 and the ΔpKs of cationic acids in methanol-water solvents, discussed in detail earlier. We will also recall that the appearance of a minimum at about the midpoint of solvent composition is characteristic of the $-H_0$ functions in mixtures of water with organic solvents in general. In Figure 6 a comparison is made between estimates of log $_{m}\gamma_{H}$ obtained by the TAB BPh$_4$ assumption (circles) and their counterparts approximated from the H_0 acidity function in the form $(-H_0 - C_{HCl})$ (solid curve). The two sets of estimates are in very good agreement up to 60 wt % ethanol, after which the function $(-H_0 - C_{HCl})$ exhibits the predictable increasing negative deviation from log $_{m}\gamma_{H}$ (*cf.* Equation 51). This deviation results from the omission of the terms $-\log \alpha, -\log {}_{s}\gamma_{H}$, and $+\log {}_{m}\gamma_{BH^+}$ (el) inherent in the approximation of log $_{m}\gamma_{H}$ by the function $(-H_0 - C_{HCl})$. The difference between the molality m and the molarity C plays a negligible role here. When numerical values for $-\log \alpha$ and $-\log {}_{s}\gamma_{H}$ are included in the calculation of log $_{m}\gamma_{H}$ for anhydrous ethanol (the most unfavorable case for a comparison of the two approximations), the estimate of log $_{m}\gamma_{H}$ rises from about 0.4 to 1.0*. Considering that log $_{m}\gamma_{BH^+}$ (el) for anhydrous ethanol should be somewhere between 0 and 1.7 (see below), this leads to fair

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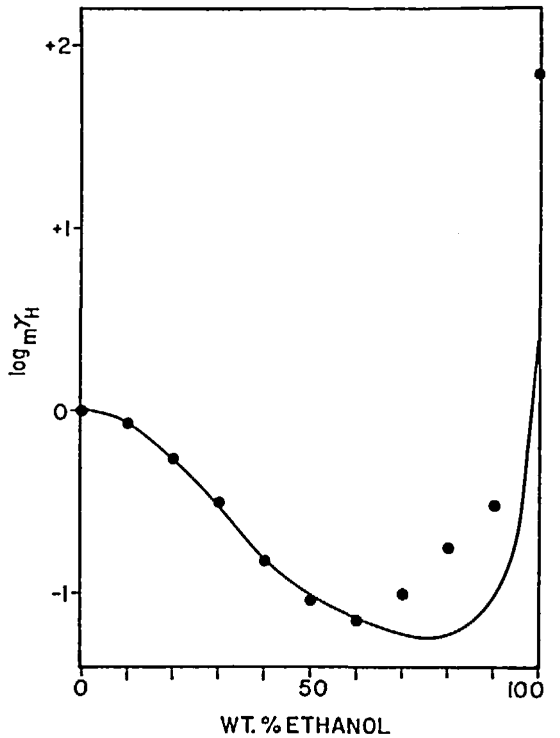
*The value of 1.5 (instead of 1.0) reported by us earlier[48] appears to be in error. In the present calculation, use is made of the definitive data of Taniguchi and Janz (*J. Phys. Chem.*, 61,688, 1957), on the basis of which the activity coefficient for 0.0951 M HCl in ethanol $y_{\pm HCl} = 0.264$ (molar scale). Because the latter already contains the degree of dissociation of HCl, α, and the concentration of HCl in the data plotted in Figure 6 is on the molarity scale, the corresponding value of log $y_{\pm HCl} = 0.6$ was used directly as an estimate of the quantity $(-\log {}_{s}\gamma_{H} - \log \alpha)$ in Equation 51.

FIGURE 6



Medium effects for the proton in ethanol-water solvents. The solid curve represents ($-H_0 - C_{HCl}$) from the data of Braude and Stern.[46] Circles are values of log $_m\gamma_H$ estimated by Popovych and Dill[10] via the TAB BPh$_4$ assumption. (Reprinted from *Anal. Chem.*, 41, 461, March 1969. Copyright (1969) by the American Chemical Society. Reprinted by permission of the copyright owner.

agreement with the value of 1.85 derived via the TAB BPh$_4$ assumption. It is noteworthy that up to 50 wt % ethanol the medium effects shown in Figure 6 also agree with those obtained by us on the basis of calculated medium effects for the potassium ion, discussed earlier.[48] These are shown in Figure 1 and Table 2. Furthermore, preliminary results obtained in our laboratory with the aid of the Ph$_4$As BPh$_4$ and the Ph$_4$P BPh$_4$ assumptions[85] yielded very nearly the same values for log $_m\gamma_H$ in ethanol-water solvents as did the TAB BPh$_4$ assumption. Thus, in the estimation of single-ion medium effects in the ethanol-water system, we have encountered a truly rare situation for this field where agreement has been observed among five different methods: the TAB BPh$_4$, Ph$_4$P BPh$_4$, and Ph$_4$As BPh$_4$ assumptions, the H_0 function, and a calculation from a modified Born equation (the last only up to 50 wt % ethanol). Furthermore, by invoking the relationship between the Δp*K*s of cationic acids and the log $_m\gamma_H$ (Equations 52 and 53), it is possible to demonstrate that the medium effects derived by the above methods are at least of the correct order of magnitude. The values of ΔpK for 12 ammonium and anilinium acids in ethanol compiled by Bell[69] range from 0.6 to 1.5 with a mean of 1.0. According to Equation 53, log $_m\gamma_H$ should be more positive than Δp*K* by the magnitude of log $_m\gamma_{BH^+}$(el)—the electrostatic component of the medium effect for the acid BH$^+$ in ethanol. When estimated from the simple Born equation for an assumed ion size of 2 Å, the latter is equal to about 1.7 log units, and, according to Strehlow's calculation with a modified Born equation, it is negligible altogether.[5] If we choose the midpoint between these extreme estimates, the medium effect for the proton in ethanol is predicted to be 1.85. The perfect agreement between this estimate and the value of log $_m\gamma_H$ obtained by the TAB BPh$_4$ assumption is undoubtedly fortuitous, but it is nevertheless gratifying.

In Table 15 the medium effects for the proton in ethanol-water mixtures derived from the TAB BPh$_4$ assumption are compared with those obtained by two independent methods specific to the proton. The results of Aleksandrov and Izmaylov[70] were obtained by the method based on the use of proton-transfer constants, K_r, which they also applied to methanol-water solvents (Table 8). We analyzed their approach at some length in connection with studies in methanol-water solvents (*cf.* Equations 55-57 and their discussion) and came to the conclusion that it was unsound. This verdict is corroborated by the nature of their results for ethanol-water solvents as well. Values of log $_m\gamma_H$ estimated by Aleksandrov and Izmaylov fail to reflect the well established maximum of solvent basicity for ethanol-water solvents (which they also failed to do for methanol-water solvents). In addition, their orders of magnitude seem to be incorrect if we accept the reasoning based on values of Δp*K* for cationic acids, which in ethanol would place the value of log $_m\gamma_H$ somewhere between 1.0 and 2.7. The estimates of log $_m\gamma_H$ from another original method—that of Grunwald and his associates[18] [19]—are in fair agreement with those of Aleksandrov and Izmaylov throughout the ethanol-water range and would seem to be incorrect for exactly the same reasons.

Stated briefly, the approach of Grunwald and his associates is based on the assumption that the Δp*K*s of acids in ethanol-water solvents obey the following relationships:

$$\Delta pK\,(\mathrm{HA}) = \log {}_m\gamma_\mathrm{H} + \bar{m}_\mathrm{HA}\, Y_- \qquad (62)$$

$$\Delta pK\,(\mathrm{BH}^+) = \log {}_m\gamma_\mathrm{H} + \bar{m}_{\mathrm{BH}^+}\, Y_0 \qquad (63)$$

where $\bar{m}$ is a function of acid structure but is independent of the solvent, while Y is a function of the solvent and of the charge type, but not of the acid structure. Through comparison with Equation 52, we identify $m_\mathrm{HA}\ Y$ as $\log ({}_m\gamma_{\mathrm{A}^-}/{}_m\gamma_\mathrm{HA})$ and $\bar{m}_{\mathrm{BH}^+}\ Y_0$ as $\log ({}_m\gamma_\mathrm{B}/{}_m\gamma_{\mathrm{BH}^+})$. It is clear from these identities that a division of the medium-effect ratios of the conjugate acid-base pairs in the manner postulated by Grunwald and co-workers is artificial. If for the sake of discussion we focus on Equation 53, which is a simplified equivalent of Equation 63, and also recall the simple Born estimate of $\log {}_m\gamma_\mathrm{H}$ (Equation 37), then a ratio of medium effects such as $\log ({}_m\gamma_\mathrm{B}/{}_m\gamma_{\mathrm{BH}^+})$ reduces to $-\log {}_m\gamma_{\mathrm{BH}^+}(\mathrm{el})$, which could be envisioned formally as the product of a solvent parameter (a dielectric-constant term) and an acid parameter (a radius term). However, the solvent parameter would have to be the same for all charge types, so that a differentiation between Y_- and Y_0 could not be accommodated. Values of $\log ({}_m\gamma_{\mathrm{BH}^+}/{}_m\gamma_\mathrm{B})$ in ethanol calculated from Grunwald's results by Bates[3] are higher by 2-3 orders of magnitude than the inverse of these ratios for uncharged acids $\log ({}_m\gamma_{\mathrm{A}^-}/{}_m\gamma_\mathrm{HA})$. These relative values are in direct opposition to the results of Strehlow's and our own calculations, according to which the first ratio should be very small, perhaps negligible, while the second should be greater than 4.

Some typical applications of $\log {}_m\gamma_\mathrm{H}$ can be illustrated if, for the sake of this discussion, we accept their numerical values estimated for ethanol-water solvents by the TAB $\mathrm{BPh_4}$ assumption. According to these results, in most ethanol-water mixtures a solution of given pa_H^* has a higher pa_H (Equation 11), *i.e.*, it is less acidic than a solution of the same nominal pH in water. The reverse is true for solutions in anhydrous ethanol, which for a given pa_H^* have a pa_H lower by 1.85 units. Using Equation 13, we can express the potential of a SHE in any ethanol-water solvent on the aqueous scale with the aid of values of $\log {}_m\gamma_\mathrm{H}$. For anhydrous ethanol, the value of ${}_wE^\circ$ $(\mathrm{H, C_2H_5OH})$ turns out to be 0.11 volts. Thus, all conventional E°s in ethanol become more positive by 0.11 volts when referred to the aqueous SHE. An interesting use of $\log {}_m\gamma_\mathrm{H}$ is in the estimation of liquid-junction potentials at the aqueous—non-aqueous boundaries in pH cells. Such an application is illustrated in Table 16.

TABLE 16
Liquid-Junction Potentials Between 3.5 *M* Aqueous KCl Bridge and Buffers in Ethanol—Water Solvents at 25 °C
(According to Popovych and Dill.[10])

Wt. % ethanol in water	$(\bar{E}_j - \log {}_m\gamma_\mathrm{H})^{21}$	$\log {}_m\gamma_\mathrm{H}$ (interpolated)	$\bar{E}_j$ pH units	Millivolts
0.0	0.000	0.00	0.00	0
16.2	0.003	−0.17	−0.17	−10
33.2	0.086	−0.61	−0.52	−31
52.0	0.221	−1.06	−0.84	−50
73.4	0.196	−0.93	−0.73	−43
85.4	−0.032	−0.64	−0.67	−40
100.0	−2.91	+1.85	−1.06	−63

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CONCLUSIONS

Throughout this review we have been critically evaluating the various existing methods for the estimation of medium effects for single ions. Our evaluations are scattered throughout the text and it is not easy for a reader to arrive at an overall assessment of the status of this field. To facilitate such an assessment, our more important conclusions, which doubtless include a good measure of subjective judgment, are compiled below:

1. The methods of Aleksandrov and Izmaylov,[70 71] of Grunwald and his coworkers,[18 19] and those which assume negligible liquid-junction potentials[8 15] appear to be unsound.
2. Methods based on the assumption of negligible medium effects for an ion (rubidium,[11] SN- transition state[8]) may be applicable in exceptional cases, but must be unsound as generalizations.
3. The extrapolation methods of Izmaylov[56–59] and of DeLigny and Alfenaar[34 39] are probably valid *in principle*, but are handicapped operationally by the present uncertainty concerning the evaluation of the neutral component of the solvation energy. The linear extrapolations of the Feakins school[61–64] appear to be an oversimplification. Extrapolation methods will always be limited in accuracy because of the necessity to determine small differences between pairs of uncertain solvation-energy values.
4. The simple Born equation seems to be an acceptable expression for the electrostatic component of the solvation energy of a very large ion. Modified Born equations without adjustable parameters are presently limited in application to mixed solvents where aqueous solvation can be presumed. The modified Born equations with empirical corrections to ionic radii are in the moot category. The implicit omission of the neutral term is one of their weak points.
5. Orders of magnitude for the medium effect of the proton can be estimated in amphiprotic media from the values of ΔpK of large cationic acids or, less reliably, from the H_0 function.
6. For more accurate estimates of medium effects, my first choice is the "reference electrolyte" method, and my second, the ferrocene electrode, with a suitable correction for the residual electrostatic component.
7. One of the most promising and urgently needed experimental approaches for progress in this field is the study of the neutral component of solvation energy by means of structural ion-molecule analogs.
8. Ultimately, we hope to be able to compare the results of the various empirical methods with those calculated from statistical-mechanical models for solvation energies on the theoretical side and with measured single-electrode potentials on the experimental side. However, to speculate on the probabilities of such developments is beyond the scope of this review.

SUMMARY

A medium effect is a measure of the difference between the free energy of a solute in its non-aqueous and its aqueous standard states. Medium effects for single ions enable us to formulate universal, solvent-independent scales for ion activities and electrode potentials referred to aqueous standard states and to evaluate liquid-junction potentials at aqueous–non-aqueous interfaces. Most existing methods for the estimation of medium effects for single ions are based on certain theoretical predictions about the relationship between the size and the solvation energy of solutes. Included here are calculations using modified Born equations, extrapolations to infinite ionic radii, assumptions of the solvent-independence of certain electrodes reversible to large "ideal" ions, the Hammett acidity functions, and the assumption that for suitable "reference electrolytes" the medium effect can be apportioned equally between its ions. A less common approach is to neglect the liquid-junction potentials at aqueous–non-aqueous interfaces. There are also two methods specific for the proton. All methods are critically evaluated and intercompared.

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