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New considerations of the Barclay–Butler rule and the behavior of water dissolved in organic solvents

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Abstract

The Barclay–Butler (B-B) rule, which states that a linear relationship exists between the standard ΔH_{vap} and ΔS_{vap} for simple, non-associated liquids and their solutions, has been used to distinguish associated ('abnormal') liquids from simple ('normal') liquids. The exact character of the B-B plots depends on the standard states chosen for the liquid/solution and vapor. We examine the effects of using number density for both vapor and liquid states for pure liquids, non-aqueous solutions, aqueous solutions and solutions in which water is the solute. The utility of B-B plots to detect solute-induced order is strengthened, and we also find remarkable changes in the modified B-B relationship: (1) the points for small, H-bonded liquids, including water, are pulled below the general B-B line; (2) many solutions containing small, simple solutes have *negative* entropies of vaporization; and (3) solutions of water in several organic solvents, relevant to studies of proteins and micelles, appear 'abnormal'.

Keywords: Thermodynamics of solution transfer; Entropy of vaporization; Solvent structure; Solvation; Enthalpy–entropy compensation

1. Introduction

It is well over 60 years ago since Barclay and Butler [1] pointed out that a linear relationship exists between the standard enthalpy and entropy changes (ΔH_{vap} and ΔS_{vap}) accompanying the vaporization of simple, non-associated pure liquids at a given temperature. The transfer of most solutes from simple, non-associated solvents to the vapor phase also gives standard enthalpy and entropy changes that fall on the Barclay–Butler (B-B) line. Frank [2] has pointed out that this behavior must reflect important aspects common to all simple liquids, and it is almost certainly related in some way to Trouton's and Hildebrand's rules. The Barclay–Butler rule is also probably one of the earliest recognitions of the empirical phenomenon now commonly referred to as enthalpy–entropy compensation (see Sharp [3] for a good review and explanation). A typical plot is shown in Fig. 1.

In general, the ΔH_{vap}, ΔS_{vap} points for associated liquids do not fall on the B-B line evinced by simple liquids. Often a different linear relationship is obtained for non-simple liquids and for many solutes in a given non-simple liquid solvent. Frank

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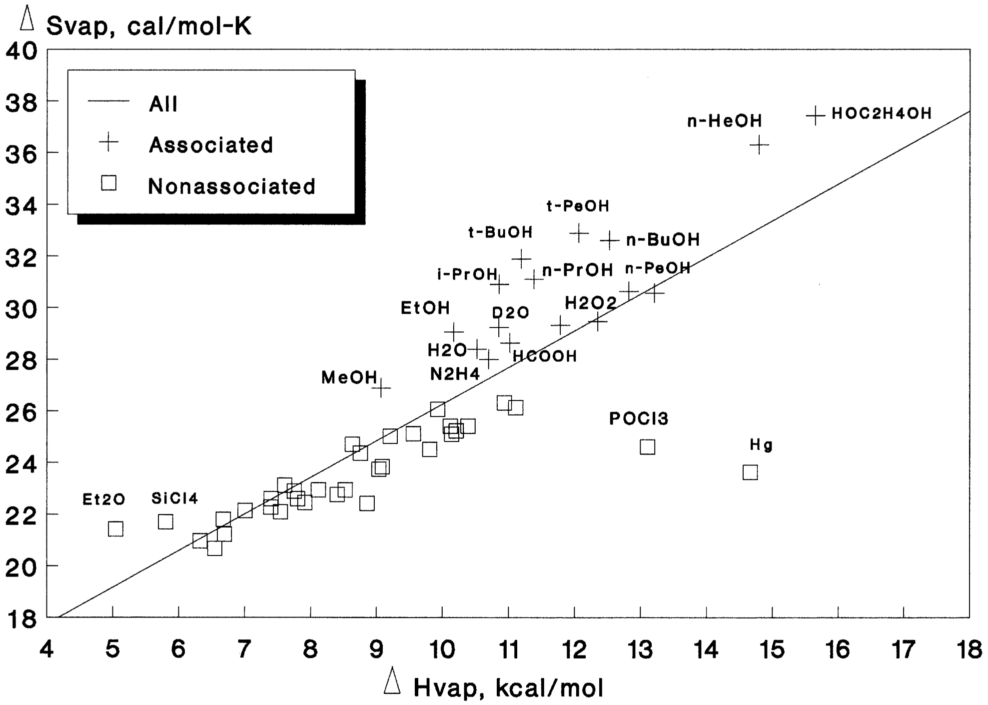

Fig. 1. Original Barclay–Butler (B-B) plot for pure liquids based on unit mole fractions.

[2] and Frank and Evans [4] pointed out that solvents and solutions could be classified as 'normal' (non-associated) or 'abnormal' (associated) on the basis of such plots. If ΔS_{vap} is plotted as the ordinate, then, in general, associated liquids, such as water and the lower alcohols and solutions in which they are solvents, give points that tend to fall above the normal B-B line.

Frank and Evans [4] showed that the deviation is particularly striking for aqueous solutions and proposed that non-electrolyte solute molecules increase the structure of the neighboring water, forming what they referred to as 'icebergs' (later more commonly called 'cages' or clathrate-like structures). Such analysis was instrumental in the early understanding of hydrophobic hydration.

The character of the B-B plots must depend to some degree on the choice of standard states employed for both the vapor and solution. Barclay and Butler [1] and Frank [2] used as the standard states a hypothetical mole fraction of unity for the solute in the solution, and unit total pressure for the solute in the vapor at 25 °C. Indeed, Frank claimed that it is necessary to use a mole fraction basis for the liquids in order to make valid comparisons among solvents and solutions [2].

Ben-Naim [5–7] has, however, criticized the use of this common choice as the standard state for solutions in general. He points out that what we really seek in understanding a solute's environment, and the attendant solvent–solute interactions, is evaluation of the free energy change (and the various thermodynamic derivatives thereof) for the hypothetical transfer process:

$$S \rightarrow K \tag{I}$$

in which a single (solute) molecule is transferred from a *fixed location and orientation* in some phase S (which might be the pure solvent, but which could also be any solution of given composition) to phase K (typically the vapor or another solvent), also in a *fixed* location and orientation. If the solute molecule possesses internal degrees of rotation (conformations), then the conformation must be fixed as well [7]. Henceforth, when we refer to a fixed position, it should be taken to mean both fixed location and orientation (and conformation, if appropriate). Ben-Naim referred to the quantities derived from such a process as local standard quantities of transfer [5–7]. To complete the transfer process and make it correspond with physical reality, the fixed solute is then released from its fixed position and allowed to move and rotate about the liquid or vapor. Obviously, referring to fixed positions is only allowable in terms of classical statistical mechanics; but there is little error in ignoring quantum effects for most solutions ordinarily encountered [5–7].

Making certain assumptions, Ben-Naim proved that, within the realms of classical statistical mechanics, the free energy change for the above hypothetical transfer step would be correctly given if the concentration units were based on number density values (i.e. molar concentration) in both phases [5–7]. Moreover, he showed that the use of number density leads to greater theoretical and practical utility, as the results obtained therefrom apply to all solutions, regardless of concentration or degree of ideality, and no reference to physically unreal or hypothetical standard states is necessary. Solution compositions described in terms of mole fractions can be valid for finding the desired free-energy change if the solution (or solutions) involved is either symmetrically ideal or regular [6]. But this situation is rare in practice and would not be the case, for instance, if the solvent and solute molecules differ appreciably in size and/or in the type and strength of their intermolecular forces.

Most of Ben-Naim's presentations of his argument have been simplified by dealing only with spherical, structureless solute molecules, possessing, for instance, no rotational degrees of freedom. He does mention in [6,7] that, in order to generalize to non-spherical solute molecules, the transfer process he describes should properly entail fixed orientation and conformation, as well as fixed location. We find that, particularly when discussing solutions involving water, it is quite helpful pedagogically to expand and generalize Ben-Naim's assumptions and derivations. As can then be demonstrated, Ben-Naim's method clearly offers, in the opinion of the present authors, unique theoretical advantages for probing the solvation properties of liquids.

Generalizing Ben-Naim's procedure to include non-spherical, polyatomic molecules, we derive a simple expression for the molar-based chemical potential of transfer and apply it to the vaporization process. Readily available solubility and vaporization data have been recalculated using standard states based on molar concentrations in order to determine their effect on the enthalpy and entropy of vaporization and the appearance of the original B-B plots.

In addition, we have applied the Barclay–Butler approach to the rarely considered but interesting solutions of water in various simple, 'normal' solvents. Perhaps contrary to expectation, we find these solutions to be 'abnormal', in that many of them yield points well above the normal B-B line. Furthermore, these solutions form their own new lines that intersect the B-B line and have steeper slopes. These results may have significance for the behavior and interactions of water molecules inside globular proteins and micelles. (See, for instance, Wade et al. in [8].)

2. Generalizing Ben-Naim's use of molar concentrations

As we noted, in the interests of clarity, Ben Naim [5–7] based his discussion on a system containing N_A molecules of A and N_B molecules of B, both of which he takes to be 'simple, spherical, structureless molecules'. He writes the classical canonical partition function as:

$$Q(T,V,N_\mathrm{A},N_\mathrm{B}) = \frac{q_\mathrm{A}^{N_\mathrm{A}} q_\mathrm{B}^{N_\mathrm{B}}}{N_\mathrm{A}!N_\mathrm{B}!\Lambda_\mathrm{A}^{N_\mathrm{A}}\Lambda_\mathrm{B}^{N_\mathrm{B}}} Z(N_\mathrm{A},N_\mathrm{B}) \tag{1a}$$

where

$$Z(N_\mathrm{A},N_\mathrm{B}) = \int \cdots \int \mathrm{d}\mathbf{R}_\mathrm{A}\mathrm{d}\mathbf{R}_\mathrm{B}\exp\left[-\beta\, U(\mathbf{R}_\mathrm{A},\mathbf{R}_\mathrm{B})\right] \tag{1b}$$

where q_A and q_B are the internal partition functions of single A and B molecules, respectively, and Λ_A and Λ_B are the reciprocals of the momentum partition functions resulting from the integration over all possible momenta of single molecules of A and B. $U(\mathbf{R}_A,\mathbf{R}_B)$ is the total potential energy of interaction among all molecules in the mixture at some particular configuration, the vector $\mathbf{R}_A$ denoting the $3N_A$ position coordinates of the centers of mass of the A molecules, and similarly for the vector $\mathbf{R}_B$. In the simplest case, Ben-Naim assumed that q_A and q_B are constant, which is not to say constant with respect to temperature or pressure, but with respect to the surroundings of A and B. If assigned 'constant' in this manner, the q values consequently cancel out during any isothermal–isobaric transfer process.

An important physical possibility is, however, obviously disregarded in writing Eq. (1a) and Eq. (1b). The 'internal partition functions' q_A and q_B, as written, include the electronic, rotational and vibrational partition functions of A and B (assumed polyatomic), and therefore include the intramolecular vibration frequencies of the A and B molecules. Suppose that either or both of A and B contain hydroxyl groups. It is well known that the O–H stretch frequency strongly depends on the hydrogen bonding arrangements and environments in which these molecules might be involved [9].

For instance, in water there is a shift of approximately 500 cm^{-1} in the O–H stretch frequency in going from the vapor (isolated water molecules) to ice (completely hydrogen-bonded molecules) [10]. Such a frequency shift produces a change in zero-point energy of approximately 3140 J mol^{-1}, which is comparable with RT at room temperature. Thus, the vibrational partition function associated with such a frequency shift would be modulated by a variable factor that could be as large as approximately 3.5 for each O–H as the solvent and solute molecules were moved and rotated in evaluating the integral in Eq. (1b). Clearly, we are not justified in treating q_A and q_B as 'constants' that can be taken out of the integral in writing Eq. (1a). Instead, we might be tempted to regard q_A and q_B as functions of *all* of the molecular coordinates, $q_A(\mathbf{R}_A,\mathbf{R}_B)$ and $q_B(\mathbf{R}_A,\mathbf{R}_B)$, and include them as part of the integrand in Eq. (1b). (Of course, this would be a bastardized way of combining quantum statistics with classical statistics—hardly a rigorous procedure for applying statistical mechanics to the problem. Yet plausible reasons can be given for justifying such an approach to an extremely complex situation.)

In addition, it is clear that, in going to non-spherical molecules such as water, we must include molecular orientation coordinates (e.g. Euler angles) as components of the vectors $\mathbf{R}_A$ and $\mathbf{R}_B$ in the integral in Eq. (1b). The result of these considerations is that, instead of commencing with Eq. (1a) and Eq. (1b), we must start with the following, more general expression:

$$Q(T,V,N_A,N_B) = Z(N_A,N_B)/(N_A!N_B!\Lambda_A^{N_A}\Lambda_B^{N_B}\Gamma_A^{N_A}\Gamma_B^{N_B}) \tag{2a}$$

$$Z(N_A,N_B) = \int\cdots\int d\mathbf{R}_A d\mathbf{R}_B \Pi\, exp\left[-\beta\, \mathrm{U}(\mathbf{R}_A,\mathbf{R}_B)\right] \tag{2b}$$

$$\Pi = \text{product over all molecules} \quad \left[q_{A_i}(\mathbf{R}_A,\mathbf{R}_B)q_{B_j}(\mathbf{R}_A,\mathbf{R}_B)\right] \quad \text{i of A and j of B.} \tag{2c}$$

The internal partition functions, q_A and q_B, now contain only the electronic and intramolecular vibration partition functions, the rotational partition function being separated out. Moreover, the q values may or may not depend on the environment in which the molecules find themselves. The new quantities, Γ_A and Γ_B, introduced for purposes of emphasis and clarity, are analogous to the momentum partition functions and result from integration over the angular momenta of single A and B molecules. In general, Γ is equal to $(2\pi kT)^{3/2}(I_xI_yI_z)^{1/2}/\sigma h^3$, where the I variables represent the molecules' moments of inertia, and σ is the symmetry number or factor (e.g. 2 for water) [11].

Generalizing to polyatomic, non-spherical molecules, which, by their very nature, reduce the likelihood of having ideal or regular solutions, in no way changes the conclusion that the proper concentration unit to use in setting up the standard states appropriate to the process Eq. (I) is the number density. The only change we must make in our interpretations is that we base them on Eq. (2a), Eq. (2b) and Eq. (2c) rather than Eq. (1a) and Eq. (1b).

Given the equations of (1) and (2), Ben-Naim [5] showed how the chemical potential of a molecule in a solution containing N_A molecules of A and N_B molecules of B can be written in the following form, which we generalize to include non-spherical molecules as:

$$\mu_A = kT\ln\left(\rho_A\Gamma_A\Lambda_A/8\pi^2\right) - kT\ln q_A - kT\ln\left\langle \exp\left[-B_A(R_A)/kT\right]\right\rangle \qquad (3)$$

where $B_A(R_A)$ is the binding energy of one A molecule, at R_A, to all the other molecules of the system at some specified configuration, and ρ_A is the number density of A. Ben-Naim [5–7] refers to the last term as the work (binding or coupling energy) required to add a molecule of A in a fixed location and orientation to a given concentration of A and B molecules [that is, either of the states K or S in the process in Eq. (I)]. He then goes on to combine the last two terms of Eq. (3) into what he calls a pseudo-chemical potential, μ_A' such that:

$$\mu_A = \mu'_A + kT\ln\left(\rho_A\Gamma_A\Lambda_A/8\pi^2\right) \qquad (4)$$

μ_A' is not a real chemical potential, because it does not contain a $kT\ln\rho_A$ term, nor is it a measurable quantity. However, differences in μ_A' are real and measurable—as we see below [5–7].

The second part of μ_A in Eq. (4) was labeled by Ben-Naim as the 'liberation free energy' [5–7]; it comes about when the added molecule of A is allowed to move about the whole system volume, V, and rotate over the full orientation space, $8\pi^2$.

For the transfer of a molecule of A from phase S to phase K, the change in the chemical potential is thus:

$$\Delta\mu_A = \mu_A^K - \mu_A^S = \mu'^K_A - \mu'^S_A + kT\ln\left(\rho_A^K/\rho_A^S\right) \qquad (5a)$$

$$= \Delta\mu'_A + kT\ln\left(\rho_A^K/\rho_A^S\right) \qquad (5b)$$

At equilibrium for the transfer of a solute molecule A from a solution of A in B (or A) to the vapor of A, we have:

$$\Delta\mu'_A = \mu'^v_A - \mu'^l_A = kT\ln\Phi \qquad (6)$$

where the superscripts v and l indicate vapor and liquid, respectively, and Φ is the Ostwald absorption coefficient [normally defined as the ratio of the molar concentration (number density) of the solute in the liquid and in the vapor at equilibrium]. The Ostwald coefficient essentially is a true equilibrium constant (partition coefficient) and, as such, is theoretically preferred for describing solutions.

We see that ΔH_{vap} and ΔS_{vap}, being temperature derivatives of $\Delta\mu_A'$, are experimentally, in fact, the temperature derivatives of the product of temperature and the logarithm of the Ostwald absorption coefficient. They are the more appropriate values to use when analyzing the vapor transfer process, because they directly reflect the environment of the transferred particle in its fixed position and do not require a physically unreal, hypothetical, or arbitrary standard state of, for instance, unit mole fraction of A surrounded by all B molecules, or unit molality [5,6].

2.1. Conversion of experimental data

The standard enthalpy and entropy of solution transfer processes (in our case, vaporization) for both pure solvents and solutions are most often calculated from data reported in either mole fractions or molality as the concentration units. As vapor and solvent have quite different volumes and coefficients of thermal expansion at the same temperature and pressure, corrections are required to convert ΔH^x_{vap} and ΔS^x_{vap} and ΔH^m_{vap} and ΔS^m_{vap} (values obtained using mole fractions and molality, respectively) to ΔH^M_{vap} and ΔS^M_{vap} (values obtained using molarity data) appropriate to the process in Eq. (I).

In their most general form, whereby solutions of any concentration can be accurately dealt with, the complete corrections for converting mole fraction- and molality-based transfer quantities to molarity-based quantities require the density, ρ (in g cm^{-3}), coefficient of thermal expansion, α, and either the 'average molecular weight' ($\langle M\rangle = x_1M_1 + x_2M_2$, where x and the subscripts 1 and 2 have their usual meanings) of the saturated solution and its temperature dependence, or the actual molality, m, of the saturated solution and its temperature dependence, all at T and P (typically 25 °C and 1 atm). Information of this kind is almost never available from compiled tables or reviews and often must be estimated from original sources.

It is understood that the solute in its saturated solution is in equilibrium with its saturated, partial pressure, the total pressure above the solution being 1 atm. This means that, for a gaseous solute at temperature T, its partial pressure is 1 atm minus the partial pressure of the solvent, while for a solute that is a liquid or solid at T, its partial pressure is that of the pure compound (neglecting solution non-idealities) at T. Thus, we have, assuming the vapors are ideal gases:

$$\Delta H^{\mathrm{M}}_{\mathrm{vap}} - \Delta H^{\mathrm{x}}_{\mathrm{vap}} = RT(\alpha T - 1 + T\,\mathrm{d}\ln\langle M\rangle/\mathrm{d}T) \tag{7a}$$

$$\Delta H^{\mathrm{M}}_{\mathrm{vap}} - \Delta H^{\mathrm{m}}_{\mathrm{vap}} = RT\Big[\alpha T - 1 + \big(TM_2/1000\big) \times \big(\mathrm{d}M/\mathrm{d}T\big)/\big(1 + mM_2/1000\big)\Big] \tag{7b}$$

$$\Delta S^{\mathrm{M}}_{\mathrm{vap}} - \Delta S^{\mathrm{x}}_{\mathrm{vap}} = R(\alpha T - 1 + T\,\mathrm{d}\ln\langle M\rangle/\mathrm{d}T - \ln(1000\rho) + \ln\langle M\rangle) \tag{7c}$$

$$\Delta S^{\mathrm{M}}_{\mathrm{vap}} - \Delta S^{\mathrm{m}}_{\mathrm{vap}} = R\Big[\alpha T - 1 - \ln(RT) - \ln\rho + \ln(1 + mM_2/1000) + \big(TM_2/1000\big)\big(\mathrm{d}M/\mathrm{d}T\big)/(1 + mM_2/1000)\Big] \tag{7d}$$

where $\mathrm{d}/\mathrm{d}T$ denotes the temperature derivative at constant total P, but not constant partial pressure or composition, both of which change as the temperatures changes.

Fortunately, for pure liquids and very dilute solutions, it is readily shown that the corrections simplify to:

$$\Delta H^{\mathrm{M}}_{\mathrm{vap}} - \Delta H^{\mathrm{x}}_{\mathrm{vap}} = \Delta H^{\mathrm{M}}_{\mathrm{vap}} - \Delta H^{\mathrm{m}}_{\mathrm{vap}} = RT(\alpha_0 T - 1) \tag{8a}$$

$$\Delta S^{\mathrm{M}}_{\mathrm{vap}} - \Delta S^{\mathrm{x}}_{\mathrm{vap}} = \Delta S^{\mathrm{M}}_{\mathrm{vap}} - \Delta S^{\mathrm{m}}_{\mathrm{vap}} = R\Big[\alpha T - 1 - \ln\big(RT/V_0\big)\Big] \tag{8b}$$

where V_0 and α_0 are the molar volume and coefficient of thermal expansion, respectively, of the pure solvent at T and P. Care must be taken that the value of R used in $\ln(RT/V_0)$ matches the units of V_0.

It should be noted here that, by virtue of having constant-volume (1l) and constant-pressure (1 atm) conditions for both the liquid and ideal vapor, there is no PV work done during our defined vaporization process. Thus, the $\Delta H^{\mathrm{M}}_{\mathrm{vap}}$ we calculate is really the energy of vaporization, $\Delta E^{\mathrm{M}}_{\mathrm{vap}}$, and we immediately recognize why the RT term is always subtracted from both $\Delta H^{\mathrm{x}}_{\mathrm{vap}}$ and $\Delta H^{\mathrm{m}}_{\mathrm{vap}}$ above. This result highlights one of the advantages, in terms of theoretical treatments of liquids and solutions, gained when using molarity (number density).

3. Results and discussion

3.1. Pure liquids

In order to observe the effects of changing from mole fraction to molarity concentration units on the Barclay–Butler rule, we have applied the corrections of Eq. (8a) and Eq. (8b) to a total of 53 pure liquids at 25 °C.

Only a few of Frank's [2] original data points have been used. Instead, we have drawn upon data compiled in the 13th edition of *Lange's Handbook of Chemistry* [12] and *The Thermodynamics of Organic Compounds* [13]. All additional information (viz. α_0 and V_0 at 25 °C) needed to convert from a mole fraction to a molarity basis was taken from either the references just mentioned or from *Organic Solvents* [14]. We note in passing that some of our converted entries for pure liquids differ somewhat from those of Ben-Naim and Marcus [15], who calculated the number density-based vaporization quantities for a myriad of pure liquids directly from the temperature dependence of the liquids' density and vapor pressure. We also mention here that all the figures are plotted using kcal mol^{-1} and cal mol^{-1} K^{-1} for the enthalpy and entropy, respectively, because the original graphs in [1,2,4] were plotted that way. Conversion to units using SI joules simply requires multiplication by 4.184. For a tabulation of much of the data graphed in this paper, see [16].

Fig. 1 is the usual B-B plot using mole fraction unity as the concentration unit for the liquid (i.e. the standard state is the pure liquid) and the partial

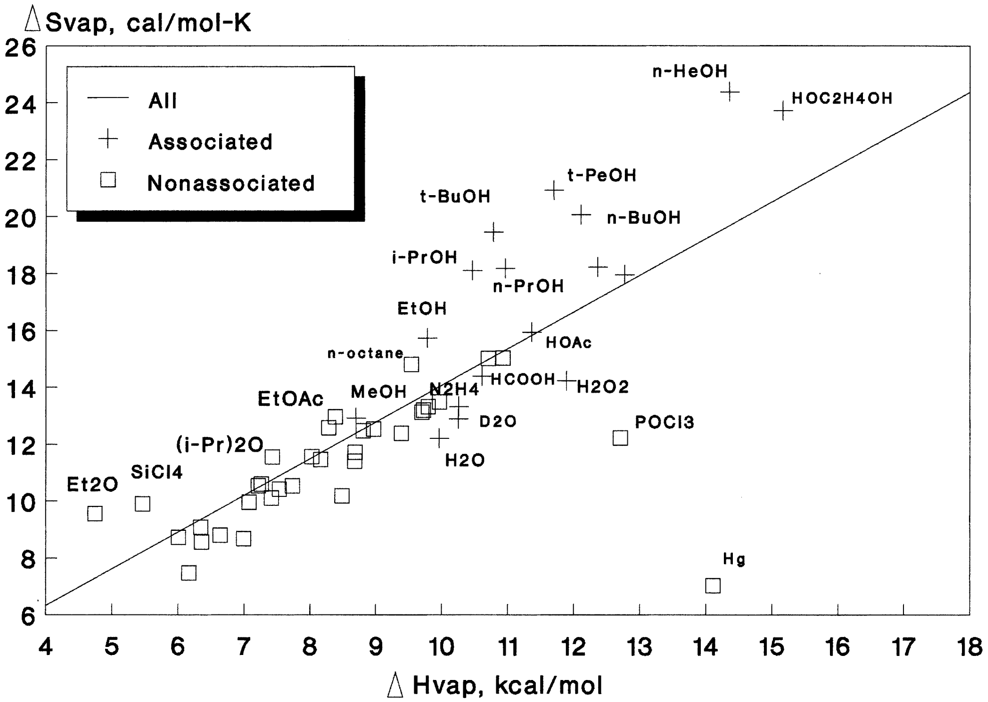

Fig. 2. Modified B-B plot for pure liquids based on number density.

pressure of the vapor at 1 atm as the standard state for the vapor. Fig. 2 is the B-B plot employing molarity at 1 atm as the concentration unit in both the vapor and liquid (i.e. inverse Ostwald absorption coefficient), in accordance with the recommendation of Ben-Naim [5–7]. Clearly, because the concentration units have been changed, and the whole 'liberation entropy' removed as a consequence, the ΔS_{vap} values in Fig. 2 are considerably lower than those in Fig. 1.

It is perhaps highly significant that the modified B-B line in Fig. 2, determined as a least-squares fit of all 53 points, extrapolates very close to the origin, with a slope not much greater than 1. But is this not exactly what we should expect in the process Eq. (I), though, if the energy of vaporization were zero? For if no energy is required to remove a molecule in a fixed location and orientation from a liquid and bring it to a fixed location and orientation in a vapor, then it is likely that there will be little, if any, overall attendant change in entropy.

The use of molar concentrations certainly does not vitiate the relationship discovered by Barclay and Butler, but it does cause some remarkable changes in the positions of the points for several liquids. Most notably and surprisingly, the points for methanol, water, hydrogen peroxide and hydrazine, all of which lie above the original B-B line in Fig. 1, now lie on or below the modified line determined by all of the 53 pure liquids in Fig. 2. Bear in mind again, though, that, by virtue of using number densities, we have removed the major contributions to ΔS_{vap} that result from the transition from hindered translations and rotations in the liquid to free translations and rotations in the vapor.

A few other features are worth noting. The point for mercury has been pulled even farther from the normal B-B line determined by all the liquids. The mercury behavior is likely due to the substantial change in its internal, electronic partition function in going from the liquid, where metallic bonding exists, to the monatomic vapor, where it does not

[17]. The fact that all the higher alkanols are still above the new B-B line implies that, relative to the strength of their intermolecular interactions, their liquids possess some unusual degree of structure, not inconsistent with the picture of winding H-bonded chains presented by Jorgensen [18,19]. Interestingly, ethyl ether, isopropyl ether and ethyl acetate, all presumably non-associated, are also above the new, general line, again hinting at the presence of some sort of enhanced order, perhaps due to weak (H-bond) interactions or packing considerations. Even more intriguing is the position of *n*-octane; but we refrain from further discussion and speculation at this time.

The observation that methanol, which, like its homologues, exists in winding chains in the liquid [19], and the other, relatively small H-bonded liquids, generally considered to be structured, now lie on or below the main line deserves special comment. It is likely that all these liquids share certain features, not present in normal liquids, that lower the $\Delta S^{\mathrm{M}}_{\mathrm{vap}}$ values from what might be expected given the type and strength of their intermolecular energies (as reflected by $\Delta H^{\mathrm{M}}_{\mathrm{vap}}$). Water happens to be the most prominent and important example of the group, and we discuss it in more detail below.

Before we do so, though, we offer the following general, heuristic discussion that might partly explain these surprising observations. Recall how we dissected the actual transfer process Eq. (I) into two steps, first transferring a solute molecule in a fixed position and then letting it translate and rotate over the available system space. Equivalently, we can just as well place the origin of the coordinate system used to evaluate the integrals in Eq. (2a)–Eq. (2c) on a randomly selected, fixed solute molecule that is either introduced or removed, and then let the surrounding solvent molecules move about it in response to achieve a new equilibrium configuration [5,6].

For the transfer process describing vaporization of a pure liquid, the key question to ask is: How much rearranging by the solvent molecules surrounding the fixed molecule is necessary to return to a local equilibrium configuration when the fixed molecule is removed? Keep in mind throughout this discussion that the $S^{\mathrm{M}}_{\mathrm{vap}}$ values should be viewed in light of the strength of the intermolecular forces, reflected by $\Delta H^{\mathrm{M}}_{\mathrm{vap}}$, which must be overcome to remove the solute molecule in the first place. Obviously, for completely structureless, isotropic liquids, there is little restructuring required. For liquids made up of large molecules or ones that engage in stronger, more directional interactions (viz. H-bonding) that putatively create some degree of order, we would expect greater restructuring. This presumably is reflected in higher $\Delta S^{\mathrm{M}}_{\mathrm{vap}}$ (and $\Delta H^{\mathrm{M}}_{\mathrm{vap}}$) values. However, the molecular rearranging needed to find another local-energy minimum for the four structured H-bonded liquids mentioned above might not be as extensive as expected because they are all relatively small, multifunctional (i.e. can engage in more than one H-bond) molecules. By comparison, molecules of *n*-propanol, for instance, having only one O–H group at the end of a three-carbon chain, might actually require more extensive rearranging after a neighboring *n*-propanol molecule is removed before they are able to return to a another local minimum-energy configuration of winding chains [19].

In addition to the simplistic picture offered above, there are certainly other possible factors to consider when explaining why the point for water, in particular, now lies below the new B-B line. It might be argued, for instance, that either water is not nearly as ordered or associated in the liquid state as generally accepted, or, as for formic and acetic acids, a major portion of its vapor exists as dimers [17]. (Note that both carboxylic acids fall more or less on the new B-B line.) The evidence, however, for water being a highly structured liquid is preponderant, and there is little indication that water vapor exists as dimers at 25 °C and 1 atm [10]. Instead, we believe that, precisely because water is such a highly associated, structured liquid, it possesses certain features, not present in normal liquids, which cause the $\Delta S^{\mathrm{M}}_{\mathrm{vap}}$ value to be diminished. For instance, if we accept that liquid water has a structure that is related to a distorted ice lattice, and which possesses residual proton disorder, as assumed by Sceats and Rice [20] and Henn and Kauzmann [21] in their random-network models of liquid water, then this contribution to the entropy is lost when water is vaporized. In addi-

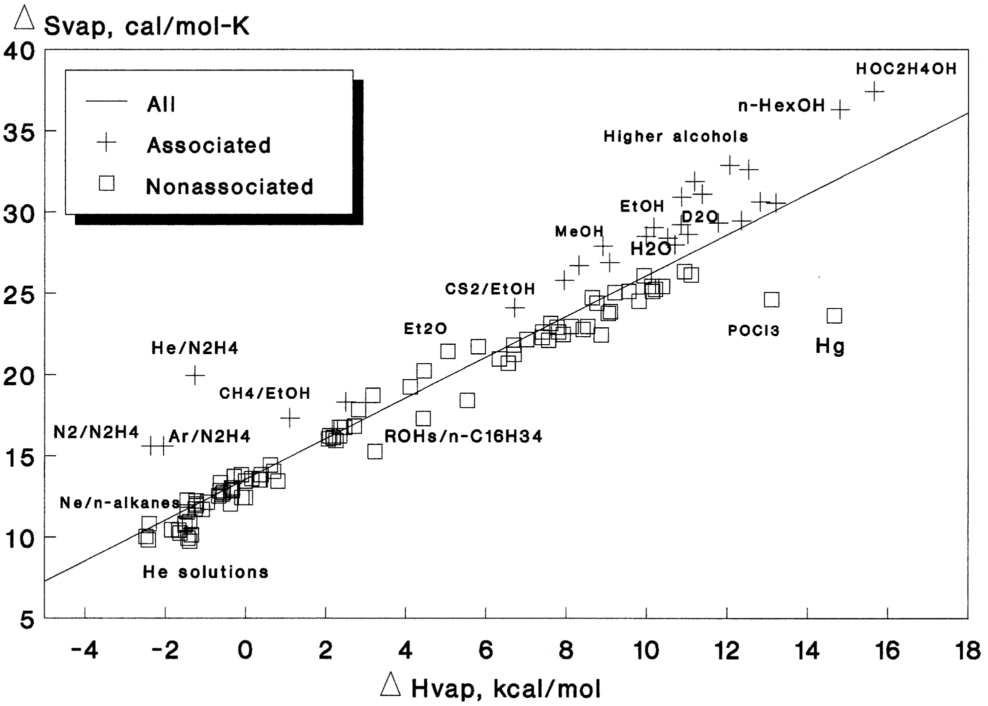

Fig. 3. Original B-B Plot for pure liquids and non-aqueous solutions based on mole fractions.

tion, as mentioned earlier, due to the strength and extent of association in the liquid phase, the intramolecular vibrational stretching frequencies of water are considerably reduced compared to the vapor [10]. As a consequence, the liquid possesses a so-called zero-point distortion energy and concomitant entropy contribution not present in the vapor [21]. Together, the residual proton disorder and zero-point distortion, both of which are not present in normal liquids, account for a loss in vaporization entropy that is estimated from the Henn–Kauzmann model of liquid water [21] to be more than 1.35 cal mol^{-1} K^{-1} (5.65 J mol^{-1} K^{-1}) at 25 °C. The addition of 1.35 cal mol^{-1} K^{-1} to the water ΔS_{vap} value would place it very close to the main B-B line. We conclude then that, given the strength of its intermolecular forces, as reflected by its enthalpy of vaporization, water does not gain as much entropy upon vaporization as might be expected if only simple structural factors are considered. Similar arguments probably apply to methanol, hydrogen peroxide and hydrazine as well. We also note that, based on their relative positions, D_2O appears to be slightly more structured than H_2O, which is generally acknowledged to be the case [7].

The factors just described can only really be revealed and appreciated when all the translational and rotational contributions to the entropy of vaporization are eliminated from the vaporization process. If data are only analyzed on the usual mole fraction basis, those important factors are totally dominated and hidden by the large translational and rotational contributions to the entropy.

3.2. Non-aqueous solutions

In Fig. 3 data based on the mole fraction concentration scale for 73 non-aqueous solutions have been added to the data exhibited in Fig. 1. A majority of these data are taken from the seminal paper of Frank and Evans [4], but quite a few are taken from the review by Wilhelm and Battino [22]. As the former [4] observed, the points for

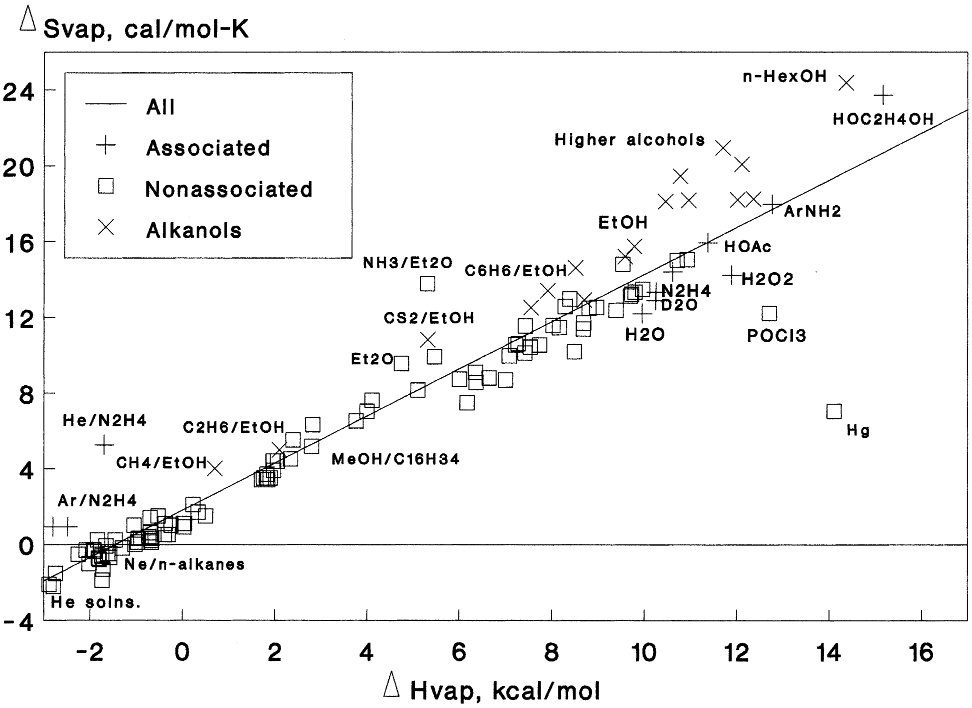

Fig. 4. Modified B-B plot for pure liquids and non-aqueous solutions using molarity.

solutions involving non-associated solvents lie on the B-B line obtained for pure, non-associated liquids. Solutions involving associated solvents lie slightly above this line, presumably for the same reason that most associated, pure liquids do.

Fig. 4 dramatically shows the effect of using the molarity concentration scale. The points corresponding to non-aqueous solutions are, if anything, brought closer to the B-B line of Fig. 2, and the line passes nearly, but not quite, through the origin. Furthermore, there are now a considerable number of points having negative values of ΔH_{vap}; even more remarkable, there are several solutions with *negative* values of ΔS_{vap}. These values belong to solutes having small molecular or atomic diameters for which the intermolecular forces are predominantly repulsive. Of the solutions presented in Fig. 4, Ne in *n*-alkanes (data from [22]) and those containing He and H_2 are, not surprisingly, particularly prominent in this regard. We propose that such solute atoms and molecules tend to loosen, or disorder, the local structure that exists in the solvent; when the solute leaves, the solvent is able to return to its slightly more ordered, regular state.

We also mention in passing a couple of other observations. It is surely significant that, despite falling slightly below the normal B-B line as a pure liquid, as water does, solutions of hydrazine (data from [22]) are above the line. This is almost certainly analogous to aqueous solutions and is suggestive of enhanced order in hydrazine induced by the solutes. In contrast, solutions of ether, except for the ammonia one, fall below the general B-B line, despite the fact that the pure solvent itself clearly lies above. The point for ammonia in ethyl ether (calculated from data taken from [23]) thus appears curiously anomalous and could be indicative of some interesting solute–solvent interactions. Perhaps, as we see for water later on, ammonia is able to induce some degree of order in certain 'normal' liquids. All these results highlight the real advantage of using molarity units when determining transfer quantities because, by

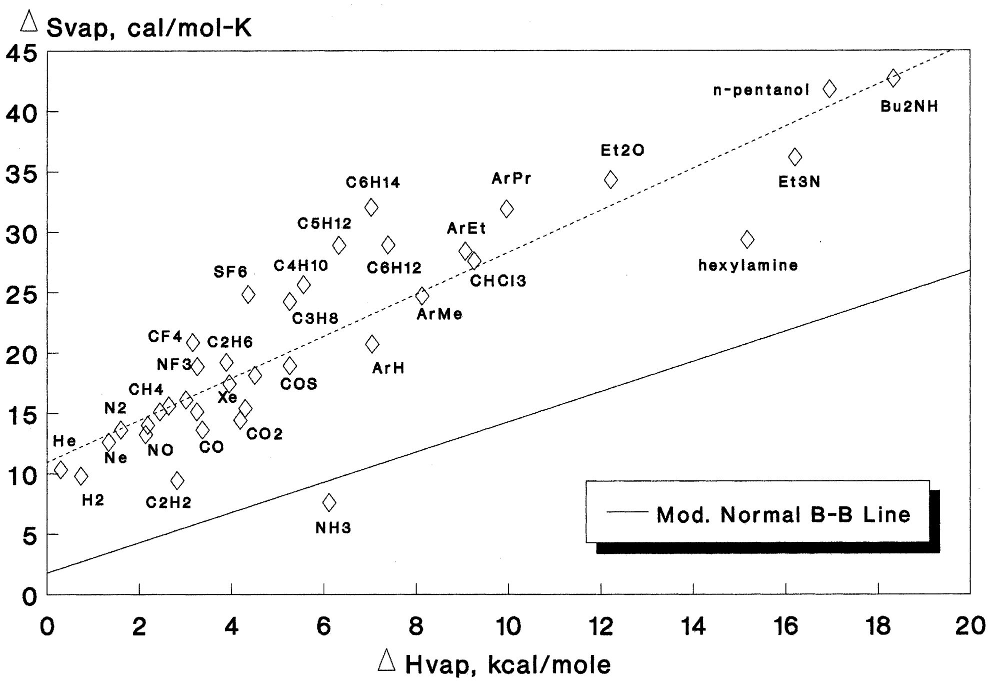

Fig. 5. Modified B-B plot for aqueous solutions of non-electrolytes based on molarity.

removing the 'liberation entropy', valuable information about the solvent and solvent–solute interactions is revealed more clearly.

3.3. Aqueous solutions of non-electrolytes

Most of the data presented here were recalculated from the paper of Frank and Evans [4]. Solutions involving miscible solutes, except for ammonia, were omitted, since the conversion from mole fraction to Ostwald coefficients could not be made accurately without knowledge of the actual solution data required in Eq. (7a) and Eq. (7c). Even though ammonia is highly soluble in water, we included it in our database because we were able to obtain the saturated solution properties mentioned in Section 2.1 (from [12,24]) necessary to convert the vaporization quantities. The corrections employed differ from those afforded for pure water (although not substantially, because the molecular weight of ammonia is almost the same as that of water), and thus our converted values for ammonia disagree slightly with those given by Ben-Naim and Marcus in [15]. Data for some aromatic hydrocarbons [25], alkanes [26], small, fluorinated compounds [27], and a few, poorly soluble, higher amines [28] have been added to the original Frank and Evans entries. The total number of data points is 37.

Fig. 5 gives a plot of ΔS_{vap} vs. ΔH_{vap} for the removal to the vapor of a number of non-electrolytes from water. The data points for all of these solutions, save ammonia, fall well above the modified normal B-B line (determined by the 53 pure liquids), still consistent with the proposal of Frank and Evans that water undergoes unusual structural changes in the vicinity of the solute molecule (i.e. so-called 'iceberg' formation [4]). Indeed, we believe that, because hindered translation and rotation contributions have been removed from the entropy of vaporization, the concept of enhanced structural changes occurring in aqueous solutions of non-electrolytes is more clearly revealed and strengthened. Incidentally, as might be expected, the *n*-alkanes and *n*-alkyl substituted benzenes separate into two groupings having different slopes. In general, as the solute size increases, so does the deviation from the average B-B line.

As noted above, the point for ammonia stands out, in that it lies substantially below the modified B-B line for aqueous solutions-and even below the normal B-B line. We note here, too, that two of the three amines included in our database fall below the overall aqueous line as well. Contrast this observation again with the point for ammonia in ethyl ether, which is well above the normal B-B line (cf. Fig. 4). Since we have observed how transfer quantities based on molarities sense solute–solvent interactions, this result suggests a tendency of relatively small, polar ammonia molecules to rearrange and reduce the structure of neat water around it (i.e. be a so-called 'structure breaker'), much like certain ions do[4]. At the very least, the solute–solvent interactions in aqueous ammonia solutions clearly must differ from those occurring in all the other aqueous solutions presented here. Again we see how the use of number densities helps to strengthen the supposition of solvent structure rearrangement in aqueous solutions of polar and non-polar compounds.

3.4. Solutions of water in non-polar and slightly polar organic solvents

Little attention seems to have been paid to obtaining and interpreting data on the solubility of water in non-polar and slightly polar organic solvents, especially as a means of gaining information on the state of water in similar environments. This subject is of considerable interest to those concerned with the role of water inside globular proteins, surfactant micelles and cell membranes. See, for instance, the work of Wade et al. [8] and Wolfenden and Radzicka [29] on the hydration probabilities of protein cavities or the small-angle neutron scattering studies of Dill et al. [30] in search of localized water in surfactant micelles. Unfortunately, there is a paucity of accurate solubility data, particularly as a function of temperature, suitable for elucidating the presence and role of water in such environments.

Solutions with polar chlorinated and fluorinated solvents were not included in the present study because deviations from Henry's law indicate that water in these solvents exists in polymeric form [31,32], which only complicates our interpretation of the data. We have used data (from [29] and [33–42]) for solutions at temperatures bracketing 25 °C and which give a reasonably good linear correlation ($r^2 \geq 0.925$) between the natural logarithm of the solubility and the reciprocal of the absolute temperature. There are strong indications [43] that the heat of vaporization for such systems is independent of temperature near 25 °C. Unfortunately, measurements for many of the solutions were made at only two or three temperatures, and the solubility of water is quite low, all of which can lead to wide discrepancies—despite claims of relative errors of a few percent. For example, values of ΔH_{vap} for water in benzene (the most frequently studied system because of the relatively high solubility of water in benzene) ranged from 4.10 to 4.96 kcal mol^{-1} and ΔS_{vap} varied from 7.82 to 10.21 cal mol^{-1} K^{-1} (cf. Table 1). Therefore, all results in this section must be viewed with a certain amount of caution. Nevertheless, the few ΔH_{s} values generated by calorimetric studies performed on water in hydrocarbons [43,44], from which we can calculate ΔH_{vap} values, agree reasonably well with the ΔH_{vap} values obtained by the van't Hoff method, despite the fact that the former provides an integral heat of solution, while the latter gives a differential heat solution. (The two are theoretically only equivalent at infinite dilution, but these solutions, for the most part, are so dilute in water that they can probably be considered infinitely dilute.) It should be mentioned here that all the data listed in Table 1, including multiple entries for the same solvent, are plotted in Fig. 6 in order to help show the range of experimental results currently available.

The results of our analysis are listed in Table 1 and plotted in Fig. 6. It is evident, surprisingly, that there is a definite tendency for most of the water-in-solvent points to lie *above* the average modified B-B line determined by the 53 pure liquids. This is in strong contrast with solutions of methanol and ethanol in hexadecane [45], both of which fall nicely along the normal B-B line (cf. Fig. 4). Moreover, the alkanes and the aromatics seem to lie along steeper lines of their own, as was observed with the aqueous solutions. Except

Table 1
Enthalpy and entropy of vaporization of water from various organic solvents at 25 °C

Solvent class/ compound	$\Delta H^{\mathrm{M}}_{\mathrm{vap}}$ (kcal mol^{-1})	$\Delta S^{\mathrm{M}}_{\mathrm{vap}}$ (cal mol^{-1} K^{-1})	Reference
n-Alkanes			
Pentane	1.55	3.23	[36]
Hexane	2.75	7.36	[36]
	2.46	6.69	[41]
Heptane	2.53	5.44	[35]
	2.85	7.81	[36]
Octane	2.28	5.91	[36]
	1.91	4.61	[42]
Decane	2.25	5.93	[34]
Undecane	2.22	5.84	[34]
Dodecane	1.67	4.12	[34]
Tridecane	1.45	3.49	[34]
Hexadecane	1.91	5.23	[34]
Branched & cyclic alkanes			
Isopentane	2.38	6.12	[36]
Isohexane	2.99	8.15	[36]
Isooctane	2.21	5.67	[36]
Cyclohexane	1.91	4.67	[32]
	2.92	7.99	[41]
	1.40	4.68	[29]
3-Methylhexane	2.89	8.00	[36]
2,2,5-Trimethylhexane	3.04	8.63	[36]
Benzene	4.10	7.81	[35]
	4.96	10.1	[36]
	4.25	7.96	[37]
	4.38	8.90	[38]
	4.81	9.56	[32]
	4.53	8.58	[41]
Substituted benzenes			
Toluene	4.64	9.57	[36]
	4.80	10.4	[37]
	5.52	12.5	[39]
	5.11	11.3	[40]
Ethylbenzene	3.39	5.88	[37]
	4.35	9.01	[36]
	4.19	8.45	[42]
Butylbenzene	3.80	7.35	[37]
o-Xylene	4.40	9.07	[36]
m-Xylene	4.85	10.8	[36]
Chlorobenzene	4.43	9.51	[37]
Bromobenzene	5.25	11.9	[37]
Iodobenzene	5.37	11.9	[37]
1-Heptene	2.55	9.90	[35]
	4.28	9.90	[40]
Carbon tetrachloride	3.93	9.35	[32]
	4.35	10.8	[39]

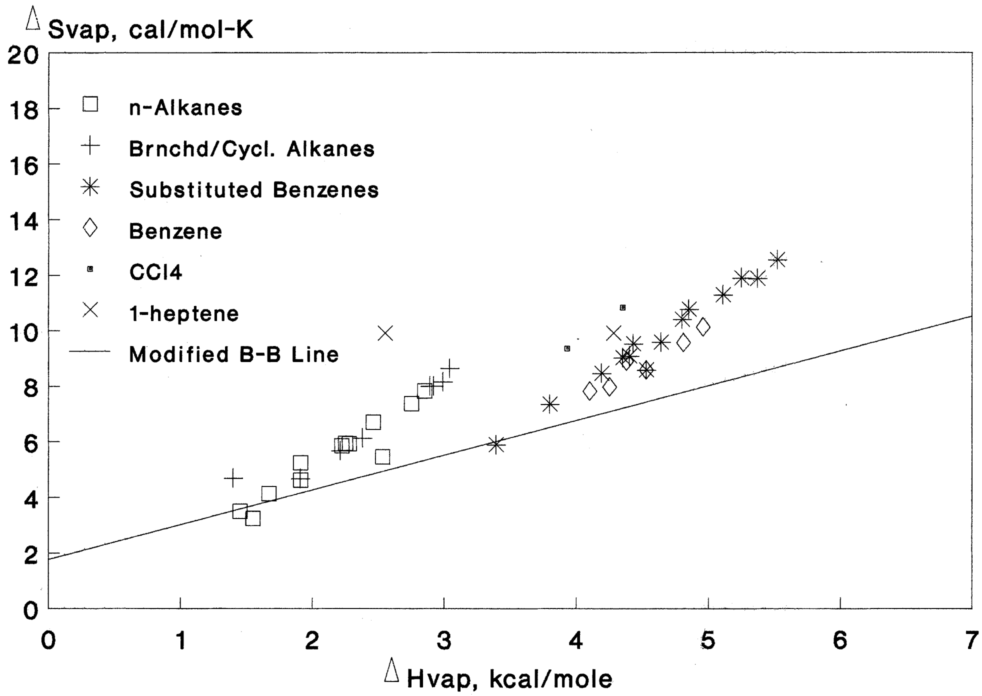

Fig. 6. Modified B-B plot for solutions of water in organic solvents based on molarity.

for the questionably high 1-heptene points [35,40], the substituted benzenes and carbon tetrachloride deviate the most from the normal B-B line. Unfortunately, the present data are not of sufficient quality or breadth, we believe, to observe firm trends with respect to carbon number or chain branching of the alkanes and alkyl substituents.

We refrain from speculating much on the meaning of any of these observations at this time. However, we do offer our results as additional evidence for H-bond-like interactions between water and aromatic rings [9,46,47], carbon tetrachloride [33,46] and double bonds [48]. Furthermore, we suggest that, in a role reversal of sorts, water, due to its unique molecular character, induces or enhances the degree of local structure, or order, in many of the solvents in which it is the solute. The mechanism for this postulated effect is probably related to the small size of water, its high dipole moment and its strongly directional bonding. Water may not be entirely alone in this regard, though, as the point for ammonia in ethyl ether perhaps hints at similar behavior for the ammonia molecule (vide supra).

Recently, Marmur [49] argued that the low solubility of water in non-polar or slightly polar liquids (as well as the low solubility of non-polar solutes in water) is due solely to molecular aggregation of the solute, which he associates with a general ‘solvophobic effect’. In contrast, our results indicate that water again exhibits its unusual character. For, despite existing essentially as a monomer in non-polar solvents, water still apparently causes these solutions to deviate from being ideal or ‘normal’, at least as defined by their deviations from the Barclay–Butler plot.

Clearly, the acquisition of more extensive and better data would be desirable to increase our understanding of water in non-polar and slightly polar solvents. Indeed, whereas Franks and Reid [50] years ago had called all such binary solutions ‘normal’, our analysis indicates that many of these solutions may yet prove to be hardly that.

4. Conclusion

The introduction of the procedure recommended by Ben-Naim to treat solution transfer quantities based on molarity (number density) has, in general, strengthened the theoretical understanding and utility of Barclay–Butler plots to sense structural changes in solvents induced by solutes because the translational and rotational contributions ('liberation' entropy) to the entropy of vaporization are removed. In particular, the substantial deviations of the points for aqueous and hydrazine solutions almost certainly result from the ability of non-polar molecules to enhance local order in those associated solvents. In contrast, the result of converting to number density seemingly blurs the distinction between associated and non-associated *pure* liquids, since most of the liquids are brought closer to the main, overall modified B-B line. This is to be expected to some degree, because conversion to molarity removes the 'liberation' entropy, which varies from liquid to liquid. However, other factors germane to H-bonded liquids then come to light when the 'liberation' contribution is removed. There are a few major surprises in the modified B-B plots—most notably in the positions of pure water and other substances containing multiple hydrogen-bonding groups—the occurrence of *negative* entropy of vaporization, and the position of water in various organic solvents. Solution transfer quantities based on molarity are confirmed as very useful, general tools for probing interactions between solutes and solvents, and revealing information about the structure of solvents. More detailed explanation and speculation await a later paper, but we hope that the present work stimulates further discussion on the use of standard thermodynamic solution-transfer quantities and highlights the need for additional studies of water in various solvents.

Acknowledgments

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References

[1] M. Barclay, J.A. Butler, The entropy of solution, Trans. Faraday Soc. 34 (1938) 1445–1454, and references therein.

[2] H.S. Frank, Free volume and entropy in condensed systems. Part II. Entropy of vaporization in liquids and the pictorial theory of the liquid state, J. Chem. Phys. 13 (11) (1945) 493–507.

[3] K. Sharp, Entropy–enthalpy compensation: fact or artifact, Protein Sci. 10 (2001) 661–667.

[4] H.S. Frank, M.S. Evans, Free volume and entropy in condensed systems. Part III. Entropy in binary liquid mixtures; partial molal entropy in dilute solutions; structure and thermodynamics in aqueous electrolytes, J. Chem. Phys. 13 (11) (1945) 507–531.

[5] A. Ben-Naim, Water and Aqueous Solutions: Introduction to a Molecular Theory, Plenum Press, New York, 1974.

[6] A. Ben-Naim, Standard thermodynamics of transfer, J. Phys. Chem. 82 (71) (1978) 792–803.

[7] A. Ben-Naim, Hydrophobic Interactions, Plenum Press, New York, 1980.

[8] R.C. Wade, M.H. Mazor, J.A. McCammon, F.A. Quiocho, A molecular dynamics study of thermodynamic and structural aspects of the hydration of cavities in proteins, Biopolymers 31 (1991) 919–931.

[9] G. Pimentel, A. McClellan, The Hydrogen Bond, Freeman and Co, San Francisco, 1960.

[10] D. Eisenberg, W. Kauzmann, The Structure and Properties of Water, Oxford University Press, New York, 1969.

[11] N. Davidson, Statistical Mechanics, McGraw-Hill Book Co, New York, 1962.

[12] J.A. Dean (Ed.), 1985. Lange's Handbook of Chemistry, 13th ed. McGraw-Hill Book Co, New York.

[13] D.R. Stull, E.F. Westrum, G.E. Sinke, The Chemical Thermodynamics of Organic Compounds, John Wiley & Sons Inc, New York, 1969.

[14] W.B. Bunger, J.A. Riddick, Organic Solvents, 3rd ed., Wiley-Interscience, New York, 1970.

[15] A. Ben-Naim, Y. Marcus, Solvation thermodynamics of non-ionic solutes, J. Chem. Phys. 81 (4) (1984) 2016–2027.

[16] A.R. Henn, Theoretical Studies of Liquid Water, PhD Thesis, Princeton University, 1982.

[17] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed., Wiley-Interscience, New York, 1972.

[18] W.L. Jorgensen, Simulation of liquid ethanol including internal rotations, J. Am. Chem. Soc. 103 (1981) 345–350.

[19] W.L. Jorgensen, Optimized intermolecular potential functions for liquid alcohols, J. Phys. Chem. 90 (7) (1986) 1276–1284.

[20] M.G. Sceats, S.A. Rice, A random network model for water, J. Phys. Chem. 85 (1981) 1108, and references therein.

[21] A.R. Henn, W. Kauzmann, Equation of state of a random network, continuum model of liquid water, J. Phys. Chem. 93 (1989) 3770–3783.

[22] E. Wilhelm, R. Battino, Thermodynamic functions of the solubilities of gases in liquids at 25 °C, Chem. Rev. 73 (1) (1973) 1–9.

[23] H. Stephens, T. Stephens (Eds.), 1963. Solubilities of Inorganic and Organic Compounds, Part I. MacMillan, New York.

[24] D.W. Green (Ed.), 1984. Perry's Chemical Engineers' Handbook, 6th ed. McGraw-Hill, New York.

[25] S.J. Gill, I. Wadso, An equation of state describing hydrophobic interactions, Proc. Natl. Acad. Sci. USA 73 (9) (1976) 2955–2958.

[26] E. Wilhelm, R. Battino, R.J. Wilcock, Low-pressure solubility of gases in liquid water, Chem. Rev. 77 (2) (1977) 219–262.

[27] J.T. Ashton, R.H. Dawe, K.W. Miller, E.B. Smith, B.J. Stickings. The solubility of certain gaseous fluorine compounds in water. J. Chem. Soc. A. (1968) 1793–1796.

[28] F.M. Jones, E.M. Arnett, Thermodynamics of ionization and solutions of aliphatic amines in water, in: A. Streitwieser, R.W. Taft (Eds.), Progress in Physical Organic Chemistry, vol. 11, John Wiley, New York, 1974, pp. 263–322.

[29] R. Wolfenden, A. Radzicka, On the probability of finding a water molecule in a non-polar cavity, Science 265 (1994) 936–937.

[30] K.A. Dill, D.E. Koppel, R.S. Cantor, J.D. Dill, D. Bendedouch, S.-H. Chen, Molecular confirmations in surfactant molecules, Nature 309 (1984) 42–45.

[31] J.R. Johnson, S.D. Christian, H.E. Affsprung. The molecular complexity of water in organic solvents, Part III. J. Chem. Soc. A. (1967) 1924–1928.

[32] S.D. Christian, A.A. Taha, B.W. Gash, Molecular complexes of water in organic solvents and in the vapor phase, J. Chem. Soc. Q. Rev. 24 (1974) 20–36.

[33] S. Goldman, The determination and statistical mechanical interpretation of the solubility of water in benzene, carbon tetrachloride, and cyclohexane, Can. J. Chem. 52 (1974) 1668–1680.

[34] P. Schatzberg, Solubilities of water in several normal alkanes from C7 to C16, J. Phys. Chem. 67 (1963) 776–779.

[35] C. Black, G.C. Joris, H.S. Taylor, The solubility of water in hydrocarbons, J. Chem. Phys. 16 (5) (1948) 537–543.

[36] J. Polak, B.C.-Y. Lu, Mutual solubilities of hydrocarbons and water at 25 °C, Can. J. Chem. 51 (1973) 4018–4023, The solubilities of water in various organic solvents were measured at only two temperatures, 0 and 25 °C, but we considered the data of sufficient quality to warrant using it for determining the mole fraction-based entropies and enthalpies of vaporization at 25 °C, which were then converted to molarity-based quantities.

[37] J.R. Jones, C.B. Monk, 1963. Determination of the solubility of water in some organic liquids by means of tritium. J. Chem. Soc. A. (1963) 2633–2635.

[38] R. Karlsson, Solubility of water in benzene, J. Chem. Eng. Data 18 (3) (1973) 290–292.

[39] P.K. Glasoe, S.D. Schultz, Solubility of H_2O and D_2O in carbon tetrachloride, toluene, and cyclohexane at various temperatures, J. Chem. Eng. Data 17 (1) (1972) 66–68, While it met our criteria for inclusion, the result for water in cyclohexane was rejected because it fell so far above every other point we obtained for any solvent, and was therefore considered an outlier.

[40] B.A. Englin, A.F. Plate, V.M. Togolukov, M.A. Pryanishnikova, Solubility of water in individual hydrocarbons, Khim. Tekhnol.: Topliv Masel 10 (9) (1965) 42–46, CA 63:14608. Much of the data generated here is questionable, we believe, mostly because the solubility of the H_2 resulting from the reaction of water with CaH_2 was not properly accounted for when determining water solubility at different temperatures.

[41] C. Tsonopoulos, G.M. Wilson, High-temperature mutual solubilities of hydrocarbons and water, Part I, Am. Inst. Chem. Eng. J. 29 (6) (1983) 990–999.

[42] J.L. Heidman, C. Tsonopoulos, C.J. Brady, G.M. Wilson, High-temperature mutual solubilities of hydrocarbons and water, Part II, Am. Inst. Chem. Eng. J. 31 (3) (1985) 376–384.

[43] S.-O. Nilsson, Enthalpies of solution of water in benzene and in some alkanes, J. Chem. Thermodyn. 18 (1986) 877–884.

[44] D.S. Reid, M.A.J. Quickenden, F. Franks, Direct calorimetric measurement of the heats of solution of some liquid hydrocarbons in water, Nature 224 (1969) 1293–1294.

[45] E.E. Tucker, S.D. Christian, Alcohol association studies, 3: vapor pressure measurements for the ethanol–*n*-hexadecane systems, J. Phys. Chem. 81 (13) (1977) 1295–1299.

[46] J. Kirchnerova, G.C. Cave, The solubility of water in low-dielectric solvents, Can. J. Chem. 54 (1976) 3909–3916.

[47] S.C.P. Hwa, W.T. Ziegler, Temperature dependence of the excess thermodynamic properties of ethanol–methylcyclohexane and ethanol–toluene systems, J. Phys. Chem. 70 (8) (1966) 2572–2593.

[48] C. Tanford, The Hydrophobic Effect, 2nd ed., Wiley-Interscience, New York, 1980.

[49] A. Marmur, Dissolution and self-assembly: the solvophobic/hydrophobic effect, J. Am. Chem. Soc. 122 (2000) 2120–2121.

[50] F. Franks, D.S. Reid, Thermodynamic properties: water in crystalline hydrates and aqueous solutions of simple non-electrolytes, in: F. Franks (Ed.), Water: A Comprehensive Treatise, vol. 2, Plenum Press, New York, 1973, p. 372.