

## Selective solvation of Ag(I) iodate in methanol-dimethyl sulphoxide mixtures

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**Abstract.** The selective solvation of silver(I) iodate was studied in methanol-dimethyl sulphoxide mixtures at 30° C by solubility and EMF measurements. The solubility of the salt increases continuously with the addition of dimethyl sulphoxide after a slight decrease upto  $X_{\text{DMSO}} = 0.1$ . The Gibbs energy of transfer of silver cation (determined on the basis of ferrocene reference method) decreases continuously while that of the iodate ion increases with the addition of dimethyl sulphoxide. The solvent transport number passes through a maximum ( $\Delta = 2.0$ ) around  $X_{\text{DMSO}} = 0.5$ . These results were interpreted as arising due to a hetero-selective solvation of the salt, the silver ions being preferentially solvated by dimethyl sulphoxide and the iodate ion by methanol in these mixtures.

**Keywords.** Selective solvation; silver iodate; methanol-dimethyl sulphoxide mixtures; solubility; EMF method.

### 1. Introduction

In a binary mixed solvent containing an electrolyte, the possibility that the electrolyte is heteroselectively or homoselectively solvated exists (Schneider 1976b). Hitherto, only few reports of this nature dealing with selective solvation of electrolytes in mixed solvents are available in literature (El-Harakany and Schneider 1973; Rodehuser and Schneider 1976; Kalidas and Sivaprasad 1979; Kalidas and Schneider 1980). In continuation of our earlier work on this subject (Janardhanan and Kalidas 1980), we report the results on the selective solvation of silver iodate in methanol-dimethyl sulphoxide mixtures in the present paper.

### 2. Experimental

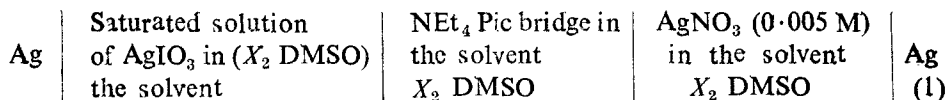
Dimethyl sulphoxide (BDH, LR) was purified by the method of Maricle and Hodgson (1965) and subsequently dried over 5 Å molecular sieves. Methanol

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(BDH, LR) was refluxed initially over neutral alumina and distilled. It was finally dried over anhydrous sodium sulphate and fractionally distilled. Silver iodate was prepared as described earlier (Janardhanan and Kalidas 1980).

In view of the low solubility of silver iodate in these mixtures, a potentiometric method, similar to that adopted by Kolthoff and Chantooni (1973), was employed in solubility measurements of the salt. The following concentration cell



in which a 0.1 M solution of tetraethyl ammonium picrate in the particular solvent mixture placed in an inverted U-tube whose ends were covered with fine porosity fritted discs served as the bridge electrolyte, was used. The e.m.f. of cell (1) is related to the activity of the silver ion in the saturated solution of the salt by

$$E = \frac{RT}{F} \ln \frac{(a_{\text{Ag}^+})_{\text{ref}}}{(a_{\text{Ag}^+})_{\text{satd. soln.}}} \quad (2)$$

The solvent transport number  $\Delta$  of DMSO for silver iodate in the complete range of methanol-DMSO mixtures was determined by setting up a concentration cell (Wagner 1966; Janardhanan and Kalidas 1980) in which the two half cells are saturated with silver iodate and the mole fraction difference of DMSO,  $X_2'' - X_2'$  between them was maintained constant at 0.1. Freshly prepared silver electrodes according to the method of Carmody (1929) were used in all EMF-measurements. Further details have been described earlier (Janardhanan and Kalidas 1980).

### 3. Results and discussion

#### 3.1. Solubility measurements

Using the silver ion activity in saturated silver iodate solutions, the Gibbs energy of transfer of silver iodate from methanol to methanol-DMSO mixtures was obtained from the relation

$$\Delta G_{i(\text{salt})}^0 = 2.303 RT \log \frac{K_{sp}(\text{MeOH})}{K_{sp}(\text{solvent})} \quad (3)$$

in which  $K_{sp}$  represents the thermodynamic solubility product of the salt. Utilising the transfer energy of the silver ion in these mixtures determined earlier (Rodehuser and Schneider 1976), the Gibbs energy of transfer of iodate ion (Reference solvent: methanol) was obtained as a difference between the transfer energy of the salt and of the silver ion. All these results are given in table 1.

The solubility of silver iodate continuously increases with the addition of DMSO after a slight decrease upto  $X_{\text{DMSO}} = 0.1$  which is in complete contrast to its solubility behaviour in water-DMSO mixtures. Thus,  $\Delta G_{i(\text{AgIO}_3)}^0$  decreases continuously with the addition of DMSO after an initial increase upto  $X_{\text{DMSO}} = 0.1$ .

The continuous decrease of the Gibbs transfer energy of silver ion with the addition of DMSO (table 1) which indicates a preferential solvation of this ion by DMSO in these mixtures can be explained on the basis of the specific back bonding of this cation with the  $\pi^*$  orbitals of the sulphoxide group. In addition, the strong electrostatic interactions between the cation and the negative charge on the oxygen may also be a contributing factor (Parker *et al* 1974). The transfer energy of iodate ion continuously increases with the addition of DMSO indicating that it is preferentially solvated by methanol in these mixtures. The strong solvation of iodate ion by methanol in these mixtures has been attributed to its pyramidal structure with the halogen at the apex (Kolthoff and Chantooni 1973). Thus a heteroselective solvation of the salt in these mixtures is observed.

### 3.2. Solvent transport number from EMF measurements

The solvent transport number  $\Delta$  of DMSO was calculated from the EMF data on the appropriate cell as described earlier (Wagner 1966). The Washburn number of DMSO,  $W_{\text{DMSO}}$  with methanol as the reference solvent is given by

$$W_{\text{DMSO}} = \Delta / X_{\text{MCH}_3}$$

and these data are presented in table 2. The magnitude of  $W_{\text{DMSO}}$  tends to a limiting value of 3.7 and this result is in good agreement with the coordination number four for  $\text{Ag}^+$  with respect to DMSO obtained by Rodehuser and Schneider (1976a) from NMR measurements. The  $\Delta$  which is related to the solvation numbers of the cation and anion by the respective solvent components (Schneider 1976a) is positive over the entire range mole fractions of DMSO and indicates a net transport of DMSO towards the cathode in a Hittorf experiment. The large increase of  $\Delta$ , which passes through a maximum ( $\Delta = 2.0$ ) at  $X_{\text{DMSO}} = 0.45$  with the addition of DMSO supports the heteroselective solvation of the electrolyte and is in agreement with the large  $\Delta$  values obtained for heteroselectively

Table 1. Solubility and transfer free energy data for  $\text{AgIO}_3$ ,  $\text{Ag}^+$  and  $\text{IO}_3^-$  ions in methanol-DMSO mixtures at 30° C

Mole fraction of DMSO	$a_{\text{Ag}^+}$ in saturated $\text{AgIO}_3$ mol kg <sup>-1</sup>	Solubility product $K_{sp}$	$\Delta G_f^\circ$ ( $\text{AgIO}_3$ ) kcal g ion <sup>-1</sup>	$\Delta G_f^\circ$ ( $\text{Ag}^+$ ) kcal g ion <sup>-1</sup>	$\Delta G_f^\circ$ ( $\text{IO}_3^-$ ) kcal g ion <sup>-1</sup>
0	$4.38 \times 10^{-6}$	$1.92 \times 10^{-11}$	0	0	0
0.1	$2.56 \times 10^{-6}$	$6.55 \times 10^{-12}$	0.65	-2.00	2.65
0.2	$4.65 \times 10^{-6}$	$2.16 \times 10^{-11}$	-0.07	-2.84	2.77
0.3	$5.30 \times 10^{-6}$	$2.81 \times 10^{-11}$	-0.23	-3.92	3.69
0.4	$9.60 \times 10^{-6}$	$9.22 \times 10^{-11}$	-0.95	-4.88	3.93
0.5	$1.03 \times 10^{-5}$	$1.06 \times 10^{-10}$	-1.03	-5.55	4.52
0.6	$1.08 \times 10^{-5}$	$1.17 \times 10^{-10}$	-1.09	-6.10	5.01
0.7	$2.15 \times 10^{-5}$	$4.62 \times 10^{-10}$	-1.92	-6.57	4.65
0.8	$2.47 \times 10^{-5}$	$6.10 \times 10^{-10}$	-2.08	-6.91	4.83
0.9	$2.66 \times 10^{-5}$	$7.08 \times 10^{-10}$	-2.17	-7.29	5.12
1.0	$2.92 \times 10^{-5}$	$8.53 \times 10^{-10}$	-2.28	-7.46	5.18

Table 2. EMF data, solvent transport number,  $\Delta$ , and Washburn number,  $W_{\text{DMSO}}$  of  $\text{AgIO}_3$  in methanol-DMSO mixtures at 30° C.

Mole fraction of of DMSO	$\frac{\partial \ln f_2}{\partial \ln x_2}$	$-E$ mV	$\Delta$	$W_{\text{DMSO}}$
0.05	-0.50	8.0	0.29	0.31
0.15	0.20	11.0	0.49	0.58
0.25	0.61	20.0	0.89	1.19
0.35	0.68	25.0	1.30	2.00
0.45	0.71	36.0	2.00	3.64
0.55	0.62	28.0	1.63	3.62
0.65	0.49	20.0	1.17	3.34
0.75	0.33	17.0	0.92	3.68
0.85	0.62	18.0	0.54	3.60
0.95	-0.60	12.0	0.41	..

solvated electrolytes in other binary solvent systems (Harakany and Schneider 1973; Kalidas and Schneider 1980).

### References

- Carmody W R 1928 *J. Am. Chem. Soc.* **51** 2901  
 El-Harakany A A and Schneider H 1973 *J. Electroanal. Chem.* **46** 255  
 Janardhanan S and Kalidas C 1980 *Bull. Chem. Soc. Jpn* (in press)  
 Kalidas C and Schneider H 1980 *Z. Phys. Chem. N.F.* **120** 145  
 Kalidas C and Sivaprasad P 1979 *Indian J. Chem.* **A18** 532  
 Kolthoff I M and Chantooni M K 1973 *J. Phys. Chem.* **77** 523  
 Maricle D L and Hodgson W G 1965 *Anal. Chem.* **37** 1562  
 Rodehusen L and Schneider H 1976 *Z. Phys. Chem. N.F.* **100** 119  
 Schneider H 1976a *Electrochim. Acta* **21** 711  
 Schneider H 1976b *Solute-solvent interactions* ed J F Coetzee and C D Ritchie (New York : Marcel Dekker) vol. 2, p. 155  
 Parker A J, Diggle J W and Avraamides 1974 *Aust. J. Chem.* **27** 721  
 Wagner C 1966 *Advances in electrochemistry and electrochemical engineering* (New York : Wiley-Interscience), vol. 4 pp. 1-46