The ferrocene potential is 0.18 v more positive in acetonitrile than in water. With $r_+ = 3.8$ A[35] and $r_+'$ values of 0.72 and 0.81 A for water and acetonitrile, respectively, eq 5 applied to ferricinium ion accounts for 0.06 v of this positive shift. It may appear that the remaining 0.12 v must be the result of a lower solvation energy of ferrocene in water than in acetonitrile. However, the actual ratio of the solubilities of ferrocene in water and acetonitrile is smaller than would be expected on this basis. Kolthoff and Thomas[10] determined a solubility value of $1.7 \times 10^{-5}$ m voltametrically for an aqueous 0.1 M Et$_4$NClO$_4$ solution; we found a value of $2 \times 10^{-5}$ m by extracting a saturated solution of ferrocene in pure water with carbon tetrachloride, evaporating (caution: ferrocene sublimes easily), and weighing. In acetonitrile we found a solubility of 0.19 m. Assuming that in both solvents the activity coefficient of ferrocene is near unity, the expected shift in standard potential resulting from this cause would be near 0.24 v, rather than 0.12 v. It is possible that this decrease of 0.12 v in positive shift is caused by hydrophobic repulsion, which would decrease the stability of ferricinium ion in water. Finally, the observed solubility ratio of ferrocene in the two solvents corresponds to 18 eu, which may be attributed quite reasonably to the reduced entropy expected on the basis of the Frank–Evans model[14] as a result of possible formation of cage structures between ferrocene and water. We conclude that both ferrocene and ferricinium ion may be involved in specific interactions with water, and hence that this couple is unsuitable for our purpose.

The ferroin potential is 0.23 v (or 0.20 v based on the data in ref 36) more positive in acetonitrile than in water. This shift corresponds to an average "effective" radius term in the Born equation of ca. 2.5 A, a value which is uncertain but not unreasonable. Although the ligand molecules are large, the structure of the iron(III) and iron(II) complexes is quite open, permitting close approach of both water and acetonitrile molecules. An additional complication was reported by Kratochvil and Knoeck.[36] Partial molal entropy values for the ferroin couple in acetonitrile indicate, as expected, a greater degree of solvent ordering around the iron(III) than around the iron(II) complex, but in water the situation is reversed. This difference in solvent ordering was attributed to preferential hydrogen bonding of water to localized regions of electronegativity on the iron(II) complex. Clearly specific interactions occur.

It therefore appears that complexes such as ferrocene and ferroin, which contain large organic ligands, may be useful for comparisons among relatively similar nonaqueous solvents, but not for comparisons with water, which is involved in a variety of specific interactions with such ligands, the details of which at present are incompletely understood.

In conclusion, it is likely that application of the Born equation in the restricted manner described in this communication results in a significant improvement in the reliability of comparisons of potentials in water and acetonitrile. However, it should be stressed that unambiguous proof of the validity of any split of solvation energies in any solvent is impossible at present.

(35) D. R. Stranks, Discussions Faraday Soc., 29, 73 (1960).

(36) B. Kratochvil and J. Knoeck, J. Phys. Chem., 70, 944 (1966).

# Solute–Solvent Interactions. II. Relative Activities of Anions in Acetonitrile and Water

J. F. Coetzee[1] and J. J. Campion[2]

Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213. Received December 12, 1966

Abstract: The free energies of transfer of the halides and of nitrate, perchlorate, and picrate ions from water to acetonitrile have been evaluated. Striking differentiation in the activities of these ions occurs in acetonitrile, to such an extent as to justify the statement that the chemistry of electrolytes in this solvent generally is dominated by differences in the properties of anions. The implications of this statement are discussed.

Considerable circumstantial evidence indicates that in solvents which are dipolar but essentially aprotic, such as acetonitrile, acetone, nitromethane, N,N-dimethylformamide, and dimethyl sulfoxide, anions are solvated more weakly and therefore possess higher activities than is the case in water. Only two examples will be given here. (a) Bimolecular reactions of anions which pass through large, polarizable transition states containing the anion proceed much more rapidly in aprotic solvents than in others. For example, the relative rates of the following S$_N$2 reaction

$$Cl^- + CH_3I \longrightarrow I^- + CH_3Cl$$
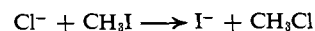
in methanol, formamide, N-methylformamide, and N,N-dimethylformamide are 1, 12.5, 45.3, and 1.2

(1) Address all correspondence to this author.
(2) From the Ph.D. thesis of this author, University of Pittsburgh, 1966.

**Table I.** Comparison of Free Energies of Solvation of Anions (X⁻) in Acetonitrile and Water Based on Solubility Products of Thallium(I) Salts and Potassium Picrate

| Salt | Acetonitrile | | | Water | | | $\Delta p K_{SP}$ | Log $_M\gamma_{X^-}$ [i] |
|------|------|------|------|------|------|------|------|------|
| | Sol[a] | $\gamma_{\pm}$[e] | $pK_{SP}$ | Sol[a] | $\gamma_{\pm}$ | $pK_{SP}$ | | |
| TlCl | $3.19 \times 10^{-7}$ [b] | 1.00 | 12.99 | | | 3.76[i] | 9.23 | 5.6 |
| TlBr | $4.25 \times 10^{-7}$ [b] | 1.00 | 12.74 | | | 5.47[i] | 7.27 | 3.7 |
| TlI | $8.07 \times 10^{-7}$ [b] | 1.00 | 12.19 | | | 7.19[i] | 5.00 | 1.4 |
| TlSCN | $9.04 \times 10^{-5}$ [b] | 0.97 | 8.11 | | | 3.77 | 4.34 | 0.8 |
| TlNO₃ | $5.03 \times 10^{-4}$ [c] | 0.93 | 6.66 | $4.407 \times 10^{-1}$ [c] | 0.497[h] | 1.32 | 5.34 | 1.8 |
| TlClO₄ | $3.31 \times 10^{-2}$ [c] | 0.65 | 3.33 | $5.22 \times 10^{-1}$ [f] | 0.525[h] | 1.12 | 2.21 | -1.4 |
| KPi | $1.53 \times 10^{-2}$ [d] | 0.72 | 3.92 | $2.42 \times 10^{-2}$ [g] | 0.88[e] | 3.34 | 0.58 | -2.6 |

[a] Solubility, as molality. [b] This work, results of tracer experiments. [c] This work, results of evaporating and weighing. [d] Kolthoff and Chantooni;[5] complete dissociation assumed. [e] Molal activity coefficient, calculated from the Debye–Hückel equation with $a = 5$ A. [f] Arithmetic mean of solubilities at 20 and 30° given in ref 9. [g] Reference 10. [h] Experimental values, ref 11. [i] Extrapolated values, ref 12. [j] Based on adjusted rubidium scale, according to which log $_M\gamma_{X^-} = \Delta p K_{SP(TlX)} - 3.59 = \Delta p K_{SP(KX)} - 3.22$; see text.

$\times 10^6$, respectively.[3] Such striking differences in rates have many important implications in organic chemistry in particular; for details refer to the extensive discussions by Parker and co-workers.[3,4] (b) Many Brønsted acids dissociate in aprotic solvents, S, according to the following over-all scheme

$$HA + S + HA \rightleftharpoons SH^+ + AH \cdots A^-$$

in which the high activity of A⁻ results in "homoconjugation" (a term coined by Kolthoff) with the parent acid. Such reactions have been studied extensively in acetonitrile, particularly by Kolthoff and Chantooni,[5] and also by others.[6]

The chemistry of electrolytes in aprotic solvents generally differs markedly from that in other solvents. Many of the most striking differences are dominated by variations in the activities of anions, such as those described above. However, present knowledge about the quantitative aspects of these variations in activity is unsatisfactory. This communication is concerned with the evaluation of such effects.

It is important to improve our understanding of the chemistry of electrolytes in aprotic solvents, because in such solvents a clearer picture of the intrinsic properties of solutes can be obtained than is possible in a strongly masking solvent such as water. However, for various reasons water must remain a solvent of unique importance, and the complex spectrum of interactions occurring between water and solutes has far-reaching implications in many branches of science. It is evident that comparisons of solute properties in water and in "nonwaterlike" solvents are bound to clarify our understanding of interactions occurring with water.

In the first paper of this series,[7] we have presented the results of an extrathermodynamic evaluation of the free energy of transfer of certain reference cations, such as rubidium ion and also of thallium(I) ion, from water to acetonitrile. In the present paper the complementary quantities are evaluated for a series of anions from the relative solubilities of the corresponding thallium(I) salts in the two solvents. The results show striking differences in activity of anions in water and acetonitrile.

(3) A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(4) B. W. Clare, D. Cook, E. C. F. Ko, Y. C. Mac, and A. J. Parker, *J. Am. Chem. Soc.*, **88**, 1911 (1966), and earlier papers.

(5) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Phys. Chem.*, **70**, 856 (1966), and earlier papers.

(6) J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2534 (1965); J. F. Coetzee and G. R. Padmanabhan, *J. Phys. Chem.*, **69**, 3913 (1965).

(7) J. F. Coetzee and J. J. Campion, *J. Am. Chem. Soc.*, **89**, 2513 (1967).

## Experimental Section

**Preparation and Purification of Chemicals.** Eastman White Label tetraethylammonium chloride and bromide were recrystallized from 2-propanol and dried *in vacuo* at 50°. Tetraethylammonium iodide was prepared by titrating Eastman Yellow Label tetraethylammonium hydroxide solution with Eastman 50% hydrogen iodide. The solution was concentrated by heating, and the crystals were filtered off and recrystallized from ethanol. The product was dissolved in a 1:1 mixture of ethanol and acetone, then precipitated with ether, and finally dried *in vacuo* at 50°. Tetraethylammonium thiocyanate was prepared directly in acetonitrile by treating a solution of tetraethylammonium chloride with a 1% excess of Baker Analyzed Reagent potassium thiocyanate and then filtering off potassium chloride, which is virtually insoluble in acetonitrile. The solution was standardized by titration with silver nitrate. Fisher Purified thallium(I) nitrate was recrystallized from water and dried at 120°. Other chemicals were treated as described.[7]

**Potentiometric Experiments.** The apparatus was the same as that described previously. Solubility products of the thallium(I) halides and thiocyanate were determined by measuring the potential of a thallium amalgam electrode in a solution prepared by adding $5 \times 10^{-4}$ to $5 \times 10^{-3}$ M thallium(I) perchlorate to $5 \times 10^{-2}$ M tetraethylammonium halide or thiocyanate.

**Radioactivity Measurements.** All measurements were made with a Geiger counter coupled with a Nuclear Chicago decade scaler (Model 181). Samples were counted on stainless steel planchets mounted on aluminum cards and covered with Mylar. Radioactive thallium(I)-204 nitrate supplied by the Oak Ridge National Laboratory was diluted with water to give an activity of *ca.* 1 mcurie/ml, and this solution was then used to dissolve an accurately weighed 100-fold excess of inactive thallium(I) perchlorate and to make it up to exactly 10 ml, giving a 0.500 M labeled solution. Precipitates of labeled TlCl, TlBr, TlI, and TlSCN were prepared by treating exactly 1 ml of this labeled solution with exactly 1 ml of 0.525 M reagent quality NaCl, KBr, KI, and NaSCN, respectively. The precipitates were washed at least four times with distilled water, transferred to polypropylene bottles, and dried *in vacuo* at 60°. Acetonitrile was added, and the bottles were sealed with serum caps and shaken for 24 hr. Aliquots then were transferred to propylene centrifuge tubes by means of plastic syringes and centrifuged. Aliquots (1 ml) were withdrawn with polypropylene pipets and evaporated on planchets under an infrared lamp. A Duco cement-ethyl acetate mixture (1 ml) was then added to each planchet and also evaporated, after which the samples were counted. Aliquots (1 ml) of $5.00 \times 10^{-5}$ M labeled TlClO₄ (prepared by diluting the 0.500 M stock solution of TlClO₄) served as standards. It was necessary to use plastic ware, because it was found that glass adsorbed appreciable amounts of thallium. Several measurements were made with each precipitate, with a reproducibility of *ca.* ±5% in the number of counts.

## Results

The solubilities of a variety of thallium(I) salts and potassium picrate in acetonitrile and water are compared in Table I.[8–12] The values listed for the halides

(8) I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **87**, 4428 (1965).

(9) "International Critical Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p 220.

(10) A. Seidell, "Solubilities of Inorganic and Metal Organic Com-

and thiocyanate in acetonitrile were obtained by tracer measurements and were checked potentiometrically as described in the Experimental Section. The potentiometric data gave the following $pK_{SP}$ values: TlCl, 12.6; TlBr, 12.4; TlI, 11.8; and TlSCN, 8.0. We prefer the tracer data, because of the uncertainty involved in estimating the activity coefficients required in treating the results of the potentiometric experiments, which were primarily designed to detect possible formation of anion complexes. The Stokes radii of I$^-$ and Br$^-$ are 2.33 and 2.37 A, respectively,[13] and that for Cl$^-$ is near 2.5 A, as computed from the approximate data of Walden and Birr.[14] Hence, as before,[7] we assume that $a = 5$ A in the Debye–Hückel equation. In a typical experiment with a mixture of $5.0 \times 10^{-2}$ $M$ tetraethylammonium halide and $5.0 \times 10^{-3}$ $M$ thallium(I) perchlorate, $S \sim 4.5 \times 10^{-2}$, assuming complete dissociation of the quaternary ammonium salt[7,13] and no significant complexation beyond the TlX$_2^-$ stage. (Actually, no complexation whatever was detected.) We obtain $f_\pm^2 = 0.35$, a value which is small enough to introduce considerable uncertainty. For further details, see ref 2.

## Discussion

**Anion Activities.** It will be convenient here to refer the activity coefficient of an ion in acetonitrile to its infinitely dilute solution in *water* as standard state. The conversion factor required for this purpose is the "medium activity coefficient," $_M\gamma_i$.

$$_W\gamma_{i,AN} = (_{AN}\gamma_{i,AN})(_M\gamma_i) \tag{1}$$

Here, $_{AN}\gamma_{i,AN}$ is the conventional Debye–Hückel molal activity coefficient of the ion in acetonitrile referred to acetonitrile as standard state,[7] and $_W\gamma_{i,AN}$ is the desired over-all activity coefficient. It is clear that the medium activity coefficient simply represents the free energy of transfer of the ion from acetonitrile to water

$$\Delta G_i^\circ = G_i^\circ{}_{AN} - G_i^\circ{}_W = RT \ln {}_M\gamma_i \tag{2}$$

For further information, refer to the discussions by Bates[15] and Popovych.[16]

Medium activity coefficients are tabulated in the last column of Table I for several anions. The numbers are based on log $_M\gamma_i$ values for Tl$^+$ and K$^+$ ions of 3.23 and 2.86, respectively, and a correction term of 0.36 for interconversion with the "aquamolality scale."[7] The immediate significance of medium activity coefficients can be illustrated as follows. Compare the activity of chloride ion in $10^{-2}$ $m$ solutions of lithium chloride in water and acetonitrile, referred in both cases to an infinitely dilute solution in water as standard state. In water, $_W\gamma_{Cl^-,W} \sim 0.9$; hence, $_Wa_{Cl^-,W} \sim 9 \times 10^{-3}$. In acetonitrile, $_{AN}\gamma_{Cl^-,AN} \sim 0.8$ (calculated from the Debye–Hückel equation) and $_M\gamma_{Cl^-} = 4 \times 10^5$; hence, $_Wa_{Cl^-,AN} \sim 3 \times 10^3$.

All anions tested, except perchlorate and picrate ions, favor water over acetonitrile as solvent. In water, anions are stabilized mainly by strong hydrogen bonding as a result of the localized positive charges of the water dipoles. Although the dipole moment of acetonitrile is high (3.37 D.), and in a nitrile the positive pole apparently is localized mainly on the cyanide carbon atom,[17,18] the charge density there is likely to be less than on the small water protons; in addition, a certain degree of charge delocalization nevertheless is likely to occur. Steric factors probably also impede solvation of anions by acetonitrile. Thus, because of the vicinity of the electron cloud of the C≡N bond, an anion probably will be forced to take up the specific position indicated in structure I, resulting in loss of freedom of rotation. Furthermore, solvation of a (small) anion by more than one acetonitrile molecule then becomes improbable. The same is not true for the cylindrically symmetrical solvate of a cation, indicated in structure II.
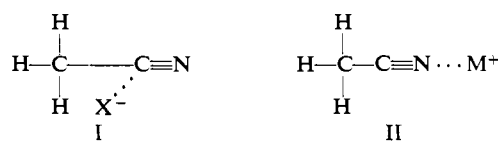
Direct measurement of the medium activity coefficient of fluoride ion is likely to be prone to large errors. Fluoride ion should be a very strong base in acetonitrile, and traces of acidic impurities (such as water) should cause a large increase in the solubility of sparingly soluble fluorides. However, it may be possible to estimate an approximate value for its medium activity coefficient from those of the other halide ions. A plot of log $_M\gamma_{X^-}$ vs. the reciprocal of the crystallographic radius is linear (Figure 1), which on extrapolation to $r = 1.36$ A gives log $_M\gamma_{F^-} \sim 14$. The corresponding value for potassium ion, which has virtually the same radius (1.33 A), is only 2.86, or 11 units smaller. On the other hand, iodide ion and a hypothetical alkali metal ion of the same radius should have approximately the same medium activity coefficient. These estimates illustrate one aspect of the strong differentiation in the properties of electrolytic solutes occurring in acetonitrile.

The two intercepts in Figure 1 predict that a hypothetical alkali metal ion with a radius near 13 A (the exact value is uncertain) should have equal solvation energies in acetonitrile and water, and that for a halide ion the analogous radius is only 2.3 A. We attribute the fact that neither value is infinity (which may have implications for Izmailov's splits; see below) to the influence of other factors, in addition to that which may be termed a first-order (Born) electrostatic effect. The polarizabilities of the ions, which increase rapidly with increasing radius, may be such an additional effect. The polarizability of a halide ion is greater than that of an alkali metal ion of equal radius, and the difference increases with increasing radius.[19] Hence, it is to be expected that this additional effect will cause equal solvation of a halide ion in the two solvents to occur

pounds," Vol. I, 3rd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1940, p 710.

(11) R. A. Robinson, *J. Am. Chem. Soc.*, **59**, 84 (1937).

(12) "Stability Constants," Part II, "Inorganic Ligands," The Chemical Society, London, 1958.

(13) J. F. Coetzee and G. P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2529 (1965).

(14) P. Walden and E. J. Birr, *Z. Physik. Chem.*, **114**, 269 (1929).

(15) R. G. Bates, "Determination of pH," John Wiley and Sons, Inc., New York, N. Y., 1964.

(16) O. Popovych, *Anal. Chem.*, **38**, 558 (1966).

(17) F. E. Murray and W. G. Schneider, *Can. J. Chem.*, **33**, 797 (1955).

(18) W. Dannhauser and A. F. Flueckinger, *J. Phys. Chem.*, **68**, 1814 (1964).

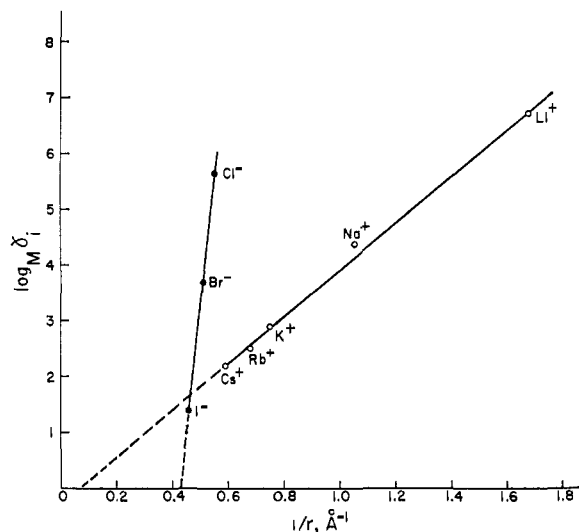(19) E. S. Rittner, *J. Chem. Phys.*, **19**, 1030 (1951).

Figure 1. Dependence of medium activity coefficients of halide and alkali metal ions on radii.

at a smaller radius than would be the case for an alkali metal ion, as observed. Another factor which must be involved is the structure-making and structure-breaking properties of the ions in water.[7]

The very polarizable picrate ion is more stable in acetonitrile than in methanol, which has approximately the same dielectric constant, and in which log $_M\gamma_i$ = −1.1.[16] This is yet another illustration of the fact that the bulk dielectric constant of the solvent is not a very useful parameter in predicting the properties of solutes. The affinity of perchlorate ion for acetonitrile (or, more likely, its phobia for water) is puzzling.

The well-known fact that the solubility of a salt in acetonitrile (and other aprotic solvents) is particularly sensitive to the nature of the anion is clearly illustrated by the data in Table I.

It is obvious that it now becomes possible to calculate the solubilities of numerous salts in acetonitrile from the known values in water, by using the log $_M\gamma_i$ values for anions reported in Table I and those calculated from the shifts in potential given in the previous paper.[7] This will be true whether or not our original split of solvation energies into the ionic components was accurate. The only requirement is that for a given salt the sum of the two log $_M\gamma_i$ values be accurate.

Our results can be compared to two other estimates based on data appearing in the literature. Izmailov[20] split solvation energies of electrolytes into the ionic components by extrapolating plots of the solvation energies of the hydrogen halides, and of the differences in solvation energy between the hydrogen halides and the corresponding alkali metal halides, vs. the reciprocal of the radius of the varying ion to infinite radius; or, of appropriate combinations of solvation energies vs. the quantity $1/n^2$ to $n = \infty$, where $n$ is the principal quantum number involved. The following log $_M\gamma_i$ values were obtained: Rb+, 1.6 (our value is 2.52); Cl−, 8.0; Br−, 5.0; I−, 2.3. This split obviously indicates a greater difference between cation and anion activities than ours does. Izmailov's extrapolation is long and uncertain, a fact which undoubtedly contributes to the discrepancy (also see above).

(20) N. A. Izmailov, Dokl. Akad. Nauk SSSR, 149, 1364 (1963).

Another estimate can be obtained from the solubility data of Pavlopoulos and Strehlow[21] for the alkali metal halides in acetonitrile. The rubidium halides[22] have the following molal solubilities[23] and molal mean activity coefficients,[11] respectively, in water: RbCl, 7.77, 0.58; RbBr, 7.04, 0.52; RbI, 7.72, 0.52. For acetonitrile the corresponding solubilities[21] and activity coefficients (calculated from the Debye–Hückel equation with $a$ = 5 A) are: RbCl, 2.6 × 10⁻⁴, 0.95; RbBr, 2.6 × 10⁻³, 0.86; RbI, 8.0 × 10⁻², 0.56. Using our values of 2.52 for log $_M\gamma_{Rb^+}$ and 0.36 for conversion to the aquamolality scale, we calculate log $_M\gamma_{X^-}$ values of 5.6, 3.5, and 1.0 for the halides, in reasonable agreement with the numbers in Table I.

**Liquid Junction Potentials.** Many polarographic measurements in acetonitrile (and other nonaqueous solvents) have been carried out with an aqueous saturated calomel electrode (sce) as reference. Various estimates have been made of the magnitude of the liquid junction potential (see pertinent papers listed in ref 7). Provided the mobilities in both solvents and the medium activity coefficients of all ions involved are known, it should be possible, in principle, to calculate the junction potential *ab initio*. This required information is now available (for Et₄N⁺, we estimate log $_M\gamma_i$ ∼ −0.3 from the relative solubilities of Et₄NI in water and acetonitrile), but various other factors introduce gross uncertainties into such calculations. Typically we are dealing with the following complex interface

acetonitrile
Et₄N⁺———→
ClO₄⁻ ———→
←——— K⁺
←——— Cl⁻
water
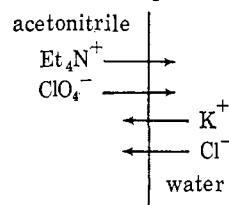
where the water phase may or may not contain agar. Furthermore, the exact profile of the interface is unknown (acetonitrile and water are miscible in all proportions). However, a semiempirical value of the junction potential can be obtained from our derived value of +0.503 v for the potential of the Pleskov electrode referred to the normal hydrogen electrode in water,[7] i.e., +0.257 v referred to sce, and Iwamoto's experimental value of +0.291 v for the Pleskov electrode vs. sce with 0.1 M Et₄NClO₄ as salt bridge.[24] The junction potential then is 0.291 − 0.257 = 0.034 v, of such sign as to make all potentials measured directly vs. sce too positive by 0.034 v. One may speculate that this relatively small value does not appear unreasonable in view of the marked compensating activity effects occurring across the interface. Thus, the medium activity coefficients of the four ions involved show qualitatively that the net effect is that the water phase is favored by an anion (Cl−), and the acetonitrile phase also by an anion (ClO₄⁻). Finally, it should be noted that, since potentials measured in acetonitrile against the sce certainly are reproducible to within a few milli-

(21) T. Pavlopoulos and H. Strehlow, Z. Physik. Chem. (Frankfurt), 2, 89 (1954).
(22) We are omitting from consideration those salts which form hydrates and for which comparisons therefore are more prone to error. In addition, the solubility reported for CsBr in acetonitrile appears to be inconsistent with the other data.
(23) Reference 10, pp 1429, 1433, 1437.
(24) R. C. Larson, R. T. Iwamoto, and R. N. Adams, Anal. Chim. Acta, 25, 371 (1961).

volts, a very large value of the junction potential appears to be unlikely.

# Hydration of Undissociated Salts in Acetonitrile[1]

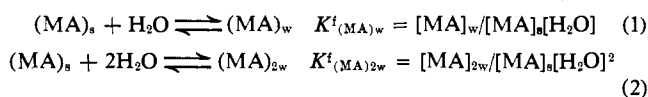## I. M. Kolthoff and M. K. Chantooni, Jr.

*Contribution from the School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. Received January 6, 1967*

**Abstract:** An equation has been derived to calculate from the total and ionic solubilities of potassium picrate, salicylate, 3,5-dinitrobenzoate, and 3,5-dinitrophenolate in acetonitrile (AN) in the presence of known concentrations of water the individual formation constants $K^f_{(MA)_w}$ and $K^f_{(MA)_{2w}}$ of dissolved, undissociated mono- and dihydrated salts, $(MA)_w$ and $(MA)_{2w}$. Using these values and the previously determined values of formation constants of hydrated ions in AN, it has been possible to calculate the concentration of all species present in saturated solutions of the above salts in the presence of water. This allowed the calculation of the ionic dissociation constant $K^d_{(MA)_w}$ which was found to be greater than $K^d_{(MA)_s}$ (unhydrated salt). Unexplained is the result that $K^d_{(MA)_{2w}}$ of potassium salicylate was found smaller than the corresponding constant of the anhydrous salt. In the presence of water the dissociation constant of the anhydrous salt was found to be virtually unaffected up to a water concentration of 0.6 $M$. The red solid salt, potassium 3,5-dinitrophenolate, changes into a yellow solid in the presence of small concentrations of water in AN. This solid was found to be a monohydrate. No hydrated solid was formed with the other salts used. The ionic dissociation constant of the monohydrate was found greater than that of the anhydrous salt, while the constant of the dihydrate was found considerably greater than that of the monohydrate.

In a previous paper[2] the equilibrium constant of the hydration of several monovalent ions $I^\pm$ was determined. In that study it was not necessary to consider a reaction between the dissolved undissociated anhydrous salt, $(MA)_s$ ($M^+$ and $A^-$ both being monovalent ions), and water.

In the present investigation the formation constants of the hydrates of the potassium salts of picric, salicylic, and 3,5-dinitrobenzoic acids and 3,5-dinitrophenol were determined. The potassium ion forms only a monohydrate with a formation constant of 1, while the sodium ion is much more strongly hydrated and forms at least a mono- and a dihydrate. For this reason sodium salts have not been used in the present study as they are expected to form higher hydrates than those of potassium. On the basis of the uncertainty in the assumptions made and in the experimental results, the hydration and dissociation constants calculated for sodium salts would be considerably more uncertain than those of hydrated potassium salts.

Denoting $(MA)_s$ as the unhydrated potassium salt and $(MA)_{\Sigma yw}$ as the hydrated salts, the following equilibria can be written

$$(MA)_s + H_2O \rightleftharpoons (MA)_w \quad K^f_{(MA)_w} = [MA]_w/[MA]_s[H_2O] \quad (1)$$

$$(MA)_s + 2H_2O \rightleftharpoons (MA)_{2w} \quad K^f_{(MA)_{2w}} = [MA]_{2w}/[MA]_s[H_2O]^2 \quad (2)$$

From the total molar solubility, $s_t$, and the total ionic solubility, $i_t$, in presence of known concentrations of water eq 3 results, $[MA]_s$ being the solubility of undissoci-
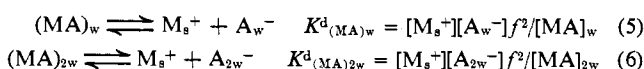
(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-28-65.
(2) M. K. Chantooni, Jr., and I. M. Kolthoff, *J. Am. Chem. Soc.*, **89**, 1582 (1967).

$$s_t = i_t + [MA]_s + [MA]_{\Sigma yw} \quad (3)$$

ated anhydrous salt in absence of water and $[MA]_{\Sigma yw}$ the total concentration of hydrated undissociated salts in presence of water. From the experimentally determined values of $s_t$, $i_t$, and $[MA]_s$, $[MA]_{\Sigma yw}$ is readily obtained. Assuming that the ratio of the solubility product and dissociation constant of $(MA)_s$, $K_{sp}/K^d_{(MA)_s}$, equal to $[MA]_s$, does not change with water content, the values of the individual formation constants $K^f$ of the hydrates (eq 1 and 2) are found from the relation

$$\frac{s_t - i_t - [MA]_s}{[MA]_s[H_2O]} = \frac{[MA]_{\Sigma yw}}{[MA]_s[H_2O]} = K^f_{(MA)_w} +$$

$$[H_2O]K^f_{(MA)_{2w}} \quad (4)$$

which is derived by combining eq 1–3. A plot is made of $s_t - i_t - [MA]_s/[MA]_s[H_2O]$ vs. $[H_2O]$. If the slope of the linear plot is zero or close to zero, it is safe to conclude that $y = 1$ and only a monohydrate is formed. When the linear plot does not have a slope of 0, $y = 2$, the intercept being equal to $K^f_{(MA)_w}$ and the slope $K^f_{(MA)_{2w}}$.

From the experimental data it was also possible to calculate the dissociation constant of the salt $(MA)_w$ and of $(MA)_{2w}$ (eq 5 and 6). The over-all dissocia-

$$(MA)_w \rightleftharpoons M_s^+ + A_w^- \quad K^d_{(MA)_w} = [M_s^+][A_w^-]f^2/[MA]_w \quad (5)$$

$$(MA)_{2w} \rightleftharpoons M_s^+ + A_{2w}^- \quad K^d_{(MA)_{2w}} = [M_s^+][A_{2w}^-]f^2/[MA]_{2w} \quad (6)$$

tion constant $K^d_{\Sigma(MA)_{s+w}}$ (eq 7) is calculated in the following

$$K^d_{\Sigma(MA)_{s+w}} = i_t^2 f^2/s_t =$$

$$\frac{[[M_s^+] + [M_w^+]][[A_s^-] + [A_w^-] + [A_{2w}^-]]f^2}{[MA]_s + [MA]_{\Sigma yw}} \quad (7)$$