Preferential Solvation of Silver(I) Bromate in Methanol-Dimethylsulfoxide Mixtures

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The solubiltiy of silver bromate, the Gibbs transfer energy of Ag^+ and BrO_3^- and the solvent transport number in methanol-dimethyl sulfoxide mixtures are reported. The solubility of silver bromate increases with addition of DMSO. The Gibbs energy of transfer of the silver ion (based on the ferrocene reference method) decreases, while that of the bromate ion becomes slightly negative with the addition of DMSO. The solvent transport number Δ passes through a maximum ($\Delta = 1.0$ at $X_{DMSO} = 0.65$. From these results, it is concluded that the silver ion is preferentially solvated by DMSO whereas the bromate ion shows no preferential solvation.

Introduction

Preferential solvation of ions in mixed solvents profoundly affects the solubilities, rates of chemical reactions, phase separation in binary mixtures and electrode potentials [1]. It finds application in the electrorefining and electrowinning of metals [2, 3]. Further, the sign and magnitude of the solvent transport number provide valuable information on the composition of the solvation shells of ions in mixed solvents [4].

The selective solvation behaviour of some silver salts in water-DMSO mixtures, which possess strong solvent-solvent interaction, has received considerable interest in recent years [5, 6]. The present paper deals with the selective solvation of silver bromate in methanol-DMSO mixtures, whose solvent-solvent interaction differs markedly [7] from that of water-DMSO mixtures.

Materials and Methods

DMSO and methanol were purified as described in [8]. The preparation of silver bromate has been reported in [6]. The solubility measurements in the solvent mixtures were carried potentiometrically as described in [6]. The silver electrodes required for the emf measurements were prepared by electrolytically coating silver onto platinum wires sealed in glass tubes according to the method of Carmody [9].

The solvent transport number Δ in methanol-DMSO mixtures was determined by setting up a concentration cell as suggested by Wagner [10], in which the two half cells are saturated with silver bromate and the mole fraction difference of DMSO between them was maintained constant at 0.1. Further details have been described in [6].

The dielectric constants, ε, of various methanol-DMSO mixtures at 30 °C were measured by means of a DK meter 60 GK (Franz Kustner Nachf. KG Dresden) using methanol-water mixtures as calibration liquids.

Results and Discussion

The solubility, S, of silver bromate and the solubility product, K_{sp}, of the salt calculated from

$$K_{sp} = S^2 \gamma_\pm^2 \qquad (1)$$

are given in Table 1. The mean molal activity coefficient $\gamma_\pm$ of the salt was obtained from the extended Debye-Hückel equation with $a = 6.5$ Å using the dielectric constant data from Table 1. It is interesting to point out [4, 6] that the solubilities of many silver-salts in water-DMSO mixtures first decrease with the addition of DMSO but then increase whereas a continuous increase of the solubility with the addition of DMSO in methanol-DMSO mixtures is generally observed. The Gibbs energy of transfer of $AgBrO_3$ from pure methanol to pure DMSO was then calculated from

$$\Delta G_t^0 = -RT \ln \frac{K_{sp,S}}{K_{sp,MeOH}}. \qquad (2)$$

The results are given in Table 1. The Gibbs energy of transfer of silver ion in methanol-DMSO mixtures, (on the basis of the ferrocene reference method reported by Rodehüser and Schneider [7])

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Table 1. Dielectric constant ε of methanol-DMSO mixtures, solubilities S and transfer energies[a] of the salt and the silver and bromate ions at 30 °C.

Mole fraction of DMSO	ε	$S \times 10^2$/mol kg^{-1} [a]	$\Delta G^0_{t(AgBrO_3)}$/ kcal mol^{-1}	$\Delta G^0_{t(Ag^+)}$/ kcal mol^{-1}	$\Delta G^0_{t(BrO_3^-)}$/ kcal mol^{-1}
0.0	31.80	0.005	0.0	0.00	0.00
0.1	35.75	0.024	− 1.86	− 1.15	− 0.71
0.2	38.80	0.079	− 3.26	− 2.42	− 0.84
0.3	41.60	0.186	− 4.26	− 3.50	− 0.76
0.4	44.00	0.362	− 5.03	− 4.50	− 0.53
0.5	45.20	0.640	− 5.68	− 5.25	− 0.43
0.6	46.01	1.00	− 6.18	− 5.88	− 0.30
0.7	46.45	1.54	− 6.66	− 6.35	− 0.31
0.8	46.60	2.20	− 7.05	− 6.69	− 0.36
0.9	46.45	3.03	− 7.40	− 7.00	− 0.40
1.0	46.00	3.79	− 7.64	− 7.26	− 0.38

[a] ΔG^0_t values accurate to ± 0.05 kcal/mol.

and the transfer energy of the anion in these mixtures calculated from

$$\Delta G^0_{t(AgBrO_3)} = \Delta G^0_{t(Ag^+)} + \Delta G^0_{t(BrO_3^-)} \tag{3}$$

are also given in Table 1.

The Gibbs energy of transfer of $AgBrO_3$ (Table 1) continuously decreases from methanol to DMSO. The transfer energy of the bromate ion in slightly negative less than 0.5 kcal/mol beyond $X_{DMSO} = 0.4$) at all solvent compositions and thus appears to be not preferentially solvated by methanol or DMSO. The Gibbs transfer energy of the silver ion, however, continuously decreases with the addition of DMSO indicating that it is selectively solvated by DMSO in these mixtures.

Table 2. EMF data and solvent transport number, Δ, of DMSO for silver bromate in methanol-DMSO mixtures at 30 °C.

Mol. fraction of DMSO	$-E$/mV[a]	Δ
0.05	7.0	0.25 ± 0.04
0.15	10.5	0.43 ± 0.04
0.25	11.5	0.51 ± 0.05
0.35	12.0	0.62 ± 0.05
0.45	15.0	0.83 ± 0.04
0.55	15.5	0.90 ± 0.06
0.65	17.0	1.00 ± 0.06
0.75	17.0	0.92 ± 0.05
0.85	11.0	0.33 ± 0.03
0.95	8.5	0.39 ± 0.04

[a] EMF values accurate to ± 1 mV.

Solvent Transport Number Measurements

The EMF data of the Wagner cell [10] in these mixtures and the solvent transport numbers calculated from these data using the relation

$$E = -\frac{RT}{F}\left(\frac{X_S'' - X_S'}{X_S(1 - X_S)}\right)\Delta\left(1 + \frac{\partial \ln f_s}{\partial \ln x_s}\right) \tag{4}$$

where $X_S = \frac{1}{2}(X_S'' + X_S')$ (S = DMSO in the present case), are given in Table 2. The activity coefficient term in (4) accounts for the non-ideal behaviour of the solvent mixtures, and $X_S'' - X_S' = 0.1$ was maintained throughout. The Δ values are positive throughout with a maximum value of 1.0 around $X_{DMSO} = 0.65$, indicating that a net increase of 1.0 mole of DMSO per Faraday (relative to the mean molar velocity of the solvent mixture as reference) occurs in the cathode compartment when solutions of the salt are electrolysed at the given composition of the solvent mixture. The solvent transport number of DMSO is related to the partial solvation numbers of cation and anion and the ionic transference numbers [11]:

$$\begin{aligned} \Delta &= \Delta_+ - \Delta_-, \\ \Delta_+ &= (X_M n_D^+ - X_D n_M^+)\, t_+, \\ \Delta_- &= (X_M n_D^- - X_D n_M^-)\, t_-, \end{aligned} \tag{5}$$

where the X's refer to the mole fractions of the two solvent components and the n's refer to the partial solvation numbers of Ag^+ and anion by the solvents indicated by the subscripts. Δ_+ and Δ_- are the solvent transport numbers due to the cation and anion. In the present case, the anionic contribution to the solvent transport, i.e. Δ_-, appears to be negligible in view of the fact that $\Delta G^0_{t(BrO_3^-)} \approx 0$, and thus the considerable positive Δ values observed in this case are entirely due to the transport of DMSO towards the cathode by the silver ion.

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