Critical Reviews in Analytical Chemistry

Non-Aqueous Solvent Chemistry - Some Recent Studies

L. M. Mukherjee; J. F. Coetzee

PLEASE SCROLL DOWN FOR ARTICLE

NON-AQUEOUS SOLVENT CHEMISTRY — SOME RECENT STUDIES

Author: **L. M. Mukherjee**
Chemistry Department, Faculty of Science
Banaras Hindu University
Varanasi, India

Referee: J. F. Coetzee
Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania

TABLE OF CONTENTS

I. INTRODUCTION

Over the years, interest in solution chemistry has greatly expanded due to the availability of a large number and variety of organic substances having good solvent properties. Many of these organic solvents are routinely used in commerce as reaction media and have proven useful in separations and in analytical determinations.

The physicochemical properties of a solution can be looked upon as the net result of mutual interactions of the solute and the solvent molecules. These interactions may involve such processes as dissociation or aggregation of the solute species, and then specific solvation of the various particles so produced. The latter would certainly be an important factor in determining the relative stability of the various forms of the solute species and would, therfore, be of consequence in governing the behavior of a particular solution.

Although the dielectric constant of a solvent plays a dominant role, especially when ion association is involved, quantitative comparisons among solvents based on their bulk dielectric constants seldom prove adequate. The literature abounds with generalizations based on the chemical reactivity of the solvent, its hydrogen bonding ability, the existence of ion-dipole inter-actions (also dispersion forces), and steric considerations in attempts to comprehend the significance and nature of the solvation phenomena. In this context, consideration of the behavior of solutions in dipolar aprotic solvents appears highly interesting.

This review presents a critical survey of studies reported during the past decade or so in pyridine and two other dipolar aprotic solvents, viz., sulfolane and propylene carbonate, which have come to prominence lately. The areas that are covered relate mostly to fundamental studies with comparatively less emphasis on the techniques or methodologies per se. Thus, it is the rationale of an approach, rather than its experimental details, that is given primary consideration. However, attempts have been made to accommodate, within the present framework, pertinent details that are not too obvious and may be considered new or somewhat unusual.

Insofar as pyridine solvent chemistry is concerned, attention is directed toward the recent polarographic studies of Brønsted acids, with special reference to the influences of background electrolytes on half-wave potentials. In addition, a detailed review is given of the quantitative aspects of acid-base equilibria and the properties of univalent salts of silver(I), on which the pH and pAg scales in this solvent are based. For sulfolane

and propylene carbonate, the results of studies on the behavior of electrolytes through conductance measurements are reviewed, and the important conclusions drawn from them regarding ion-solvent interactions in these two systems are presented. Also, the reports on the thermo-dynamic behaviors of reversible electrodes in propylene carbonate, especially the alkali metal electrodes and the Li$^+$-sensitive glass electrode, are examined in detail, and the results on the measurements of heats of solution of electrolytes in both sulfolane and propylene carbonate are discussed. In a separate section, the available estimates of medium activity coefficients for several cations are compared for a general assessment of the solvent affinities and the activity levels of these ions in the three solvents considered.

It is hoped that the present review will be of use to those actively engaged in research in non-aqueous solvent chemistry, and of help in inspiring new ideas for further studies and correlations including applications in analytical and preparative fields of chemistry.

II. CHEMISTRY IN PYRIDINE

Pyridine is a stable, heterocyclic base (fp -41.7; bp 115.3°) with a low dielectric constant (12.3). It is truly aprotic[1] in nature, having only a negligible tendency for self-association in the liquid state (Trouton's constant = 21.7). It can form strong complexes with Ag(I) and other transition-metal ions, and its stable complex with Li(I) is also known.[2,3] In addition, pyridine is a good solvent for a variety of inorganic and organic substances. These interesting properties offer a wide scope for diverse, fundamental studies of this solvent and for investigation of the different aspects of acid-base chemistry in particular. Indeed, the importance of pyridine as a solvent has long been recognized.

A. Purification of Pyridine — Physicochemical Properties

Commercial samples of pyridine can be easily purified. The recommended[4] procedure involves prolonged treatment with solid KOH, followed by fractional distillation over Linde 5A molecular sieve and solid KOH. To prevent contamination with carbon dioxide and water from the air, the purified solvent should be stored in a sealed reservoir with an arrangement for dispensing it automatically, when required, under pressure of pure nitrogen gas.

Some important physicochemical properties of pyridine are given in Table 1.

B. Recent Studies in Pyridine

The two areas in pyridine solvent chemistry that have received most attention lately relate to (1) the investigation of the polarographic behavior of certain Brønsted (and Lewis*) acids by Elving and his co-workers,[12-18] and (2) the work in the reviewer's laboratory on the establishment of the pH and pAg scales in the solvent, the interpretation of neutralization curves, and studies of some complex equilibria of fundamental

TABLE 1

Properties of Pyridine

|	
Density (g cm^{-3}, 25°)	0.97824[5]
Viscosity (cP, 25°)	0.884[5]
Surface tension (dynes cm^{-1}, 20°)	38.0[6]
Specific heat (cal g^{-1} deg^{-1}, 21−108°)	0.431[6]
Heat of fusion (cal g^{-1})	22.4[6]
Molal elevation constant (deg mole^{-1} kg^{-1})	2.69[7]
Molal depression constant (deg mole^{-1} kg^{-1})	4.97[6]
Dipole moment (D)	2.23[8]
Dielectric constant	12.3[a,9], 12.5[b,10]
Refractive index (n_D^{21})	1.50919[6]
Specific conductivity (mho cm^{-1}, 25°)	<1 × 10^{-9}[11]
pK$_b$ in water (25°)	8.81[6]
Spectral cut-off (λ, nm)	~290[4]

[a]Low frequency.
[b]High frequency.

*Consideration of the polarographic behavior of Lewis acids has been omitted from the present discussion.

importance through a generous application of spectrophotometry and potentiometry as well as conductance and differential vapor pressure (DVP) measurements.[19-26] Some spectroscopic studies[2,27] are also reported which seem significant and relevant in the present context.

1. Polarographic Behavior of Brφnsted Acids

Because of the importance of hydrogen ion, or available proton, in certain electrochemical reactions,[28] pyridine has assumed a rather unique distinction as a genuinely aprotic organic solvent. Likewise, studies on the polarographic behavior of pyridine solutions of Brφnsted acids have become a subject of much interest.

In 0.1 M lithium perchlorate solution as the background electrolyte, Brφnsted acids of pK_a^{aq} less than 9 were found[12] to yield fairly well-defined cathodic waves at a DME. These are accompanied by a small "prewave," possibly due to

$$\text{pyrH}^+ + e \longrightarrow \text{pyrH}^\bullet$$

$$2\text{pyrH}^\bullet \longrightarrow \text{Hpyr-pyrH}$$
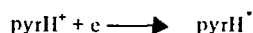
(pyr denotes a molecule of pyridine)

For most acids, the half-wave potentials of the main wave were found to be close to -1.3 V (vs. a normal silver electrode in pyridine), and the diffusion current constant was about 2 on the basis of the combined height of the 2 waves, i.e., the prewave and the main wave. In 0.1 M tetraethylammonium perchlorate as the background electrolyte,[13] no prewave appeared before the main reduction wave; moreover, the diffusion current constant showed considerable variation and was significantly smaller in each case than the almost constant value of 2 realized in 0.1 M lithium perchlorate solutions. Also, it is interesting to note that the half-wave potentials in 0.1 M tetraethylammonium perchlorate were appreciably different from those obtained in 0.1 M lithium perchlorate, and showed a strong dependence on the nature of the acid used (except in the case of relatively strong acids such as nitric acid, trifluoroacetic acid, and dichloroacetic acid. For instance, the half-wave potentials of nitric, benzoic, and acetic acids were -1.31, -1.62, and -1.72 V (Table 2; Figure 1).

Elving and co-workers[13] initially considered
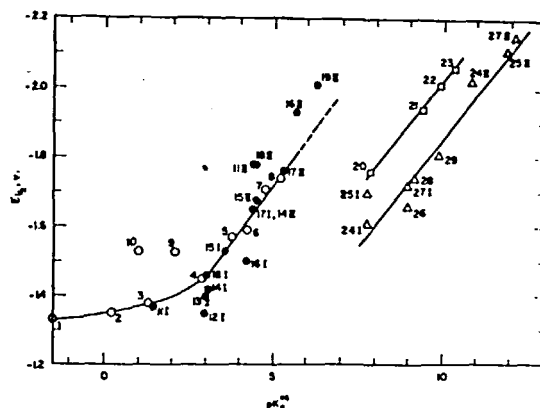
FIGURE 1. Relation between the half-wave potentials of Brφnsted acids in pyridine containing 0.1 M tetraethylammonium perchlorate at 25° and the aqueous pK_a-values of the acids: o nitric and monocarboxylic acids; • salicylic and dicarboxylic acids; □ phenols; and ∧ purines. Numerals refer to the acids as listed in Table 2. (Reprinted from Anal. Chem., 41, 286 (1969). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)

the difference between the half-wave potentials in the two background electrolytes to be related to the difference in electrocapillary effects. However, such an explanation does not account for the observed dependence of the half-wave potential on the nature of the acid when tetraethylammonium perchlorate is used as the background electrolyte. Hence, the authors assumed[15] the following reactions:

$$\underset{\text{I}}{\text{pyr} + \text{HA}} \;\rightleftharpoons\; \underset{\text{II}}{\text{pyrHA}}$$

$$\underset{\text{III}}{\text{pyrH}^+ \, \text{A}^-} \;\rightleftharpoons\; \underset{\text{IV}}{\text{pyrH}^+ + \text{A}^-}$$
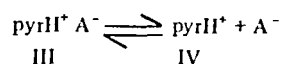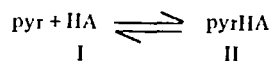
and argued that since (1) for acids of $pK_a^{aq} \geqslant 3.4$, the sum of the concentrations of the associated species II and III in pyridine will be nearly equal to the total analytical concentration, and (2) the observed diffusion currents are proportional to the total concentrations, it will be reasonable to consider species II and III as the diffusing species in these cases. These species may then undergo a preceding chemical step to produce the pyridinium ion (pyrH$^+$) responsible for the wave. For acids that are appreciably dissociated in pyridine, it could be assumed that the predominant diffusing species was pyrH$^+$ together with some II and/or III. In fact, the half-wave potentials do approach a

TABLE 2

Polarographic Behaviors of Solutions of Brønsted Acids in Pyridine Containing 0.1 M Et$_4$NClO$_4$

No.[a]	Acid	pK_a^{aq}	$-E_{1/2}$, V	I[b]	ΣI	$E_{1/4} - E_{3/4}$, mV
1	HNO$_3$	−1.3	1.33	1.79		51
2	CF$_3$COOH	0.23	1.35	1.92		57
3	Cl$_2$CHCOOH	1.29	1.38	1.90		76
4	ClCH COOH	2.87	1.49	1.47		86
5	HCOOH	3.75	1.57	2.00		85
6	C$_6$H$_5$COOH	4.20	1.59	1.85		85
7	CH$_3$COOH	4.73	1.71	2.04		82
8	(CH$_3$)$_3$CCOOH (pivalic)	5.20	1.74	2.02		78
9	Nicotinic	2.07	1.53	2.15		89
10	Picolinic	1.01	1.53	1.87		119
11	Oxalic	I 1.46	1.37	1.79		
		II 4.40	1.78	1.67	3.46	73
12	Phthalic	I 2.96	1.35	1.71	1.71	64
		II 5.51				
13	Salicylic	I 2.97	1.40	1.90	1.90	66
		II 13.00				
14	Tartaric	I 3.03	1.42	1.76		
		II 4.37	1.65	1.77	3.53	72
15	Terephthalic	I 3.54	1.53[c]	d		d
		II 4.46	1.68[c]		3.69	
16	Succinic	I 4.21	1.50	1.59		
		II 5.64	1.93	1.56	3.15	70
17	Adipic	I 4.41	1.65	d		d
		II 5.28	1.76		3.29	
18	Fumaric	I 3.02	1.46	1.82		65
		II 4.45	1.78	1.45	3.27	150
19	Maleic	I 2.00	e	1.83		e
		II 6.26	2.01	1.57	3.40	60
20	2,4-Dichlorophenol	7.85	1.76	2.03		104
21	p-Chlorophenol	9.38	1.94	2.01		89
22	Phenol	9.89	2.01	1.90		99
23	3,4-Dimethylphenol	10.30	2.06	1.74		92
24	6-Mercaptopurine	I 7.40	1.61	1.44		
		II 10.84	2.02	1.27	2.71	88
25	2,6-Dihydroxypurine	I 7.74	1.70	f	f	87
		II 11.86	2.11			59
26	Purine	8.93	1.66	1.74		96
27	6-Hydroxypurine (hypoxanthine)	I 8.94	1.72	1.61		
		II 12.10	2.15	1.17	2.78	74
28	6-Methoxypurine	9.16	1.74	1.35		166
29	6-Aminopurine (adenine)	9.83	1.81	1.48		116

[a]No. 1: nitric acid added as pyridinium nitrate; Nos. 2 to 10: monobasic carboxylic acids; Nos. 11 to 19: dibasic carboxylic acids; Nos. 20 to 23: phenols; Nos. 24 to 29: purines.
[b]Diffusion current constant, $I = i_l/Cm^{2/3}t^{1/6}$.
[c]Measured, assuming that the observed wave consists of two waves of equal heights.
[d]The two waves merged or nearly merged.
[e]Anomalous wave.
[f]The polarogram was recorded with a saturated solution because of the low solubility of the compound. Based on wave height, the concentration was about 0.7 mM.

(Reprinted from *Anal. Chem.*, 41, 286 (1969). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)

constant value (Figure 1) with decreasing pK_a^{aq}, indicating that in these limiting cases the reduction of a common species (i.e., pyrH$^+$) is taking place.

Tsuji and Elving[15] further suggested that the single wave given by phthalic acid, in contrast to terephthalic acid, was most likely due to the stabilization of the hydrogen-bonded cyclic form of the monoanion in the former case. The observed deviations of wave I (Figure 1) for oxalic, salicylic, tartaric, and succinic acids from the monocarboxylic-acid line are also to be attributed to such an effect. The fact that adipic and fumaric acids do conform to this line is probably an indication that for these acids stable, intramolecularly hydrogen-bonded ring structures are difficult to form. The case of maleic acid is considered anomalous and may involve reduction either of the double bond or of an easily reducible charge-transfer complex. The fact that wave II appears for oxalic, succinic, fumaric, and maleic acids well above the monocarboxylic-acid line may be partly due to the dielectric effect.

The observed "leveling effect" of lithium perchlorate is discussed in connection with the metathetical reactions involving proton exchange. It may be mentioned here that the possibility of similar exchange reactions in the case of the tetraalkylammonium perchlorates, viz., Et_4NClO_4 or Bu_4NClO_4,[29] is restricted due to the small charge density on these bulky, symmetrical cations which reduces their ion-pairing ability.

2. Determination of Absolute Values of pK_a of Uncharged Acids — Establishment of pH Scale

Although relative pK_a-values are easier to obtain from hydrogen-electrode measurements,[30] determinations of absolute dissociation constants* of such systems require knowledge of the hydrogen-ion activities of the solutions, and therefore necessitate standardization of the reference electrode used.

a. Standardization of the Reference Electrode

According to Mukherjee and co-workers,[19] both $Hg/HgCl_2(s)$, $LiCl(s)$ and $Zn(Hg)/ZnCl_2(s)$ electrodes proved satisfactory as reference electrodes in pyridine. However, most of their mea-

surements were carried out with the help of the $Zn(Hg)/ZnCl_2(s)$ electrode. It was prepared by adding a saturated solution of $ZnCl_2 \cdot 2C_5H_5N$[†] in pyridine to the amalgam contained in a suitable electrode vessel. (An amalgam containing 3 percent of zinc by weight was used; two alternative methods of preparation have been given.[19]) An equilibration period of 24 hr was normally allowed before use. For standardization of this electrode, the cell

Cell I $Zn(Hg)/ZnCl_2(s) // HX$ in pyridine/H_2 (1 atm), Pt
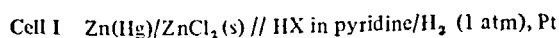
could be utilized provided an acid HX of known dissociation constant or one which is completely dissociated was available. Since most acids are incompletely dissociated in pyridine, the initial step in the standardization reduced to the task of determining the dissociation constant of a suitable acid such as HNO_3 or HBr in this solvent. It was considered[19] that a spectrophotometric approach would be the most appropriate for the purpose. With this objective, solutions of different concentrations of two indicator acids, 2,4- and 2,5-dinitrophenol in pyridine were studied. Assuming the model $HIn \rightleftharpoons H^+ In^- \rightleftharpoons H^+ + In^-$, and taking into account the contributions made to the absorbance by all of the indicator species, viz., the molecular form HIn, the ion-pair $H^+ In^-$, and the anion In^- at the selected wavelength, the pK_a-values of the two nitrophenols were calculated from the equation

$$\epsilon_{app} = \epsilon_{In} - \frac{(\epsilon_{app} - \epsilon')^2 \, C_t \, f_i^2}{(\epsilon_{In} - \epsilon') \, K_{HIn}} \qquad (1)$$

where ϵ_{app} denotes the apparent molar absorptivity at the total indicator concentration C_t, ϵ_{In} represents the molar absorptivities of H^+In^- and In^-, and ϵ' is the limiting molar absorptivity of the indicator[31] in the presence of an excess of a non-absorbing acid, the value of f_i being obtained from the Debye-Hückel limiting law ($-\log f_i = 8.191\sqrt{\mu}$). These pK_a-values were subsequently used in the studies of mixtures with the non-absorbing acids HBr and HNO_3. The corresponding data treatment involved a trial-and-error procedure: The ratio of the dissociation constant

*Without any specific reference as to the states of solvation of the various species involved, the dissociation of an acid, HX, in pyridine can be represented as $HX \overset{K_i}{\rightleftharpoons} H^+ X^- \overset{K_d}{\rightleftharpoons} H^+ + X^-$. However, HX and H^+X^- are not distinguishable potentiometrically, and both count as undissociated species. Thus, only estimates of the overall dissociation constant $[K_{HX} = K_iK_d/(1 + K_i)]$ are obtainable from such measurements.

†$ZnCl_2$ was not used because of its hygroscopic nature.

of the indicator acid (K_{HIn}) to that of the particular non-absorbing acid (K_{HX}) was adjusted for a best fit with the equation

$$\frac{[HX]}{C_{HIn}} = -\frac{K_{HIn}}{K_{HX}} + \frac{K_{HIn}^2 \, C_{HIn}}{K_{HX} \, f_i^2 \, [In^-]^2} \qquad (2)$$

using ionic activity coefficients calculated in the manner indicated above. The dissociation constants of HBr and HNO_3 were then calculated from the final values of K_{HIn}/K_{HX} and the weighted averages of K_{HIn} derived from the pure indicator runs and the slope: intercept ratios for the plots of Equation 2. Substitution of these values of pK_a of hydrobromic or nitric acid into the expression

$$E = E_j - E_{ref} + 0.02956 \log K_{HX} + 0.02956 \log C_{HX} \qquad (3)$$

for the e.m.f. of cell I at 25° yielded a value of -0.788 ± 0.001 V for $E_j - E_{ref}$ over a range of acid concentrations, suggesting that the junction potential E_j was either very small or practically constant and independent of the nature of the junction involved. The said value (-0.788 V vs. N.H.E. in pyridine) was, therefore, reliably used as the potential of the $Zn(Hg)/ZnCl_2(s)$ reference electrode (inclusive of the contribution of E_j) in determining ionic activities and for related measurements in the solvent.

b. Overall Dissociation Constants of Acids and Lithium Salts

The pK_a values of $HClO_4$, HI, and HCl were obtained from potentiometric measurements using the Pt/H_2 electrode. Also, from hydrogen-electrode studies of HX-LiX mixtures*, the dissociation constants of a few lithium salts were determined. The vales of pK_a for acetic and benzoic acids, which are very weakly dissociated in pyridine, were determined from e.m.f. measurements using a calibrated glass electrode and buffer solutions containing the appropriate tetrabutyl-ammonium salts.[23] A summary of the pK-values of the various acids and lithium salts is given in Table 3.

The present estimates of the acid dissociation constants do indeed substantiate earlier conclusions[32,36] on the differentiating effect of pyridine toward acids that are leveled in water. Also, it is to

TABLE 3

Summary of the Values of pK of Acids and Lithium Salts at 25°

Acid or salt	pK	
	In pyridine	In EDA[a]
$HClO_4$	3.26[b] 3.12[c]	3.10
HI^{d}	3.39[b] 3.23[c]	2.97
HNO_3	4.06[e] 4.30[c]	3.20
HBr	4.36[b] 4.38[e]	3.73
HCl	5.66[b] 6.14[c]	4.01
2,4-Dinitrophenol	4.38[e] 4.00[c]	
2,5-Dinitrophenol	5.76[e] 5.15[c]	
Benzoic acid	9.8[f]	
Acetic acid	10.1[f]	
LiCl	6.07[b]	
LiBr	4.28[b]	
LiI	3.61[b]	
$LiNO_3$	4.97[b]	
$LiClO_4$	4.38[b]	

[a]Reference 31.
[b]Reference 19 (potentiometric; $\delta_{pK} \leqslant \pm0.1$).
[c]References 11 and 32 to 34.
[d]A pK-value of 3.11 was obtained from DVP measurements, at 37°, on the basis of the relation

$$K_{HX} = \frac{(\Sigma m - m_s)^2 \, f_i^2}{2m_s - \Sigma m} \qquad (4)$$

where Σm represents the molarity as determined from these measurements for a stoichiometric molarity m_s, and f_i denotes the ionic activity coefficient estimated from the Marshall-Grunwald equation.[35]
[e]Reference 19 (spectrophotometric; $\delta pK \leqslant \pm0.1$).
[f]Reference 23 (Potentiometric; $\delta pK \sim \pm0.2$).

be noted that the acids, in general, appear to be less dissociated in pyridine than in the isodielectric solvent ethylenediamine (EDA) (D = 12.9). A plausible explanation of this behavior may be that, being a stronger base (pK_b in water = 4.15), EDA is able to interact more intensively with the undissociated acid molecules facilitating the formation of the ion-pairs, which would eventually lead to a larger overall extent of dissociation.

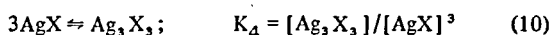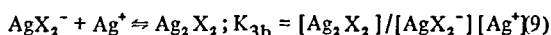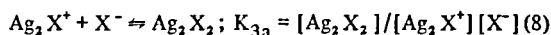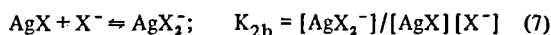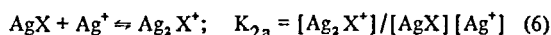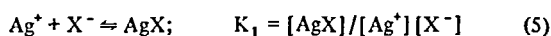*No homoconjugation could be detected in any of the acids studied.

The pK-values of the lithium salts indicate that all of the salts, except LiBr, are less dissociated than the corresponding acids. A similar trend was also observed in EDA.[31],[37]

3. Interpretation of the Behavior of Some Monovalent Silver Salts and Establishment of pAg Scale

Previous conductance studies[11],[38] indicate that silver nitrate, perchlorate, and picrate behave in a simple manner in pyridine and have dissociation constants of 9.3×10^{-4}, 1.91×10^{-3}, and 3.06×10^{-3}, respectively. In contrast, however, the weakly conducting solutions of the chloride, cyanide, and thiocyanate of silver(I) appear to involve complicated equilibria. Mukherjee and co-workers quantitatively explained the conductance data of Mathews and Johnson[39] on these systems and their own data on silver bromide on the basis of the following equilibria:[20],[21]

$$Ag^+ + X^- \rightleftharpoons AgX; \qquad K_1 = [AgX]/[Ag^+][X^-] \qquad (5)$$

$$AgX + Ag^+ \rightleftharpoons Ag_2X^+; \quad K_{2a} = [Ag_2X^+]/[AgX][Ag^+] \quad (6)$$

$$AgX + X^- \rightleftharpoons AgX_2^-; \quad K_{2b} = [AgX_2^-]/[AgX][X^-] \quad (7)$$

$$Ag_2X^+ + X^- \rightleftharpoons Ag_2X_2; \quad K_{3a} = [Ag_2X_2]/[Ag_2X^+][X^-] \quad (8)$$

$$AgX_2^- + Ag^+ \rightleftharpoons Ag_2X_2; \quad K_{3b} = [Ag_2X_2]/[AgX_2^-][Ag^+] \quad (9)$$

$$3AgX \rightleftharpoons Ag_3X_3; \qquad K_4 = [Ag_3X_3]/[AgX]^3 \qquad (10)$$

If one assumes that $K_{2a} = K_{2b} = K_2$ and that $K_{3a} = K_{3b} = K_3$, substitution for the equilibrium concentrations of AgX, Ag_2X^+, AgX_2^-, Ag_2X_2, and Ag_3X_3 in terms of $[Ag^+]$ leads to the following expression for the total concentration C_{AgX}:

$$C_{AgX} = [Ag^+] + K_1[Ag^+]^2 + 3K_1K_2[Ag^+]^3 + 2K_1K_2K_3[Ag^+]^4 + 3K_1^3K_4[Ag^+]^6 \qquad (11)$$

Thus, for a series of assumed values of $[Ag^+]$ and with a given set of values of K_1, K_2, K_3, and K_4, it is possible to generate the corresponding values of C_{AgX}; likewise, the equivalent conductances at these total concentrations can be obtained from the equilibrium concentrations of all relevant ionic species and the available estimates of their mobilities. In practice, a family of plots of log Λ_c against log C can be constructed with different sets of values for K_1, K_2, K_3, etc. The particular set of values of these parameters which provides the best fit between the simulated plot and the experimental one can be finally accepted as reasonable and representative for a given system. The actual curve-fitting in different cases under study is illustrated in Figures 2 and 3. To obtain additional verification of the constants used, the case of AgBr was subjected to further studies, which involved comparing the calculated value of the sum, Σ C, (Equation 12) of the molarities of all the species with the total concentration as determined from differential-vapor-pressure measurements for a series of solutions of known stoichiometric concentrations (Figure 4). It should be pointed out in this connection that although the values of K

$$\Sigma C_{AgBr} = 2[Ag^+] + K_1[Ag^+]^2 + 2K_1K_2[Ag^+]^3 + K_1K_2K_3[Ag^+]^4 + K_1^3K_4[Ag^+]^6 \qquad (12)$$

introduced in the present treatment are formal constants, activity correction for the monomer dissociation — the predominant process at low concentrations — will be relatively unimportant. Thus, the reciprocals of K_1 for silver chloride, bromide, cyanide, and thiocyanate should be closely comparable with the corresponding thermodynamic dissociation constants. According to this, the monomeric dissociation constant of AgCl is estimated to be 8.3×10^{-8}. The value of 8.4×10^{-5} for the dissociation constant of silver chloride as obtained from ultraviolet spectrophoto-metric studies[40] is not corroborated in the present work.

The existence of large aggregates of AgX, such as the dimers and trimers in solution, provides an interesting topic for further investigation by physical methods.

a. Calculation of the Standard Potential of the Silver Ion-Silver Electrode in Pyridine

Calculation of the total concentration (C_{AgX}) for an arbitrary value of $[Ag^+]$ in the case of silver chloride, bromide, cyanide, or thiocyanate has
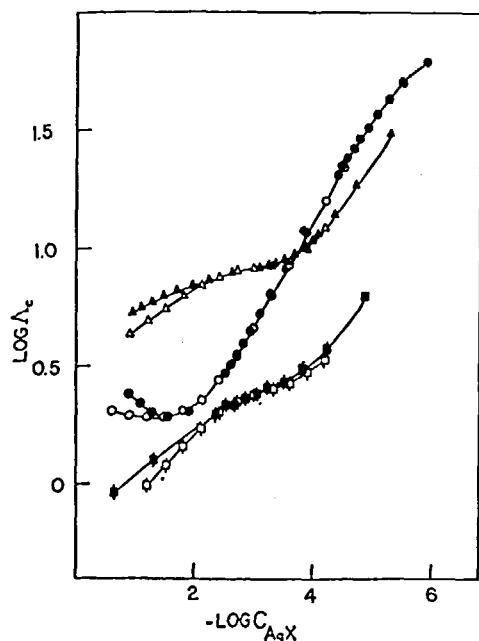
FIGURE 2. Plots of log Λ_c against $-\log C_{AgX}$. AgCl: ϕ (exptl.), ϕ (calcd. with $K_1 = 1.2 \times 10^7$, $K_2 = 1.6 \times 10^4$, and $K_3 = 6.5 \times 10^5$); AgSCN: o (exptl.), • (calcd. with $K_1 = 2.9 \times 10^5$, $K_2 = 1.0 \times 10^2$, and $K_3 = 0$); AgCN: $\triangle$ (exptl.), $\blacktriangle$ (calcd. with $K_1 = 7.5 \times 10^5$, $K_2 = 2.0 \times 10^4$, and $K_3 = 2.0 \times 10^4$). (Reprinted from *J. Phys. Chem.*, 73, 580 (1969). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)
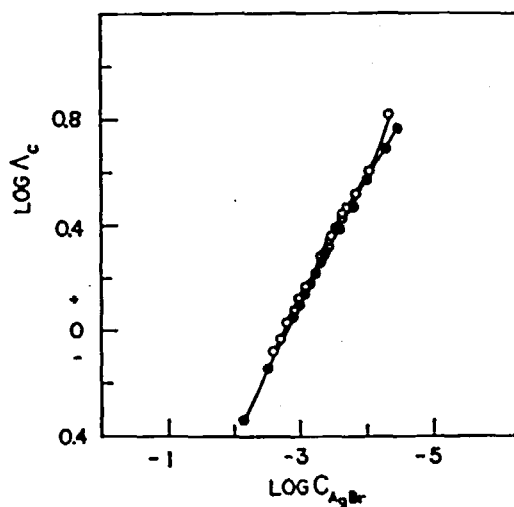
FIGURE 3. Plot of log Λ_c against log C_{AgBr}. o: exptl.; •: calcd. with $K_1 = 5 \times 10^6$, $K_2 = 3 \times 10^3$, $K_3 = 1 \times 10^6$, and $K_4 = 1 \times 10^6$. (Reprinted from *J. Phys. Chem.*, 73, 3115 (1969). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)
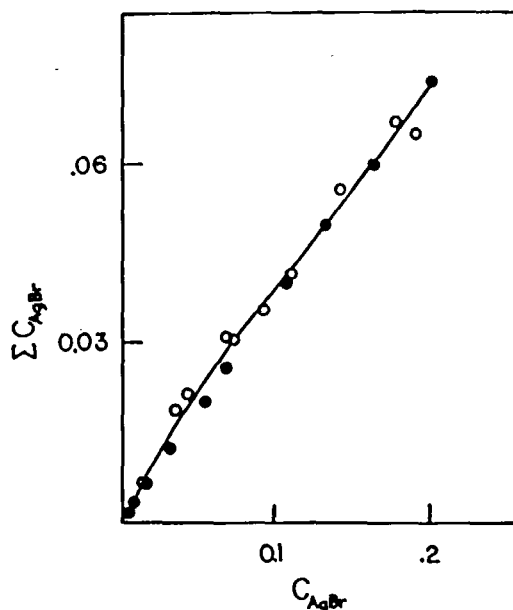
FIGURE 4. Plot of ΣC_{AgBr} against C_{AgBr}: o, exptl.; •, calcd. from Equations 11 and 12. Mean line shown in the plot. (Reprinted from *J. Phys. Chem.*, 73, 3115 (1969). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)

already been discussed (cf. Equation 11). Now, since the ionic strengths of these solutions are given by the relation $[Ag^+] + K_1 K_2 [Ag^+]^3$, the silver-ion concentrations can be transformed into activities using the Debye-Hückel limiting law. Similarly, values of a_{Ag^+} for various concentrations of silver nitrate and picrate can also be generated on the basis of Equation 13 after incorporating the value of the dissociation constant, K_{AgX}, and that of the activity coefficient, f_i.

$$C_{AgX} = [Ag^+] + [Ag^+]^2 \, f_i^2 / K_{AgX} \qquad (13)$$

Mukherjee and others[20,21] organized the results of such activity calculations for the above silver salts in the form of plots of 0.05916 log a_{Ag^+} against $-\log C_{AgX}$. These plots were then compared with those of E against $-\log C_{AgX}$ (cf. Equation 14) based on the actual e.m.f. measurements using cell II at 25°.

$$E = E^0 \,_{Ag^+/Ag} - E_{ref} + 0.05916 \log a_{Ag^+} \qquad (14)$$

Cell II   Zn(Hg)/ZnCl$_2$ (s)//AgX/Ag(s)

In all cases, the plots of the calculated values of 0.05916 log a_{Ag^+} against $-\log C_{AgX}$ were linear

below about 10^{-3} M, but curvature was noticed at higher concentrations, possibly suggesting the inapplicability of the Debye-Hückel limiting law at these concentrations. The plots of E against $-\log$ C_{AgX} for all the systems were linear over the concentration ranges studied, and their slopes compared favorably with those of the linear portions of the plots of $0.05916 \log a_{Ag^+}$ against $-\log C_{AgX}$. It is to be pointed out that the slopes for the chloride, bromide, cyanide, and thiocyanate were in good agreement with the value of 0.02956 V predicted for weak electrolytes; the slightly higher values (about 0.047 V) observed in the case of the nitrate and picrate are most likely due to the relatively greater degrees of dissociation of these salts (Figures 5, 6, and 7).

For the evaluation of $E_{Ag^+/Ag}$, the values of the e.m.f. (E) of cell II and those of $0.05916 \log$ a_{Ag^+} for all 6 silver salts, viz., the chloride, bromide, cyanide, thiocyanate, nitrate, and picrate, were compared in the range of concentrations where both the experimental and the calculated plots were linear and had approximately the same slopes. Normally, the comparison was made at three different concentrations. Using the value of -0.788 V for the potential of the $Zn(Hg)/ZnCl_2(s)$ reference electrode (cell II, cf. Equation 14), a value of 0.550 ± 0.001 V vs. N.H.E. in pyridine was calculated for $E^0_{Ag^+/Ag}$ as the net result of comparison of data on the various systems studied.
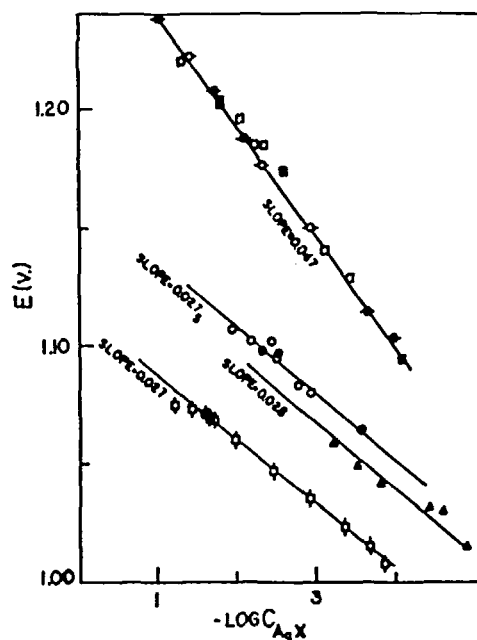
FIGURE 6. Plots of E against $-\log C_{AgX}$ for AgCl (ϕ), AgCN (△), AgSCN (○), AgNO₃ (⊡), and Ag picrate (⊙) (vs. $Zn(Hg)/ZnCl_2(s)$ reference electrode); and for AgSCN (•), AgNO₃ (■), and Ag picrate (⊕) (vs. $Hg/HgCl_2(s)$, LiCl(s) reference electrode). All values of E are referred to the $Zn(Hg)/ZnCl_2(s)$ reference electrode. (The e.m.f. of the cell $Zn(Hg)/ZnCl_2(s)//LiCl(s)$, $HgCl_2(s)/Hg$ is 1.2245 V.) (Reprinted from *J. Phys. Chem.*, 73, 580 (1969). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)
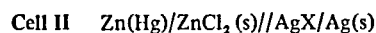

FIGURE 5. Plots of $0.05916 \log a_{Ag^+}$ against $-\log C_{AgX}$ for AgCl (ϕ), AgCN (△), AgSCN (○), AgNO₃ (□) and Ag picrate (⊙). (Reprinted from *J. Phys. Chem.*, 73, 580 (1969). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)

FIGURE 7. Plots of (A) and (B) 0.05916 log a_{Ag^+} vs. log C_{AgBr}. (Reprinted from *J. Phys. Chem.*, 73, 3115 (1969). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)
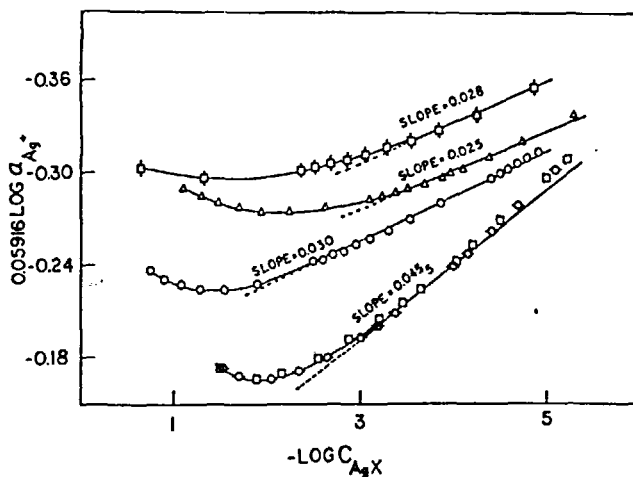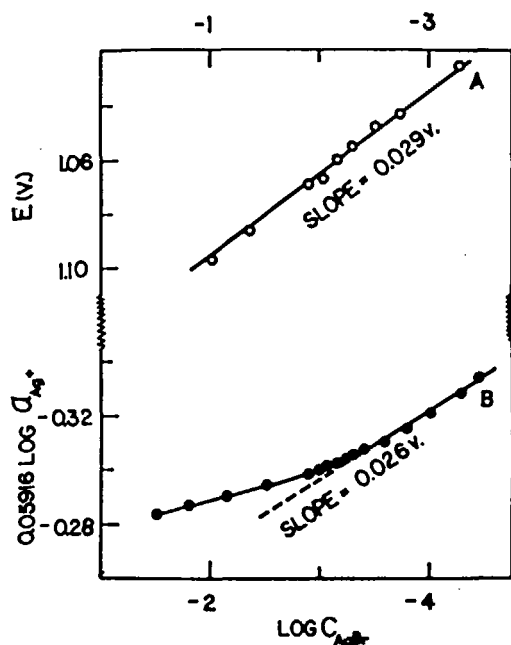
4. Acid-Base Titrations in Pyridine

Indicators such as thymol blue, azo violet, phenolphthalein, and thymolphthalein have been used previously[41-44] in determining the end-points in neutralization reactions in pyridine. Fritz and Gainer[45] attempted to assign values to the color-change potentials of a number of such acid-base indicators on an arbitrary e.m.f. scale. Approximate estimates of the pK-values of these indicators are now being worked out in the reviewer's laboratory.

Streuli and Miron[46] used a methanolic saturated calomel-glass electrode combination and tetrabutylammonium hydroxide as the base for titrating several organic acids, including some aliphatic and aromatic mono- and dicarboxylic acids and phenols. Meta- and parasubstituted benzoic acids and aliphatic monocarboxylic acids were found to maintain the same relative relationships in both pyridine and water. Most orthosubstituted acids became weaker, but most short-chain dicarboxylic acids behaved as stronger acids. Acids capable of anion stabilization through hydrogen bonding became stronger. From an analysis of the half-neutralization potentials

relative to benzoic acid, these investigators were able to obtain a broad classification of the various acids and to formulate criteria for their resolution on the basis of the characteristic linear dependence of the half-neutralization potentials on pK_a^{aq}. It is claimed that dibasic acids for which $pK_2 - pK_1$ exceeds 0.94 unit in water will give 2 titration breaks in pyridine; also, monobasic acids of the same type with pK-differences of this magnitude are expected to give distinctly separate end points.

Bos and Dahmen[47,48] titrated a few acids in pyridine with uncharged bases, using a glass electrode. From an analysis of titration data together with their results of supplementary studies involving spectrophotometric, potentiometric, differential-vapor-pressure* and measurements on the acids and salts, the following order of base strengths was found: tetramethylguanidine > n-butylamine > triethylamine > morpholine. The reported values of $K_d^{BH^+}$ are: 2.4×10^{-10} for tetramethylguanidine, 3.5×10^{-6} for n-butylamine, 1.7×10^{-4} for triethylamine, and 3.1×10^{-4} for morpholine. Unfortunately, there seems to be considerable disagreement among the acid dissociation constants obtained by these workers using different methods. Their estimate of pK for picric acid, for instance, varies between 3.0 and 3.5, and there are similar discrepancies for 2,4-, 2,5-, and 2,6-dinitrophenol. Moreover, the reported values of pK_a for acetic acid (12.0) and benzoic acid (11.0), which were derived from titrations using tetramethylammonium hydroxide solution in pyridine, are higher by about two units and one unit, respectively, than those obtained from more rigorous studies.[23] The authors' conclusion that ion-pair intermediates are · not involved in the dissociation of the nitrophenols and sulfonphthaleins does not appear reasonable.

Mukherjee et al. employed conductance and thermometric techniques for titrating acids in pyridine, using 1,3-diphenylguanidine as the base. A typical example of the conductometric titrations has already been reported.[22] As the acid — in this case, nitric acid — was progressively titrated, the conductance of the solution decreased linearly up to the end point and then rose gradually, also in a linear fashion. A complete analysis of the titration curve was given on the basis of the following equilibria:

$$HX (H^+ X^-) \xrightleftharpoons{K_{HX}} H^+ + X^- \qquad (15)$$
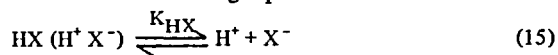
*The important activity-coefficient term has been left out of the equation used in the data treatment.

$$B + H^+ \underset{}{\overset{K_B}{\rightleftharpoons}} BH^+ \qquad (16)$$

$$BH^+ + X^- \underset{}{\overset{K'}{\rightleftharpoons}} BH^+ X^- \text{ (BHX)} \qquad (17)$$
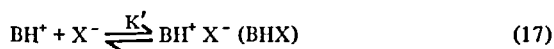
where B represents the uncharged base, 1,3-diphenylguanidine.

Assuming that the activity coefficients of all of the ionic species are given by f_i and that those of the molecules and ion-pairs are unity, at any point during the titration when the molarity B of the base attains a value C_B, application of the principles of mass balance and charge neutrality yields

$$K'K_B{}^2 [H^+]^2 \, f_i{}^2 [B]^2 + (1 + K_B[H^+] +$$

$$K'K_B \, [H^+]^2 \, f_i{}^2)[B] = C_B \qquad (18)$$

where $[H^+]$ and $[B]$ represent the equilibrium concentrations of the species indicated. If K', K_B, and $[H^+]$, and f_i are correctly ascertained, Equation 18 can be solved for $[B]$, and the resulting value can then be substituted into the relations

$$[BH^+] = K_B \, [H^+][B] \qquad (19a)$$

and

$$[X^-] = [H^+] + [BH^+] \qquad (19b)$$

to evaluate $[BH^+]$ and $[X^-]$. Using Equation 20, the conductance $(1/R)$ of the solution can be subsequently calculated.

$$\frac{1}{R} = \frac{\lambda_{H^+}[H^+] + \lambda_{BH^+}[BH^+] + \lambda_X - [X^-]}{1000 \, \theta} \qquad (20)$$

In calculating the theoretical curve for nitric acid, a trial-and-error procedure was actually adopted. A rough estimate of f_i was initially obtained from the ratio of the hydrogen-ion activity of the pure acid solution, as determined from glass-electrode measurements, to the equilibrium concentration of hydrogen ion, as calculated from the product of the molarity of the acid and the factor Λ_c/Λ_o. For nitric acid, K_{HX} and the reciprocal of K' are almost equal, and the ionic strength, and hence the ionic activity coefficients, could therefore be assumed to remain practically constant throughout the entire titration. Using the experimental value of 1.011×10^4 for K', the best fit was obtained with the adjusted values of 2.2×10^5 and 0.800 for K_B and f_i, respectively.

In the thermometric titrations,[26] the neutralizations of $HClO_4$, HI, HNO_3, HBr, picric acid, o-nitrobenzoic acid, 2,4- and 2,5-dinitrophenol, acetic acid, and benzoic acid were studied, using 1,3-diphenylguanidine as the base titrant. With the exceptions of 2,5-dinitrophenol and the two very weak acids (acetic and benzoic acids), the titration curves showed detectable end points and were resonably satisfactory (Figures 8 and 9). The approximate heats of neutralization (kcal mol^{-1}) are calculated to be 11.27 for HBr, 11.19 for 2,4-dinitrophenol, 9.35 for HI, 8.85 for o-nitrobenzoic acid, 8.12 for HNO_3, 7.74 for picric acid, and 5.74 for $HClO_4$, assuming a 1:1 reaction of each acid with the base. Excluding o-nitrobenzoic acid, for which no estimate of pK_a is available, and HI, for which the experimental error may be unusually large becasue the concentration of this acid used in the titration was unusually small, the heats of neutralization of the remaining acids
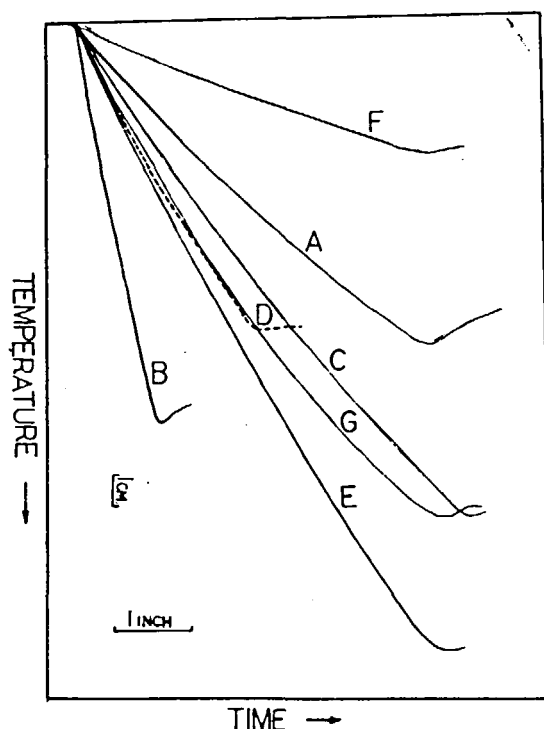
FIGURE 8. Plots of temperature against time for thermometric titrations of: A — $HClO_4$ (0.1000 M); B — HI (0.0247 M); C — HNO_3 (0.1105 M); D — HBr (0.0479 M); E — 2,4-dinitrophenol (0.1013 M); F — picric acid (0.1013 M); and G — o-nitrobenzoic acid (0.1013 M). The full-scale recorder sensitivity was 3 mV for plots, A, C, D, E, and G; 1 mV for plot B; and 10 mV for plot F. (Reprinted from *Talanta*, 21, 303 (1974), by permission of the copyright owner.)
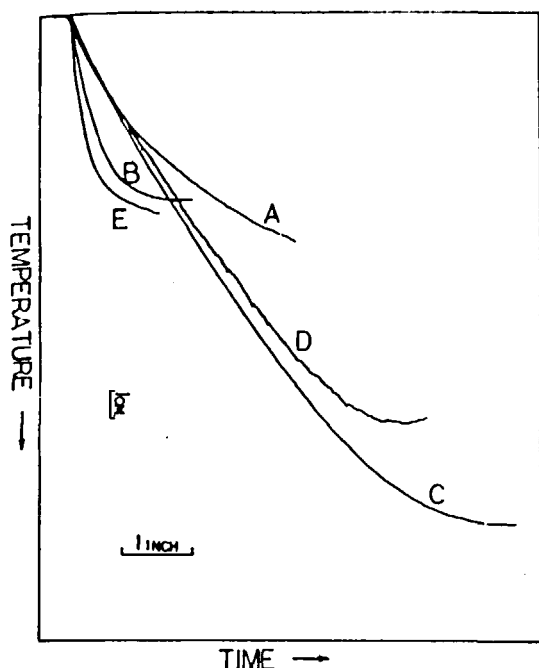
FIGURE 9. Plots of temperature against time for thermometric titrations of: A — acetic acid $(0.0112 M)$; B — benzoic acid $(0.0116 M)$; C — benzoic acid $(0.1164 M)$; D — 2,5-dinitrophenol $(0.0990 M)$; and E — 2,5-dinitrophenol $(0.0099 M)$. The full-scale recorder sensitivity has 1 mV for plots A, B, and E, and 3 mV for plots C and D. (Reprinted from *Talanta*, 21, 303 (1974), by permission of the copyright owner.)

appear to be in the same order as their pK_as. This interesting trend is being further investigated.

5. Metathetical Reactions Involving Exchange of Protons

In connection with studies of the common-ion effect on HX-LiX mixtures (Table 3), it seemed worthwhile to investigate the behavior of mixtures of the type HX-LiY as well. Mixtures of the latter type may conceivably involve a proton exchange of the type

$$HX + LiY \overset{K}{\rightleftharpoons} Hy + LiX; \quad K = \frac{[HY][LiX]}{[HX][LiY]} \tag{21}$$
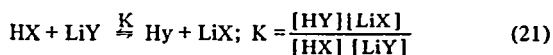
Since the overall dissociation constants of HX, HY, LiX, and LiY are given by

$$K_{HX} = \frac{a_{H^+} a_{X^-}}{[HX]} \tag{22a}$$

$$K_{HY} = \frac{a_{H^+} a_{Y^-}}{[HY]} \tag{22b}$$

$$K_{LiX} = \frac{a_{Li^+} a_{X^-}}{[LiX]} \tag{22c}$$

and

$$K_{LiY} = \frac{a_{Li^+} a_{Y^-}}{[LiY]} \tag{22d}$$

the equilibrium constant K for reaction 21 can be rewritten as

$$K = \frac{K_{HX} K_{LiY}}{K_{LiX} K_{HY}} \tag{23}$$

and can easily be evaluated if the ratios of dissociation constants K_{HX}/K_{LiX} and K_{HY}/K_{LiY} are known. Now, using the charge neutrality rule and assuming that the activity coefficients of all ions are equal, the hydrogen-ion activity of a given HX-LiY mixture can be expressed in either of the two equivalent forms:

$$a_{H^+} = \sqrt{\frac{K_{HX}[HX] + K_{HY}[HY]}{1 + \frac{K_{LiX}[LiX]}{K_{HY}[HY]}}} \tag{24a}$$

and

$$a_{H^+} = \sqrt{\frac{K_{HX}[HX] + K_{HY}[HY]}{1 + \frac{K_{LiX}[LiX]}{K_{HX}[HX]}}} \tag{24b}$$

For a particular mixture of HX and LiY, it is possible to calculate the equilibrium concentrations of HX, HY, LiX, and LiY from the value of K (Equation 23), and then to obtain the corresponding hydrogen-ion activity using Equation 24a or 24b. The latter can be used together with the known value of the potential of the $Zn(Hg)/ZnCl_2(s)$ reference electrode for calculating the e.m.f. of the cell

Cell III $Zn(Hg)/ZnCl_2$ (s)//HX, LiY in pyridine/H_2
(1 atm) Pt
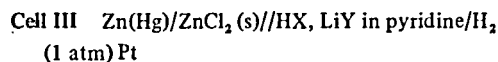
and the validity of the postulated proton-exchange reaction in a given case can be judged on the basis of the agreement of this calculated value of the e.m.f. with the experimental one.

Since lithium perchlorate had already come to be of some interest because of its "leveling effect" on the polarographic half-wave potentials of acids,[12] mixtures of HNO_3 and $LiClO_4$ were the first ones to be studied[19] as a test case. A comparison of the observed and the calculated

TABLE 4

Comparison of Calculated and Observed Values of the E.M.F. of Cell III with HNO₃-LiClO₄ Mixtures

$10^4 \times$ Concn. (M) of HNO_3	$10^3 \times$ Concn. (M) of $LiClO_4$	E, V	
		Observed	Calculated from Equation 24b
9.22	1.50	0.597	0.593
9.22	7.41	0.5945	0.593
9.22	17.1	0.589	0.589

values of the e.m.f. of cell III, which were based on a value of 0.60_5*for K 9cf. Equation 23 and Table 3) in this case, is presented in Table 4. The excellent agreement found for the three mixtures strongly suggests that the reaction

$$HNO_3 + LiClO_4 \rightleftharpoons HClO_4 + LiNO_3 \qquad (25)$$
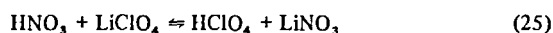
does indeed occur. It should be mentioned in this connection that Tsuji and Elving[17] subsequently used this concept of proton-exchange in explaining the observed leveling of the half-wave potentials of acids in $LiClO_4$ as the background electrolyte. A comprehensive survey of similar proton-exchange reactions in pyridine involving the application of the conventional techniques and nmr measurements[50] is now in progress in the reviewer's laboratory.

6. Silver Halide Adducts of the Type AgX·MX

In pyridine, the acids $HClO_4$, HNO_3, HBr, and HCl seemed to conform to rather simple equilibria. Likewise, the behavior of the alkali halides[51] appeared relatively simple in this solvent. On the other hand, solutions of certain univalent silver(I) salts, such as AgCl, AgBr, AgCN, and AgSCN, were found to be complex, and their behaviors suggested the existence of triple ions, dimers, and even larger self-associated aggregates like the trimers, as discussed earlier. In view of these differences, Mukherjee and co-workers[21,24] considered it interesting to explore the possibility of interaction of the AgX moities, such as AgCl and AgBr, in pyridine with the corresponding halides containing the organic cations Et_4N^+, Bu_4N^+, diphenylammonium ($DPAH^+$), and 1.3-

diphenylguanidinium ($DPGH^+$), and also wi: LiBr, and HBr from measurements of the si activities of the mixtures, which were m using a silver indicator electrode. Sample lations for obtaining the value of the for constant K_c for a 1:1 adduct of the $AgX·MX$, are given in connection with the of the AgBr·HBr adduct.[21]

The values of the formation constants (T: ranged from 1.57×10^2 to 5.96×10^4. All no explanations of the absolute values of constants were offered, certain correlations be established. The chlorides were found t rise to weaker adducts than the bromides. the formation constants in either series seen decrease (1) as MCl or MBr became less d ated, and (2) as the size of M^+ (gauged fr ionic mobility) increased. The trend for DP/ and DPG·HCl was possibly due to the coope effect of the size of M^+ and the dissociabil MCl acting in the same direction. The sitt with regard to the AgCl·LiCl adduct might : sent the net result of the effects of the size and the smaller dissociation constant of LiCl.

It should be mentioned that in EDA, wh also a coordinating solvent of almost equal d tric constant (D = 12.9), similar 1:1 adduc considerably lower formation constants[37] be detected among silver iodide and the iodide. Na(I), K(I), Rb(I) and Cs(I). In this solvent silver iodide and the alkali iodides dissociate as simple weak electrolytes.

The above adducts are particularly interesting on account of their inherent difference from the complexes of the usual π donor — (unfilled d) acceptor type that are known to be formed

---

*It is of interest to note that the magnitude of this value is comparable with those of the equilibrium constants of metathetical reactions between the substituted ammonium salt ion-pairs and the alkali acetate ion pairs in glacial acetic acid (D = 6.13) as solvent.[49]

TABLE 5

Formation Constants (K_c) of the Adducts Formed by the Reaction

$$AgX + MX \ (or \ HX) \overset{K_c}{\rightleftharpoons} AgX \cdot MX \ (or \ AgX \cdot HX)$$
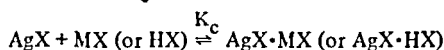
MX or HX	Dissociation constant of MX or HX	Mobility of cation	$10^3 \ K_c$[a]
(DPGH)Cl	2.30×10^{-6}[a]	18.6[a]	0.157 ± 0.0134
LiCl ·	8.55×10^{-7}[a]	24.9[b]	0.298 ± 0.043
(DPAH)Cl	4.41×10^{-6}[a]	23.4[a]	0.852 ± 0.059
(DPGH)Br	4.31×10^{-5}[a]	–	1.76 ± 0.10
LiBr	5.24×10^{-5}[a]	–	3.71 ± 0.67
HBr	4.36×10^{-5}[c]	49.6[b]	7.5 ± 0.9
(DPAH)Br	1.25×10^{-4}[a]	–	12.7 ± 1.3
(Bu$_4$N)Br	2.50×10^{-4}[b]	24.0[b]	48.2 ± 8.0
(Et$_4$N)Br	5.82×10^{-4}[a]	25.5[a]	59.6 ± 10.8

[a]Reference 24; cf. Table 3 for the dissociation constants of LiCl and LiBr.
[b]Reference 11 and 38.
[c]Reference 19; cf. Table 3.

TABLE 6

ν_2 Vibration Frequencies of the Nitrate Ion (cm^{-1})

	NH_4NO_3	$LiNO_3$	$C_5H_5N \cdot HNO_3$	$AgNO_3$
Saturated solution in pyridine	830	828	823	828, 831
Aqueous pyridine	830	816, 829	827, 831	830
Aqueous solution	833	833	833	816

between some aromatic hydrocarbons and silver nitrate or perchlorate.[52-54] Attempts are under way in the reviewer's laboratory to isolate the adducts formed in pyridine and to study their nature of bonding and other physical properties such as the optical characteristics and electrical conductivity[55] in the solid state. Studies related to new adducts of similar types, and a critical appraisal of the role of pyridine in promoting the formation of such adducts, are also in progress.

7. Spectroscopic Studies in Pyridine

Thompson[2] found that the infrared spectrum of lithium nitrate in pyridine shared many of the characteristics of the pyridine–water system and corresponded roughly to 0.3 mol of water per mole of pyridine insofar as the pyridine vibrations were concerned. Since the polarizing power of a cation is determined by the degree of shielding due to solvation, the two ν_2 frequencies of the nitrate ion (Table 6) for lithium nitrate in aqueous pyridine were attributed to the presence of two different forms of the lithium ion:

The situation of pyridinium nitrate was considered to be similar, differing only in that a hydrated pyridinium cation, rather than a hydronium ion solvated with pyridine, may be involved.

The spectrum of a saturated solution of silver nitrate in pyridine was found to correspond to a solution containing 0.2 mol of water for each mole of pyridine. The appearance of two ν_2 frequencies

of similar intensity for the nitrate ion in this case was believed to imply that, in addition to the two strongly coordinated pyridine molecules, there are others that are held in a secondary solvation shell. On the other hand, the appearance of only one ν_2 frequency in aqueous pyridine would suggest that only one form of solvated Ag^+, viz., the strongly coordinated complex $Ag(C_5H_5N)_2^+$, is possible in this medium.

The fact that there is only one ν_2 band for ammonium nitrate in either pyridine or aqueous pyridine, and that it has the same frequency in these media, suggests that the structure of the ion pair is the same in both pyridine and water. Perturbation of the nitrate ion due to hydrogen bonding may be responsible for this similarity in structure.

Interestingly, potassium thiocyanate was found to dissolve in pyridine without producing any changes in pyridine frequencies. This was considered to be due to the lack of cation solvation in this case.

Popov and his co-workers have recently reported[27,56,57] some systematic studies of ion solvation through infrared and nmr spectroscopy in various aprotic and basic solvents including pyridine. Their investigation[27] on the solvation of sodium ion, using ^{23}Na nmr spectroscopy in solutions of $NaBPh_4$, $NaClO_4$, NaI, and $NaSCN$ with reference to aqueous solutions of sodium chloride, reveals that the chemical shifts for the first two salts are independent of concentration, whereas those for the iodide and, to a lesser extent, for the thiocyanate depend on the salt concentration, indicating the existence of contact ion pairs in these cases. For sodium chloride, which is free from contact ion pairs, the chemical shifts were found to bear a good linear relationship with Gutmann's donor numbers[58] in the solvents nitromethane, acetonitrile, dimethylformamide, dimethylsulfoxide, pyridine, and hexamethylphosphoramide.

III. CHEMISTRY IN SULFOLANE

Sulfolane (tetramethylenesulfone, TMS) is of intermediate dielectric constant (43.3) and belongs to the family of protophobic aprotic solvents. The high viscosity of the substance and its remarkably low heat of fusion suggest a well-developed structure in the liquid state.[59]

The value of pK_a (S) of TMS as a Brønsted acid

is estimated to be greater than 31,[60] and in addition TMS is known to behave as a very weak base $[pK(SH^+) = -12.9$.[61] Thus the solvent is expected to cover an acidity range of over 40 pH-units. The ability of TMS to solvate ions or to form hydrogen bonds is presumed to be weak.[62-64]

The substance offers a major practical advantage as a medium for the determination of very weak acids and bases, and also for the resolution of mixtures of strong acids and bases that are normally leveled in other solvents. In addition, the large freezing-point-depression constant, which is about 35 times greater than that of water, holds considerable promise for TMS as an interesting solvent for cryoscopic studies.

Industrially, TMS has proven to be a good solvent for polymers and to be useful in the extraction of aromatics and the removal of acidic gas constituents.[65]

A. Purification of Sulfolane — Physicochemical Properties

A simple procedure for purification[64] of TMS consists of refluxing the commercial material over sodium hydroxide pellets and successive distillations under reduced pressure (11 torr) at 140° until the distillate ceases to produce a detectable brown coloration upon treatment with concentrated sulfuric acid. Two or three distillations are usually required to reach this point. A final distillation over calcium hydride is carried out to remove the last traces of water that may be retained by the solvent. The purified material should be stored in sealed containers.

A more elaborate method of purification has been described by Coetzee et al.[66] According to this method, commercial samples (Shell or Phillips) should be heated in 1-liter batches with 10 to 15 g of solid NaOH, at 170 to 180°, for 24 hr. During heating, the liquid should be purged with a slow stream of pure nitrogen gas. This treatment decomposes the thermally unstable sulfolene and removes other volatile impurities. The product, which is dark reddish-brown in color, should be decolorized by stirring with 10 to 15 g of Fischer Norit-A Decolorizing Carbon-Neutral, at 80 to 90°, for 6 hr. The filtrate is passed through a 4-ft column packed with a mixed bed of acidic and basic macroreticular ion-exchange resins (Rohm and Haas Amberlyst-15 and A-21). The column should be kept heated to 70 to 80° in order to

increase the rate of exchange and the flow rate, since the viscosity of TMS is high. The clear effluent, having a specific conductivity of about 2 $\times$ 10^{-9} mho/cm^{-1}, should be vacuum-distilled from calcium hydride at a pressure of 0.01 to 0.02 torr and an oil-bath temperature of 90 to 100°. The 80% middle cut should be collected and stored under nitrogen gas.

The single distillation step involved in the above procedure has some obvious advantages.

Some characteristic physical properties of TMS are given in Table 7. In view of the fact that the substance is a solid at normal room temperature, most of these properties and the reported measurements in this solvent are referred to 30°.

B. Recent Studies in Sulfolane

The recent studies in TMS consist of acid-base titrations and some fundamental studies, which can be divided into three categories: (1) the development of pH standards, (2) the examination of the behaviors of electrolytes and some complexes, and (3) polarographic investigations and other studies concerning the energetics of ion solvation in this medium.

1. Acid-Base Titrations

The advantages of the differentiating properties of the sulfolanes in acid-base titrations have been clearly demonstrated by Morman and Harlow.[62] These workers titrated a variety of acids and bases potentiometrically in 3-methylsulfolane, a solvent analogous to TMS, using a glass electrode. Their base titrant consisted of 0.2 M n-Bu$_4$NOH in isopropanol; for the titration of bases, an 0.2 M solution of perchloric acid in dioxane was used. Later, Coetzee and Bertozzi[68] demonstrated the feasibility of conductometric titration of HClO$_4$ in TMS, using simply water as the reagent (!) (Figure

10). In a more recent study,[69] they have further explored the possibility of conductometrically titrating predominantly anhydrous perchloric acid with various types of mono- and bifunctional weak bases, including alcohols, ketones, and amines, and also substances that are themselves important dipolar aprotic solvents, such as acetonitrile, nitrobenzene, dimethylformamide, and dimethylsulfoxide. Four categories of titration curves have been described. Acetonitrile and nitrobenzene produced drawn-out curves indicating a very gradual rise in conductance. Apparently the proton-transfer reaction in these cases is not complete, but it is significant in that the proton-accepting power of acetonitrile and nitrobenzene is demonstrated to be greater than that of TMS.

2. Hydrogen Ion Activities of Solutions — pH Standards

For obvious reasons, the quantitative assessment of acidities is the most important consideration in dealing with acid-base chemistry in a given solvent. The determination of acidity in TMS solutions poses serious experimental difficulties, presumably because of the inability of the solvent to stabilize the molecular part of the acid or the anion involved in a dissociation equilibrium. Indeed, the preliminary attempts of Coetzee and Bertozzi[70] in this direction, through potentiometric measurements using a hydrogen or a glass electrode, were unsuccessful. In their subsequent work,[68] they also failed to achieve good reproducibility of the calibration constant of the hydrogen electrode, and suggested a provisional value for the same. Their first set of measurements, on mixtures of 2,6-dihydroxybenzoic acid and tetrabutylammonium salts, does not exhibit a systematic trend. Furthermore, if the result for salicylic acid is taken into consideration with those

TABLE 7

Properties of Sulfolane

Melting point (°C)	28.37,[64] 28.9[63]
Boiling point (°C, 760 mmHg)	285[62]
Heat of fusion (cal g^{-1}, 26°)	2.73 ± 0.03[63]
Molal depression constant (deg mole^{-1} kg^{-1})	66.2 ± 0.6[63]
Density (g cm^{-3}, 30°)	1.2614[67]
Viscosity (cP, 30°)	9.89,[63] 10.286[67]
Refractive index (30°)	1.4820[67]
Dielectric constant (30°)	43.3[67]
Specific conductivity (mho cm^{-1}, 30°)	~2 $\times$ 10^{-9} [66]
Spectral cut-off (λ, nm)	~220
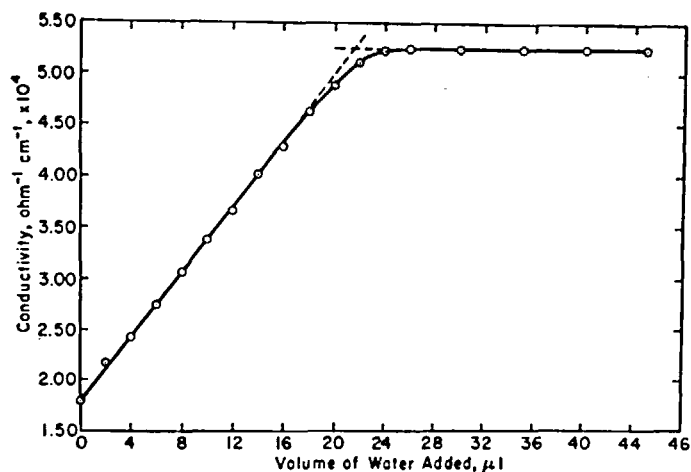
FIGURE 10. Conductimetric titration of anhydrous perchloric acid in 28 ml of a solution containing 5.0×10^{-2} M total acid. Solvent: sulfolane. Titrant: water. (Reprinted from *Anal. Chem.*, 43, 961 (1971). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)
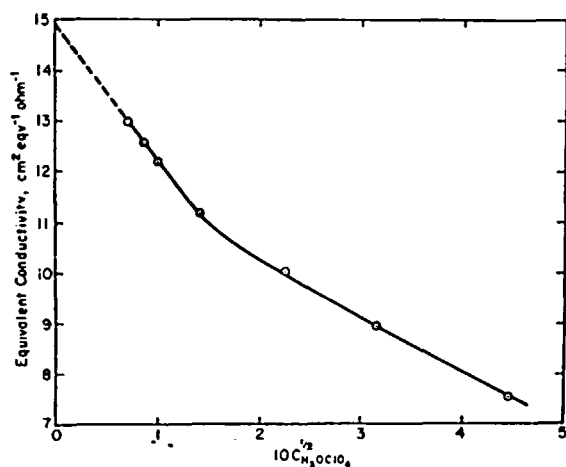
FIGURE 11. Concentration dependence of equivalent conductivity of hydronium perchlorate in sulfolane as solvent. (Reprinted from *Anal. Chem.*, 43, 961 (1971). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)

of the other measurements, it becomes evident that the potential of an identical hydrogen-glass electrode combination depends markedly on the nature of the solutions used. However, on prolonged equilibration (for 30 to 60 min), Nernstian response stable within ± 1 mV was observed for the glass electrode in later studies[69] of the 2,6-dihydroxybenzoic acid-tetrabutylammonium salt system, and the results seemed to be in general agreement with the postulated existence of the homoconjugated species $(HA)A^-$ and $(HA)_2A^-$.

The estimates of pK given by Coetzee and Bertozzi[68,69] are: 23.6 for salicylic acid, 18.8 for pyridinium ion, 18.8 for 2,6-dihydroxybenzoic acid, 17.4 for picric acid, 14.5 for HCl, and 3.0 for $HClO_4$, which indicates an average increase of 6 to 7 pK-units in comparison to the values obtained in acetonitrile. It should be mentioned here that the pK_a-values of the last two acids were arrived at through measurements independent of the potentiometric acidity scale calibration constant. The value for hydrochloric acid was determined from potentiometric titrations of anhydrous hydrochloric acid with anhydrous silver perchlorate solution in TMS using a silver indicator electrode, whereas the dissociation constant of anhydrous perchloric acid in TMS was derived in a rather ingenious way from the specific conductivity of hydronium perchlorate (Figure 11) and the data on titration of the acid with water (Figure 10).

Apparently with the object of re-examining the potentiometric approach, Benoit and Pichet[71] recently investigated the optimum conditions for the functioning of a glass electrode in TMS. They used 3 different types of electrodes: 1 was a commercial Radiometer G 202B electrode, and the other 2 were modified varieties having as internal electrode either a silver wire in contact with an 0.1 M solution of silver perchlorate or simply a platinum wire dipped in a pool of triple-distilled mercury. An $Ag/AgClO_4$ (0.01 M) or a Pt/I_3^- (0.01 M), I^- (0.1 M) electrode was used as the

reference. A slope of 0.060 V for the plot of E vs. log [B]/[BH$^+$] was obtained in solutions containing the base pyridine with a constant molarity of pyridinium picrate, which presumably held the liquid-junction potential at a steady value. The authors suspect that any deviation from the Nernstian response is due to the variation of the junction potential. It should be further stated that, according to these authors, the nature of the internal reference of a glass electrode was of no consequence.

Benoit and Pichet[71] successfully titrated several amines with perchloric acid in TMS, using a glass electrode; their calculated values of H$_0$ for 0.1 M solutions of acids are -1.5 for HCl, -4.5 for HBr, -6.4 for HClO$_4$, and -7.3 for HSbCl$_6$, which is completely dissociated, with o-nitroaniline as the reference base. These H$_0$-values compare favorably with the values reported by Adler and co-workers,[72] which are -1.2 for HCl, -4.5 for HBr, -7.2 for HClO$_4$, and -8.2 for HPF$_6$. The values of pK$_a$ arrived at by Benoit and Pichet are 2.8 for HClO$_4$ (a value of 2.7 had been obtained from earlier work[73]), 3.3 for HSO$_3$F, 5 for H$_2$S$_2$O$_7$, 14.3 for picric acid, and 20.6 for salicylic acid.

From the H$_0$-values derived in the TMS-sulfuric acid system with 4-chloro-2-nitroaniline [pK$_a$ (BH$^+$) = -1.03] as the reference base, Arnett and Douty[64] were able to obtain the dissociation constants of the conjugate acids of nitrobenzene, anthraquinone, benzalacetophenone, and several nitroanilines.

From hydrogen-electrode* measurements in an 0.1 M solution of perchloric acid in TMS, using the ferrocene electrode as the second electrode, a potential of 0.20 V was calculated for N.H.E.(S) vs. E^o of the ferrocene couple in the solvent. Combining this value with that of E^o of the ferrocene system (0.59 V) vs. N.H.E.(W) in TMS, which was estimated through the medium activity coefficient of Ag$^+$,[66,75] Benoit and Pichet[71] finally calculated a pH of -12.8 for 1 M SH$^+$ in the solvent. The latter apparently suggests that a very high proton activity is attainable in TMS.

3. Conductance Behavior of Electrolytes

Fundamental studies on conductance of electrolytes in TMS are mostly due to Fernandez-Prini and Prue,[59] and Della Monica and his co-

*An "activated" bright platinum electrode[74] was used.

workers.[76-80] The former investigators fitted their data on LiCl, LiBr, LiI, LiClO$_4$, NaI, NaClO$_4$, KI, KClO$_4$, RbClO$_4$, CsClO$_4$, Et$_4$NI, and KPF$_6$ to Pitts' equation (to better than 0.1%) by introducing association constants. In order to rationalize the differences between the distances of closest approach ($\mathring{a}$) and the sums of the crystallographic radii of the ions, which were mostly larger, it was necessary to consider dielectric saturation. The association constants of lithium chloride and bromide were found to be 1.39 $\times$ 10^4 and 2.78 $\times$ 10^2; for the other salts they were small (<10). The limiting conductances obtained by these workers are presented in Table 8, together with those reported in dimethylsulfoxide[81] for the purpose of comparison. As is evident, there is a decrease in conductance from cesium perchlorate to sodium perchlorate, which is followed by a sharp rise at lithium perchlorate in contrast with the normal behavior in other solvents such as water,[82] methanol,[83] formamide,[84] dimethylformamide,[85] and pyridine,[11] besides dimethylsulfoxide.[81] The present behavior is believed to suggest that ion mobility depends in some way on structural factors; a reorganization or disruption of the parent structure of the solvent might be involved.

The reported ionic mobilities[76-80] are summarized in Table 9. The radii obtained for Cl$^-$, Br$^-$, I$^-$, and ClO$_4$$^-$ by the Robinson and Stokes method are close to the crystallographic values,

TABLE 8

Limiting Conductances of Electrolytes

Salt	Sulfolane (30°)[a]	Dimethylsulfoxide (25°)[b]
LiCl	13.63	35.3
LiBr	13.25	35.2
LiI	11.53	–
LiClO$_4$	11.05	35.7
NaI	10.865	37.6
NaClO$_4$	10.325	38.3
KI	11.25	38.2
KClO$_4$	10.75	39.1
KPF$_6$	9.995	–
RbClO$_4$	10.84	39.4
CsClO$_4$	11.03	–
Et$_4$NI	11.20	–

[a] η = 10.29 cP, D = 43.3.
[b] η = 1.96 cP, D = 46.6.

TABLE 9

Limiting Ionic Conductances in Sulfo-
lane at 30°

Ion	$\lambda°$
$n\text{-}Am_4N^+$	2.50
Bu_4N^+	2.80
Pr_4N^+	3.23
Na^+	3.61
Et_4N^+	3.95
K^+	4.05
Rb^+	4.16
Cs^+	4.27
Me_4N^+	4.31
Li^+	4.33
NH_4^+	— 4.97
$Picrate^-$	5.28
PF_6^-	5.95
ClO_4^{-*}	6.68,
I^-	7.22
Br^-	8.92
Cl^-	9.30
SCN^-	9.64

*From transference-number measure-
ments.[77]

indicating that these anions do not also[86] undergo
any solvation in TMS and remain as practically
bare ions in this solvent. The corrected solvated
radii of the ions Na^+, K^+, Rb^+, Cs^+, and NH_4^+
decrease systematically in that order, whereas Li^+
seems to be exceptional in the sense that its
solvated radius is less than that of Na^+. Similar
behavior of Li^+ was also observed in acetonitrile.[87]

4. Complexes of Silver (I) with Cl^-, Br^-, I^-, and SCN^-

Della Monica, Lamanna, and Senatore,[88] deter-
mined the solubility products of AgI, AgBr, and
AgSCN and the overall formation constants (β) of
the complexes $AgBr_2^-$, $Ag_3I_4^-$, and $Ag(SCN)_2^-$ in
TMS at $\mu = 0.1$ from potentiometric as well as
conductometric titrations of $AgClO_4$ using, for the
former, a spongy silver-wire indicator electrode.
The solubility products so obtained are $6.6 \times
10^{-19}$ for AgBr, 3.3×10^{-19} for AgI, and $5.4 \times
10^{-17}$ for AgSCN. The overall formation
constants (β) are reported to be 2.1×10^{19} for

$AgBr_2^-$, 3.3×10^{56} for $Ag_3I_4^-$, and 1.1×10^{16}
for $Ag(SCN)_2^-$. In subsequent studies, Benoit et
al.[89] obtained $pK_{sp} = 18.5$ for AgCl and 18.9 for
AgBr, and $\log\beta = 20.3$ for $AgCl_2^-$ and 20.2 for
$AgBr_2^-$ at zero ionic strength.

5. Polarographic Studies in Sulfolane — Reference of Potentials in Sulfolane to the Water Scale; Heats of Solution of Electrolytes

Among the polarographic studies reported in
TMS, only the work of Coetzee and his co-
workers[66,90] is discussed here since the other
investigations[91,92] refer to temperatures substan-
tially above or below 30°.*

Coetzee et al.[66] determined the half-wave
potentials of Li^+, Na^+, K^+, Rb^+, and Cs^+ [vs. an
$Ag/AgClO_4$ (0.1 M) electrode in TMS] in TMS,
using the perchlorate salts. Apparently, their
principal object in this study was to relate the
potential scales of TMS and water. On the basis of
the modified Born equation

$$\Delta G_+^0 = -\frac{Ne^2}{2}(1 - \frac{1}{D})\left(\frac{z_+^2}{r_+ + r_+'}\right) \tag{26}$$

they first evaluated the difference between the
solvation energies of Cs^+ and Li^+ in water as 49.1
kcal/mol^{-1}. From the difference between the
differences in the half-wave potentials of the same
pair of cations in water and TMS ($\Delta\Delta E_{1/2} = 5.3$
kcal/mol^{-1}) they obtained a solvation-energy
difference of 43.8 kcal/mol^{-1} between Cs^+ and Li^+
in TMS and a cation-radius correction of 0.81 Å
for the solvent. Finally, this correction term was
used together with $r_t' = 0.72$ Å for water to show
that the half-wave (or standard) potentials of
lithium, sodium, potassium, rubidium, and cesium
ions are more positive in TMS than in water by
0.36, 0.26, 0.19, 0.16, and 0.14 V, respectively,
on the molal scale.

Choux and Benoit[93] measured heats of solu-
tion of various salts, including $AsPh_4I$ and the
tetraphenylborates of $Na(I)$, $K(I)$, $Rb(I)$, and
$Cs(I)$, in TMS, and were able to separate the
cationic and anionic enthalpies of transfer from
water on the basis of the extrathermodynamic

*Headridge et al.[91] reported polarographic and voltammetric data at 40° for 22 inorganic systems, including ferrocene and
cobalticinium ion, in 0.1 M sodium or tetraethylammonium perchlorate as the background electrolyte. A silver-silver
chloride electrode, prepared with a saturated solution of tetraethylammonium chloride in TMS, was used as a reference
electrode. For most of the systems the behavior in TMS resembled that in water, but this was not true for bromide,
oxygen, and the rare-earth ions europium(III) and samarium(III).

assumption that $\Delta H_t(AsPh_4^+) = \Delta H_t(BPh_4^-)$.[94] Apparently, attempts were made to determine the enthalpy of transfer of $AsPh_4BPh_4$ directly; however, due to its very low solubility in water, the heat of precipitation had to be determined, and the results lacked reproducibility. The average value of -12.1 kcal/mol^{-1}, when combined with the heat of solution of the salt in TMS, led to a value of -2.0 kcal/mol^{-1} for the enthalpy of transfer in comparison with the calculated value of -5.7 kcal/mol^{-1}.

The implications of the above single-ion enthalpies of transfer and the results of Coetzee and co-workers on the reference of potentials in TMS and water are discussed in Sections IV.B.3 and V.

IV. CHEMISTRY IN PROPYLENE CARBONATE

Propylene carbonate (PC) is a stable aprotic substance (fp $-49.2°$, bp $241.7°$) of a moderately high dielectric constant (64.4). It is a good solvent for many inorganic and quaternary ammonium salts. Also, it does not react with the alkali metals; in fact, a number of alkali metals (and alkaline earths) have been successfully electrodeposited from PC solutions. Apparently, it is this inertness toward alkali metals that makes PC a particularly suitable solvent for "high energy" electrochemical reactions.[95]

According to the pioneering studies of Harris,[96] the solubilities of the alkali halides in PC increase in the order K < Na < Li, i.e., as the cation size decreases. These studies further suggest that cations are more solvated in PC than anions are, an effect which probably arises from the disposition of charges in the solvent dipole. The negative end of the dipole is localized on the carbonyl oxygen, which is relatively easily accessible to the cations, whereas the positive charge is distributed over the atoms in the chain $H_3C\text{-}CH\text{-}CH_2\text{-}$, and therefore becomes too weak to attract the anions. Harris also noticed that, in general, solutions of the sodium or potassium halides and tetrafluoroborates were much more ionic than those of the alkaline-earth halides and other higher valent metal halides.

A. Purification of Propylene Carbonate — Physicochemical Properties

PC can be prepared in the laboratory by the reaction of 1,2-propanediol and diethyl carbonate at 110 to 135° in the presence of an alkali metal catalyst.[97] Commercially, it is produced by the reaction of 1,2-propylene oxide and carbon dioxide. The yield from this reaction is low unless a catalyst, such as a quaternary ammonium halide, is used.[98] The typical impurities in the commercial product are[99] propylene glycol (2,000 ppm), water (450 ppm), propylene oxide (33 ppm), allyl alcohol (10 ppm), and carbon dioxide. In addition, propionaldehyde may be present in detectable amounts.

Although PC is quite stable at ordinary temperatures, it is decomposed on heating and therefore it cannot be purified by slow distillation at atmospheric pressure. Fast distillation under reduced pressure[99] is normally used. Practically all low-boiling impurities are removed by two such distillations, although a small amount (11 ppm) of propylene glycol (bp 189°) may still remain in the distillate. Samples of PC obtained from distillation under vacuum in the presence of CaO, SiO$_2$, or lithium metal appear to contain no appreciable amounts of impurities of any kind. For routine purification[100] two successive distillations of the commercial sample (Jefferson) from CaO at a pressure of 1 torr have been found to suffice, the middle fraction being taken each time. The specific conductance of the twice-distilled solvent varied between 1.0×10^{-8} and 2.0×10^{-8} mho cm^{-1}. Analysis by vapor-phase chromatography indicated the absence of any appreciable impurities. The carbon dioxide content was below 0.02 mol %, and no other extraneous peak could be observed. Water could not be detected by Karl Fischer titration. Additional details on purification and tests for purity of PC are given by Fujinaga and Izutsu.[101]

Some important physicochemical properties of PC are presented in Table 10.

B. Recent Studies in Propylene Carbonate

Recent studies in PC comprise mainly (1) investigations of the conductances and viscosities of solutions of electrolytes; (2) potentiometric studies of the thermodynamics of alkali-metal and thallous-ion indicator electrodes, including some polarographic and voltammetric investigations; (3) measurements of heats of solution of electrolytes; and (4) some acid-base titrations.

TABLE 10

Properties of Propylene Carbonate

Density, ρ (g cm^{-3}, 25°)	1.198,[96] 1.200[101]
d ln ρ/dT (deg^{-1})	-0.001[96]
Viscosity, η(cP, 25°)	2.530,[96] 2.480[100]
d ln η/dT (deg^{-1})	-0.018[96]
Refractive index (20°)	1.4209[102]
Dielectric constant, D (25°)	64.4,[96] 65.1[103]
d ln D/dT (deg^{-1})	-0.0037[103,104]
Specific heat (cal g^{-1} deg^{-1})	0.615 (20°),[102] 0.682 (100°),[102] 0.777 (150°)[102]
Specific conductivity (ohm^{-1} cm^{-1}, 25°)	~1.0 × 10^{-8}[100]

1. Conductance and Viscosity Studies

Fuoss and his co-workers[105] studied the conductance of tetra-n-butylammonium tetraphenylborate in PC and concluded that the association of the salt was negligible. The $\overset{\circ}{a}$ parameter was found to be 5.5 Å, which is considerably smaller than the value expected from molecular models. Fuoss and Hirsch[106] found a value of 5.1 Å, which was again in poor agreement with the value obtained from viscosity measurements.

A careful study of conductance and viscosity of a selected group of 1:1 electrolytes was undertaken by Mukherjee et al.[100,107] The method of Fuoss and Accascina[108] was used in analyzing their data on the conductances of solutions of LiCl, LiBr, LiClO$_4$, KI, KClO$_4$, Et$_4$NCl, Et$_4$NClO$_4$, n-Bu$_4$NBr, n-Bu$_4$NClO$_4$, (i-Am)$_4$NI, and (i-Am)$_4$ N (i-Am)$_4$B. Of these salts, only lithium chloride and bromide were found to be associated, having association constants of 557 and 19, respectively. As in the case of TMS, the larger bromide ion with its lower charge density appeared to have a much smaller affinity for the lithium ion than the chloride ion.

The experimental value of the viscosity coefficient A ($\eta/\eta_0 = 1 + AC^{1/2} + FC$) of tetraisoamylammonium tetraisoamylborate was found to be in satisfactory agreement with the value calculated from the relation

$$A = \frac{327.88}{320\,\eta_0\,(DT)^{1/2}\,\Lambda^\circ_{(i\text{-Am})_4 N(i\text{-Am})_4 B}} \qquad (27)$$

which is based on equality of the conductances of the ions (i-Am)$_4$N$^+$ and (i-Am)$_4$B$^-$. Accordingly, in establishing the mobilities of other ions, it was assumed that

$$\lambda^\circ_{(i\text{-Am})_4 N^+} = \lambda^\circ_{(i\text{-Am})_4 B^-} = \tfrac{1}{2}\Lambda^\circ_{(i\text{-Am})_4 N(i\text{-Am})_4 B} \qquad (27a)$$

The transference number of ClO$_4^-$, calculated from values of the e.m.f. of the concentration cell Li(Hg) (2 mol %)/LiClO$_4$ (C$_1$)/LiClO$_4$ (C$_2$)/Li(Hg) (2 mol %), was also used to verify the results. Table 11 presents the ionic mobilities obtained from this study, together with the values reported by Courtot and L'Her[109] from a parallel investigation on the basis of the Onsager plots and the Fuoss-Hirsch assumption that $\lambda^\circ_{Bu_4 N^+} = \lambda^\circ_{BPh_4}^-$. More recent data obtained by Jansen and Yeager are also included in this table for comparison.

With the exception of (i-Am)$_4$B$^-$, BPh$_4$, and the picrate ion, the conductances of the anions do not differ appreciably, but this is not true for the cations (Table 11). The mobilities of the alkali metal ions seem to increase in the order Li$^+$ < Na$^+$ < K$^+$ < Rb$^+$ < Cs$^+$ as the crystallographic radius of the cation increases. This apparently reverse trend of a systematic increase in mobility in the order indicated has also been observed in most aprotic solvents (except TMS) as well as in water, and is presumably due to the tightly held sheath of solvent molecules attracted by the intense field associated with a small ion. The Stokes radii (Å) for the alkali-metal ions in PC are estimated to be[110] 5.1 for Li$^+$, 3.8 for Na$^+$, 3.1$_5$ for K$^+$, 2.9 for Rb$^+$ and 2.8 for Cs$^+$.

The limiting conductances of the perchlorates[100] indicate that the mobility of Li$^+$ is noticeably lower than those of n-Bu$_4$N$^+$ and Et$_4$N$^+$. Moreover, the viscosity coefficient F for the same series of salts is found to decrease in the order LiClO$_4$ > n-Bu$_4$NClO$_4$ > Et$_4$NClO$_4$. Thus, in all probability, the relative sizes of these three cations are Li$^+$ > n-Bu$_4$N$^+$ > Et$_4$N$^+$, which would suggest that lithium ions are substantially solvated in PC. Of further interest in this connection is the fact that, in contrast to what is true of the quaternary ammonium salts, the agreement

TABLE 11

Ion Conductances in Propylene Carbonate at 25°

Ion	Courtot and L'Her[110]	Mukherjee et al.[100,108,a]	Jansen and Yeager[111,112,b]
Li$^+$	6.5	7.30	8.89
(i-Am)$_4$N$^+$	–	8.185	8.17
n-Bu$_4$N$^+$	8.6	9.39	8.98
Na$^+$	8.8	–	9.45
K$^+$	10.5	11.97	11.17
Ag$^+$	11.3	–	–
Rb$^+$	11.4	–	11.90
Cs$^+$	12.0	–	12.66
Tl$^+$	12.4	–	–
Me$_4$N$^+$	–	–	14.16
Et$_4$N$^+$	13.0	13.28	13.18
Pr$_4$N$^+$	–	–	10.46
(i-Am)$_4$B$^-$	–	8.185	8.17
BPh$_4$$^-$	8.6	–	–
Picrate$^-$	13.0	–	–
Trifluoroacetate	–	–	17.87
Cl$^-$	18.5	20.20	18.26
PF$_6$$^-$	18.6	–	–
I$^-$	–	18.765^c, 18.78^d	18.35
ClO$_4$$^-$	19.6	18.78^d	18.44
Br$^-$	20.0	19.26	18.91
NO$_3$$^-$	–	–	20.42
SCN$^-$	–	–	22.12

^{a}The following additional constants are given in the format salt, $\overset{\circ}{a}$ parameter (A), viscosity F-coefficient: LiCl, 2.525, –; LiBr, 2.66, 1.25; LiClO$_4$, 2.75, 1.30; KI, 3.70, 0.904; KClO$_4$, 3.175, 0.874; Et$_4$NCl, 4.73, 0.51; Et$_4$NClO$_4$, 3.60, 0.54; n-Bu$_4$NBr, 3.525, 0.96; n-Bu$_4$NClO$_4$, 5.00, 0.83; (i-Am)$_4$NI, 3.30, 0.96; (i-Am)$_4$N(i-Am)$_4$B, 5.22, 1.27.

^{b}[λ°(i-Am)$_4$N$^+$ = λ°(i-Am)$_4$B$^-$ = 8.17.

^{c}λ°(i-Am)$_4$N$^+$ = λ°(i-Am)$_4$B$^-$ = 8.185.

^{d}From transference number of ClO$_4$$^-$.

between the sums of the crystallographic radii and the values of $\overset{\circ}{a}$ for the lithium salts is generally good (Table 11). On this basis, it may be surmised that, for the lithium salts, it is the bare ions rather than their solvated cospheres that are involved in the event of ion-ion contacts.

The values of $\overset{\circ}{a}$ derived for the two tetraisoamylammonium salts are almost half of the values expected from the summation of crystallographic radii of the corresponding ions.* Much the same thing is true for Et$_4$NClO$_4$, n-Bu$_4$NBr, and n-Bu$_4$NClO$_4$. One possible explanation for the deviation may lie in the somewhat arbitrary assumption that ionic association does not occur at all, which is implied in the treatment of the data

by the equation $\Lambda = \Lambda^\circ - SC^{1/2} + EC \log C + JC - F \Lambda^\circ C$. In fact, plots of $\Lambda - \Lambda^\circ + SC^{1/2} \cdot EC \log C + F \Lambda^\circ C$ against C for these five quaternary ammonium salts do exhibit divergences from linearity, as is shown by Figure 12, at concentrations above about 0.005 M, and this may suggest that there is a small but significant degree of association in each case. It should be remarked in this connection that the data for (i-Am)$_4$NI show the least departure from linearity, although the relative difference between the value of $\overset{\circ}{a}$ and the sum of the crystallographic radii is greatest for this salt. The omission from the present treatment of the $-J_2C^{3/2}$ term in the more comprehensive Fuoss-Onsager equation may also be responsible in

*The radius of (i-Am)$_4$N$^+$ [or (i-Am)$_4$B$^-$] is calculated to be 4.69 A from the observed value of the viscosity F coefficient, yielding a total center-to-center distance of 9.38 A for tetraisoamylammonium tetraisoamylborate. This value of 9.38 A is only slightly less than the value of 10.8 A calculated from molecular models,[113] but it is much greater than the value (5.22 A) of $\overset{\circ}{a}$ estimated from the conductance measurements.
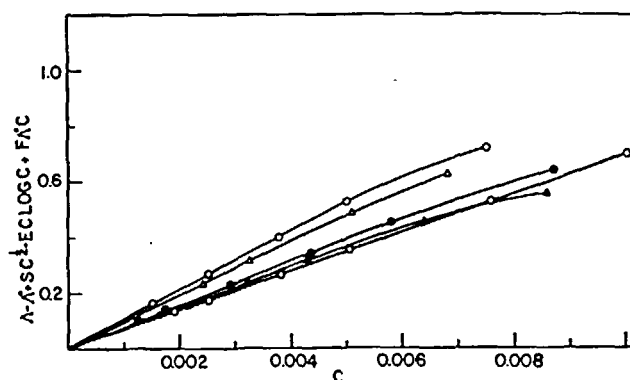
FIGURE 12. Plots of $\Lambda - \Lambda° + SC^{1/2} - EC$ log C + $F\Lambda°C$ against C for n-Bu$_4$NClO$_4$ (○), Et$_4$NClO$_4$ (△), (i-Am)$_4$N(i-Am)$_4$B (●), (i-Am)$_4$NI (◯), and n-Bu$_4$NBr (▲). (Reprinted from *J. Phys. Chem.*, 74, 1942 (1970). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)

part for the low values of the $\overset{\circ}{a}$ obtained for the tetraalkylammonium salts.

2. Thermodynamics of Electrode Reactions — Polarographic and Voltammetric Studies

The fact that the Li$^+$/Li electrode exhibits Nernstian behavior in PC was first reported by Boden, Buhner, and Spera,[114] who showed that the Nernst equation was obeyed over the range of concentrations from 0.1 to 1.0 M. Burrows and Jasinski[115] later made an assessment of three different forms of the lithium electrode as a reference electrode in 1.0 M solutions of lithium perchlorate. Electrodeposited lithium electrodes were found to be very susceptible to poisoning by impurities present in the electrolyte. Electrodes constructed from lithium powder packed into a glass tube were stable over long periods of time and showed little hysteresis in micropolarization tests, but had high ohmic resistances. Lithium-ribbon electrodes were found to be stable and reproducible to ± 1 mV, and showed negligible hysteresis. Bauke and Tobias[116] showed that thallium-thallous halide electrodes were stable and reversible in PC; the pure Tl/TlCl system was found to be suitable as a reference electrode.

The standard potentials of Li, Na, K, Rb, and Cs, as well as of Ca and Tl [Tl(I)/Tl], at 25° are summarized in Table 12. Although there is a discrepancy of about 20 mV for potassium, the standard potentials of lithium and thallium as reported by the two groups of investigators are in good agreement.

In their measurements L'Her and Courtot[117]

employed a sodium-coated platinum electrode, while their potassium, rubidium, cesium, and calcium indicator electrodes consisted of amalgams of the respective metals. (The form of the thallium electrode used is not mentioned in the publication cited.) The standard potential of the Li$^+$/Li couple was determined from the e.m.f. of the cell.[119]

K(s)/KI // LiI/Li(s)
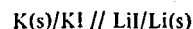
Of the three systems (Li, K, and Tl) that were investigated by Mukherjee and Boden,[118] solid metal indicator electrodes were used only for lithium, while the potassium and thallium electrodes were in the form of amalgams. In both investigations, the ultimate reference electrode was a Pt/ferricinium, ferrocene (1:1) electrode in PC.

Mukherjee and Boden observed that the e.m.f. of the cell

Reference electrode/MX/M(s) or M(Hg)
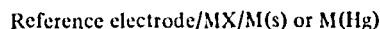
was linearly dependent on the logarithm of the activity of lithium, potassium, or thallous ion. The least-squares values of the individual slopes were found to be 0.0668 V for LiCl, 0.0678 V for LiBr, 0.0647 V for LiClO$_4$, 0.0607 V for KClO$_4$, and 0.0737 V for TlClO$_4$. The slope for potassium is remarkably close to the theoretical value of 0.05916 V at 25°. The slopes exhibited by solutions of the three lithium salts are somewhat higher, but consistent. Although the polarographic reduction of lithium ion in PC is believed to be irreversible,[117] in the absence of further evidence

TABLE 12

Average Values of Standard Potentials and Temperature Coefficients for the Reaction

$$M^+ + e \rightleftharpoons M(s) \text{ at } 25°$$
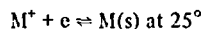
M	E°(V)		$\delta E°/\delta T$ (V deg^{-1})[b]
	Courtot and L'Her[a]	Mukherjee and Boden[b]	
Li	−3.265	−3.2705[c]	0.000877
Na	−3.050	−	−
K	−3.354	−3.3335	0.000688
Rb	−3.379	−	−
Cs	−3.399	−	−
Tl	−0.767	−0.7648	0.000191
Ca	−3.050	−	−

[a]vs. E° of ferricinium, ferrocene couple (Reference 114).
[b]vs. Pt/ferricinium picrate (0.005 M), ferrocene (0.005 M) in PC; the half-cell Ag/AgCl(s), LiCl(s) in PC served as the working reference electrode (Reference 115). A range of 10° (20−30°) was covered in temperature-coefficient measurements.
[c]The value represents the grand average of results obtained using LiCl, LiBr, and LiClO$_4$.

it would be inexpedient to consider the observed deviation (∼ 5 mV) of these slopes as a definite indication of departure from reversibility. The relatively large value, 0.0737 V, for the Tl(Hg)/TlClO$_4$ system is most probably associated with the unstable nature of the thallous perchlorate solutions in PC, which causes the actual activities of Tl$^+$ to be somewhat smaller than those calculated from the stoichiometric molarities used in constructing the plot.

Boden[114] and McClure and Reddy[120] investigated the behaviors of cation-sensitive glass electrodes in solutions of alkali and alkaline earth metal salts in PC. Mukherjee and Boden[121] examined the equilibrium response characteristics of a Li$^+$-sensitive glass electrode in solutions of pure lithium salts in PC, and also in the presence of certain univalent cations which are likely to interfere with the electrode response. Considering the exchange equilibrium

$$I^+_g + Li^+_s \rightleftharpoons Li^+_g + I^+_s$$
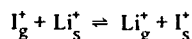
between Li$^+$ and the interfering ion, I$^+$, these workers derived[121] the following general equation for the potential of a glass electrode in a solution containing both Li$^+$ and I$^+$ ions at a fixed ionic strength:

$$E_g = E^*_g + \frac{RT}{F} \ln \left[C_{I^+_s} \exp \left\{ \frac{p}{RT} (V_{Li^+} - V_{I^+})_g \right\} + C_{Li^+_s} \right] \tag{28}$$

where V_{Li^+} and V_{I^+} denote the specific ionic volumes of the respective ions in the glass phase, $C_{Li^+_s}$ and $C_{I^+_s}$ represent the concentrations of lithium ion and the interfering ion in the solution phase, and p determines the swelling pressure in the glass matrix. As is evident, Equation 28 does not contain any empirical constant; the term involving the specific volumes of the ions in the glass phase is particularly significant since it relates to ionic volumes which can be estimated from the crystallographic radii.

When the solution contains no interfering ions, Equation 28 can be simplified to

$$E_g = E^*_g + \frac{RT}{F} \ln C_{Li^+_s} \tag{29}$$

The above relationship will also be approached in the presence of a very large interfering cation, for which $V_{I^+} \gg V_{Li^+}$. If V_{I^+} is exactly equal to V_{Li^+} the exponential term in Equation 28 will become unity, so that

$$E_g = E^*_g + \frac{RT}{F} \ln (C_{I^+_s} + C_{Li^+_s}) \tag{30}$$

The electrode response in such a case will accordingly depend on the relative values of $C_{I_S}^+$ and $C_{Li_S}^+$. For ions of comparable sizes ($V_{I^+} \approx V_{Li^+}$), Equation 30 similarly predicts that the plot of E_g against $\log C_{Li^+}$ will assume a slope of 0.05916 V at 25° only at high concentrations of lithium ion. The effects of K+ (r = 1.33 Å) and NH_4^+ (r = 1.48 Å) on the response to lithium ion (r = 0.60 Å) are shown in Figure 13 and illustrate this behavior. In comparison, the total absence of interference exhibited by Et_4N^+ (r = ca. 4.0 Å) must be due to its relatively large size, which makes the exponential term (Equation 28) very small and consequently permits the electrode potential to be determined by Equation 29. It should be stated in this connection that with Mg^{2+}, which has the same size (r = 0.65 Å) as Li^+, the Nernstian response was found[102] to develop at a much lower concentration than in the case of the larger K^+, so it may be possible that the concentration above which the glass electrode begins to behave reversibly to Li^+ depends on the size as well as the charge of the competing ion.

The polarographic reductions of the alkali metal ions, with the exception of Li^+, have been found to proceed reversibly in PC. The observed
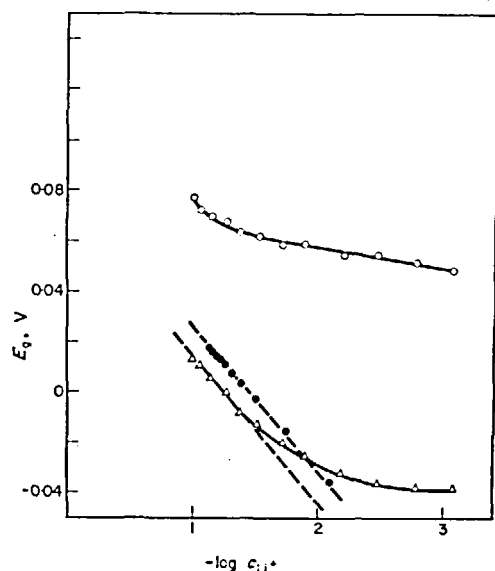

FIGURE 13. Plot of E_g against $-\log C_{Li^+}$ in mixtures containing a univalent cation and having an ionic strength of 0.25 M. ○: Li^+ + KSCN; ▵: Li^+ + NH_4SCN; ●: Li^+ + Et_4NClO_4. (Reprinted from Electrochim. Acta, 17, 965 (1972), by permission of the copyright owner.)

diffusion current constants at 25° are 0.85 for Li^+, 1.1 for Na^+, 1.2 for K^+, 1.2 for Rb^+ and Cs^+, as compared to the values 1.8, 2.2, 2.6, 2.8, and 3.3, respectively, in water ($\eta = 0.937$ cP). (The report by Broadhead and Elving[122] that the diffusion current constant of Li^+ in PC is large, possibly because of negligible solvation of the ion, is not corroborated in this study.) Furthermore, according to L'Her and Courtot,[117] the alkaline earth metals give irreversible waves in PC.

From voltammetric studies using a platinum electrode, Courtot and L'Her[123] determined the stability constants of I_3^- and I_5^- in PC. From similar studies,[124] they found that the reduction of Ag^+ was diffusion-controlled and that the wave height was proportional to the concentration of the ion. Although the analysis of the current-potential curves did not suggest a strict reversibility, a slope of 0.058 V (at 22°) could be obtained from the plot of E (at zero current) against $\log [Ag^+]$ over the range of concentrations from 10^{-3} to 8.5×10^{-2} M. The standard potential of the Ag^+/Ag system was estimated to be 0.50 V more positive than that of the ferricinium-ferrocene couple. Potentiometric studies using a silver indicator electrode subsequently yielded the formation constants of $AgCl_2^-$, $AgBr_2^-$, AgI_2^-, $Ag_3I_4^-$, $Ag(SCN)_2^-$, and $Ag(SCN)_3^{2-}$, as well as the solubility products of AgCl, AgBr, AgI, AgSCN, and $AgBPh_4$ in PC. Good agreement seems to have been obtained with the overall formation constant of $AgCl_2^-$ and the solubility product of AgCl reported earlier by Butler.[125]

The relatively high viscosity of PC is likely to reduce convective mass transfer in the solvent. This is considered advantageous[126,127] for certain voltammetric studies, especially for those involving the application of EPR techniques, where homogeneous electron transfer between the generated radical and the parent species is to be minimized.

3. Heats of Solution of Salts — Single-Ion Enthalpies of Transfer

The energetics of ion solvation in non-aqueous solvents have been a subject of much investigation. In particular, dipolar aprotic solvents have currently assumed a special interest in this regard.

From the heats of solutions of salts in PC and water, Wu and Friedman[128] derived the enthalpies of transfer of the alkali metal ions between the two solvents on the basis of Na^+ as the reference

ion, with the result that the relatively small ions Cs^+ and I^- appeared ultimately to have the same ΔH_t = values. Their subsequent studies[129-132] on heats of solution revealed that the enthalpies of transfer of R_4N^+ ions from dimethylsulfoxide to PC comprised additive contributions from the $-CH_2$ groups, which were the same as those for the transfers of the primary alcohols between these solvents. Using this as the basis, a method has been developed for obtaining the single-ion contributions to the enthalpies of transfer of electrolytes. It is interesting to note that the enthalpy of transfer of $AsPh_4^+$ is calculated to be the same as that of BPh_4^- according to this procedure. Friedman and Krishnan[130] further observed that there was roughly a constant contribution of -2 kcal mol^{-1} per phenyl group in the enthalpy of transfer from water to PC. Although the overall transfer enthalpies fail to characterize the effects in any one member of a solvent pair, it was suggested that Me_4N^+ was a net structure breaker, that the structure-making and structure-breaking effects mutually cancelled for Et_4N^+, and that the structure-making effects predominated for Pr_4N^+, Bu_4N^+, and Am_4N^+ ions. Comparison of the results for the primary, secondary, and tertiary alkylammonium ions[132] indicated that there is a sizeable contribution from hydrogen bonding of the ions to the solvent. The contribution was found to be fairly sensitive to the nature and number of the alkyl chains attached to the nitrogen.

Choux and Benoit[93] evaluated the single-ion enthalpies of transfer from water to four aprotic solvents including PC and methanol (Table 13), on the assumption that $\Delta H_t(AsPh_4^+) = \Delta H_t(PBh_4^-)$. According to their results, the order dimethylsulfoxide > dimethylformamide > TMS > PC appears to represent the solvating strengths of these aprotic solvents toward Na^+, K^+, and Rb^+. The somewhat anomalous position of the lithium ion may signify that its specific interactions with dimethylsulfoxide are stronger than those with dimethylformamide. The order of solvating strength toward the anions is found to be dimethylformamide > dimethylsulfoxide > TMS > PC. The single-ion enthalpies of solvation obtained by Choux and Benoit for the anions (Table 14) further suggest that the order of solvation $Cl^- > Br^- > I^- > ClO_4^-$ is the same for water, methanol, and the four aprotic solvents considered. It should be pointed out, however, that the small anions appear to be less solvated and the large anions more solvated in the aprotic solvents than in water or methanol. Although Choux and Benoit[93] demonstrated that both the cationic and anionic enthalpies of transfer from PC to any of the other aprotic solvents could not be accounted for in terms of coulombic interactions alone, Salomon[133] utilized an essentially electrostatic model and based his calculations of the conventional single-ion free energies and enthalpies of solvation in PC on Li^+ as the standard: the values of ΔG°_{solv} and ΔH°_{solv} for this reference cation

TABLE 13

Single-ion Enthalpies of Transfer from Water to Some Non-aqueous Solvents (kcal mol^{-1})

Ion	TMS	PC	Dimethylformamide	Dimethylsulfoxide	Methanol
Li^+	5.4	−0.05	1.5	−6.5	−3.7
Na^+	−4.05	−3.3	−5.9	−7.2	−4.8
K^+	−6.4	−6.0	−7.5	−8.45	−4.7
Rb^+	−6.8	−6.7	−7.2	−	−4.7
Cs^+	−6.3	−7.4	−6.8	−8.25	−3.8
Me_4N^+	−	−4.8	−0.6	−	−0.05
Et_4N^+	0.3	−0.8	1.6	0.6	1.4
$AsPh_4^+$	−2.85	−2.6	−2.15	−2.3	0.8
Cl^-	6.7	7.45	2.8	5.1	1.9
Br^-	3.35	4.35	−1.35	1.1	0.9
I^-	−1.6	0.1	−5.4	−2.6	−0.4
ClO_4^-	−4.7	−3.05	−7.9	−4.8	−1.1
BPh_4^-	−2.85	−2.6	−2.15	−2.3	0.8

(Reprinted from *J. Am. Chem. Soc.*, 91, 6221 (1969). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)

TABLE 14

Enthalpies of Solvation, kcal mol^{-1}

Anion	H$_2$O	TMS	PC	Dimethylformamide	Dimethylsulfoxide	Methanol
Cl$^-$	86.8	80.1	79.3	84.0	81.7	84.9
Br$^-$	80.3	77.0	76.0	81.6	79.2	79.4
I$^-$	70.5	72.1	70.4	75.9	73.1	70.9
ClO$_4$$^-$	57	61.7	60.1	64.9	61.8	58.1

(Reprinted from *J. Am. Chem. Soc.*, 91, 6221 (1969). Copyright by the American Chemical Society. Reprinted by permission of the copyright owner.)

were calculated to be -95.0 and -106.2 kcal mol^{-1}, respectively. It should be added, in this connection, that comparison of the enthalpies of transfer obtained by different approaches reveals substantial deviations in several instances.

The investigations of Mukherjee and Boden[118] indicate that the entropy changes (Table 12) associated with the process M(s) $\rightleftharpoons$ M$^+$ + e, which may determine the order-promoting ability of a cation in PC, are -20.223 for Li$^+$, -15.865 for K$^+$, and -4.40 for Tl$^+$ in Cal deg^{-1} mol^{-1}. From a consideration of the crystallographic radii, which are 0.60 Å for Li$^+$, 1.33 Å for K$^+$, and 1.40 Å for Tl$^+$, this trend may suggest that such ordering in the case of PC — a "structureless" solvent[134] — is primarily a result of electrostatic solvation and is confined within the immediate vicinity of the ions. The somewhat large decrease in entropy for the formation of the lithium ion reflects a relatively high degree of solvation of this particular cation in PC, and corroborates the conclusion from the conductance studies (cf. Table 11) that a solvated Li$^+$ is even larger than the ion (i-Am)$_4$N$^+$. The free energies of transfer from water (D = 78.54) to PC (D = 64.4) are calculated to be + 3.64 for Li$^+$, -0.577 for K$^+$, and - 1.05 for Tl$^+$, in kcal mol^{-1} on the molar scale.* Although there is an approximately linear relationship between these free energies of transfer and the reciprocals of the crystallographic radii of the ions, neither the magnitudes nor the signs of these free-energy changes are readily understandable in terms of the Born equation or any of its modifications, such as the Latimer-Pitzer-Slansky equation. The relatively large decrease of free energy associated with the transfer of Tl$^+$ might be attributed to fairly strong,

short-range interactions encountered by the ion due to its empty 5f orbital.[135] According to the present estimates, the difference between the enthalpies of transfer of a mole of Li$^+$ and a mole of K$^+$ from water to PC is calculated to be 9.22 kcal as compared to the values, 5.95[93] and 5.6[130] kcal, deduced from other studies.

4. Acid-Base Reactions

Although PC is believed to be susceptible to decomposition in the presence of acids, a few acid-base studies in the solvent have been reported recently. The relative acidities of some substituted benzoic acids, mono- and dicarboxylic acids, and phenols have apparently been established on the basis of their half-neutralization potentials.[136] Courtot and L'Her[137] found HPF$_6$ to be completely dissociated in PC. The values of pK$_a$ obtained by them for the acids HSbCl$_6$, H$_2$S$_2$O$_7$, and HFSO$_3$, from Kraus and Bray plots of conductance data, are 1.0, 1.8 and 2.0, respectively. Their conductance titrations of water with HFSO$_3$, of HCl with SbCl$_5$, and of PF$_5$ with HF are interesting, but more facts are needed to understand the shapes of the curves, especially in the first two instances. The hydrogen electrode was polarized in solutions of these acids and did not respond to proton activity.

Preliminary results of Courtot and L'Her[137], from the Hammett acidity measurements indicated the possibility of attainment of a high acidity level in PC and, hence, a low proton affinity of the solvent. However, comparison of the H$_0$-values for 0.001 *M* solutions of H$_2$S$_2$O$_7$ suggests that PC (H$_0$ = -5) is more basic than nitromethane (H$_0$ = -6.7).

*Using the correct conversion factors (cf. Reference 118), the corresponding values on the rational scale are +2.72 for Li$^+$ -1.495 for K$^+$, and -1.965 for Tl$^+$, in kcal mol^{-1}.

MEDIUM EFFECTS FOR SINGLE IONS IN PYRIDINE, SULFOLANE, AND PROPYLENE CARBONATE

Although the conclusions derived from the enthalpies of transfer and other measurements mentioned earlier offer a good deal of insight into ionic solvation in pyridine, TMS, and PC, estimates of medium effects characteristic of these solvents are considered desirable for a more generalized basis of comparison. The accumulated data on the medium activity coefficients of several cations with respect to these three solvents are summarized in Table 15.

The proton medium effect $(\log_m \gamma_{H^+})$ in pyridine was determined by Mukherjee[25] to be -3.85 (molal scale) on the basis of the ferrocene assumption.[138]* As is evident, this value is in order with that (-3.25) obtained by combining $\log_m^M \gamma^W_{H^+} = -1.95$[136,137] and $\log_m^M \gamma^{DMSO}_{H^+} = -5.2$[137] (w = water; m = methanol; DMSO = dimethylsulfoxide) for dimethylsulfoxide, which is a weaker base. It may be stated here that the previous estimate of ca. -5.2 as given by Courtot et al.[141] for $\log_m \gamma_{H^+}$ for dimethylsulfoxide appears doubtful.

The standard potential of the Ag^+/Ag couple in pyridine was found to be 0.550 V vs. N.H.E. (pyridine). Accordingly, the value for $\log_m \gamma_{Ag^+}$ in this solvent is calculated to be -8.1 (molal

TABLE 15

Medium Effects of Single Ions ($\log_m^{water} \gamma_{M^+}^{solvent}$ on the molal scale)

Ion	Pyridine	TMS	PC
H$^+$	-3.85[a]	14.0[b]	–
Ag$^+$	-8.1[a]	3.3[b]	1.6[c]
Li$^+$	–	6.1[b]	2.8[c]; 2.8[d]
Na$^+$	–	4.4[b]	1.0[c]
K$^+$	–	3.0[b]	-0.5[c]; -0.2[d]
Rb$^+$	–	2.7[b]	-1.0[c]
Cs$^+$	–	2.4[b]	-1.3[c]
Tl$^+$	–		-7.2[d]

[a]Reference 25; also cf. References 20 and 21.
[b]Reference 66.
[c]References 114, 121.
[d]Reference 115.

scale), which indicates a profound affinity of silver ion for pyridine and a relatively low activity of the ion in this solvent. (The values of $\log_m \gamma_{Ag^+}$ reported for dimethylsulfoxide are, incidentally, -8.0[141] and -5.6[75])

The medium activity coefficients of the alkali metal ions and Ag$^+$ for TMS, which are listed in Table 15, are based on the procedure adopted by Coetzee et al.[66] for relating the potential scales of the solvent and water using a modified Born approach (Section III.B.4) The proton medium effect ($\log_m \gamma_{H^+} = +14.0$) was estimated from the differences of potential between the Ag/AgClO$_4$ (0.1 M in TMS) reference electrode and an aqueous S.C.E.[66] or the N.H.E. in TMS,[68] as reported by the same group of workers. It should be mentioned that this value of $\log_m \gamma_{H^+}$ is in the neighborhood of that suggested from the estimate of -12.8 obtained by Benoit and Pichet[71] for the pH of a 1 M solution of SH$^+$ in TMS, and it supports the notion that a very high acidity level is attainable in this solvent.

The value, 3.3, for $\log_m \gamma_{Ag^+}$ for TMS is reasonably close to that reported by Parker and co-workers[75] from their assumption that the junction potential is negligible.

For the solvent PC, the tabulated values of the medium activity coefficients of the cations were derived from the corresponding standard potentials[117,118,124] on the basis of the ferrocene assumption. It is interesting to note in this connection that, for both TMS and PC, the values of $\log_m \gamma_{M^+}$ decrease systematically from Li$^+$ to Cs$^+$ among the alkali-metal ions. However, the individual values in PC for the entire series appear to be lower than in TMS and, as such, do not conform to the general order established from the enthalpies of transfer which suggested PC to be a poorer solvator than TMS.

The value of 1.6 for $\log_m \gamma_{Ag^+}$ is lower than the estimate (4.0 on the molal scale) given by Parker et al.[75] for PC. The large negative value (-7.2) for $\log_m \gamma_{Tl^+}$ is indicative of fairly strong interaction of the ion with PC and approximates the value for Ag$^+$ in dimethylsulfoxide.

*No spectral changes could be observed in solutions of either ferrocene or ferricinium picrate during several days after the instant of preparation. The monomeric nature of ferrocene and dissociation of ferricinium picrate as a weak electrolyte in pyridine were established in advance by separate experiments.

VI. SUMMARY AND CONCLUSIONS

1. Both pyridine and sulfolane behave as "differentiating" solvents toward acids. Based on the limited evidence, propylene carbonate also appears to possess similar differentiating properties.

2. Electrolytes are found to be weakly dissociated in pyridine, the overall dissociation constants of acids being smaller than in the isodielectric solvent ethylenediamine. This behavior may be attributed to the fact that the basicity of pyridine is much lower than that of ethylenediamine. The general lack of association of electrolytes in sulfolane and propylene carbonate may be a consequence of the higher dielectric constant of the two solvents.

Although there is no convincing evidence for the occurrence of homoconjugation of acids in pyridine, the stabilization through intramolecular hydrogen bonding of the monoanions of dibasic acids, such as phthalic acid,[15] is interesting and should be studied in detail.

3. In agreement with earlier notions, the medium effects for hydrogen and silver ions (Table 15) as well as the results of spectroscopic studies[2] in pyridine reflect a strong tendency of the solvent for solvating cations in general. On the other hand, the cation medium effects and the single-ion enthalpies of transfer[93] for both cations and anions in general suggest that sulfolane and propylene carbonate solvate ions less strongly than do other dipolar aprotic solvents such as dimethylsulfoxide and dimethylformamide. Also, acetonitrile and nitrobenzene appear to exercise greater proton affinity than sulfolane,[69] and propylene carbonate appears to be a stronger base than nitromethane.[137] The situation of hydrogen ion in sulfolane is indeed remarkable; as is evident from its medium activity coefficient (Table 15), the pa_H of a 1 M solution of SH^+ in the solvent would be equivalent to a pa_H somewhere between -12.8 and -14.0 in the aqueous scale (cf. $\log_m \gamma_{H^+} = -13.2$ in hydrazine and -15.8 in ammonia.[142]

4. The position of Li^+ in sulfolane seems to be best understood in terms of disruption and/or reorganization of the parent structure of the solvent. Although the degree of structuring of the parent solvent seems debatable,[143] the possibility of existence of structure in pure liquid sulfolane has not been ruled out.[144]

Though this is not reflected in its medium activity coefficient, lithium ion is most probably extensively solvated in propylene carbonate as suggested by other evidence, and its solvation may be due chiefly to electrostatic effects confined to the immediate vicinity of the ion. Thallous ion, on the other hand, appears to be involved in fairly strong, short-range interactions with the solvent molecules, possibly by virtue of its empty 5f orbital.

5. Self-aggregation of the AgX moities and their ability to form reasonably stable adducts of the type AgX · MX in pyridine are viewed as being related in some way to an inherent aggregation-promoting influence of the solvent on such systems. Although this is a mere speculation at the moment, the matter deserves careful study.

6. The single-ion enthalpies of transfer from water to propylene carbonate and to sulfolane could not be directly related to coulombic interactions, and the solvating strength of sulfolane for both cations and anions was suggested to be greater than that of propylene carbonate.[93] However, consideration of the available estimates of the medium activity coefficients, especially of those of the alkali metal ions, seems to indicate a reversal of the order of the solvating strength of these two solvents. This, along with the discrepancy observed in the values of $\log_m \gamma_{Ag^+}$ for propylene carbonate using the ferrocene assumption as well as the assumption that the liquid-junction potential is negligible, presents difficulty in accepting the validity of any of the individual extrathermodynamic assumptions used in obtaining the results.

Although the present review does not permit any elaborate observation, it can be briefly remarked that the prevailing uneasiness regarding the extrathermodynamic assumptions in general warrants vigorous study in the direction of sophisticated theoretical approaches as well as experimental verification of the energies of ionic solvation by more direct methods. In this context, the approach of Goldman and Bates[145] and the mass spectrometric studies of solvation parameters by Kebarle[146-149] seem more meaningful and promising. The technique proposed by Oppenheim[150] for obtaining single-electrode potentials, which has been totally neglected so far, also merits trial.

VII. ACKNOWLEDGMENTS

VIII. REFERENCES

1. Kolthoff, I. M., *J. Polarogr. Soc.*, 10, 22 (1964).
2. Thompson, W. K., *J. Chem. Soc.*, 4028 (1964).
3. Broadhead, J. and Elving, P. J., *Anal. Chem.*, 41, 1814 (1969).
4. Lindauer, R. and Mukherjee, L. M., *Pure Appl. Chem.*, 27, 267 (1971).
5. Helm, R. V., Lanum, W. J., Cook, G. L., and Ball, J. S., *J. Phys. Chem.*, 62, 858, (1958).
6. *International Critical Tables of Numerical Data*, Washburn, E. W., Ed., McGraw-Hill, New York, 1930.
7. *Dictionary of Organic Compounds*, Heilborn, I. M., Ed., Oxford, 1965.
8. Leis, D. G. and Curran, B. C., *J. Am. Chem. Soc.*, 67, 79 (1945).
9. Maryott, A. A. and Smith, E. R., *Circ. U.S. Natl. Bur. Stand.*, 514 (1951).
10. Boyer, P., *C. R. Acad. Sci. Paris*, 254, 4153 (1962).
11. Burgess, D. A. and Kraus, C. A., *J. Am. Chem. Soc.*, 70, 706 (1948).
12. Spritzer, M. S., Costa, M., and Elving, P. J., *Anal. Chem.*, 37, 211 (1965).
13. Hickey, J. E., Spritzer, M. S., and Elving, P. J., *Anal. Chim. Acta*, 35, 277 (1966).
14. Floch, L., Spritzer, M. S., and Elving, P. J., *Anal. Chem.*, 38, 1074 (1966).
15. Tsuji, K. and Elving, P. J., *Anal. Chem.*, 41, 286 (1969).
16. Elving, P. J. and Tsuji, K., in *Coordination Compounds in Non-Aqueous Solvents*, Cais, M., Ed., Elsevier, New York, 1968, 760.
17. Tsuji, K. and Elving, P. J., *Anal. Chem.*, 41, 1571 (1969).
18. Elving, P. J., *J. Electroanal. Chem. Interfacial Electrochem.*, 29, 55 (1971).
19. Mukherjee, L. M., Kelly, J. J., Baranetzky, W., and Sica, J., *J. Phys. Chem.*, 72, 3410 (1968).
20. Mukherjee, L. M., Kelly, J. J., Richards, M., and Lukacs, J. M., Jr., *J. Phys. Chem.*, 73, 580 (1969).
21. Mukherjee, L. M. and Lukacs, J. M., Jr., *J. Phys. Chem.*, 73, 3115 (1969).
22. Mukherjee, L. M., Suwala, D. W., and Schultz, R. S., *Anal. Chim. Acta*, 60, 247 (1972).
23. Mukherjee, L. M. and Schultz, R. S., *Talanta*, 19, 707 (1972).
24. Mukherjee, L. M., Czaban, J. D., Schultz, R. S., Atwell, R. W., and Krohn, R. J., *J. Inorg. Nucl. Chem.*, 34, 3944 (1972).
25. Mukherjee, L. M., *J. Phys. Chem.*, 76, 243 (1972).
26. Vidal, R. and Mukherjee, L. M., *Talanta*, 21, 303 (1974).
27. Erlich, R. H. and Popov, A. I., *J. Am. Chem. Soc.*, 93, 5620 (1971).
28. Michielli, R. F. and Elving, P. J., *J. Am. Chem. Soc.*, 90, 1989 (1968).
29. Nigretto, J. M. and Jozefowicz, M., *Electrochim. Acta*, 18, 145 (1973).
30. Mukherjee, L. M. and Kelly, J. J., *J. Phys. Chem.*, 71, 2348 (1967).
31. Mukherjee, L. M., Bruckenstein, S., and Badawi, F. A. K., *J. Phys. Chem.*, 69, 2537 (1965).
32. Davies, M. M., *Trans. Faraday Soc.*, 31, 1561 (1935).
33. Corey, E. J., *J. Am. Chem. Soc.*, 75, 1172 (1953).
34. Angerstein, H., *Rocz. Chem.*, 30, 855 (1956).
35. Marshall, H. P. and Grunwald, E., *J. Chem. Phys.*, 21, 2143 (1953).
36. Hantzsch, A. and Caldwell, K. S., *Z. Phys. Chem. (Frankfurt)*, 61, 227 (1908).
37. Bruckenstein, S. and Mukherjee, L. M., *J. Phys. Chem.*, 64, 1601 (1960).
38. Luder, W. F. and Kraus, C. A., *J. Am. Chem. Soc.*, 69, 2481 (1947).
39. Mathews, J. H. and Johnson, A. J., *J. Phys. Chem.*, 21, 294 (1916-1917).
40. Bruckenstein, S., and Osugi, J., *J. Phys. Chem.*, 65, 1868 (1961).
41. Cundiff, R. H. and Markunas, P. C., *Anal. Chem.*, 28, 792 (1956).
42. Johnson, J. B. and Funk, G. L., *Anal. Chem.*, 28, 1977 (1956).

43. Mauermeyer, R. K., Margosis, M., and Ma, T. S., *Microchim. Acta*, 177 (1959).
44. Fauth, M. I., Frandsen, M., and Havlik, B. R., *Anal. Chem.*, 36, 380 (1964).
45. Fritz, J. S. and Gainer, F. E., *Talanta*, 13, 939 (1966).
46. Streuli, C. A. and Miron, R. R., *Anal. Chem.*, 30, 1978 (1958).
47. Bos, M, and Dahmen, E. A. M. F., *Anal. Chim. Acta*, 53, 39 (1971).
48. Bos, M. and Dahmen, E. A. M. F., *Anal. Chim. Acta*, 55, 285 (1971).
49. Price, E. and Frunwald, E., *J. Phys. Chem.*, 68, 3876 (1964).
50. Mukherjee, L. M., paper presented at the 159th National Meeting of the American Chemical Society, Houston, Texas, February 1970.
51. Mukherjee, L. M. and Goodloe, G. W., unpublished results; Goodloe, G. W., B.S. thesis, Polytechnic Institute of Brooklyn, New York, 1968.
52. Rundle, R. E. and Goring, J. H., *J. Am. Chem. Soc.*, 72, 5337 (1950).
53. Smith, H. G. and Rundle, R. E., *J. Am. Chem. Soc.*, 80, 5075 (1958).
54. Avinur, P. and Eliezer, I., *Anal. Chem.*, 42, 1317 (1970).
55. Bradley, J. N. and Greene, P. O., *Trans. Faraday Soc.*, 62, 2069 (1966).
56. William, M. B. and Popov, A. I., *J. Am. Chem. Soc.*, 91, 20 (1969).
57. Herlem, M. and Popov, A. I., *J. Am. Chem. Soc.*, 94, 1431 (1972).
58. Gutmann, V., *Coordination Chemistry in Non-Aqueous Solvents*. Springer-Verlag, New York, 1968.
59. Fernandez-Prini, R. and Prue, J. E., *Trans. Faraday Soc.*, 62, 1257 (1966).
60. Bordwell, F. G., Imes, R. H., and Steiner, E. C., *J. Am. Chem. Soc.*, 89, 3905 (1967).
61. Hall, S. K. and Robinson, E. A., *Can. J. Chem.*, 42, 1113 (1964).
62. Morman, D. H. and Harlow, G. A., *Anal. Chem.*, 39, 1869 (1967).
63. Burwell, R. L., Jr. and Langford, C. H., *J. Am. Chem. Soc.*, 81, 3799 (1959).
64. Ernett, E. M. and Douty, G. F., *J. Am. Chem. Soc.*, 86, 409 (1964).
65. Phillips Petroleum Co., Technical Bulletin on Sulfolane.
66. Coetzee, J. F., Simon, J. M., and Bertozzi, R., *Anal. Chem.*, 41, 766 (1969).
67. Vaughn, J. W. and Hawkins, C. F., *J. Chem. Eng. Data*, 9, 140 (1964).
68. Coetzee, J. F. and Bertozzi, R. J., *Anal. Chem.*, 43, 961 (1971).
69. Coetzee, J. F. and Bertozzi, R. J., *Anal. Chem.*, 45, 1064 (1973).
70. Coetzee, J. F. and Bertozzi, R. J., *Anal. Chem.*, 41, 860 (1969).
71. Benoit, R. L. and Pichet, P., *J. Electroanal. Chem. Interfacial Electrochem.*, 43, 59 (1973).
72. Adler, R. W., Chalkley, G. R., and Whiting, M. C., *Chem. Commun.*, 405 (1966).
73. Benoit, R. L., Buisson, C., and Choux, G., *Can. J. Chem.*, 48, 2353 (1970).
74. Hills, G. J. and Ives, D. J. G., in *Reference Electrodes. Theory and Practice*, Ives, D. J. G. and Janz, G. J., Eds. Academic Press, New York, 1961, 111.
75. Alexander, R., Parker, A. J., Sharp, J. H. and Waghorne, W. E., *J. Am. Chem. Soc.*, 94, 1148 (1972).
76. Della Monica, M., Lamanna, U., and Jannelle, L., *Gazz. Chim. Ital.*, 97, 367 (1967).
77. Della Monica, M., Lamanna, U., and Senatore, L., *J. Phys. Chem.*, 72, 2124 (1968).
78. Della Monica, M. and Lamanna, U., *J. Phys. Chem.*, 72, 4329 (1968).
79. Della Monica, M. and Senatore, L., *J. Phys. Chem.*, 74, 205 (1970).
80. Bruno, P. and Della Monica, M., *J. Phys. Chem.*, 76, 1049 (1972).
81. Non-aqueous Electrolytes Handbook, Vol. 1, Janz, G. J. and Tomkins, R. P. T., Eds., Academic Press, New York, 1972.
82. Robinson, R. A. and Stokes, R. H., *Electrolyte Solutions*, Butterworths, London, 1959, 463.
83. Jervis, R. E., Muir, D. R., Butler, J. P., and Gordon, A. R., *J. Am. Chem. Soc.*, 75, 2855 (1953).
84. Notley, J. N. and Spiro, M., *J. Phys. Chem.*, 70, 1502 (1966).
85. Prue, J. E. and Sherrington, P. J., *Trans. Faraday Soc.*, 57, 1795 (1961).
86. Parker, A. J., *Rev. (London)*, 16, 163 (1962).
87. Mine, S. and Werblan, L., *Electrochim. Acta*, 7, 257 (1962).
88. Della Monica, M., Lamanna, U., and Senatore, L., *Inorg. Chim. Acta*, 2, 363 (1968).
89. Benoit, R. L., Beauchamp, A. L., and Deneux, M., *J. Phys. Chem.*, 73, 3268 (1969).
90. Coetzee, J. F. and Simon, J. M., *Anal. Chem.*, 44, 1129 (1972).
91. Headridge, J. B., Pletcher, D., and Callingham, M., *J. Chem. Soc. A.*, 684 (1967).
92. Desbarres, J., Pichet, P., and Benoit, R. L., *Electrochim. Acta*, 13, 1899 (1968).
93. Choux, G. and Benoit, R. L., *J. Am. Chem. Soc.*, 91, 6221 (1969).
94. Grunwald, E., Baughman, G., and Kohnstam, G., *J. Am. Chem. Soc.*, 82, 5801 (1960).
95. Jasinski, R. J., *High Energy Batteries*, Plenum Press, New York, 1967.
96. Harris, W. H., Ph.D. thesis, University of California, Berkeley, 1958, UCRL Report 8381.
97. Chabrier, P., Najer, H., and Giudicelli, R., *C. R.*, 238, 108 (1954).
98. Lichtenwalter, M. and Cooper, J. F., U.S. Patent 2,773,070 (1956).
99. Jasinski, R. J. and Kirkland, S., *Anal. Chem.*, 39, 1663 (1967).
100. Mukherjee, L. M. and Boden, D. P., *J. Phys. Chem.*, 73, 3965 (1969).

101. Fujinaga, T. and Iutsu, K., *Pure Appl. Chem.*, 27, 275 (1971).
102. Boden, D. P., Ph.D. thesis, Polytechnic Institute of Brooklyn, New York, 1970.
103. Jefferson Chemical Co., Technical Bulletin on Propylene Carbonate.
104. Watanabe, M. and Fuoss, R. M., *J. Am. Chem. Soc.*, 78, 527 (1956).
105. Kempa, R. and Lee, W. H., *J. Chem. Soc.*, 1936 (1958).
106. Fuoss, R. M., Berkowitz, J. B., Hirsch, E., and Petrucci, S., *Proc. Natl. Acad. Sci., U.S.*, 44, 27 (1958).
107. Fuoss, R. M. and Hirsch, E., *J. Am. Chem. Soc.*, 82, 1013 (1960).
108. Mukherjee, L. M., Boden, D. P., and Lindauer, R., *J. Phys. Chem.*, 74, 1942 (1970).
109. Fuoss, R. M. and Accascina, F., *Electrolyte Conductance*, Interscience, New York, 1959, 191.
110. Courtot-Coupez, J. and L'Her, M., *C. R. Acad. Sci., Paris, Ser. C.*, 271, 357 (1970).
111. Jansen, M. L. and Yeager, H. L., *J. Phys. Chem.*, 77, 3089 (1973).
112. Jansen, M. L. and Yeager, H. L., *J. Phys. Chem.*, 78, 1380 (1974).
113. Coetzee, J. F. and Cunningham, G. P., *J. Am. Chem. Soc.*, 87, 2529 (1965).
114. Boden, D. P., paper presented at the Electrochemical Society Meeting, Dallas, Texas, May 1967; Boden, D. P., Buhner, H. R., and Spera, V. J., first quarterly report, Contract DA-28-043-AMC-01394(E), ESB, Inc., Research Center, Yardley, Pa., October 1965.
115. Burrows, B. and Jasinski, R. J., *J. Electrochem. Soc.*, 115, 365 (1968).
116. Bauke, F. G. K. and Tobias, C. W., *J. Electrochem. Soc.*, 116, 34 (1969).
117. L'Her, M. and Courtot-Coupez, J., *Bull. Soc. Chim. Fr.*, 9, 3645 (1972).
118. Boden, D. P. and Mukherjee, L. M., *Electrochim. Acta*, 18, 781 (1973).
119. Salomon, M., *J. Electroanal Chem.*, 26, 319 (1970).
120. McClure, J. E. and Reddy, T. B., *Anal. Chem.*, 40, 2064 (1968).
121. Mukherjee, L. M. and Boden, D. P., *Electrochim. Acta*, 17, 965 (1972).
122. Broadhead, J. and Elving, P. J., *J. Electrochem. Soc.*, 118, 63 (1971).
123. Courtot-Coupez, J. and L'Her, M., *C. R. Acad. Sci., Paris, Ser. C.*, 266, 1286 (1968).
124. Courtot-Coupez, J. and L'Her, M., *Bull. Soc. Chim. Fr.*, 2, 675 (1969).
125. Butler, J. N., *Anal. Chem.*, 39, 1799 (1967).
126. Marcoux, L., Prater, K., Prater, B., and Adams, R. N., *Anal. Chem.*, 37, 1446 (1965).
127. Nelson, R. and Adams, R., *J. Electroanal. Chem.*, 13, 184 (1967).
128. Wu, Y-C. and Friedman, H. L., *J. Phys. Chem.*, 70, 501 (1966).
129. Friedman, H. L., *J. Phys. Chem.*, 71, 1723 (1967).
130. Krishnan, C. V. and Friedman, H. L., *J. Phys. Chem.*, 73, 3934 (1969).
131. Krishnan, C. V. and Friedman, H. L., *J. Phys. Chem.*, 74, 2356 (1970).
132. Krishnan, C. V. and Friedman, H. L., *J. Phys. Chem.*, 74, 3900 (1970).
133. Salomon, M., *J. Phys. Chem.*, 74, 2519 (1970).
134. Criss, C. M. and Mastroianni, M. J., *J. Phys. Chem.*, 75, 2532 (1971).
135. Coetzee, J. F. and Campion, J. J., *J. Am. Chem. Soc.*, 89, 2513 (1967).
136. Baranov, N. A., Vlasov, N. A., and Potekhina, L. P., *Zh. Anal. Khim.*, 27, 2333 (1972); cf. Lagowski, J. J., *Anal. Chem.*, 46, 460R (1974).
137. L'Her, M. and Courtot-Coupez, J., *J. Electroanal. Chem. Interfacial Electrochem.*, 48, 265 (1973).
138. Strehlow, H., *Z. Elektrochem.*, 56, 827 (1952); cf. also Koepp, H. M., Wendt, H., and Strehlow, H., *Z. Elektrochem.*, 64, 483 (1960).
139. Popovych, O. and Dill, A. J., *Anal. Chem.*, 41, 456 (1969).
140. Kolthoff, I. M. and Chantooni, M. K., Jr., *J. Phys. Chem.*, 76, 2024 (1972).
141. Courtot-Coupez, J., Madec, C., and Le Demezet, M., *C. R. Acad. Sci., Paris, Ser. C*, 270, 1397 (1970).
142. Izmaylov, N. A., *Dokl. Akad. Nauk SSSR*, 149, 1364 (1963).
143. Della Monica, M., Jannelli, L., and Lamanna, U., *J. Phys. Chem.*, 72, 1068 (1968).
144. Coetzee, J. F. and Sharpe, W. R., *J. Soln. Chem.*, 1, 1 (1972).
145. Goldman, S. and Bates, R. G., *J. Am. Chem. Soc.*, 94, 1476 (1972).
146. Kebarle, P., Searles, S. K., Zolla, A., Scarborough, J., and Arshadi, M., *Adv. Mass Spectrom.*, 4, 621 (1968).
147. Searles, S. K., Dzidic, I., Kebarle, P., *J. Am. Chem. Soc.*, 91, 2810 (1969).
148. Dzidic, I. and Kebarle, P., *J. Phys. Chem.*, 74, 1466 (1970).
149. Arshadi, M., Yamdagni, R., and Kebarle, P., *J. Phys. Chem.*, 74, 1475 (1970).
150. Oppenheim, I., *J. Phys. Chem.*, 68, 2859 (1964).