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# Preferential Solvation of Silver(I) Acetate in Water, Methanol and Their Mixtures with Dimethyl Sulfoxide

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The solvent transport number, Δ, of dimethyl sulfoxide and *Gibbs* solvation energies of silver acetate in the binary solvent systems, water—*DMSO* and methanol—*DMSO*, were determined by employing *EMF* and solubility measurements. While the transfer free energy of the salt increases from water to water—*DMSO* mixtures (up to $X_{DMSO} = 0.7$) and then decreases, it continuously decreases from methanol to methanol—*DMSO* mixtures. In both mixed solvents, $\Delta G^{\circ}_{t(\mathrm{Ag}+)}$ decreases down to pure *DMSO* and that of acetate ion increases with increasing composition of *DMSO* indicating that silver ion is preferentially solvated by *DMSO* and acetate ion by water or methanol in these mixtures. The solvent transport numbers, Δ, of *DMSO* are positive throughout, passing through a maximum at $X_{DMSO} = 0.45$ ($\Delta = 1.0$) in the case of water—*DMSO* mixtures and at $X_{DMSO} = 0.25$ ($\Delta = 1.8$) in methanol—*DMSO* mixtures. This observation is shown to be in accord with the conclusions arrived at from the transfer energy data of the salt in the two mixtures.

*(Keywords: Electromotive force; Solvent transport number; Thermodynamics)*

### *Bevorzugte Solvatation von Silber(I)acetat in Wasser, Methanol und deren Mischungen mit Dimethylsulfoxid*

Es wurde die Lösungsmitteltransportzahl (Δ) von Dimethylsulfoxid und die *Gibbs*sche Solvatationsenergie von Silberacetat in den binären Lösungsmittelsystemen Wasser—*DMSO* und Methanol—*DMSO* mittels *EMK*- und Löslichkeitsmessungen ermittelt. Während die freie Energie des Transfers des Salzes beim Übergang von Wasser zu Wasser—*DMSO*-Mischungen zunächst ansteigt (bis $X_{DMSO} = 0{,}7$) und dann abfällt, ist für das System Methanol bzw. Methanol—*DMSO* ein kontinuierlicher Anstieg feststellbar. In beiden Mischsystemen fällt $\Delta G^{\circ}_{t(\mathrm{Ag}^+)}$ bis zu reinem *DMSO*, der entsprechende Wert für Acetat steigt bei größeren Anteilen von *DMSO* an. Das zeigt, daß das Silber(I)ion bevorzugt von *DMSO* solvatisiert wird, Acetat von der jeweils anderen Komponente (Wasser bzw. Methanol). Die Lösungsmitteltransportzahl Δ für *DMSO* ist stets positiv mit Maxima bei $X_{DMSO} = 0{,}45$ ($\Delta = 1{,}0$) für

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Wasser—*DMSO* und $X_{DMSO} = 0{,}25$ ($\Delta = 1{,}8$) für Methanol—*DMSO*. Diese Beobachtung steht im Einklang mit Rückschlüssen, die aus den Transferenergiedaten des Salzes in den zwei untersuchten Systemen getroffen werden können.

## Introduction

Selective solvation of ions in mixed solvents profoundly influences many chemical phenomena such as rates of chemical reaction, phase separation in binary mixtures, solubilities, electrode potentials etc.[1]. It also has potential technological value[1–3]. Two experimental parameters, solvent transfer numbers, $\Delta$, and the *Gibbs* energies of solvation provide valuable information on the nature of solvation[4], i.e., whether an electrolyte is homoselectively or heteroselectively solvated in the mixed solvent system under consideration. In particular, the sign and magnitude of $\Delta$, offers a new approach of obtaining at least qualitative information about the composition of ionic solvation shells in mixed solvents.

In previous investigations from this laboratory[5,6], the selective solvation of silver bromate in water—*DMSO* and of silver iodate in water—*DMSO* and methanol—*DMSO* mixtures was investigated. Both these systems belong to a small group of binary mixtures of polar solvents possessing stronger solvent—solvent interaction[7] compared to the interaction in pure solvents. In this paper, we report the results on the selective solvation of silver(I) acetate in these mixtures at 30 °C in order to consider the effect of strong solvent—solvent interactions in these systems on ion solvation.

## Experimental

Dimethyl sulfoxide (BDH, LR Grade) was purified by the method of *Maricle* and *Hodgson*[8] and subsequently dried over 5 Å molecular sieves. Double distilled water was used in the preparation of water—*DMSO* mixtures. Methanol (BDH, LR Grade) was purified as described earlier[6].

The solubility of the salt in the various compositions of solvent mixtures and its *Gibbs* transfer free energy from water or methanol to mixed solvents were determined as described earlier[5]. The solvent transport number, $\Delta$, was determined by employing a galvanic cell with transfer as suggested by *Wagner*[9].

$$\mathrm{Ag}\;\left|\;\begin{array}{l}\mathrm{Ag(CH_3COO)_{satd.}}\\ X'_{DMSO} = 1 - X'_{\text{(water or methanol)}}\end{array}\;\right|\;\begin{array}{l}\mathrm{Ag(CH_3COO)_{satd.}}\\ X''_{DMSO} = 1 - X''_{\text{(water or methanol}}\end{array}\;\right|\;\mathrm{Ag}$$

and the *EMF* measurements were carried out over the complete range of water—*DMSO* and methanol—*DMSO* mixtures keeping the mole fraction difference at 0.1 throughout. Further details are described previously[5].

## Results and Discussion

The solubility and transfer free energy of the salt (from water or methanol to the mixtures with *DMSO*) calculated from the relation.

$$\Delta G^{\circ}_{t\,(\mathrm{salt})} = 2.303\, RT \log \frac{K_{sp\ (\text{water or methanol})}}{K_{sp\ (\text{solvent})}} \tag{1}$$

in different compositions of the two mixed solvent systems are given in Table 1. The solubility of the salt is related to the thermodynamic solubility product by the relation

$$K_{sp} = S^2 f_{\pm}^2 . \tag{2}$$

Where $f_{\pm}$ is the mean molal activity coefficient of the electrolyte calculated from the extended *Debye-Hückel* equation with $a = 6.5$ Å. The *Gibbs* energy of transfer of silver ion in water—*DMSO* and methanol—*DMSO* mixtures, determined on the basis of ferrocene reference method and taken from literature[10, 4], is also given in Table 1. The transfer free energy of the salt can be expressed in terms of the transfer energies of the corresponding ions by

$$\Delta G^{\circ}_{t\,(\mathrm{CH_3COOAg})} = \Delta G^{\circ}_{t\,(\mathrm{Ag^+})} + \Delta G^{\circ}_{t\,(\mathrm{CH_3COO^-})} . \tag{3}$$

The transfer energy of the anion in these mixtures calculated from eq. (3) is incorporated in Table 1.

It is seen (Table 1) that the solubility of silver acetate decreases up to 0.7 mole fraction of *DMSO* and then slightly increases in water—*DMSO* mixtures whereas it is found to increase continously from methanol to methanol—*DMSO* mixtures. The $\Delta G^{\circ}_{t\,(\mathrm{salt})}$ thus increases from water to water—*DMSO* mixtures (up to $X_{DMSO} = 0.7$) and then decreases but the same decreases from methanol to methanol—*DMSO* mixtures. However, the transfer energies of silver ion decrease down to pure *DMSO* in both mixed solvents and that of acetate ion increases with increasing composition of *DMSO* indicating that silver ion is preferentially solvated by *DMSO* and acetate ion by water or methanol. It must be pointed out that the transfer energy of the silver ion is nearly equal to zero at $X_{DMSO} = 0.1$ indicating that this ion behaves as if it is in pure water presumably because of the strong solvent—solvent interactions between *DMSO* and water molecules at low mole fractions of *DMSO*. A heteroselective solvation of the salt in these mixtures may therefore be inferred.

Table 1a. *Solubility and transfer free energies for* $CH_3COOAg$, $Ag^+$ *and* $CH_3COO^-$ *in water–DMSO mixtures at 30 °C*

| Mole fraction of *DMSO* | Solubility of $CH_3COOAg(S \cdot 10^2)$ $mol\,kg^{-1}$ | $\Delta G_t^\circ$ (salt) $kcal\,mol^{-1}$ | $\Delta G_t^\circ$ ($Ag^+$) $kcal\,g\,ion^{-1}$ | $\Delta G_t^\circ$ ($CH_3COO^-$) $kcal\,g\,ion^{-1}$ |
|---|---|---|---|---|
| 0.0 | 7.20 | 0.00 | 0.00 | 0.00 |
| 0.1 | 4.19 | 0.62 | —0.61 | 1.23 |
| 0.2 | 2.57 | 1.18 | —2.52 | 3.70 |
| 0.3 | 1.79 | 1.60 | —4.30 | 5.90 |
| 0.4 | 1.44 | 1.86 | —5.75 | 7.61 |
| 0.5 | 1.26 | 2.03 | —7.09 | 9.12 |
| 0.6 | 1.15 | 2.15 | —8.00 | 10.15 |
| 0.7 | 1.13 | 2.17 | —8.80 | 10.97 |
| 0.8 | 1.17 | 2.16 | —9.55 | 11.71 |
| 0.9 | 1.25 | 2.10 | —10.10 | 12.20 |
| 1.0 | 1.33 | 2.07 | —10.57 | 12.64 |

Table 1b. *Solubility and transfer free energies for* $CH_3COOAg$, $Ag^+$ *and* $CH_3COO^-$ *in methanol—DMSO mixtures at 30 °C*

| Mole fraction of *DMSO* | Solubility of $CH_3COOAg(S \cdot 10^2)$ $mol\,kg^{-1}$ | $\Delta \overset{\circ}{G_t}$ (salt) $kcal\,mol^{-1}$ | $\Delta \overset{\circ}{G_t}$ ($Ag^+$) $kcal\,g\,ion^{-1}$ | $\Delta \overset{\circ}{G_t}$ ($CH_3COO^-$) $kcal\,g\,ion^{-1}$ |
|---|---|---|---|---|
| 0.0 | 0.09 | 0.00 | 0.00 | 0.00 |
| 0.1 | 0.18 | —0.82 | —2.00 | 1.18 |
| 0.2 | 0.31 | —1.45 | —2.84 | 1.39 |
| 0.3 | 0.43 | —1.85 | —3.92 | 2.07 |
| 0.4 | 0.56 | —2.15 | —4.88 | 2.73 |
| 0.5 | 0.68 | —2.38 | —5.54 | 3.16 |
| 0.6 | 0.81 | —2.58 | —6.09 | 3.51 |
| 0.7 | 0.93 | —2.73 | —6.57 | 3.84 |
| 0.8 | 1.05 | —2.88 | —6.91 | 4.03 |
| 0.9 | 1.17 | —2.99 | —7.29 | 4.30 |
| 1.0 | 1.33 | —3.14 | —7.46 | 4.32 |

*Solvent Transport Number Measurements*

*Wagner* showed that in a galvanic cell which consists of two half cells containing solvent mixtures of similar composition both saturated with a sparingly soluble salt the chemical potential of the electrolyte remains constant throughout the cell. Considerable *EMF* can, however, be obtained due to the difference in the chemical potential of the solvent in the two compartments. This *EMF* can be related to the solvent transport number, Δ, which is a function of the selective solvation of the ions by

$$E = \frac{-RT}{F}\,\frac{(X''_{DMSO} - X'_{DMSO})\,\Delta}{X_{DMSO}(1 - X_{DMSO}}\left(1 + \frac{\partial \ln f_{DMSO}}{\partial \ln X_{DMSO}}\right). \tag{4}$$

Where

$$X_{DMSO} = \frac{X''_{DMSO} + X'_{DMSO}}{2} \quad \text{and} \quad \frac{\partial \ln f_{DMSO}}{\partial \ln X_{DMSO}}$$

represents the variation of the activity coefficient of *DMSO* with the mole fraction of *DMSO*. The *EMF*, $\frac{\partial \ln f_{DMSO}}{\partial \ln X_{DMSO}}$ taken from literature[11, 4] and Δ values of *DMSO* in solutions saturated with silver acetate in both solvent mixtures are given in Table 2. The values are positive throughout, passing through a maximum at $X_{DMSO} = 0.45$ ($\Delta = 1.0$) in the case of water—*DMSO* mixtures and at $X_{DMSO} = 0.25$ ($\Delta = 1.8$) in methanol—*DMSO* mixtures. Thus an increase of 1.0 and 1.8 moles of *DMSO* occurs in the case of water—*DMSO* and methanol—*DMSO* mixtures respectively per *Faraday* relative to the mean molar velocity of the solvent mixture as reference, in the cathode compartment when solutions of the salt are electrolysed at the given compositions of the solvent mixture. Detailed interpretation of Δ is made difficult by the non-availability of information on *n*'s and also of ionic transfer numbers as a function of solvent composition. The solvent transport number, Δ, is related to the solvation numbers of cation and anion $n_{1+}$, $n_{2+}$, $n_{1-}$ and $n_{2-}$ by the solvent components and the ionic transfer numbers (*t*'s) by

$$\Delta = (X_1\,n_{2+} - X_2\,n_{1+})\,t_+ - (X_1\,n_{2-} - X_2\,n_{1-})\,t_- \tag{5}$$

where subscript 1 refers to water or methanol and 2 refers to *DMSO*.

The positive values of Δ for both the salts is in agreement with the conclusion arrived at from the transfer energy data of the salt in the

Table 2. *EMF data on cell (1) and solvent transport number for* $CH_3COOAg$ *in water—DMSO and methanol—DMSO mixtures*

| Mole fraction of *DMSO* | Water—*DMSO* mixtures | | | Methanol—*DMSO* mixtures | | |
|---|---|---|---|---|---|---|
| | $1+\frac{\partial \ln f_2}{\partial \ln X_2}$ | $-E$ (mV) | $\Delta$ | $1+\frac{\partial \ln f_2}{\partial \ln X_2}$ * | $-E$ (mV) | $\Delta$ |
| 0.05 | 1.175 | 7 | 0.1 | 0.500 | 34 | 1.2 |
| 0.15 | 1.245 | 10 | 0.4 | 1.199 | 37 | 1.5 |
| 0.25 | 1.365 | 12 | 0.7 | 1.611 | 40 | 1.8 |
| 0.35 | 1.515 | 15 | 0.8 | 1.677 | 33 | 1.7 |
| 0.45 | 1.705 | 19 | 1.0 | 1.708 | 30 | 1.7 |
| 0.55 | 1.920 | 9 | 0.5 | 1.626 | 25 | 1.5 |
| 0.65 | 2.155 | 9 | 0.3 | 1.485 | 23 | 1.4 |
| 0.75 | 2.235 | 9 | 0.3 | 1.328 | 21 | 1.1 |
| 0.85 | 2.235 | 8 | 0.2 | 1.618 | 18 | 0.6 |
| 0.95 | 2.235 | 8 | 0.1 | 0.400 | 15 | 0.7 |

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* Calculated from Ref. [4].

two mixtures. The transport of *DMSO* into the cathode compartment occurs largely through the silver ion while the anions transport water or methanol into the anode compartment. The two effects are combined, characterising the hetroselective solvation with significantly large $\Delta$. The preferential solvation of $Ag^+$ by *DMSO* in these mixtures may be ascribed to specific interactions between the $d^{10}$ cation and the $\pi$ orbital of the sulfoxide group in *DMSO* whereas the selective solvation of the anion by methanol or water is due to the strong hydrogen bonding interactions between the solvents and the anion.

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