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## Solute–Solvent Interactions. I. Evaluations of Relative Activities of Reference Cations in Acetonitrile and Water

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**Abstract:** Extrathermodynamic methods that have been used to split solvation energies of electrolytes into the ionic components and to compare single ion activities in different solvents are reviewed critically. In this work, the application of the Born equation is restricted in such a manner that the probable reliability of the comparisons is improved significantly. The free energy of transfer from acetonitrile to water associated with potentially useful reference couples, including the rubidium, thallium, ferrocene, and ferroin systems, is evaluated. The relative advantages of these couples are discussed.

It is well known that the properties of electrolytic solutes quite generally are modified substantially by interaction with the solvent. However, quantitative information about this important process is limited. In order to assess the relative extent of such interactions in various solvents, it is necessary to estimate single ion activities in different solvents relative to a common standard state.

The basic problem of evaluating single ion activities and Galvani potentials, and the related ones of comparing potentials in different solvents and splitting the solvation energies of electrolytes into the ionic components, constitute classical dilemmas of chemistry which have received much attention.[3–5] The essential point is that, since the problem is not accessible to exact thermodynamics, it is necessary to follow extrathermodynamic procedures. Perhaps the most promising approach at present is based on an assumed ideal (nonspecific) behavior of certain solutes with respect to their oxidation–reduction or their solubility properties. Thus various authors have assumed that the standard potentials of couples such as rubidium ion–rubidium amalgam,[6,7] ferricinium ion–ferrocene,[8] or the iron(III–II) complexes of the phenanthrolines[9,10] are relatively insensitive to specific solvation effects and therefore should be reasonably constant in different solvents. In a related approach, Popovych[11] has estimated single ion solvation energies from solubility data by assuming that in any given solvent the cation and anion of an appropriate reference electrolyte, such as triisoamylbutylammonium tetraphenylboride, will have equal free energies of solvation. These assumptions all suffer from certain limitations. Thus, the assumed equality of the free energy of solvation of the ions of the above reference electrolyte is based on the transport properties of the ions, specifically the approximate equality of the Stokes radii in methanol and water.[12] However, no simple correlation necessarily exists between the transport properties and the free energy of solvation of an

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[2] From the Ph.D. thesis of this author, University of Pittsburgh, 1966.

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[9] I. V. Nelson and R. T. Iwamoto, *Anal. Chem.*, **33**, 1795 (1961); **35**, 867 (1963).

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[12] J. F. Skinner and R. M. Fuoss, *J. Phys. Chem.*, **68**, 1882 (1964).

ion, because other factors also affect transport properties. One such factor is the additional frictional force produced as a result of the dielectric relaxation induced by ionic motion in a polar medium;[13] another is the change in local viscosity produced by the structure-making and structure-breaking properties of ions in a solvent such as water;[14] and, finally, the size and effective "number" of the solvent molecules accompanying the ion during its migration also enter into its transport properties. This problem would persist even if a more ideal reference electrolyte, such as tetraisoamylammonium tetraisoamylboride,[15] were used. The uncertainty would be particularly large in a dipolar aprotic solvent, such as acetonitrile, which solvates anions (except those that are highly polarizable) much more poorly than cations. For such solvents, splitting solvation energies of electrolytes on any basis involving directly or even indirectly the properties of an anion probably should be avoided. Furthermore, reference electrolytes of the type under discussion have quite high solubilities in dipolar aprotic solvents, and the required activity coefficients for the saturated solutions may be difficult to measure. Nevertheless, Popovych's approach may be eminently suitable for comparisons among solvents of similar relative solvating power for cations and anions, such as the water–methanol pair actually studied.[11]

As far as the use of reference redox couples for the comparison of potentials in different solvents is concerned, desiderata include the lowest and most shielded charge possible, maximum size and symmetry, and minimum polarizability. Other factors to be considered are listed in ref 8. The high-charge type of the iron(III–II)-phenanthroline couples presents a serious problem; the Born equation (see below) predicts that for equal effective radii the free-energy difference associated with a III–II couple will be five times as large as that for a I–0 couple. This problem persists even after due allowance has been made for the effect of ionic strength on the formal potentials in both solvents (through activity coefficients and possible incomplete electrolytic dissociation). Furthermore, specific solvation effects generally are magnified with ions of high-charge type.

For the reasons mentioned above, we prefer to base our comparisons on I–0 couples, such as the rubidium (or cesium) and the ferrocene systems. The latter has the important advantage of considerably greater size, but a serious uncertainty comes from the fact that the reduced form of the couple is also present in solution, so that its solvation energy is involved, and this may vary considerably from one solvent to another (see below). For this reason we place prime emphasis on the rubidium scale, adjusted by a suitable modification of the Born equation, as described in this paper. The thallium(I–0) potential is then placed on this scale, and from the solubilities of thallium(I) salts the relative activities of anions in acetonitrile and water are evaluated, as described in the next paper.

## Experimental Section

**Preparation and Purification of Chemicals.** Matheson Coleman and Bell practical grade acetonitrile was purified as described before.[16] Thallium(I) perchlorate was prepared by treating 10 g of Fisher Purified thallium(I) nitrate with 40 ml of 3 *M* perchloric acid, evaporating to dryness, and then recrystallizing three times from water and drying at 120°. Tetraethylammonium perchlorate was prepared as described elsewhere.[17] Thallium amalgam was prepared by adding Fisher Purified thallium metal to Bethlehem Apparatus Co. triple-distilled mercury and heating with an infrared lamp under a nitrogen atmosphere. Analysis of the amalgam by acidimetric titration[18] showed that it contained 0.74 mole % of thallium. It was stored under 0.01 *M* aqueous sulfuric acid.

**Potentiometric Experiments.** Measurements were made with a Leeds and Northrup Model 8687 precision potentiometer. An H-type cell was constructed with 10-mm diameter fritted glass disks of fine porosity inserted 5 cm apart in the horizontal (salt bridge) section of the cell. Between the two disks a vertical tube was provided for the introduction or removal of salt bridge solution. In all experiments, one working (vertical) compartment of the all-acetonitrile cell contained an Ag¦(0.01 *M* $AgNO_3$) electrode as reference.[19] The salt bridge compartment contained 0.1 *M* tetraethylammonium perchlorate. In the measuring compartment a thallium amalgam electrode dipped into deaerated 0.01 *M* tetraethylammonium perchlorate containing varying amounts of thallium(I) perchlorate. Immediately before use the thallium amalgam was washed twice with deionized water and then twice with acetonitrile, after which it was introduced into a J-tube electrode.[20] An atmosphere of nitrogen saturated with acetonitrile was maintained during all measurements.

## Results and Discussion

In Table I the crystallographic radii and polarographic half-wave potentials of the alkali metals in acetonitrile and water are compared.[7,21,22] In Table II the standard reduction potentials of various couples in the same solvents are compared.[8,10,23–25]

**Standard Potential of Thallium.** From the results of three different series of experiments with 0.74 mole % thallium amalgam in the following cell

$$\mathrm{Tl(Hg)|TlClO_4}\ (C) + \mathrm{Et_4NClO_4}\ (10^{-2}\ M)\,¦\,\mathrm{Et_4NClO_4}\ (10^{-1}\ M)\,|\,\mathrm{AgNO_3}\ (10^{-2}\ M)|\mathrm{Ag}$$

plots of emf *vs.* log *C* were linear with slopes near the theoretical value of 59 mv for values of *C* in the range $10^{-3}$ to $10^{-4}$ *M*. Extrapolation to $C = 0$ gave a formal potential (on the molar scale) $E_0'$ for the particular amalgam used in $10^{-2}$ *M* $Et_4NClO_4$ of $-0.521 \pm 0.003$ v *vs.* the Pleskov reference electrode, hereafter designated as PE.

The Debye–Hückel equation for the rational activity coefficient, $f_\pm$, of a 1:1 electrolyte in acetonitrile is

$$-\log f_\pm = \frac{1.64S^{1/2}}{1 + (0.485aS^{1/2})} \qquad (1)$$

where *S* represents the ionic strength. Rational and molal activity coefficients in acetonitrile are related as follows through the molality, *m*, of the electrolyte and the molecular weight, *M*, of acetonitrile.

$$\gamma_\pm = f_\pm/(1 + 2 \times 10^{-3}\ mM) = f_\pm/(1 + 0.082\ m) \qquad (2)$$

It is evident that at molalities below 0.1 the two scales

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**Table I.** Comparison of Polarographic Half-Wave Potentials of Alkali Metal Ions in Acetonitrile (AN) and Water (W)

| Ion | $r_+$[a] | $-(E_{1/2})_{AN}$[b,c] | $(E_{1/2}')_{AN}$[d] | $-(E_{1/2})_W$[b,c] | $(E_{1/2}')_W$[e] | $\Delta E_{1/2}'$[f] | $\Delta E_{1/2}'_{,\text{calcd}}$[g] |
|---|---|---|---|---|---|---|---|
| $Li^+$ | 0.60 | 1.95 | 0.03 | 2.33[h] | −0.20 | 0.23 | 0.25 |
| $Na^+$ | 0.95 | 1.85 | 0.13 | 2.12 | 0.01 | 0.12 | 0.11 |
| $K^+$ | 1.33 | 1.96 | 0.02 | 2.14 | −0.01 | 0.03 | 0.02 |
| $Rb^+$ | 1.48 | 1.98 | 0.00 | 2.13 | 0.00 | 0.00 | 0.00 |
| $Cs^+$ | 1.69 | 1.97 | 0.01 | 2.09 | 0.04 | −0.03 | −0.02 |

[a] Crystallographic radius, A; ref 21. [b] Volts *vs.* aqueous sce. [c] Reference 7. [d] Volts *vs.* $(E_{1/2})_{AN}$ of $Rb^+$. [e] Volts *vs.* $(E_{1/2})_W$ of $Rb^+$. [f] $\Delta E_{1/2}' = (E_{1/2}')_{AN} - (E_{1/2}')_W$. [g] Values of $\Delta E_{1/2}'$ calculated from the modified Born equation with $r_+'$ values of 0.81 and 0.72 for AN and W, respectively; see text. [h] Reference 22.

**Table II.** Comparison of Standard Reduction Potentials in Acetonitrile (AN) and Water (W) Based on an Adjusted Rubidium Molal Scale

| Couple | Measured in AN, v *vs.* Ag\|0.01 *M* $AgNO_3$ (AN) | Derived for AN, v *vs.* nhe (W) | Value in W, v *vs.* nhe (W) |
|---|---|---|---|
| Rubidium(I–0) | −3.282[a] | −2.779[d] | −2.928[e] |
| Thallium(I–0) | −0.648[b] | −0.145 | −0.336[f] |
| Ferrocene(I–0) | +0.074[c] | +0.577 | +0.394[c] |
| Ferroin(III–II) | +0.846[c] | +1.349 | +1.120[c] |

[a] Computed from amalgam potential given in ref 19; see text. [b] This work. [c] Reference 10; also see ref 8 and 35. [d] Born correction of +0.149 applied to value for water. On this basis the Ag|0.01 *M* $AgNO_3$ (AN) reference electrode has a potential of +0.503 v referred to nhe (W); see text. [e] Reference 23. [f] Reference 24.

differ by less than 1%. Salts such as $Et_4NClO_4$, which contain relatively "ideal" ions, are completely dissociated in acetonitrile at concentrations which are as low as $10^{-2}$ *M*;[15] hence $S \sim 10^{-2}$. Assuming that the ion-size parameter $a$ can be approximated by the Stokes radii[15] for $Et_4N^+$ (2.79 A) and $ClO_4^-$ (2.29 A), it is found that $a \sim 5$ A and hence $\gamma_\pm \sim f_\pm = 0.74$. The formal potential, $E_0'$, is related to the standard (reduction) potential, $E_0$, as

$$E_0' = E_0 + 0.059 \log f_{Tl^+}/(fx)_{Tl(Hg)} \qquad (3)$$

where $x$ is the mole fraction of thallium in the amalgam. Assuming that for the very dilute amalgam used $f_{Tl(Hg)} = 1$, it is found that $E_0 = -0.639$ v *vs.* PE. Applying the small correction of −0.0025 v for the free energy of amalgamation of thallium,[25] a final value of $E_0 = -0.642$ v *vs.* PE is obtained. Since the density of acetonitrile is equal to 0.777 g $ml^{-1}$, the corresponding value of $E_0$ on the *molal* scale is −0.642 − 0.006 or −0.648 v *vs.* PE.

**Standard Potential of Rubidium.** Pleskov[19] measured an emf of 2.3275 v for the following all-acetonitrile cell with 0.54 mole % amalgam.

$$Rb(Hg)|RbI\ (10^{-2}\ M)|AgNO_3\ (10^{-2}\ M)|Ag$$

The Stokes radii of $Rb^+$ and $I^-$ are 2.75 and 2.33 A, respectively. Hence, assuming a value of 5 A for the ion-size parameter for RbI, we calculated from eq 1 that $f_\pm = 0.74$. Lewis and Argo[23] determined the free energy of amalgamation of Rb by measurements on the following cell: Rb(Hg)|RbI in $EtNH_2$ containing 7.9 mole % $NH_3$|Rb. With 0.54 mole % amalgam (the same concentration as that used later by Pleskov), the emf was 1.0745 v. Consequently the standard potential of Rb in acetonitrile (on the molal scale) is given by

$$E_0 = -2.3275 - 0.059 \log (0.74 \times 10^{-2}) - 1.0745 - 0.006 = -3.282 \text{ v } vs. \text{ PE}$$

**Rubidium Potential Referred to the Water Scale. Modification of the Born Equation.** The main purpose of this paper is to refer the potentials measured in acetonitrile *vs.* PE (listed in the second column of Table II) to that of the normal hydrogen electrode in water. Our reasons for selecting the rubidium potential for this purpose have been given in the introductory section.

The change in *electrostatic* free energy occurring when a mole of electrolyte is transferred from the gas phase to a medium of dielectric constant $D$ is given as a first approximation by the Born equation

$$\Delta G_\pm^\circ = -\frac{N\epsilon^2}{2}\left(1 - \frac{1}{D}\right)\left(\frac{z_+^2}{r_+} + \frac{z_-^2}{r_-}\right) \qquad (4)$$

where $r_+$ and $r_-$ are the crystallographic radii of the cation and anion, respectively, and other symbols have their customary meaning. However, it is well known that the Born equation has the serious limitations that it recognizes neither specific solvation nor dielectric saturation. For the relatively ideal solutes considered here, specific solvation effects are likely to be unimportant, but the same is not true of the differences in dielectric saturation that may be expected in water and acetonitrile. There is no consensus about the quantitative aspects of dielectric saturation in water,[26] although a modification of the Born equation which explicitly allows for this perturbation has been used with apparent success to calculate free energies of transfer from water to deuterium oxide[27] and to water–alcohol mixtures.[28] Too little is known about dielectric saturation in acetonitrile to allow a quantitative treatment here. However, from a rough comparison of the known polarizability of the C≡N bond in HCN (31 $A^3$)[29] and the average polarizability of the water molecule (14 $A^3$),[30] it can be predicted qualitatively that dielectric saturation may be even more pronounced in acetonitrile than in water. (The dipole moments of acetonitrile and water are 3.37 and 1.84 D., respectively.)

In the absence of a reliable estimate of the effective dielectric constants of water and acetonitrile, the only practical approach is the well-known one introduced by Latimer, Pitzer, and Slanski,[31] in which the effective

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radii of the solute ions, rather than the dielectric constant of the solvent, are corrected.

$$\Delta G_{\pm}{}^{\circ} = -\frac{N\epsilon^2}{2}\left(1 - \frac{1}{D}\right)\left(\frac{1}{r_+ + r_+'} + \frac{1}{r_- + r_-'}\right) \quad (5)$$

A single pair of values for the correction terms $r_+'$ and $r_-'$ gives a fairly self-consistent match of calculated and experimental solvation energies for the alkali metal halides in water. This self-consistency provides some justification for the use of eq 5 to split solvation energies into the ionic components. Strehlow and his co-workers[8] have carried out such a split for acetonitrile by comparing the solubilities ($S$) of the alkali metal halides in water (W) and acetonitrile (AN)

$$\Delta G_{\pm}{}^{\circ}{}_{\mathrm{AN}} = \Delta G_{\pm}{}^{\circ}{}_{\mathrm{W}} + 2RT \ln \frac{S_{\mathrm{W}}}{S_{\mathrm{AN}}} \quad (6)$$

and then fitting the $\Delta G_{\pm}{}^{\circ}{}_{\mathrm{AN}}$ values to eq 5. Omitting activity coefficients (which are unknown), the results lead to average correction terms $r_+'$ and $r_-'$ of 0.72 and 0.61 A for acetonitrile, as compared to Latimer, Pitzer, and Slanski's values (subsequently revised; see below) of 0.85 and 0.25 A, respectively, for water. However, the fluctuations in these values for the individual salts in acetonitrile are quite large. Furthermore, the smaller value of $r_+'$ in acetonitrile means that the alkali metal ions are more strongly solvated in that solvent than in water, which is the opposite of what polarographic and other data unambiguously show to be the case. For example, the second last column of Table I shows that the half-wave potentials of the smaller alkali metal ions referred to that of rubidium or cesium are more negative (corresponding to more difficult reduction of the ion) in water than in acetonitrile, and that this negative shift increases smoothly with decreasing size of the ion. It is clear that all of these ions must be more strongly solvated in water than in acetonitrile. The stronger solvation of cations by water, as compared to that by acetonitrile, is not restricted to the alkali metals. In particular, high-charge type ions [*e.g.*, Eu(III)] show large positive shifts in half-wave potential in acetonitrile,[7] and spectrophotometric and a host of other data show that the proton is solvated much more strongly by water than by acetonitrile.[32]

We now assume that the Born equation can be modified empirically according to the approach of Latimer, Pitzer, and Slanski to account for this negative shift in water. This is done with due cognizance of the demonstrated limitations of the Born equation in predicting absolute values of the electrostatic free energy of transfer of ions from the gas phase to water. However, by restricting the use of the equation to the difference between water and acetonitrile, and by imposing *still another restriction* by comparing this difference for rubidium with those for the other ions, many of the uncertainties inherent in the Born treatment should be eliminated. We assume that the "neutral" part of the solvation energy differences is the same in both solvents (zero-energy assumption[21]).

**Sample Calculation.** The second to last column in Table I shows that the difference between the half-wave potentials of lithium and cesium ions is 0.26 v smaller in acetonitrile than in water, corresponding to a difference in solvation energy which is 0.26(96,500 × 10$^{-3}$)/4.18 or 6.0 kcal mole$^{-1}$ smaller in the former solvent. From Noyes' recent tabulation,[21] the average value of $r_+'$ for water is 0.72 ± 0.03. Equation 5 with $D$ = 78.5 then predicts a difference in solvation energy of lithium and cesium of 56.1 kcal mole$^{-1}$ in water. Hence, in acetonitrile this difference amounts to 56.1 − 6.0 = 50.1 kcal mole$^{-1}$. On substituting this value, and $D$ = 36.0, for acetonitrile into eq 5, it follows that

$$50.1 = 161\left(\frac{1}{0.60 + r_+'} - \frac{1}{1.69 + r_+'}\right)$$

from which the value of $r_+'$ for acetonitrile is found to be 0.81 A. Similar calculations for the pairs Li$^+$–K$^+$ and Na$^+$–K$^+$ (for which the differences in solvation energy are reasonably large) give $r_+'$ values of 0.80 and 0.82 A, respectively. We therefore assume an average value of 0.81, which on substitution into eq 5 leads to calculated positive shifts in the half-wave (or standard) potentials in acetonitrile as compared to water of 0.42, 0.28, 0.19, 0.17, and 0.15 v for Li, Na, K, Rb, and Cs, respectively. The last column of Table I shows an internally consistent agreement between calculated and observed differences in half-wave potentials. Virtually the same differences are calculated if the comparisons are based on the correction factor of Latimer, *et al.*, rather than that of Noyes. For exact comparisons of free-energy values in two different solvents it is necessary to allow for the difference in solvent molality in the two solvents. Such allowance is included in Gurney's $J$ factors[33] and Frank and Rasaiah's "aquamolality" scales.[34] A correction of −0.021 v is required for this purpose. Consequently the standard potential of rubidium becomes 0.17 − 0.021 = 0.149 v more positive in acetonitrile than in water. The standard potentials for the thallium, ferrocene, and ferroin couples in acetonitrile reported in the third column of Table II are based on this value.

In principle it should be preferable to apply the modified Born treatment to standard potentials, rather than half-wave potentials. However, the standard potential of lithium in water is uncertain[24] and that reported for lithium in acetonitrile[19] appears to be seriously in error. We have discussed elsewhere[7] factors to be considered in the comparison of half-wave potentials in different solvents. Many of the uncertainties associated with such comparisons should be minimized here, since only differences among the alkali metal ions are involved. For example, conductance data show that the influence of M$^+$ClO$_4^-$ ion-pair formation should be similar for all alkali metal ions and is quite small.

**The Thallium, Ferrocene, and Ferroin Potentials.** The positive shift in the standard potential of the thallium(I–0) couple (0.191 v) is considerably larger than those for rubidium (0.149 v) or potassium (0.169 v), even though its crystallographic radius (1.40 A) is intermediate between those of the two alkali metals (1.48 and 1.33 A). We attribute this additional shift to the "abnormally" strong hydration of Tl$^+$,[21] which may be the result of its empty 5f orbital.

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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* $Et_4NClO_4$ 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.

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

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**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 SN2 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

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