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Applications of Potentiometric Ion Sensors in the Characterization of Nonaqueous Solvents

J. F. COETZEE,* B. K. DESHMUKH, and C.-C. LIAO

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

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I. Introduction

A highly significant merit of a potentiometric ion sensor is that it measures the activity of the "free" (solvated) ion, irrespective of whether the ion is also present in other states, e.g., covalently bound complexes or electrostatically bound ion aggregates. This desirable property has been demonstrated for a wide variety of potentiometric sensors in a range of polar solvents varying from water and other amphiprotic solvents, e.g., alcohols, to such dipolar aprotic solvents as acetonitrile and dimethyl sulfoxide and even low-permittivity solvents such as tetrahydrofuran. In all of these solvents various potentiometric sensors under carefully controlled conditions give Nernstian response over a wide range of ion activities, particularly in buffered solutions but also in relatively unbuffered solutions *provided the solvents are relatively free from impurities reacting with the analyte ion.* This important requirement of adequate solvent purity will be discussed later.

It is important to stress at the outset certain fundamental and practical limitations of potentiometry. For a potentiometric ion sensor giving Nernstian response a relation such as that in eq 1 applies, where a_i is the

$$E = k + \frac{RT}{z_iF} \ln a_i \qquad (1)$$

individual ion activity, which, in turn, is related to the ion concentration as $a_i = \gamma_i m_i$. The activity coefficient γ_i can be defined by eq 2 where G_e is the nonideal

$$\ln \gamma_i = (RT)^{-1}(\delta G_e/\delta n_i)_{T,p,n_{j\neq i}} \qquad (2)$$

component of the Gibbs free energy and n_i and n_j are mole numbers. Since it is impossible in any real experiment to vary the mole number of only the *i*th kind of ion without varying any other mole numbers or the temperature or pressure, a fundamental question concerning the physical reality of the single-ion activity arises. This dilemma has been intensely debated because the concept of single-ion activity, uncertain though it may be fundamentally, has proven exceptionally useful operationally, e.g., in pH measurements. It is obviously necessary to invoke extrathermodynamic assumptions in any operational definition of a single-ion activity scale. For example, the conventional pH scale is based on the assumption that for a cell without transference, of the type H_2,Pt|HA(m_1) + KCl(m_2)|Ag,AgCl, the activity coefficient of chloride ion can be calculated from the Debye–Hückel equation. The authoritative discussion by Bates[1] should be consulted for details about the operational definition of the pH scale for aqueous solutions. Similar considerations apply to single-ion activity scales in other solvents, e.g., the pH* scale for which the standard state is an infinitely dilute solution in the particular solvent; in this standard state the activity coefficient of hydrogen ion is set equal to unity. Consequently, a different pH* scale exists for every solvent considered. If it is desired to place all pH* scales on a single scale, e.g., that for pH, then the free energies of transfer of hydrogen ion from the various solvents to water must be used as conversion factors. The evaluation of these single-ion transfer energies, once again, falls outside the realm of rigorous thermodynamics, so that extrathermodynamic assumptions must be introduced, e.g., the assumption that the transfer energies of tetraphenylarsonium and tetraphenylborate ions are equal. The merits and limitations of this and other assumptions have been intensively debated[2] and will not be discussed here, other than to urge authors to guard against the indiscriminate acceptance of any of these assumptions (see section V).

A second limitation applies to potentiometry in certain nonaqueous, particularly dipolar, aprotic solvents for which viable cells without transference cannot be constructed. For example, the Ag,AgCl internal reference electrode cannot be used in such solvents due to the fact that in these solvents chloride ion is only weakly solvated and therefore has high reactivity, leading to solubilization of AgCl by formation of $AgCl_2^-$ and higher chloro complexes. Consequently, external reference electrodes must be used with these solvents, thereby introducing liquid-junction potentials that increase uncertainties in equilibrium constants and other thermodynamic data derived from potentiometry. Silver ion–silver and triiode ion–iodide ion external reference electrodes in a wide variety of solvents function satisfactorily[3] although in dipolar aprotic solvents liquid-junction potentials cannot always be minimized as effectively as in water because electrolytes having all of the desirable properties for use in salt bridges of high solubility, low reactivity, and equitransference of the component ions do not exist.

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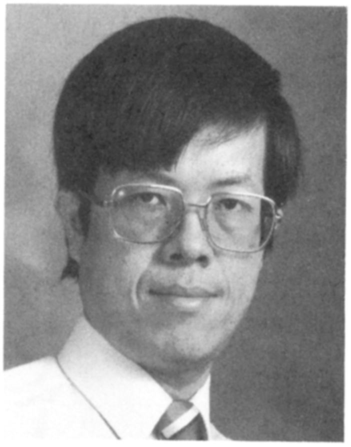
Johannes F. Coetzee received his Ph.D. degree from the University of Minnesota under the direction of I. M. Kolthoff in 1956. He joined the faculty of the University of Pittsburgh as Assistant Professor in 1957, becoming Professor in 1966. His research has been in electroanalytical chemistry and in the study of interactions occurring in solutions, particularly solutions of electrolytes in dipolar aprotic solvents, using electrochemical and various spectroscopic probes. He has served as Chairman of the Commission on Electroanalytical Chemistry of the International Union of Pure and Applied Chemistry and in various other professional organizations. He is the recipient of the 1986 University of Minnesota Distinguished Achievement Award and the 1989 Pittsburgh ACS Award.

Balasaheb K. Deshmukh received his Ph.D. degree from Nagpur University, India, in 1978 and served as lecturer at the same institution until 1982, publishing extensively on the development of methods for environmental analysis. He joined the research group of J. F. Coetzee at the University of Pittsburgh as an India National Scholar for the period 1982–1984 and again for the period 1986–1989, doing research on the development of new potentiometric sensors and on novel applications of existing sensors.



Chaochuan Liao received his B.S. degree from Tunghai University, Taiwan, and Ph.D. degree in 1986 from the University of Pittsburgh. His research at Pittsburgh involved the characterization of reactive impurities in acetonitrile and the study of complexation reactions of cadmium ion in the same solvent. Since 1986 he has been a postdoctoral associate in the Departments of Physiology and Surgery of the Hershey Medical Center, Pennsylvania State University.

An obvious requirement is that the sensor material should have negligible solubility in the analyte solution and should not react with it. This requirement rules out most liquid-membrane ion-selective electrodes (ISEs) for use in organic solvents. However, many other types of potentiometric sensors can be used in a wide variety of nonaqueous solvents, e.g., solid state and glass-membrane ISEs and indicator electrodes of the first kind (e.g., Ag) and of the second kind (e.g., Ag/AgCl in protic solvents). On the other hand, certain sensors malfunction in particular solvents. Examples are the hydrogen electrode in the majority of dipolar aprotic solvents and the copper(II) solid-state ISE in acetonitrile. One possible reason for the failure of the hydrogen electrode in such solvents as acetonitrile may be catalytic hydrogenation of the solvent in the presence of platinum. On the other hand, the copper(II) ISE, which has the composition $Cu^{I}_{0.45}Ag^{I}_{1.55}S$, fails in acetonitrile as a result of the cumulative effect of the weak solvation of copper(II) ion and the exceptionally strong solvation of the d^{10} copper(I) and silver(I) ions, so that, as shown by ESCA,[4] the latter ions are replaced by the highly reactive copper(II) ion in the surface of the sensor.

It is widely accepted that in aqueous solution the response mechanism of such ISEs as glass and lanthanum fluoride electrodes involves ion-exchange processes occurring in gel layers established on the surface of the membranes. If such gel layers indeed are essential to the response of the sensors, then it is to be expected that these ISEs will gradually passivate in nonaqueous solvents, particularly such highly hygroscopic solvents as methanol or acetone, as the gel layers become dehydrated and therefore deactivated. The literature in fact contains scattered reports of passivation of the glass hydrogen ISE in particular, but we and many other workers have encountered no such problems, at least if the electrode is stored only in aqueous solutions and is conditioned in the particular nonaqueous solvent for perhaps 1 h before use.

The literature also contains many reports of aberrations in the response of ISEs and other indicator electrodes in nonaqueous media, particularly non-Nernstian response and restricted dynamic range in unbuffered solutions. We shall show later that these aberrations usually are caused by the presence of impurities reacting with the analyte ions; in buffered solutions these problems therefore are less severe. The question of whether a particular sensor *inherently responds in strictly Nernstian manner* is important and must be addressed. It is frequently observed that the response of ISEs tends to deviate by a few percent from the Nernstian slope of $59/z_i$ mV/decade in activity of the analyte i. The question then arises whether reliable thermodynamic data can be obtained with such an electrode, particularly when the analyte activity is much smaller than the activities used for calibration of the electrode. Caution should be exercised in the rationalization of such deviations from strictly Nernstian response. Apart from impurity effects, these deviations

TABLE I. Properties and Parameters of Dipolar Aprotic Solvents Correlated with Solvation of Polar Solutes and Ions[a]

property or parameter	W	AN	DME	MC	DMF	DMA	SL	DMS	DMSO	THF	2MTHF	DO	PC	4BL	NMP
rel permittivity	78.5	36.0	7.2	8.9	36.7		43.3	22	46.6	7.6	6.2	7.1	65.1	39.1	32.0
dipole moment, D	1.8	4.1		1.1	3.8	3.8	4.8		4.3				4.9		4.1
polarizability, Å^3/molecule	1.5	4.5			7.9	9.7			8.0				8.6		10.3
Kosower polarity param, Z[b]	(92)	71.3		64.2	68.5		70.6		70.2						
Dimroth polarity param, E_T[c]	63.1	46.0	38.2	41.1	43.8	43.7	44.0		45.0	36.0			46.6		
Kamlet–Taft param[d]															
α	(1.13)	(0.15)	0	(0.22)	0	0	0		0	0			0	0	0
β	(0.18)	(0.31)	(0.41)	0	0.69	0.76			0.76	0.55				0.49	0.77
π^*	(1.09)	(0.85)	(0.53)	(0.80)	0.88	0.88	0.98		1.00	0.58			(0.81)	0.87	0.92
Gutmann donor no., DN[e]	(18)	14.1			26.6		14.8		29.8	20.0			15.1		
Mayer–Gutmann acceptor no., ACN[f]	54.8	18.9	10.2		16.0				19.3	8.0			18.3		

[a] Abbreviations: W, water (included for comparison); AN, acetonitrile; DME, dimethoxyethane; MC, methylene chloride; DMF, dimethylformamide; DMA, dimethylacetamide; SL, sulfolane; DMS, dimethyl sulfite; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran; 2MTHF, 2-methyltetrahydrofuran; DO, 1,3-dioxolane; PC, propylene carbonate; 4BL, 4-butyrolactone; NMP, *N*-methylpyrrolidinone. Temperatures: 303 K for sulfolane; 298 K for all other solvents. [b] A proposed measure of the polarity of the solvent, based on solvatochromic shifts induced in the longest wavelength charge-transfer band of 1-ethyl-4-carbomethoxypyridinium iodide. [c] Similar to Z, but based on pyridinium *N*-phenol betaine. [d] Based on average solvatochromic shifts for seven indicators (for π^*). These are compared with corresponding shifts for additional indicators chosen to reveal hydrogen bond donor (α) and acceptor (β) abilities of solvents. The resolution of these three classes of interactions represents a major advance over previous "polarity" scales. For reviews of polarity scales, see refs 8 and 9. [e] A measure of the electron-donor strength of the solvent, based on its enthalpy of reaction with antimony pentachloride in 1,2-dichloroethane as solvent. [f] A measure of the electron-acceptor strength of the solvent, based on the ^{31}P chemical shift of triethylphosphine oxide in the solvent.

may be caused by slow approach of the potential to its equilibrium value or to fluctuations in the potential of the reference electrode and in the liquid-junction potential if an external reference electrode is used. The electrode may also be responding to other ions. The selectivity of an ISE generally is solvent-dependent; for example, the glass hydrogen ISE responds much more strongly to lithium ion in 1,3-dioxolane than in water.[5] Finally, another possibility is that the response of the ISE is perturbed by a solvent-dependent interference with its ion-exchange properties; examples are partial dehydration or other deleterious modification of its gel layer and the malfunction of the copper(II) ISE in acetonitrile already referred to. In such cases it is highly desirable to compare the response of the ISE with that of other indicator electrodes for the same ion, if available. This has been done in a number of instances. For example, it has been shown that in several solvents the response of typical glass hydrogen ISEs parallels that of the hydrogen electrode. Similarly, in a particularly useful study Nakamura showed that the response of a so-called cation-sensitive glass electrode (Beckman No. 39047) to Li^+, Na^+, K^+, Rb^+, Cs^+, and Tl^+ paralleled that of the corresponding amalgam electrodes in water, methanol, acetonitrile, propylene carbonate, dimethyl sulfoxide, and dimethylformamide as solvents.[6]

The conclusion is that, with due caution, many ISEs can be used to obtain reliable thermodynamic data in a wide range of polar solvents.

II. Important Polar Solvents in Which Potentiometric Ion Sensors Can Be Used

Apart from purely analytical applications of potentiometric ion sensors, both in absolute potentiometry (e.g., the measurement of pH) and as equivalence point detectors in potentiometric titrations, these devices provide fundamental information on the reactivities of solutes and, hence, on the interactions occurring between solutes and solvents. When complemented by other probes of such interactions, particularly conductometry and various spectroscopic techniques, including infrared, Raman, and nuclear magnetic resonance spectroscopy as well as microwave dielectric and ultrasonic relaxation measurements, many of the details of the complex interplay of interactions occurring in electrolyte solutions can be resolved.

It was pointed out in section I that many potentiometric sensors can be used in a wide variety of polar solvents. Early work was limited mainly to water and the lower alcohols. Indicator electrodes used in the alcohols included the hydrogen electrode, the glass hydrogen ISE, the glass alkali-metal ISEs, and the lanthanum fluoride ISE for fluoride ion, while the silver–silver chloride electrode was used extensively as internal reference electrode. In water many additional indicator electrodes could be used, including liquid-membrane electrodes based on charged as well as on neutral carriers, enzyme electrodes, etc.; applications of these sensors in aqueous solutions have been extensively discussed.[7] Later work dealt increasingly with the class of dipolar aprotic solvents; these solvents are particularly useful in many important applications, some of which will be referred to in section IV. Examples of such solvents and of their key properties are given in Table I, which also includes water for comparison. While all dipolar aprotic solvents are weak hydrogen bond or proton donors (as shown, for example, by their low Kamlet–Taft α parameters), they differ widely in their strengths as nucleophiles, ranging from the very weak methylene chloride to the relatively weak acetonitrile, sulfolane, and propylene carbonate to the strong nucleophiles dimethylformamide and dimethyl sulfoxide (compare β or DN parameters). Relative

TABLE II. Overall Dissociation Constants of Acids Best Suited to Calibration of Hydrogen Ion Indicator Electrodes in Selected Dipolar Aprotic Solvents (References in Parentheses)

solvent	$HClO_4$	FSO_3H	CH_3SO_3H	CF_3SO_3H	HPi[a]
dimethyl sulfoxide	0.5 (14)	1.0 (15)	1.6 (14)	0.6 (14)	0.3 (16), −1.0 (17)
sulfolane (30 °C)	3.0 (18)	3.3 (19)		3.4 (16)	
acetonitrile	1.6 (15), 2.1 (20)		8.4 (15), 10.0 (21)		11.0 (21)
propylene carbonate	1.3 (22)	2.0 (23), 4.7 (15)	7.2 (15), 8.3 (24)	1.3 (15)	9.3 (24), 11.4 (22)
methyl isobutyl ketone	4.5 (25)	6.0 (15)	7.3 (15)	4.7 (15)	11.0 (25)
tetrahydrofuran[b]	7.7 (5)			8.1 (5)	11.6 (5)

[a] Picric acid (2,4,6-trinitrophenol). Typically, electrodes are calibrated in HPi–R_4NPi buffers where pK_a values of HPi have been obtained by potentiometric comparison with the strongest acids, the pK_a values of which in turn have been obtained conductometrically. It is important to note uncertainties discussed in the text. [b] In this low-permittivity solvent the dissociation constant K_a refers to the following overall process so that $K_a = K_iK_d/(1 + K_i)$.

$$HA + S \overset{K_i}{\rightleftharpoons} SH^+A^- \overset{K_d}{\rightleftharpoons} SH^+ + A^-$$

values of solvation parameters depend on the reference nucleophiles and electrophiles used. More specific information on reactivities of solvents is provided by thermodynamic quantities for a variety of reactions, e.g., dissociation constants of acids and bases. In evaluation of such constants, potentiometric sensors played a key role; some examples are given in section III.

Other solvents in which potentiometric sensors have been used include protogenic amphiprotic solvents, e.g., acetic acid (using the chloranil electrode as hydrogen ion sensor), and the protophilic amphiprotic solvents ethylenediamine and liquid ammonia in which the hydrogen electrode could be used, in the latter solvent under the extreme condition of a temperature of −60 °C.

Details about the potentiometric sensors used in this wide range of solvents are scattered throughout the extensive literature dealing with the chemistry of nonaqueous solutions. The key bibliography appears in the next section.

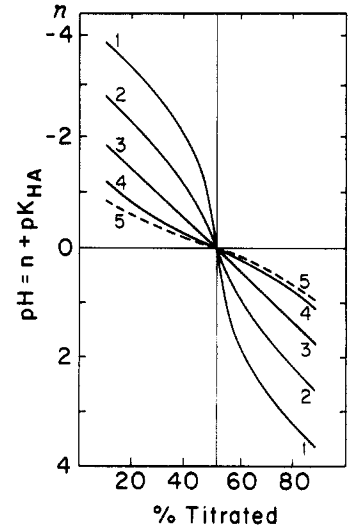


Figure 1. Calculated potentiometric titration curve of HA with Et_4NOH for various values of log K_f, where K_f is the formation constant of the homoconjugate AHA^-: (1) 3; (2) 2; (3) 1; (4) 0; (5) simple dissociation of HA, $K_f = 0$ (reprinted from ref 21; copyright 1965 American Chemical Society).

III. General Applications of Potentiometric Sensors in Nonaqueous Solutions

A comprehensive compilation with 330 references of applications of ISEs in nonaqueous and mixed solvents has been published by Pungor et al.[10] The key role of potentiometric sensors in the study of nonaqueous solution chemistry is illustrated throughout the literature of the field, particularly in the fairly recent critical and informative discussions of acid–base equilibria by Kolthoff and Chantooni (general introduction), Popov and Caruso (amphiprotic solvents), Kolthoff and Chantooni (dipolar aprotic solvents), and Popov (inorganic solvents) in Kolthoff and Elving's *Treatise on Analytical Chemistry*[11] and by Popovych and Tomkins in their monograph *Nonaqueous Solution Chemistry*.[12] A useful and detailed compilation by Izutsu of acid–base dissociation constants (determined primarily by potentiometry) in 12 dipolar aprotic solvents will be published.[13] In view of these recent reviews, acid–base reactions will not be discussed here, other than to point out a few of the salient features. (a) Proton transfer and other acid–base reactions are exceptionally solvent-dependent, so that a rich diversity in reactivities is observed in the wide range of solvents studied. For example, in dipolar aprotic solvents the dissociation of Brønsted acids is much more differentiated than in a leveling solvent such as water. Much of this information was obtained with the glass hydrogen ISE and, in a few solvents, with the hydrogen electrode. For example, in dimethyl sulfoxide as solvent, pK_a values of picric acid, nitromethane, and triphenylmethane, determined by potentiometric titration with dimsylcesium at the glass electrode calibrated with *p*-toluenesulfonic acid behaving as a strong acid, are −0.3, 16.5, and 30, respectively.[11] (b) In aprotic solvents (S) many proton-transfer reactions are strongly influenced by the homoconjugation reaction $HA + S + HA \rightleftharpoons SH^+ + AH\cdots A^-$ when the anion A^- is "hard" (e.g., chloride) or has a localized charge (e.g., acetate), requiring hydrogen bonding for stabilization. One result of such homoconjugation is that it strongly modifies the shape of potentiometric titration curves, producing a potential break at 50% titrated, as shown in Figure 1, while reducing the break at 100% titrated, which is undesirable from the analytical point of view. (c) In solvents of low permittivity (e.g., acetic acid), especially if the solvent is also aprotic (e.g., tetrahydrofuran), all chemical reactions involving ionogens or ionophores, including proton-transfer reactions, are greatly complicated by ion association leading to ion pairs of various types and higher aggregates. (d) In many solvents, particularly those that are only weak solvators of the analyte ion and/or have low permittivities, the calibration of an indicator electrode is a nontrivial matter. The uncertainties encountered in the calibration of hydrogen ion

TABLE III. Comparison of Equilibrium Constants on the Molar Scale for Reactions of Silver(I) with Halide Ions in Nonaqueous Solvents and Water[a]

	$-\log S_0$			$\log \beta_2$			$\log K_{s2}$			
solvent	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-	Cl^-	Br^-	I^-	ref
Activity Constants at 25 °C										
acetonitrile	13.0	13.3	15.0	13.7	14.1	15.6	0.7	0.8	0.6	27
sulfolane (30 °C)	18.5	18.9		20.3	20.2		1.8	1.3		28
propylene carbonate	20.2			21.2			1.0			29
dimethylformamide	15.2			17.0			1.8			30
water	9.7	12.2	16.0	5.0	7.2	10.6[b]	-4.7	-5.0	-5.4[b]	31
Concentration Constants near 25 °C										
acetonitrile[c]	12.4	13.2	14.2	12.6	13.4	14.6	0.2	0.2	0.4	32
nitromethane[c]	19.2	19.7	20.5	19.5	19.7	22.0	0.3	0.0	1.5	33
nitroethane[c]	21.1	21.8	22.6	22.2	22.5	23.5	1.1	0.7	0.9	32
propylene carbonate[c]	20.0	20.5	21.8	20.9	21.2	22.8	0.9	0.7	1.0	34
dimethyl sulfoxide[c]	10.4	10.6	12.0	11.9	11.7	13.1	1.5	1.1	1.1	32
acetone[d]	16.4	18.7	20.9	16.7	19.7	22.2	0.3	1.0	1.3	32
methanol[e]	13.0	15.2	18.2	8.0	10.9	14.8	-5.0	-4.3	-3.4	32

[a] Reprinted from ref 26; copyright 1983 Wiley. [b] In 4 M $NaClO_4$. [c] In 0.1 M Et_4NClO_4. [d] In 0.1 M $LiClO_4$. [e] In 1 M $LiClO_4$.

indicator electrodes in several dipolar aprotic solvents is illustrated by the data in Table II showing, in some cases, considerable differences between different workers. There are several known reasons for these differences. One problem is that while perchloric acid and the three sulfonic acids listed in Table II are extensively dissociated in dimethyl sulfoxide, sulfolane, acetonitrile, and propylene carbonate, solutions of these relatively strong acids in all solvents listed except sulfolane are not ideally stable. The problem is particularly acute in acetonitrile and propylene carbonate. A second serious problem is that in solvents that are weak proton acceptors (sulfolane, acetonitrile, propylene carbonate) the effect of basic impurities can be disastrous. This important matter is discussed in section IV. Finally, in the aprotic and low-permittivity solvent tetrahydrofuran interpretation of the response of hydrogen ion indicator electrodes is greatly complicated by ion association reactions.

In comparison to the extensive studies of acid–base reactions in nonaqueous solvents, much less has been done on complexation and precipitation reactions, and while oxidation–reduction reactions have received much attention, the great majority of studies involved voltammetry rather than potentiometry. A brief review of precipitation titrations in nonaqueous solvents has appeared.[26] Representative examples of equilibrium constants obtained by potentiometric titration of halide ions with silver(I) ion at the silver metal indicator electrode are listed in Table III, where S_0 is the solubility product constant, β_2 is the overall formation constant for the reaction $Ag^+ + 2X^- \rightleftharpoons AgX_2^-$, and K_{s2} is the formation constant for the reaction $AgX\downarrow + X^- \rightleftharpoons AgX_2^-$. Polynuclear silver complexes may also form in these reactions, as illustrated in Figure 2.

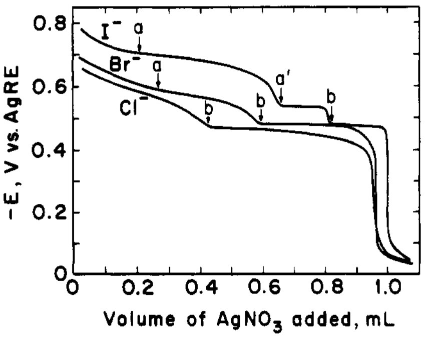


Figure 2. Potentiometric titration of halide ions (X^-) with silver(I) in acetonitrile: Cl^-, 10.0 mL of 0.0238 M Et_4NCl with 0.251 M $AgNO_3$; Br^-, 10.0 mL of 0.0240 M Et_4NBr with 0.250 M $AgNO_3$; I^-, 10.0 mL of 0.0250 M Et_4NI with 0.251 M $AgNO_3$. First precipitations: $Et_4NAg_2Br_3$ and $Et_4NAg_2I_3$ (a); $Et_4NAg_5I_6$ (a′); AgX (b) (reprinted from ref 27; copyright 1973 American Chemical Society).

TABLE IV. Known Impurities in Propylene Carbonate and Acetonitrile (1982 IUPAC Compilation)[35]

solvent	impurities
propylene carbonate	water, carbon dioxide, propylene oxide, 1,2- and 1,3-propanediol, allyl alcohol, ethylene carbonate, unidentified impurity absorbing in the 240–340-nm region, unidentified basic impurity[a]
acetonitrile	water, propionitrile, acrylonitrile, acetone, allyl alcohol, benzene[a]

[a] By using the new approach described later in section IV, we have found additional, highly reactive, impurities in these and other solvents.

IV. Applications of Potentiometric Sensors in the Characterization of Reactive Impurities in Solvents

A specific recent application of potentiometric sensors is in the characterization of reactive impurities in solvents, which is of crucial importance throughout the field of solution chemistry.

A major obstacle in realizing the potential of any solvent, but particularly a relatively inert solvent (which is required if high solute reactivities are desired), is the presence of reactive impurities. We shall concentrate on the class of dipolar aprotic solvents that is especially useful for carrying out many chemical and electrochemical reactions of interest in chemistry, chemical engineering, and industrial technology. A list of such solvents was given in Table I. As an illustration of the kinds of impurities typically found in solvents of this type (even after purification by "standard methods"), results reported in a 1982 IUPAC compilation[35] for propylene carbonate and acetonitrile are listed in Table IV. These are two of the most thoroughly studied solvents; much less is known about impurities in most of the other solvents listed in Table I.

Examples of applications of nonaqueous solvents in which impurities are expected to seriously interfere are

TABLE V. Typical Examples of Important Applications of Nonaqueous Solvents Expected To Be Seriously Affected by Impurities

application	utility	expected interference by impurities
1. "superacids" and "superbases" (as well as "superreagents" for complexation or redox reactions) examples: 0.1 M $HClO_4$ in sulfolane, pH′ ~ -10;[a] 0.1 M cesium salt of dimethyl sulfoxide in dimethyl sulfoxide, pH′ $\sim +30$[a]	allow many additional chemical reactions: new types of chemistry	decreases the range of accessible acidities or basicities
2. electrochemical "window" for electron-transfer reactions example: extended anodic and/or cathodic range in such solvents as acetonitrile, sulfolane, methylene chloride	allows many additional electron-transfer reactions: new types of chemistry	1. decreases accessible potential range 2. increases background current decreases S/N 3. impurities themselves or their oxidation/reduction products may catalyze undesirable reactions
3. aprotic battery systems example: $Li/LiAsF_6$ in THF/TiS_2	allows higher charge densities than for aqueous batteries	1. corrodes Li anode 2. catalyzes degradation of the aprotic solvent
4. studies of reactivities of solutes and mechanisms of reactions	numerous applications in current physical–organic and inorganic chemistry	may drastically affect thermodynamics and kinetics, and even mechanisms, of reactions

[a] Pseudo-pH value based on a suitable extrathermodynamic model, e.g., by assuming that Gibbs free energies of transfer of Ph_4As^+ and Ph_4B^- from water to the solvent in question are equal.

given in Table V. We do not wish to exaggerate the importance of the concentrations of impurities typically found in nonaqueous solvents (typically 10^{-1} M or lower in water and 10^{-3} M or lower in other impurities present in reagent-grade solvents). Fortunately, many common impurities are not sufficiently reactive to interfere significantly. Certain properties of solutions (e.g., bulk dielectric properties and transport properties of unreactive ions) are relatively insensitive to impurities. In many cases it is possible or even necessary to work at relatively high concentrations (e.g., NMR spectroscopy), thereby minimizing impurity effects. However, in many other cases, as in the determination of fundamental thermodynamic quantities for reactions, it is desirable to work at the lowest possible concentrations to allow extrapolation to infinite dilution. Low concentrations are particularly desirable for solvents having only poor solvating power and/or low permittivities (in order to minimize ion association reactions) and for those probes (e.g., voltammetric methods) that are essentially limited to relatively dilute solutions. Finally, low concentrations of reactive impurities may interfere even at high solute concentrations. An example is lithium batteries[36] in which low concentrations of protic and other impurities tend either to passivate or to progressively corrode the lithium surface. In fact, as the current interest in solid–liquid interfaces develops further, it may well become apparent that such interfaces are the ultimate scavengers of reactive impurities.

The pervasive problem created by impurities originates from the cumulative effect of the following factors. (a) The nature and concentrations of impurities in a given solvent frequently vary with the source and even with the batch of solvent, exhibiting an alarming time dependence. Manufacturers often change sources of raw materials as well as synthetic methods and thereby introduce different impurities, usually without publicizing the changes. (b) Typical reagent grades of solvents (e.g., spectroscopic or HPLC grades) contain reactive impurities in sufficiently high concentrations to compromise certain important applications of the solvents. (c) Probes typically used to detect and determine impurities (especially gas chromatography) have in the past frequently failed to detect important reactive impurities, e.g., amines in alcohols, propylene carbonate, and acetonitrile, as described later in this section. (d) "Standard" purification procedures often fail to lower the concentrations of such impurities to acceptable levels, so that *new purification procedures tailored to the intended use of the solvent* must be developed.

What is really needed, therefore, is an approach allowing the *routine characterization of impurities on the basis of their reactivities toward appropriately chosen probes*, rather than on the basis of their concentrations only. We have developed an "ion probe" method providing this information.[37] This approach involves adding such highly reactive ions as hydrogen, *tert*-butoxide, silver(I), copper(II), mercury(II), and fluoride as probes while their activities are monitored, preferably in flow systems, over a wide concentration range (typically from 10^{-8} to 10^{-2} M) with the corresponding indicator electrodes. The main features of the results are these. (a) In all adequately purified polar nonaqueous solvents tested so far (including the lower alcohols, acetonitrile, propylene carbonate, dimethyl sulfoxide, tetrahydrofuran, and 1,3-dioxolane) the response of the indicator electrodes is Nernstian over the entire range of concentrations of the added probe electrolytes [down to 10^{-8} M $HClO_4$, $Bu_4N(t\text{-BuO})$, $AgClO_4$, $Cu(ClO_4)_2$, $Hg(ClO_4)_2$, and Bu_4NF with 10^{-2} M Bu_4NClO_4 for ionic strength control]. (b) Deviation from such simple Nernstian response reveals the presence of a particular class of reactive impurities: with H^+ as probe ion, the presence of proton acceptors (a very large class of impurities, particularly in weakly basic solvents such as acetonitrile and propylene carbonate); with $t\text{-BuO}^-$, proton donors; with Ag^+, Cu^{2+}, and Hg^{2+}, a large class of ligands, particularly those containing nitrogen or sulfur donor atoms; with F^-, proton donors as well as hydrogen bond donors. (c) The total concentration of a particular class of impurities is related in a simple manner to the location of point B in Figure 3, which gives plots of the deviation from simple Nernstian response for typical reactions of probe ions M with impurities L. Furthermore, the magnitude

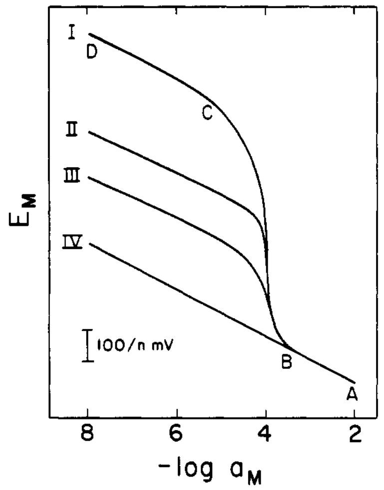


Figure 3. Calculated response of indicator electrode for M^{n+} in the presence of 10^{-4} M ligand L (reprinted from ref 37; copyright 1984 American Chemical Society). (I) log β_n = 10, 18, 24, and 28 for n = 1–4 (e.g., Hg^{2+} + aliphatic amines in methanol). In regions AB (large excess of metal) and CD (large excess of ligand), slope $59/n$ mV/decade in a_M, as shown by eq 3, while in region BC the response of the indicator electrode appears to be super-Nernstian owing to significant variations in the free ligand concentration [L]. (II) log β_1 = 10 (e.g., H^+ + aliphatic monoamines in methanol). (III) log β_n = 6, 11, 15, and 18 for n = 1–4 (e.g., Cu^{2+} + aliphatic amines in methanol). (IV) No ligand present, slope $59/n$ mV/decade in a_M.

of the deviation from Nernstian response, ΔE, depends on the reactivities of the impurities, as shown by eq 3,

$$\Delta E = -S \log (1 + \beta_1[L] + \beta_2[L]^2 + ... + \beta_n[L]^n) \quad (3)$$

where S is the slope of line IV in Figure 3. It follows that predictions about the nature of probable impurities can be further refined in those cases where an adequate database of equilibrium constants is available; e.g., it may be possible to conclude that the proton donors are probably carboxylic acids, or the proton acceptors and ligands are probably amines. However, final confirmation of impurities (which will be volatile if the solvent has been distilled) requires gas chromatographic data, preferably with mass spectrometric detection. Conditions for these confirmatory measurements can now be optimized, although even then the required procedures for such highly reactive and volatile impurities as the lower amines are by no means routine.[38] (d) As a final step in this experimental protocol, purification procedures tailored to the intended use of the solvent, as in studies of reactivities of solutes or in lithium batteries, must be developed. That the recommended procedures should be as simple as possible is important if many workers are to adopt these recommendations.

We have been able to demonstrate the effectiveness of the ion probe method in several protic as well as aprotic solvents. Typical results are shown in Figure 4 for the case of copper(II) ion as probe in methanol. The response of the copper(II) ion selective electrode indicated that ca. 2 × 10^{-4} M impurity acting as a strong ligand (probably ammonia or amine) was present in Fisher Spectranalyzed methanol (as well as in other reagent grades of methanol). Careful gas chromatographic work identified the impurity as (mainly) trimethylamine. The electrode response also gave a hint that ca. 3 × 10^{-7} M copper(II) ion was present, which was confirmed by atomic absorption spectroscopy (after evaporation of 90% of the methanol in order to reach the lower detection limit for copper). Curve E in Figure 4 shows that we were able to account quantitatively for the observed response of the electrode in the presence of these impurities.

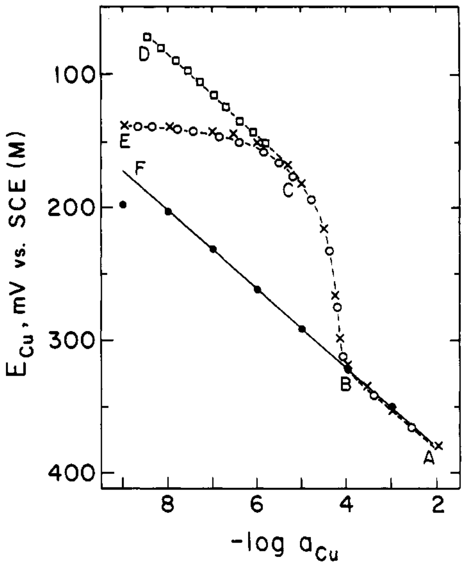


Figure 4. Response of copper(II) ion selective electrode in methanol containing 10^{-2} M Et_4NClO_4 as ionic strength control. In regions AB (large excess of copper ion) and CD (large excess of amine), slope 29.6 mV/decade in a_{Cu}, while in region CE the slope tends to zero at the lowest values of a_{Cu}. Key: open circles, observed response with Fisher Spectranalyzed methanol; squares, calculated response based on complexation of copper(II) ion with amines; crosses, calculated response based on complexation with amines as well as the presence of 3 × 10^{-7} M copper(II) ion also shown to be present as an impurity; closed circles, observed response after appropriate purification of methanol; F, theoretical response in absence of impurities (reprinted from ref 37; copyright 1984 American Chemical Society).

An additional merit of the ion probe method is that its lower detection limit (LDL) is self-adjusting in that it is lowest (most favorable) in the very solvents in which impurities are most harmful, i.e., relatively inert solvents. For example, for an arbitrary value of ΔE of −10 mV (easily discernible) and for S = 59 mV/decade, it follows from eq 3 that under conditions when n = 1, $\beta_1[L] \sim 1.5$. In such solvents as acetonitrile and propylene carbonate, β_1 for amines can be as large as 10^{19} with H^+ as probe ion, so that, in principle, the LDL can be as low as 10^{-19} M. In practice, however, nothing approaching this value can be realized, mainly because Nernstian response of the indicator electrodes in unbuffered solutions extends to only 10^{-8} M. Nevertheless, the practical LDL of between 10^{-7} and 10^{-8} M (10–1 ppb) is far superior to that attainable by gas chromatography, at least without preconcentration.

As an example of the effectiveness of the ion probe method in dipolar aprotic solvents, Figure 5 shows results obtained in a particularly interesting case, that of acetonitrile. This solvent is exceptionally important in that it is the workhorse in many proton- and electron-transfer and other studies. It owes its utility to a fortuitous combination of properties, including high polarity, high electrical conductivity of the solutions of many salts, and a wide electrochemical "window", coupled with relatively weak solvation of many solutes, so that solute reactivities can be very high. Its weak solvating ability, however, results in the complication that its intrinsic properties can be masked easily by

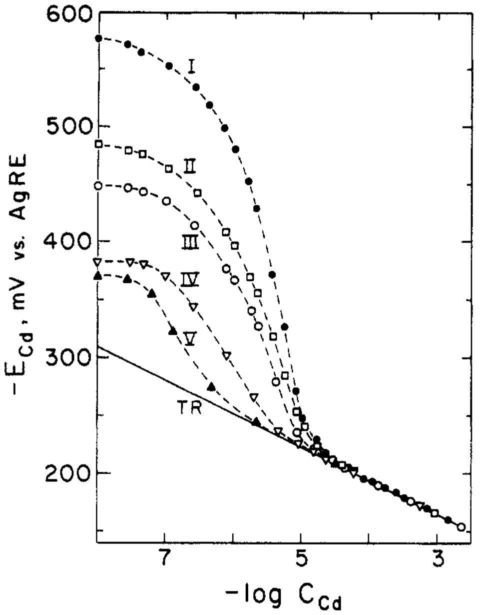


Figure 5. Response of cadmium ion selective electrode in commercial samples of acetonitrile containing 0.1 M sodium perchlorate as ionic strength control: (I) Mallinckrodt AR; (II) Aldrich, 99%; (III) Burdick and Jackson; (IV) Fisher, 99%; (V) solvent I purified by method of Carlsen.[35] TR = theoretical response in the absence of reactive impurities.

reactive impurities. In principle the ion probe method should be particularly useful in this case. Two of the more reactive probe ions, hydrogen and copper(II) ions, are of limited utility in acetonitrile, however, the first because solutions of the stronger acids in acetonitrile are unstable and the second because a reliable indicator electrode for its solutions in acetonitrile is not available (see before). Figure 5 shows results obtained with cadmium ion as probe and the cadmium ISE (solid-state membrane consisting of a mixture of cadmium and silver sulfides) as indicator electrode.[39] Total concentrations of impurities acting as ligands toward cadmium ion were found to be 4×10^{-5}, 8×10^{-6}, 3×10^{-6}, 1×10^{-6}, and 3×10^{-7} M for solvents I–V, respectively. Gas chromatography under appropriate conditions[38] showed that a major part of these impurities consisted of ethylamine and other alkylamines. The conjugate acids of these amines have pK_a values near 18 in acetonitrile,[11] so that even very weakly acidic solutes with pK_a values up to 20 (e.g., benzoic acid) will protonate the amine impurities. One result is that the measured conductivity of all but the strongest acids (see Table II) will be almost entirely (>99%) due to the reaction $HA + B \rightleftharpoons BH^+ + A^-$, where B is the amine impurity, even when the concentration of B is as low as 10^{-5} or 10^{-6} M; this illustrates the futility of attempting to determine the dissociation constants of the weaker acids by conductometry in a solvent such as acetonitrile. It is instructive to consult the original literature in order to obtain an appreciation of the difficulties encountered in obtaining a reliable pK_a value suitable for the calibration of indicator electrodes, e.g., 11.0 for picric acid.[21] Another field in which the presence of even very low concentrations of amines in acetonitrile may cause serious perturbations is in the study of ligand substitution kinetics of those metals forming stable complexes with amines; in such cases, the presence of the amine in the inner coordination sphere of the metal will labilize the remaining solvent molecules in the inner sphere, thereby greatly accelerating substitution reactions proceeding by a dissociative mechanism.[40]

Finally, several workers have commented on the presence of an unidentified, persistent basic impurity in another important dipolar aprotic solvent, propylene carbonate. This impurity may have been responsible for the inconsistencies in the pK_a values listed in Table II. Hydrogen, silver(I), and copper(II) probe ions showed that a persistent amine-type impurity survived repeated vacuum distillations. Gas chromatography showed that the impurity was triethylamine.[38] The widespread presence of amines in organic solvents is probably the result of the fact that the majority of these solvents (including the alcohols, see ref 37) are currently manufactured from petrochemicals containing some dinitrogen or nitrogen compounds.

V. Conclusions

Potentiometric ion sensors have played a key role in studies of solute–solvent interactions in a wide variety of polar solvents differing greatly in solvating abilities and permittivities. Among the more useful indicator electrodes are the hydrogen electrode (but in a limited number of solvents), the silver metal electrode, and several ion-selective glass and solid-state membrane electrodes including those for hydrogens, alkali metal, copper(II), cadmium, and fluoride ions. These sensors give Nernstian response at concentrations down to 10^{-8} M even in relatively unbuffered solutions and at activities down to 10^{-25} or even 10^{-30} in buffered solutions. The result is that solute reactivities can be measured over a very wide range with these sensors. In those solvents that are weak solvators, solute reactivities can be exceptionally high. Particularly in such solvents many impurities are sufficiently reactive to mask the intrinsic properties of the solvent, so that it is essential to devote special attention to the characterization of reactive impurities. Potentiometric sensors are especially useful for this purpose as well.

Finally, it should be reiterated (see section I) that (a) potentiometry provides for a particular solute a different activity scale for every solvent considered and (b) intercomparison of these activity scales requires extrathermodynamic assumptions. An important caveat is that the validity of such assumptions cannot be totally verified experimentally. In spite of this uncertainty, however, there is a growing tendency among many authors to indiscriminately accept without any qualification the predictions of a particular favored assumption. The most generally accepted assumption at this time is that the transfer energies of tetraphenylarsonium and tetraphenylborate ions are equal. While this indeed may be the most realistic assumption made so far, there does exist considerable spectroscopic and other evidence that there are solvent-dependent differences in the solvation of these two ions in a variety of solvents. Spectroscopic evidence includes the near-IR spectra of aqueous solutions containing these ions,[41] the solute-induced changes in ^1H NMR chemical shifts of various solvents,[42] the solvent-induced changes in ^1H, ^{13}C, ^{75}As, and ^{11}B NMR chemical shifts of the two ions in various solvents,[43] and the broadening effects of the two ions in aqueous solution on the ESR spectrum of hydrophobic nitroxide free radicals.[44] While it is possible that these spectral differences are accompanied by only relatively insignificant differences in the solvation energies of the two ions, prudence dictates that this or any other extrathermodynamic assumption used for this purpose should not be accepted indiscriminately. It remains desirable to search for new theoretical or experimental approaches to this important problem.

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