

SOLVATION OF IONS IN PURE AND MIXED SOLVENTS†

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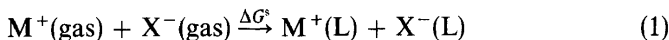
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ABSTRACT

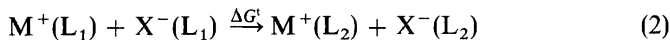
The problem of the influence of the solvent on activities of ions is discussed. Some proposals for the splitting of thermodynamic functions for electrolytes in solution into single ion values are reviewed. The effect of different solvation of ions on phenomena such as transfer of solvent in electrolysis, selective solvation in mixed solvent, phase boundary potential, surface tension and critical solution point in non-miscible solvents, and on solubilities of electrolytes in mixed solvents, may qualitatively and semiquantitatively be determined from the knowledge of single ion solvation behaviour. The most direct information on selective ion solvation in mixed solvent is provided from NMR measurements on, for example, Al^{3+} ions in a mixture of two aprotic solvents.

I. THERMODYNAMICS OF IONIC SOLVATION

The standard free enthalpy of solvation of an electrolyte MX in a solvent L is defined by the free enthalpy of the process (*Figure 1*)

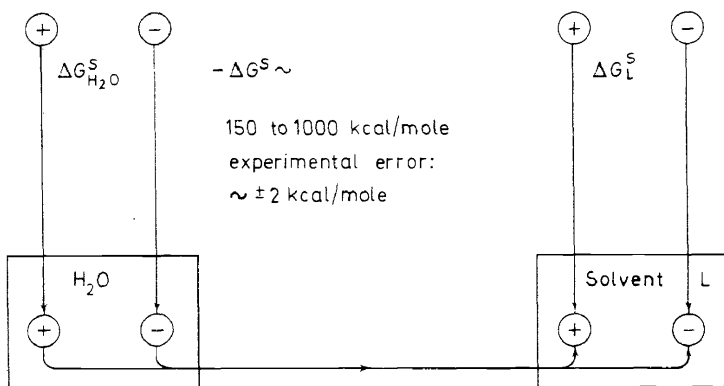


with the fugacities of the ions in the gas phase and the activities of the ions in solution being unity. This free enthalpy may be obtained with a Haber Born cycle and turns out to be of the order of from -150 kcal/mole (1-1 electrolytes) to more than -1000 kcal/mole (e.g. for Al^{3+} salts). The uncertainty involved in the calculation of these energies amounts to at least 2 kcal/mole. However, the difference of free enthalpies of solvation of a given electrolyte in two different solvents, which we shall call the free enthalpy of transfer, is a smaller quantity ($|\Delta G^{\circ}| \lesssim 20$ kcal/mole) and its experimental precision is much better, since data not precisely known, especially electron affinities of anions needed in the Haber Born cycle, cancel out in ΔG° . Process (1) is never realized in practice and is only of theoretical importance. Of much greater interest for the practical chemist is the process



† This review is not intended to be exhaustive and only covers work done in this laboratory

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$\Delta G^{\ddagger} \approx 20$ kcal/mole
 experimental error:
 $\sim \pm 0.3$ kcal/mole

Figure 1. Free enthalpy of solvation and free enthalpy of transfer

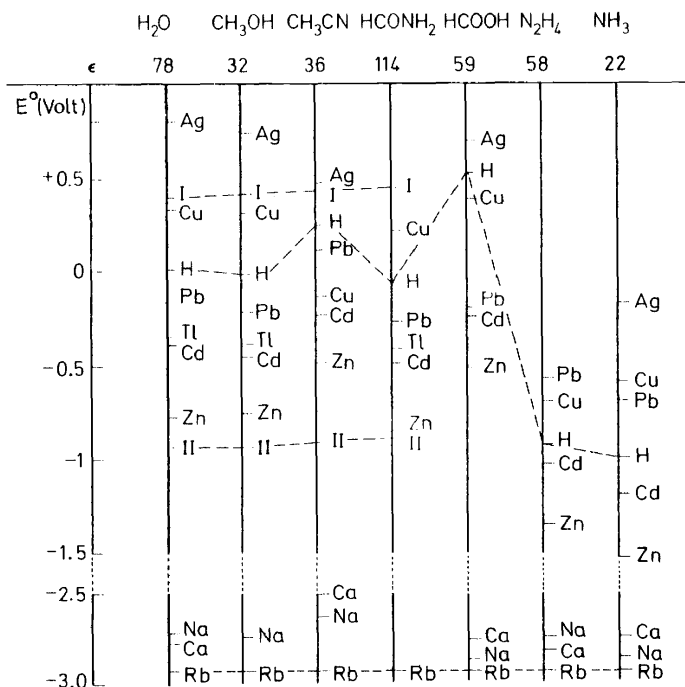
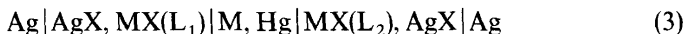


Figure 2. Voltage series in some solvents²

$E_{Rb}^{\circ} = -2.92$ volt in all solvents
 I = ferrocene/ferricinium
 II = cobaltocene/cobalticinium

The free enthalpy of such a transfer process may be obtained by different standard techniques only two of which will be mentioned.

For a galvanic cell of the type



the standard EMF, E , is proportional to the required free enthalpy of transfer

$$\Delta G^\dagger = -2FE \quad (4)$$

Another method is the measurement of the activities of MX in saturated solutions in both solvents. We have

$$\Delta G^\dagger = 2RT \ln \frac{a_{\text{satd}}(\text{L}_2)}{a_{\text{satd}}(\text{L}_1)} \quad (5)$$

The activities of the saturated solutions are obtained from solubility and activity coefficient measurements with standard techniques.

While the free enthalpies of transfer of electrolytes from one solvent to another can thus be determined, the splitting of this energy into the contributions of the single ions is not possible from pure thermodynamic values, since experimentally only uncharged species can be transferred¹. But non-thermodynamic assumptions—e.g. model calculations of the free enthalpies—lead to a splitting of this value which are of considerable interest to the chemist and which allow the prediction of the outcome of seemingly unrelated experiments as will be shown with some examples below. One well known problem of this kind arises if the acidities of solutions with different solvents are to be compared. Then the free enthalpy of transfer for H^+ is required. The free enthalpy of transfer for strong acids from water, e.g. to liquid ammonia, is of the order of -25 kcal/mole and depends only weakly on the anion. The most simple (though logically inconclusive) explanation is that the hydrogen ions are more strongly solvated by the more basic ammonia and that the difference in free enthalpy of transfer for different anions is relatively unimportant. This qualitative statement must be formulated quantitatively: what is the free enthalpy of transfer for the hydrogen ion in kcal/mole and what is the free enthalpy of transfer for the chloride ion (or other anion)? This division of the observed free enthalpy of transfer of electrolytes has been performed by different methods using more or less reasonable models. With such methods a free enthalpy of transfer from water to ammonia of about -23 kcal/mole has been estimated², which is equivalent to a standard hydrogen electrode, about 1 volt more negative in ammonia than in water. This situation is best represented by the voltage series as presented in *Figure 2*. Of course, when the free enthalpy of transfer of one ion between a given solvent pair is fixed, the analogous value is known for any other ion, the standard potential of which is known in both solvents. Therefore, for the normalization of voltage series in different solvents with only one common reference point ($E_{\text{H},\text{H}_2\text{O}}^\circ \equiv 0$ is convenient), it is sufficient to estimate the free enthalpy of transfer for only one ion from water to the other solvents.

A very simple and fruitful proposal for a suitable reference ion has been made by Pleskov³. An ideal reference ion should have the same free energy

of solvation in every solvent and therefore a free energy of transfer equal to zero. Of course, such an ion does not exist. According to Pleskov, the closest approximation of a real ion to the ideal reference ion would be that one for which the free solvation energy in every solvent is as small as possible, one which exhibits no specific interaction such as strong complex formation with the solvents, and which is only weakly polarizable. For a low free enthalpy of solvation, the charge must be low, i.e., $|z| = 1$, and the radius must be large; a low polarizability requires a cation. Therefore, Pleskov proposed that a solvent-independent electrode potential for the rubidium ion be assumed. In other words, as a first approximation, the free energy of transfer for the Rb^+ ion is considered to be zero. The large Cs^+ ion was not chosen as a reference by Pleskov, since fewer and less reliable data on this ion were available at the time of his proposal. However, it has been found that the difference between the standard potentials of Rb^+ and Cs^+ is nearly independent of the solvent. This independence is a necessary—though not sufficient—condition for the applicability of Pleskov's method. In *Figure 2* the voltage series are arranged with $E_{\text{Rb}}^\circ = \text{constant}$; and all qualitative expectations for the free energy of transfer for other ions are fulfilled. Especially the hydrogen ion is found to have a more negative standard electrode potential in basic solvents. Thus, the Pleskov method should be considered to be at least a reasonable first step towards the solution of the problem. However, merely from considerations of the difference of electrostatic interaction of the Rb^+ ion with solvents of different dielectric constant, free energies of transfer to the order of 0.1 eV can be expected. Therefore, it seems advisable to estimate this small, but finite, free energy of transfer

Only the outcome of this estimation will be discussed here. With a semi-empirical adaptation of the Born equation

$$-\Delta G^s = \frac{Ne^2}{2r} \left(1 - \frac{1}{\epsilon} \right) \quad (6)$$

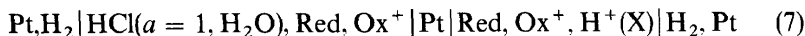
for the free energy of solvation the free enthalpy of transfer for the Rb^+ ion was found to be rather small in the cases thus far investigated, so that Pleskov's proposal proved to be a rather fortunate one².

Nevertheless, it is desirable to have other reference ions. Firstly, the measurement of standard potentials of Rb^+ is a rather difficult task and in the case of acidic media is very inaccurate because of the corrosion of rubidium amalgam in these solvents. Secondly, a reasonably correct comparison of voltage series may be ensured by the consistence of the results of different techniques.

A well known method, the measurement of Hammett acidity functions in different solvents⁴, will only shortly be mentioned. This technique provides the free enthalpy of transfer of the hydrogen ion, but it has been shown elsewhere² that it is not as reliable as Pleskov's method.

Another possibility for the comparison of voltage series is the redox function $R^{2,5}$. A large redox system of the charge type $0/+1$ should have a standard redox potential approximately independent of the solvent. Two suitable redox systems have been proposed: the ferrocene/ferricinium, and the analogous cobaltocene/cobalticinium couples. The redox function, e.g.

for the hydrogen ion $R_o(\text{H})$, is measured in the galvanic cell



with the ratio $\text{Red} | \text{Ox}^+ = 1$ in both half cells. The EMF of the cell is then

$$-FE = \Delta G^{\circ}(\text{H}^+) + \Delta G^{\circ}(\text{Red}) - \Delta G^{\circ}(\text{Ox}^+) \quad (8)$$

and with the assumption

$$\Delta G^{\circ}(\text{Red}) = \Delta G^{\circ}(\text{Ox}^+) \quad (9)$$

we have

$$-FE \cong \Delta G^{\circ}(\text{H}^+) \quad (10)$$

The redox function R_o is defined by

$$R_o(\text{H}) = -\frac{\Delta G^{\circ}(\text{H}^+)}{2.303 RT} = -\log c_{\text{H}} + f_{\text{H}^+} - \frac{\Delta G^{\circ}(\text{H}^+)}{2.303 RT} = \frac{FE}{2.303 RT} \quad (11)$$

The subscript "o" refers to the charge of the lower oxidation state: If in cell (7) the solvent X is a dilute aqueous solution, $R_o(\text{H})$ degenerates to the pH function. For a cell such as (7) with Ag/Ag^+ electrodes, we can similarly define a redox function, $R_o(\text{Ag}^+)$, which is a logarithmic measure for the activity of Ag^+ ions and similarly degenerates for $\text{X} = \text{H}_2\text{O}$ into the pAg^+ . If the right half of cell (7) also has an acid activity $a = 1$ (in the solvent X, $\lim_{c \rightarrow 0} a \rightarrow c$), $R_o(\text{H})$ is a measure of the standard free energy of transfer for the hydrogen ion. Similar arguments apply to the redox functions of other ions.

The standard redox potentials of ferrocene/ferrocinium (= dicyclopentadienyl iron [II]/dicyclopentadienyl iron [III]) are shown for some solvents [= I] and the redox potential of cobaltocene/cobalticinium [= II] in Figure 2.

The difference between the standard redox potential of the two systems is 1.33 volts and, within the experimental precision, independent of the solvent. Also the difference $E_{\text{ferrocene}}^{\circ} - R_{\text{Rb}}^{\circ}$ is very similar in the solvents investigated. These results constitute a strong argument for the efficacy of the redox method. A correction, such as applied to the free enthalpy of transfer of the rubidium ion may also be applied to the redox systems. For a simple application of the redox function the difference in half wave potentials of

Table 1. Standard electrode potential E_{M}° in some solvents with $E_{\text{H}, \text{H}_2\text{O}}^{\circ} = 0$ estimated with different methods²

Solvent	E_{H}°	Rb^{a}	H_o	Method	
				$R_o(\text{H})_{\text{ferrocene}}^{\text{a}}$	$R_o(\text{H})_{\text{cobaltocene}}^{\text{a}}$
H_2O	$E_{\text{H}}^{\circ} =$	± 0	± 0	± 0	± 0
CH_3OH	$E_{\text{H}}^{\circ} =$	+0.01	+0.02	-0.01	-0.01
CH_3CN	$E_{\text{H}}^{\circ} =$	+0.14	+0.24	+0.15	+0.16
HCONH_2	$E_{\text{H}}^{\circ} =$	-0.07	-0.04	-0.15	-0.14
HCOOH	$E_{\text{H}}^{\circ} =$	+0.47	+0.28		
Quinoline ^b	$E_{\text{H}}^{\circ} =$	-0.34	-0.30		

^a With an estimated free enthalpy of transfer $\Delta G_{\text{Rb}}^{\circ}$ and $[\Delta G^{\circ}(\text{Red}) - \Delta G^{\circ}(\text{Ox}^+)]$, respectively⁵.

^b Saturated with water.

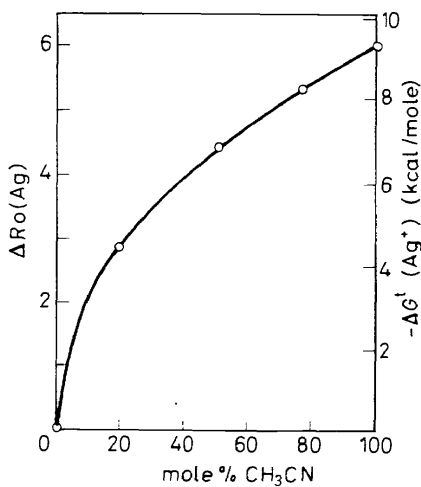


Figure 3. Redox function $R_o(\text{Ag})$ and free enthalpy of transfer of Ag^+ ion from water to water/acetonitrile

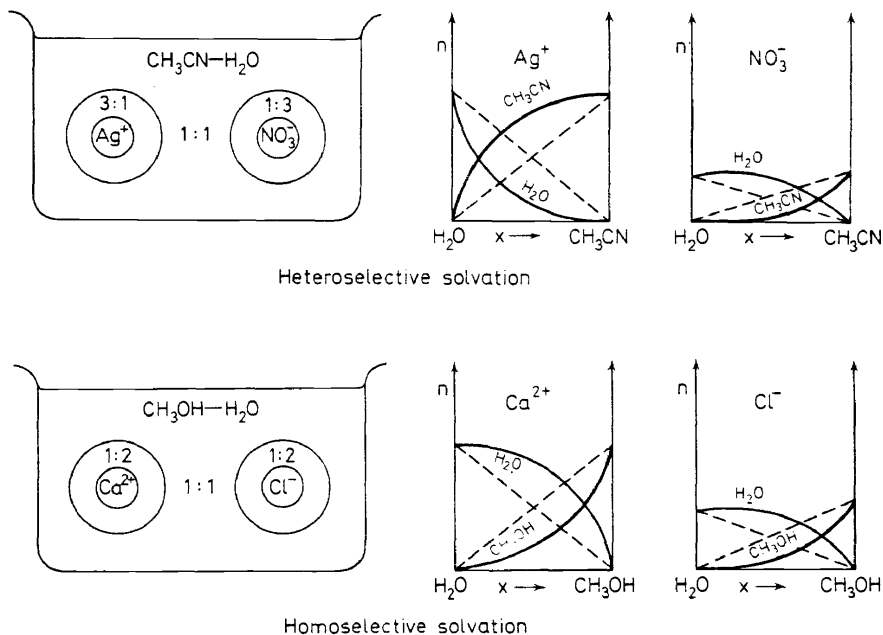


Figure 4. Solvation numbers as a function of solvent composition for homo- and heteroselective solvation

Tl^+ (or Cd^{++}) and cobaltocene/cobalticinium has been measured in some pure and mixed solvents⁶. With these data the free enthalpy of transfer for an ion is easily estimated by measuring the difference between its (reversible) half wave potential and that of Tl^+ (or Cd^{++}) in the two solvents.

The standard electrode potentials of the normal hydrogen electrode in some solvents, the reference potential being $E_{H,H_2O}^0 = 0$, are collected in *Table 1*.

An example of the free enthalpy of transfer of an ion as a function of the composition of a solvent mixture is shown in *Figure 3*⁵.

This system $AgNO_3$ in H_2O-CH_3CN will be discussed in some detail below. *Figure 1* shows that the Ag^+ ion is more strongly solvated in CH_3CN . Since the solubilities of $AgNO_3$ are comparable in the two solvents, the opposite must be true for the nitrate ion.

II. SELECTIVE SOLVATION OF IONS IN MIXED SOLVENTS

The composition of the solvation shell around an ion in a mixed solvent will, in general, differ from the stoichiometric composition of the solvent mixture. The solvent in which the ion has the more negative free enthalpy of solvation is expected to be enriched in the solvation shell. Two cases may be encountered in solutions of a binary electrolyte in a mixture of two solvents. Either both ions are preferentially solvated by the same solvent component, or, with more interesting consequences, one ion is bound more strongly by one solvent component and the other ion prefers the other solvent. The former case might be called 'homoselective' and the latter one 'heteroselective' solvation.

Figure 4 schematically shows two such cases. The expected four solvation numbers of the two solvents on the two ions are given in the diagrams of *Figure 4*. In the following, results obtained in this laboratory on selective solvation will be shortly discussed.

Since in H_2O-CH_3CN Ag^+ is more strongly solvated by CH_3CN , and NO_3^- more strongly by water (see *Figure 3*), for this system heteroselective solvation may be predicted. Different techniques for the measurement of selective solvation have been developed in recent years and will shortly be outlined below.

(a) The Hittorf Experiment

The most direct method of obtaining information on selective solvation is a modified Hittorf experiment⁷. If, for example, a current is passed through a solution as shown in *Figure 4*, the Ag^+ ion will transport CH_3CN into the cathode compartment, and the NO_3^- ion will transport water into the anode compartment. Both effects add and we get not only a change in concentration of the electrolyte in the two electrode compartments but also a change in the solvent composition. From these concentration changes we obtain the Hittorf transference numbers for the ions in the usual way and, furthermore, a solvent transport number Δ which is defined by the enrichment of one component[†] in the cathode compartment when one Faraday

[†] The non-aqueous component in mixtures with water; in mixtures not containing water this component has to be specified.

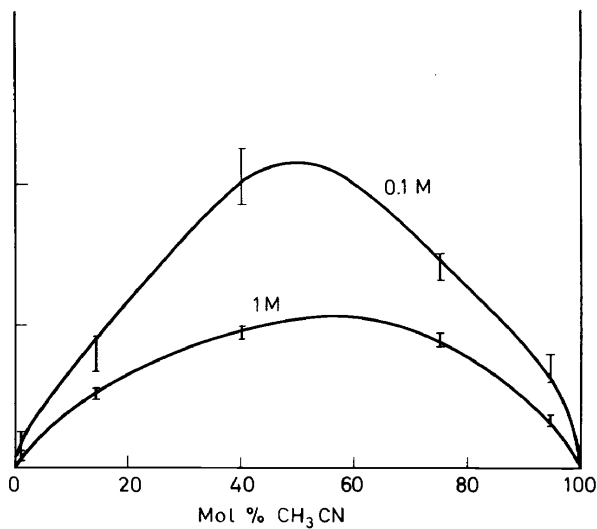


Figure 5. The solvent transport number Δ for AgNO_3 (1 M and 0.1 M) in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ mixtures (25°C) as a function of mole percent CH_3CN

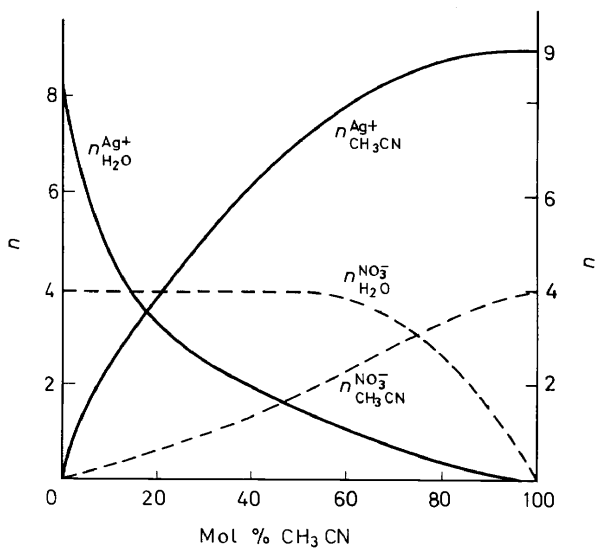


Figure 6. The four solvation numbers of AgNO_3 in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ as a function of mole percent CH_3CN

of electric charge has been sent through the solution. Of course, the selective solvation of both solvent components contribute to Δ . Since the change in solvent composition is at most 1 per cent a considerable analytical precision is required to determine this small change with sufficient accuracy. Measurements of density⁷ and of refractive index^{8,9} have been used for that purpose. In *Figure 5*, Δ for AgNO_3 in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ is plotted as a function of solvent composition for two concentrations of AgNO_3 . Δ is positive in accordance with the expectations from energetic considerations (Section I).

Δ is a function of the four solvation numbers $n_{\text{Ag}^+}^{\text{CH}_3\text{CN}}$, $n_{\text{Ag}^+}^{\text{H}_2\text{O}}$, $n_{\text{NO}_3^-}^{\text{CH}_3\text{CN}}$, and $n_{\text{NO}_3^-}^{\text{H}_2\text{O}}$. With the assumption of a monotonic dependence of the solvation numbers on solvent composition and reasonable maximum solvation numbers, the solvation numbers can be estimated semiquantitatively⁷ as shown in *Figure 6*. It should be mentioned that these solvation numbers are 'transport solvation numbers.' Every solvent molecule transported by the ion migrating in the electric field is counted, i.e. not only the composition of the inner coordination shell contributes to Δ . The strong desolvation effect with increasing concentration which manifests itself in *Figure 5* at $c_{\text{AgNO}_3} = 1\text{M}$ is another consequence of this fact. In *Table 2* results obtained by the Hittorf technique are presented. In each case the sign of Δ corresponds to that predicted from energetic considerations.

Table 2. The solvent transport number Δ and the selectivity of solvation of electrolytes in mixed solvents

Electrolyte	Solvents	Δ	Selectivity	Ref.
AgNO_3	$\text{H}_2\text{O}-\text{CH}_3\text{CN}$	+, large	heteros.	7
CaCl_2	$\text{H}_2\text{O}-\text{CH}_3\text{OH}$	-, small	homos.	8
ZnCl_2	$\text{H}_2\text{O}-\text{CH}_3\text{CN}$	-, large	homos.	9
ZnCl_2	$\text{H}_2\text{O}-\text{N}_2\text{H}_4$	+, large	heteros.	9

(b) Chemical Shift Experiments

Another possibility to measure the selectivity of ions in mixed solvents is the determination of the chemical shift of protons of both solvents as a function of solvent composition and concentration of the electrolyte. Again we have chosen the system AgNO_3 in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ for a first investigation.¹⁰ The chemical shift of the water line furnishes only qualitative information with respect to our problem, since two large effects with opposite sign are superimposed: the breaking of hydrogen bonds of water by the addition of acetonitrile and the change of the chemical shift by solvation phenomena. With acetonitrile, however, only the latter effect is observed. *Figure 7* and *Figure 8* show the results obtained. The chemical shift of CH_3CN will be a weighted average of the chemical shifts for CH_3CN molecules in the solvation sphere of an Ag^+ ion, for CH_3CN at a NO_3^- ion and for free CH_3CN

$$\delta = p_+ \delta_+ + p_- \delta_- + p_0 \delta_0 \quad (12)$$

where p_+ , p_- and p_0 are the respective mole fractions. δ_+ and δ_- , the specific chemical shifts of CH_3CN in the strong electric field of an ion, are more negative than δ_0 . Furthermore, it is known from potentiometric⁷ and spectro-

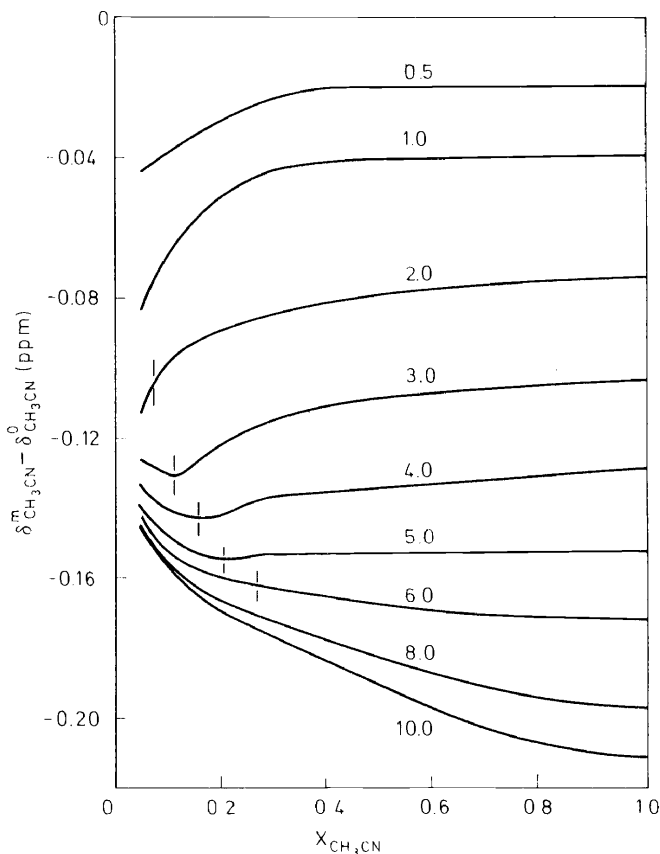


Figure 7. Chemical shift (ppm) of CH_3CN protons as a function of solvent composition in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ mixtures. Parameter: molality of AgNO_3 (25°C)

metric evidence that two CH_3CN molecules are rather strongly coordinated to Ag^+ . Let us now discuss qualitatively the curve pertaining to a 3 M AgNO_3 solution in Figure 7. By adding small amounts of CH_3CN to an aqueous AgNO_3 solution, the CH_3CN is nearly quantitatively bound by Ag^+ with a corresponding decrease in the chemical shift. When two moles of CH_3CN have been added per mole Ag^+ (the perpendicular dashed line on the curve) further acetonitrile will distribute itself between p_+ and p_0 and δ will rise again. At high mole fractions of CH_3CN also NO_3^- has to be solvated by CH_3CN and the curve flattens again. With very high concentrations of AgNO_3 every added CH_3CN molecule is likely to be bound in a solvation shell and we observe a monotonic decrease. For a quantitative discussion δ_+ , δ_- and δ_0 must be known. δ_0 is known from the electrolyte-free mixture. δ_+ can be estimated from Figure 8. At high concentrations of AgNO_3 and small mole fractions of CH_3CN every CH_3CN is likely to be bound to a silver ion. By extrapolating the plateau value in Figure 8 to

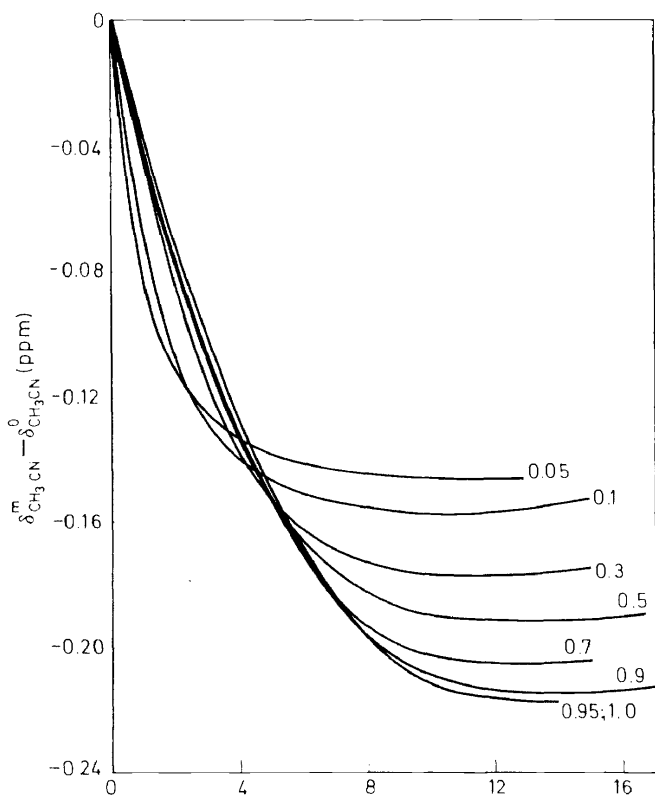
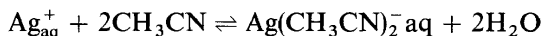


Figure 8. Chemical shift (ppm) of CH_3CN protons as a function of molality of AgNO_3 .
Parameter: mole fraction of CH_3CN in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ mixtures

vanishing CH_3CN the value of δ will be δ_+ . Similarly from the known equilibrium constants for the reaction



and the slope of the curves in *Figure 8* at small concentrations of AgNO_3 δ_+ can be obtained. A third method is the theoretical calculation of the effect of the electric field on δ . All these methods yield values for δ_+ that are in good agreement. Similarly δ_- may be estimated. With these results again semiquantitative solvation numbers have been obtained.

The plots of these solvation numbers against mole fraction look similar to those in *Figure 6* but the numbers are smaller by a factor of about two. Since the NMR method is sensitive only to the solvent molecules coordinated in the inner solvation sphere, it is reasonable that solvation numbers determined in this manner are smaller than those determined by the Hittorf method.

Incidentally, most of the information on selective solvation may be obtained from simple measurements of the slopes of the curves in *Figure 8*

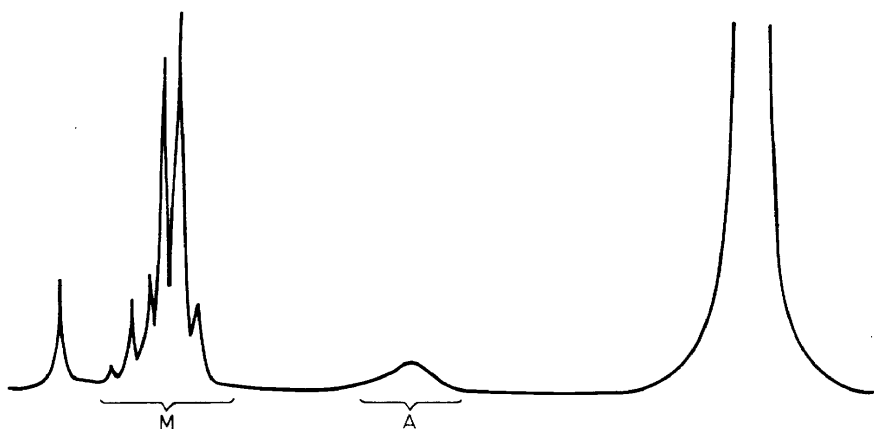


Figure 9. Proton-magnetic resonance (60 MHz) spectrum of 1 m AlCl_3 in CH_3CN with 0.5 m $(\text{CH}_3)_2\text{SO}$ at 25°C

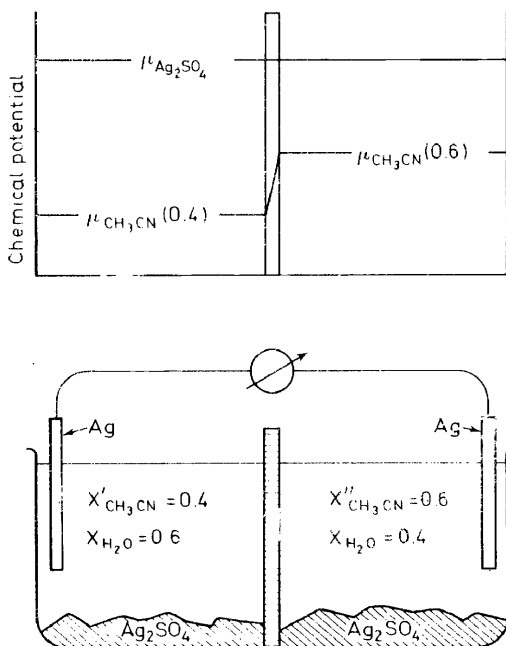


Figure 10. Scheme for the determination of the solvent transport number Δ from EMF measurements

at vanishing concentration of AgNO_3 . Experimentally this technique is much less tedious than the Hittorf technique discussed above.

In the case of slowly exchanging solvent molecules an even more direct information on selective solvation of ions in mixed solvents may be obtained by NMR. Recently, one of us (H. Schneider) investigated the system AlCl_3 in $\text{CH}_3\text{CH}-(\text{CH}_3)_2\text{SO}$. The average life times of the solvent molecules in the inner solvation sheaths of the Al^{3+} ion are long enough so that separated NMR absorption lines are observed even at room temperature. *Figure 9* shows a typical NMR spectrum.

The mole fraction of CH_3CN is about 0.98. The line at the outer left is the ^{13}C spin coupled line of the $^{13}\text{CH}_3\text{CN}$ protons (it may serve as an internal standard for the concentration of unbound CH_3CN , since its intensity is 0.505 per cent of the main absorption of CH_3CN at the right of the spectrum). The multiplet M shows the absorption lines of dimethylsulphoxide (DMSO) bound in the first solvation shell of Al^{3+} , the broadened line A is due to the bound acetonitrile. Unbound DMSO is not observed. This is an extreme case of selective solvation of DMSO on Al^{3+} . From NMR spectra of this kind very detailed information of the solvation behaviour is obtained. From the ratio of bound to unbound protons we conclude that AlCl_3 is dissolved as Al^{3+} and AlCl_4^- ions in the solvent mixture and that the solvation number is 6 for the Al^{3+} ion. The single lines in the DMSO multiplet are due to the solvated species AlA_5D , AlA_4D_2 , AlA_3D_3 , AlA_2D_4 , AlAD_5 , and AlD_6 with A = Acetonitrile and D = Dimethylsulphoxide. The broadened line at A contains the absorption of all bound CH_3CN . From the line widths exchange rates or at least higher limits to the exchange rates are obtained.

(c) Selectivity from EMF Measurements

Another possibility of determining the solvent transport number Δ has been proposed by Wagner.¹¹ Two half cells with silver electrodes contain two solvent mixtures of similar composition which are both saturated with a sparingly soluble silver salt. A system of that kind is shown in *Figure 10*. Though the chemical potential of the salt (Ag_2SO_4) is the same throughout, the EMF is different from zero, since by transporting one Faraday of electric charge through the cell, Δ moles of acetonitrile are transported from one compartment to the other. Since the chemical potential of the solvent is unequal in the two compartments, free energy is gained and an EMF is observed which is proportional to Δ . The formula for the EMF reads

$$dE = -\frac{RT}{F} \Delta \cdot \frac{dx_{\text{CH}_3\text{CN}}}{x_{\text{CH}_3\text{CN}} (1 - x_{\text{CH}_3\text{CN}})} \cdot \left(1 + \frac{d \ln f_{\text{CH}_3\text{CN}}}{d \ln x_{\text{CH}_3\text{CN}}} \right) \quad (13)$$

The results of measurements on the cell in *Figure 10* are presented in *Figure 11* (the activity coefficients have been taken from vapour pressure measurements of Vierk¹²). The heteroselectivity for Ag_2SO_4 is even stronger than for AgNO_3 . This means that in the solvent mixtures the preferential hydration of SO_4^{2-} is more pronounced than that of NO_3^- , a reasonable result.

(d) Conductivity Measurements

By determining the equivalent conductance at infinite dilution, the

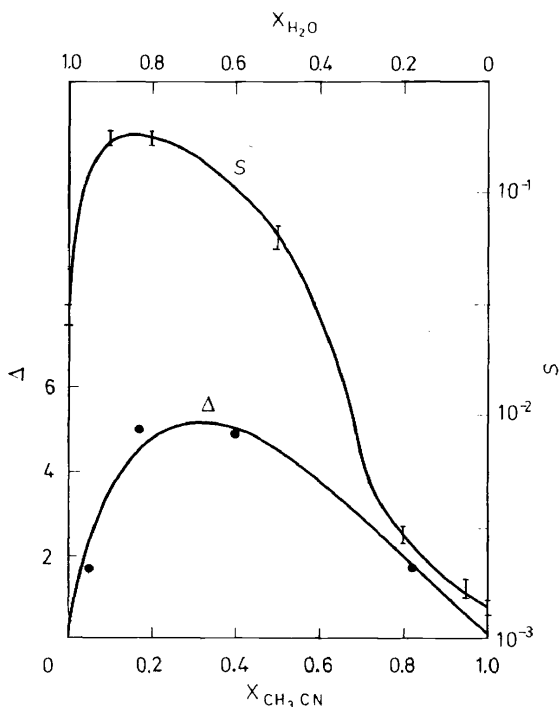


Figure 11. Solvent transport number Δ for Ag_2SO_4 in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ mixtures at 25°C . Solubility S of Ag_2SO_4 at 25°C . Ag_2SO_4 in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, Δ = selectivity number, S = solubility (mole/1000g of solvent)

transference number for AgNO_3 , and the viscosity in mixtures of water and acetonitrile, the Walden products $\Lambda_+^0\eta_0$ and $\Lambda_-^0\eta_0$, have been obtained for Ag^+ and NO_3^- as a function of solvent composition⁷. The result is given in Figure 12.

Traces of CH_3CN added to an aqueous AgNO_3 solution will strongly coordinate to Ag^+ ion, thereby increasing its effective radius of friction and diminishing its mobility (corrected for viscosity). The minimum in $\Lambda_-^0\eta_0$ reflects the maximum in total solvation number for the nitrate ion ($n_{\text{NO}_3^-}^{\text{H}_2\text{O}} + n_{\text{NO}_3^-}^{\text{CH}_3\text{CN}}$) at $x \sim 0.6$ in Figure 6. Following the procedure of Kortüm and Weller¹³, solvation numbers may be extracted from conductance measurements which prove to be similar to those obtained by the NMR technique.

(e) Special Behaviour of Heteroselective Electrolyte Solutions

Two interesting consequences of heteroselective solvation have been observed. Firstly, the solubility in such systems will generally be higher in mixtures than in the pure solvents. Such a result is shown, for example, in Figure 11 where the solubility, S , of Ag_2SO_4 is plotted as a function of the composition of a $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ mixture. This behaviour is expected, since both ions can solvate in the mixture with that solvent for which they exhibit

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the greater affinity. This rule, of course, may break down if different solid solvates are in equilibrium with different solvent mixtures.

Another unusual behaviour of heteroselective systems is found with phase separation experiments. Water and acetonitrile form a strongly nonideal mixture. Below about 0°C the two solvents are no longer miscible in all proportions. The composition-temperature phase diagram of $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ is shown in *Figure 13* (the heavily drawn curve). Adding a homoselective electrolyte, e.g. NaNO_3 , raises the critical point of solution. The addition of AgNO_3 , however, considerably lowers the coexistence curve¹⁴. The phase separation is opposed by the heteroselective electrolyte. Clusters of CH_3CN and H_2O formed in the critical region take up Ag^+ and NO_3^- , respectively. Rather small concentrations of electrolyte produce large effects, as demonstrated in *Figure 13*.

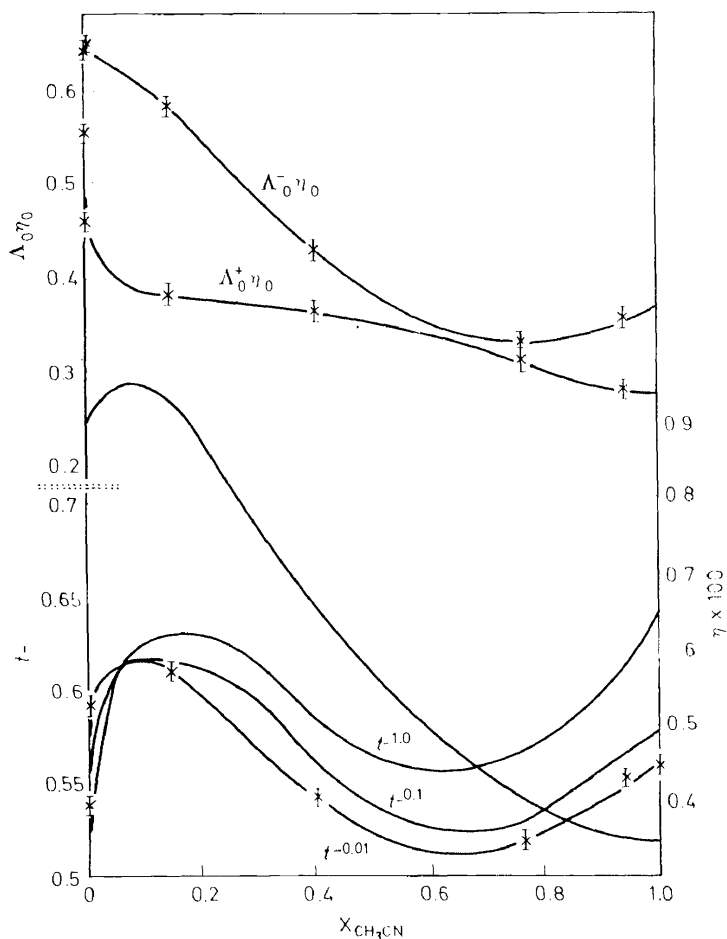


Figure 12. Viscosity η , Walden products $\Lambda_{\text{Ag}^+}^{\circ}\eta_0$ and $\Lambda_{\text{NO}_3^-}^{\circ}\eta_0$ and transference number $t_{\text{NO}_3^-}$ at 25°C in $\text{H}_2\text{O}-\text{CH}_3\text{CN}$ mixtures as a function of mole percent CH_3CN

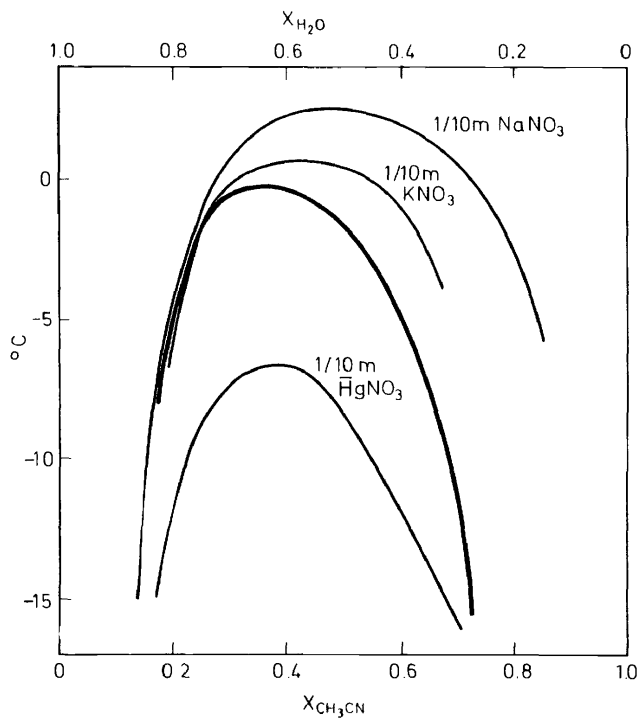


Figure 13. The T-x-phase diagram of $\text{H}_2\text{O}-\text{CH}_3\text{CN}$. Effect of addition of homoselective (NaNO_3) and heteroselective (AgNO_3) electrolytes

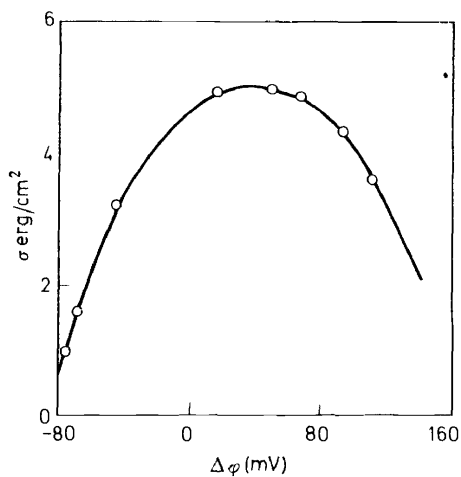
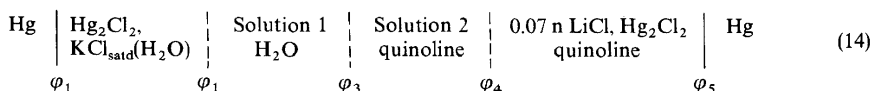


Figure 14. Electrocapillary curve on phase boundary water-quinoline (see text)

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A last example may demonstrate the effects of selective solvation on phase boundary potentials between immiscible solvents¹⁵. The solvent pair consists of water (saturated with quinoline) and quinoline (saturated with water). Electrolytes with an inorganic anion and a large organic cation or vice versa will exhibit selective solvation of the organic ion by quinoline and the inorganic ion by water, respectively. At the phase boundary an electric double layer will be formed, the polarity of which is determined by the electrolyte added to the system. By mixing two electrolytes of opposite behaviour (quinine hydrochloride = QHCl and potassium-2-phenylquinoline-4-carboxylat = KPCQ) at a total concentration of 0.1 M, the phase boundary potential may be changed and measured in the cell



Solution 1 and solution 2 are the corresponding solutions equilibrated with a salt mixture QHCl and K PQC in a molar ratio varied from 0 to 1.

The total measured EMF is given by the sum of the potentials φ_i

$$E = \varphi_1 + \varphi_2 + \varphi_3 + \varphi_4 + \varphi_5 \quad (15)$$

The diffusion potentials φ_2 and φ_4 may be neglected. φ_1 and φ_5 are known from the voltage series with the Rb-method (see *Table I*) so that φ_3 may be calculated to be +40 mV. The surface tension at this potential has its maximum value (*Figure 14*) and the electrophoretic mobilities of quinoline drops in water and of water drops in quinoline change sign at this phase boundary potential.

Thus, this system behaves most simply showing that the ionic double layer alone is responsible for the phase boundary potential whereas an orientation of the solvent dipoles is unimportant. Since the water saturated quinoline contains 61 mole per cent H₂O, this is not surprising.

At the end of this review it should be mentioned that the experimentally accessible features of selective solvation to a certain extent confirm the reliability (or possibly the unreliability) of molecular models which have been proposed for the estimation of single ion thermodynamic functions.

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