

Solvent Transference Numbers and Solvation Energies of Silver Sulphate in Mixtures of Methanol and N-methylformamide

By

C. Kalidas* and H. Schneider

Contribution from the Max-Planck-Institut für biophysikalische Chemie,
D-3400 Göttingen, West Germany

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The solvent transference number, t , of Ag_2SO_4 in mixtures of methanol and N-methylformamide (NMF) was determined by e.m.f. experiments using a galvanic cell with transference as introduced by C. Wagner [4]. The solvent composition was varied over the entire mole fraction range, corresponding to a change in the dielectric constant from 32 to 180 by about a factor of 6. The solvent transference number was always not equal zero which means that there is a preferred transport of NMF towards the cathode compartment. t passes through two maximal values with changing mole fraction and decreases to nearly zero in the mixture; this behaviour is unusual when compared with results from other polar solvent mixtures. With the help of the Gibbs energies of solvation of the ionic species obtained from additional experiments it could be shown that the special behaviour of t is due to a transition from heteroselective solvation to homoselective solvation of Ag_2SO_4 by NMF.

Mit einer galvanischen Zelle nach C. Wagner [4] wurde die Lösungsmittelüberführungszahl t für Ag_2SO_4 in Mischungen von Methanol und N-Methylformamid (NMF) untersucht. Die Zusammensetzung der Mischungen wurde über den gesamten Molenbruchbereich variiert, wobei sich die Dielektrizitätskonstante von 32 bis 180 änderte. Die Lösungsmittelüberführungszahl hat in den Solvensmischungen nur positive Werte, was einem bevorzugten Transport von NMF in Richtung zur Kathode entspricht, zeigt jedoch zwei Maximalwerte. Ein solches Verhalten und das Absinken von t gegen den Wert Null in einer Mischung ist für andere binäre Lösungsmittelsysteme bisher nicht beobachtet worden und konnte mit Hilfe der Gibbschen Solvationsenergien der Ionen aus zusätzlichen Messungen durch den Übergang von heteroselektiver Solvation von Ag_2SO_4 zu homoselektiver Solvation mit NMF erklärt werden.

* Present address: Department of Chemistry, Indian Institute of Technology, Madras-600036 India

Introduction

This paper is part of a series [1–3] dealing with ion solvation in binary solvent mixtures in terms of solvent transference numbers and Gibbs energies of solvation. The solvent transference number, Δ , is defined as the change in the number of moles of one solvent component in the cathode compartment, with the mean molar velocity of the solvent mixture as reference, when one Faraday of electricity is passed through a cell during electrolysis [4, 5]. The dependence of the solvent transference number Δ of component 2 on the number of solvent molecules n_{1+} , n_{2+} , n_{1-} , n_{2-} of components 1 and 2 solvating the cation(+) and anion(-), and on the ionic transference numbers t_+ and t_- is given for an infinitely dilute solution of a binary electrolyte by Eq. (1) [4–6]:

$$\Delta = (x_1 n_{2+} - x_2 n_{1+}) t_+ - (x_1 n_{2-} - x_2 n_{1-}) t_- \quad (1)$$

The sign and magnitude of Δ provide new ways of obtaining at least qualitative information about the composition of ionic solvation shells in mixed solvents. For example, Δ will be small and around zero for homoselective solvation [7] of an electrolyte where both ions are solvated preferentially by the same solvent component. If the ions are solvated in such a way that one ion is preferentially solvated by one solvent component while the other ion prefers the second component (i.e. heteroselective solvation [7]) then Δ will be large and its sign will also indicate the solvent components that preferentially solvate the ions. With respect to Eq. (1), Δ is positive for a heteroselectively solvated electrolyte whose cation is preferentially solvated by component 2.

In previous investigations in this laboratory, it was demonstrated that the silver ion is preferentially solvated by acetonitrile (AN) in the system $\text{AgNO}_3\text{-H}_2\text{O-AN}$ [6] and by dimethylsulphoxide (DMSO) in the systems $\text{Ag}_2\text{SO}_4\text{-H}_2\text{O-DMSO}$ [1] and $\text{Ag}_2\text{SO}_4\text{-methanol-DMSO}$ [3]. As a continuation of this work, we will now report the results of our studies on the selective solvation of Ag_2SO_4 in binary mixtures of methanol (MeOH) and N-methylformamide (NMF) over a wide range of dielectric constants in solvent mixtures with different compositions at 25°C; this work was carried out in order to understand the nature of ion-solvent interactions in this system.

Experimental

Solvents and salts

N-methylformamide (Merck) was purified according to the procedure of French and Glover [8]. The specific conductance of the solvent obtained was found to be of the order of $1 \cdot 10^{-5} \text{ Ohm}^{-1} \text{ cm}^{-1}$ at 25°C. In view of the unstable nature of the solvent as reported in the literature [9], a freshly

distilled sample was always used in all experiments. Methanol (Baker, analyzed) was purified as previously described [3].

Silver sulphate (Merck, p.a.) and silver nitrate (Merck, p.a.) dried under vacuum at 80°C and 120°C respectively, were used. Ferrocene (Merck) was recrystallized twice from ether and dried under vacuum. Ferricinium picrate was prepared according to the method of Kolthoff and Thomas [10]. The purity of these substances was checked spectrophotometrically.

Electrodes

The silver electrodes required for e.m.f. measurements were prepared by electrolytically coating silver onto platinum wires (dia. 0.6 mm, length 10 mm) sealed in glass tubes according to the method of Janz [11]. The reproducibility of the electrodes thus obtained was about ± 1 mV.

A silver wire electrode (Metrohm EA 242) and a mercury/mercurous sulphate electrode (Metrohm EA 406) were used as indicator and reference electrodes respectively.

Cells

A H-shaped cell made of Duran glass was used in the e.m.f. measurements and the liquid junction between the two half cells was established by means of a short capillary tube in order to reduce diffusion to a minimum.

E. m. f. measurements

A Philips digital multimeter (model PM 2421) was utilized in conjunction with a Knick impedance transformer (type 85, $R_{int} \geq 10^{13}$ Ohms) to measure the e.m.f. of the concentration cells employed in this work as described later. The cells were thermostatted at $25 \pm 0.05^\circ\text{C}$ by keeping them in a thermostat maintained at this temperature.

Dielectric constant measurements

The dielectric constants, ϵ , of the various methanol-NMF mixtures at 25°C were measured by means of a capacitance bridge (WTW, Weilheim). Methanol ($\epsilon = 32.7$), DMSO ($\epsilon = 46.7$) and water ($\epsilon = 78.3$) at 25°C were used as calibration liquids.

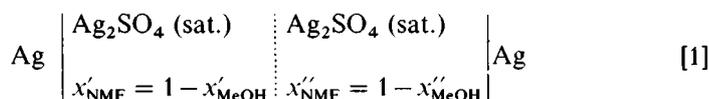
Solubility measurements

Saturated solutions of silver sulphate in the various solvent mixtures were prepared by stirring about 25 ml of the mixture with a sufficient amount of the salt in a thermostatted vessel. After about 12 h stirring saturation was

achieved and no detectable change in the concentration of the salt was noted. The liquid phase was then filtered off in a G-4 glass filter and a defined quantity of an excess solution of potassium iodide of known concentration was added to a weighed portion of the clear saturated solution. The excess potassium iodide was back titrated potentiometrically with a standard solution of silver nitrate using a modified Metrohm titroprint (E 475) for automatic evaluation of titration curves which was connected to an electronically controlled burette (Metrohm Multidosimat E 415). The solubility of the salt in the solvent mixtures was calculated from the iodide titration.

Results

The solvent transference number, Δ , was determined by employing a galvanic cell with transference as introduced by C. Wagner [4] of the type



in which the two half cells contained saturated solutions of silver sulphate in solvent mixtures differing only slightly in solvent composition ($x''_{\text{NMF}} - x'_{\text{NMF}} \leq 0.1$). The observed e.m.f. of the cell is due to solvent transport in the two half cells. The solvent transference number, Δ , is related to the e.m.f., ΔE , of the cell [1] according to

$$\Delta E = - (x''_{\text{NMF}} - x'_{\text{NMF}}) \frac{RT}{F} \frac{\Delta}{x_{\text{NMF}} (1 - x_{\text{NMF}})} \left(1 + \frac{\partial \ln f_{\text{NMF}}}{\partial \ln x_{\text{NMF}}} \right) \quad (2)$$

where x'_{NMF} , x''_{NMF} are the mole fractions of the solvent component NMF in the two half cells, and $x_{\text{NMF}} = (x'_{\text{NMF}} + x''_{\text{NMF}})/2$. f_{NMF} is the activity coefficient of N-methylformamide; the activity coefficient term in Eq. (2) accounts for deviations of the solvent mixtures from ideal behaviour.

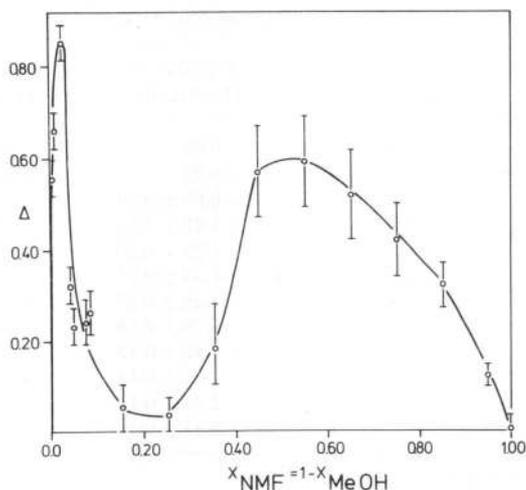
The observed ΔE values and the solvent transference numbers of NMF obtained from the above expression at various mole fractions are given in Table 1. The activity coefficient data required in the above calculations were taken from the literature [12]. The resulting Δ is plotted as a function of the mole fraction of NMF in Fig. 1. At low mole fractions, the difference between the solvent composition, $x''_{\text{NMF}} - x'_{\text{NMF}}$, had to be smaller (0.01) than at higher values of x_{NMF} (s. Table 1). The dielectric constants ϵ of the various solvent mixtures, required for the evaluation of the mean activity coefficient of the salt in the saturated solutions, are given in Table 2. The solubility, S , of silver sulphate and the solubility product, K_{sp} , of the salt calculated from

$$K_{\text{sp}} = 4 S^3 \gamma_{\pm}^3 \quad (3)$$

are recorded in Table 2. The mean molal activity coefficient γ_{\pm} of the salt was obtained from the extended Debye-Hückel equation [13]. The Gibbs energy

Table 1. *E.m.f. of cell [1] and solvent transference numbers, Δ , for NMF in the Ag_2SO_4 -methanol-NMF system at 25°C*

| x_{NMF} | $x'_{\text{NMF}} - x_{\text{NMF}}$ | ΔE (mV) | Δ |
|------------------|------------------------------------|-----------------|-----------------|
| 0.004 | 0.0078 | -29.0 ± 2 | 0.56 ± 0.04 |
| 0.010 | 0.021 | -34.0 ± 2 | 0.66 ± 0.04 |
| 0.026 | 0.051 | -43.6 ± 2 | 0.85 ± 0.04 |
| 0.043 | 0.037 | -7.5 ± 1 | 0.32 ± 0.04 |
| 0.050 | 0.051 | -6.3 ± 1 | 0.23 ± 0.04 |
| 0.075 | 0.049 | -4.3 ± 1 | 0.24 ± 0.05 |
| 0.082 | 0.041 | -3.6 ± 1 | 0.26 ± 0.07 |
| 0.152 | 0.100 | -1.0 ± 1 | 0.05 ± 0.05 |
| 0.252 | 0.100 | -0.4 ± 1 | 0.03 ± 0.03 |
| 0.355 | 0.090 | -1.7 ± 1 | 0.18 ± 0.09 |
| 0.450 | 0.100 | -5.6 ± 1 | 0.57 ± 0.10 |
| 0.551 | 0.102 | -6.0 ± 1 | 0.59 ± 0.10 |
| 0.652 | 0.090 | -5.6 ± 1 | 0.52 ± 0.09 |
| 0.749 | 0.099 | -5.4 ± 1 | 0.42 ± 0.08 |
| 0.849 | 0.102 | -6.3 ± 1 | 0.32 ± 0.05 |
| 0.950 | 0.101 | -6.6 ± 1 | 0.12 ± 0.02 |


 Fig. 1. Solvent transference number, Δ , of NMF for Ag_2SO_4 in methanol-NMF mixtures at 25°C

of transfer of Ag_2SO_4 from methanol to methanol-NMF mixtures (solvent *s*), which is the difference between the Gibbs energies of solvation of the salt in methanol and in *s*, was then calculated from

$$\Delta G_t^0 = -RT \ln \frac{K_{\text{sp},s}}{K_{\text{sp},\text{MeOH}}} \quad (4)$$

Table 2. Dielectric constant, ϵ , of the solvent, solubilities, S , and mean molar activity coefficients, γ_{\pm} , for Ag_2SO_4 in methanol-NMF mixtures at 25°C

| x_{NMF} | ϵ | $S \cdot 10^{4a}$ (mol/kg) | γ_{\pm} |
|------------------|------------|-------------------------------|----------------|
| 0.00 | 32.7 | 0.26 | 0.950 |
| 0.10 | 36.8 | 0.51 | 0.914 |
| 0.20 | 43.8 | 1.46 | 0.891 |
| 0.30 | 56.4 | 2.30 | 0.906 |
| 0.40 | 70.3 | 3.74 | 0.914 |
| 0.50 | 87.6 | 5.89 | 0.923 |
| 0.60 | 102.0 | 7.36 | 0.931 |
| 0.70 | 122.8 | 8.91 | 0.943 |
| 0.80 | 142.1 | 10.06 | 0.951 |
| 0.90 | 162.7 | 11.65 | 0.957 |
| 1.00 | 182.4 | 16.85 | 0.957 |

^a Accurate to within $\pm 1\%$

Table 3. Gibbs energies of transfer of Ag_2SO_4 and of Ag^+ and SO_4^{2-} ions from methanol to methanol-NMF mixtures at 25°C

| x_{NMF} | $\Delta G_t^0(\text{Ag}_2\text{SO}_4)^a$ (kcal/mol) | $\Delta G_t^0(\text{Ag}^+)^b$ (kcal/mol) | $\Delta G_t^0(\text{SO}_4^{2-})$ (kcal/mol) |
|-------------------|--|---|--|
| 0.00 | 0.00 | 0.00 | 0.00 |
| 0.05 ^c | -0.70 | -0.39 | +0.08 |
| 0.10 | -1.13 | -0.60 \pm 0.20 | +0.07 |
| 0.20 | -2.94 | -1.01 \pm 0.14 | -0.92 |
| 0.30 | -3.79 | -1.25 \pm 0.20 | -1.29 |
| 0.40 | -4.66 | -1.38 \pm 0.13 | -1.90 |
| 0.50 | -5.49 | -1.55 \pm 0.20 | -2.39 |
| 0.60 | -5.90 | -1.78 \pm 0.14 | -2.35 |
| 0.70 | -6.26 | -1.91 \pm 0.13 | -2.44 |
| 0.80 | -6.49 | -2.19 \pm 0.13 | -2.11 |
| 0.90 | -6.76 | -2.45 \pm 0.14 | -1.86 |
| 1.00 | -7.42 | -2.84 \pm 0.17 | -1.74 |

^a Accurate to ± 0.20 kcal/mol

^b With respect to $\Delta G_t^0(\text{Fic}^+) = \Delta G_t^0(\text{Foc})$ [14]

^c Gibbs energies obtained from plots of S and e.m.f.

and is given in Table 3. The Gibbs energy of transfer, ΔG_t^0 , of the salt is related to the Gibbs transfer energies of the constituent ions by

$$\Delta G_t^0 = 2 \Delta G_t^0(\text{Ag}^+) + \Delta G_t^0(\text{SO}_4^{2-}). \quad (5)$$

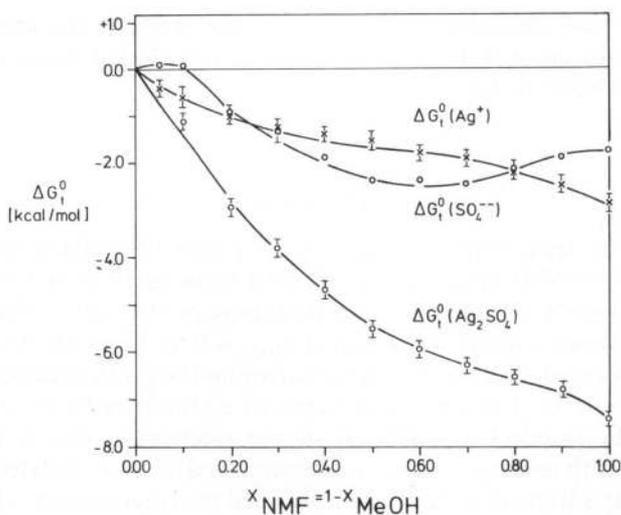
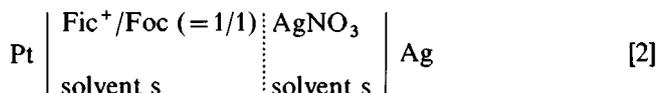


Fig. 2. Gibbs energies of transfer of Ag_2SO_4 and of Ag^+ and SO_4^{2-} ions from methanol to methanol-NMF mixtures at 25°C

The Gibbs energy of transfer of the silver ion, $\Delta G_1^0(\text{Ag}^+)$, was determined from e.m.f. measurements using cell [2]



In the above cell the concentrations of ferrocene (Foc) and ferricinium (Fic^+) picrate were both kept constant at 0.01 m and the concentration of silver nitrate was varied from 0.002 to 0.007 m; the standard potential, $E_s^0(\text{Ag}/\text{Ag}^+)$, related to $E_s(\text{Foc}/\text{Fic}^+)$ in various methanol-NMF mixtures, s , was obtained by extrapolating the plot of the parameter $(E - 2.303 \frac{RT}{F} \log m_{\text{Ag}^+})$ against the ionic strength, I , to $I = 0$. Such plots were found to be fairly linear for all solvent compositions. A bridge electrolyte was not used to separate the two compartments in the cell [2], as our calculations on the basis of the Henderson equation showed that the liquid junction potential in the cell was very small.

By using the extra-thermodynamic assumption that the standard potential of the ferrocene/ferricinium ion electrode is independent of the solvent [14], the Gibbs energy of transfer of Ag^+ from methanol to methanol-NMF mixtures, s , was calculated from

$$\Delta G_1^0(\text{Ag}^+) = -F(E_s^0 - E_{\text{MeOH}}^0). \quad (6)$$

The results and the Gibbs energies of transfer of SO_4^{2-} obtained by using Eq. (5) are given in Table 3. All these data are plotted against the mole fraction of NMF in Fig. 2.

Discussion

It can be seen from Fig. 1 and Table 1 that the solvent transference number, Δ , of NMF increases sharply to a value of about 0.9 at low mole fractions of NMF ($x_{\text{NMF}} = 0.05$) and then decreases to a value of almost zero and again shows a broad maximum at $x_{\text{NMF}} = 0.5$ ($\Delta = 0.60$). Two maxima are thus observed, the first one being sharper and larger than the second. The sharp increase of Δ in the initial stages of addition of NMF presumably indicates heteroselective solvation of the electrolyte, this is in general agreement with the large Δ values for heteroselectively solvated electrolytes in other binary solvent systems [1, 3, 6]. Detailed interpretation of Δ in terms of solvation numbers is made difficult by the lack of data about the ionic transference numbers in the solvent mixtures and about ionic association in the methanolic solutions. Due to these facts, in the following discussion it will be assumed that the influence of ion-pair formation on Δ is negligible and that striking changes of Δ with respect to the mole fraction are predominantly the result of changes in ionic solvation and not of changes in the ionic transport numbers [s. Eq. (1)].

The solvation numbers of the ions are related to the Gibbs energies of solvation, although this relationship is probably less direct in these highly associated and structured solvent mixture than in binary solvent systems of aprotic polar solvents [15]. Examination of the Gibbs energies of transfer of Ag_2SO_4 and its constituent ions in Table 3 and Fig. 2 will thus help to clarify the behaviour of Δ . It is seen that ΔG_1^0 for Ag_2SO_4 continuously decreases with addition of NMF suggesting that its transfer from methanol to the mixed solvents and to NMF is favoured and hence that it is preferentially solvated by NMF. The Gibbs energy of transfer of the sulphate ion, however, shows a different behaviour and initially increases on addition of NMF, but then passes through a shallow maximum at $x_{\text{NMF}} = 0.1$ and continuously decreases. Thus although the transfer of SO_4^{2-} from methanol to methanol + NMF mixtures is not favoured at low mole fractions of NMF, it is thermodynamically favourable at $x_{\text{NMF}} > 0.1$. This result when considered together with the constantly negative Gibbs energy of transfer of Ag^+ in these mixtures clearly shows that, at low mole fractions of NMF ($x_{\text{NMF}} < 0.1$), the electrolyte is heteroselectively solvated – the silver ion being preferentially solvated by NMF and the sulphate ion by methanol. Both ions therefore contribute additively to produce the maximum in Δ at around $x_{\text{NMF}} = 0.05$. As the mole fraction of NMF increases above 0.1, the salt is, however, homoselectively solvated, both ions being selectively solvated by NMF in the

mixtures. The competitive contribution of ionic solvation to Δ now leads to a decrease in its value to almost zero due to a favourable combination of solvation numbers and ionic transport numbers. Since $\Delta G_i^0(\text{SO}_4^{2-})$ changes only slightly at mole fractions $x_{\text{NMF}} \geq 0.55$ whilst $\Delta G_i^0(\text{Ag}^+)$ becomes increasingly negative up to pure NMF (Fig. 2), the transport of NMF by Ag^+ towards the cathode may exceed the amount of NMF carried in the opposite direction by the anion — this would lead to the second maximum in Δ .

The fact that the Gibbs energy of transfer of Ag^+ from methanol to NMF calculated on the basis of the Born equation in its original form is within its range of application very nearly equal to that obtained experimentally on the basis of the ferrocene/ferricinium ion reference method (Table 3) indicates that, in this case, there are no specific interactions similar to those found between this ion and dipolar aprotic solvents such as AN and DMSO [16]. The preferential solvation of Ag^+ by NMF in these mixtures can thus be qualitatively accounted for both in sign and in magnitude by Born-type interactions. The preferential solvation of SO_4^{2-} by NMF in these mixtures at $x_{\text{NMF}} > 0.1$ presumably arises because of the strong hydrogen bond interaction between the protonic hydrogen of the $-\text{NHMe}$ group and the negative charge of the sulphate ion. This is supported by the observations of Paul *et al.* [17] on anion solvation with NMF as a solvent. The small Gibbs transfer values of this ion at low mole fractions of NMF ($x_{\text{NMF}} < 0.1$) are similar to the results obtained with the silver ion in the $\text{Ag}_2\text{SO}_4\text{-H}_2\text{O-DMSO}$ [2] system and may be ascribed to the effect of strong solvent-solvent interactions.

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