

# Ion-Solvent Interactions of Silver(I)-18-crown-6 Perchlorate Complex in Methanol–Acetonitrile Mixtures

C. KALIDAS and R. RAGHUNATH

*Department of Chemistry, Indian Institute of Technology, Madras–36, India.*

(Received: 8 November 1993; in final form: 29 March 1994)

**Abstract.** The standard Gibbs transfer energies of the silver(I)-18-crown-6 perchlorate complex salt from methanol to various compositions of methanol–acetonitrile mixtures were determined from solubility measurements at 30°C and these data were separated into the corresponding ionic contributions by employing the negligible liquid junction potential method of Parker *et al.* The solvent transport numbers  $\Delta_{AN}$ , for the salt were also determined at various solvent compositions using a concentration cell with transference.

The Gibbs transfer energy of the silver(I)-18-crown-6 complex cation is negative and decreases with the addition of acetonitrile but the transfer energy of the anion is positive and increases under the same conditions. The solvent transport number,  $\Delta_{AN}$ , increases and passes through a maximum value of 5.48 at  $\Delta_{AN} = 0.55$ . These results indicate that the complex salt is heteroselectively solvated in these mixtures with the cation being preferentially solvated by acetonitrile and the anion by methanol molecules.

**Key words:** Silver(I)-18-crown-6 perchlorate complex, selective solvation, methanol–acetonitrile mixtures, Gibbs transfer energies, solvent transport numbers.

## 1. Introduction

Investigations on ion solvation in binary mixed solvents have revealed [1, 2] two types of solvation phenomena: (i) both ions of an electrolyte are preferentially solvated by the same solvent component of the mixture, *viz.* homoselective solvation; (ii) each of the ions is selectively solvated by the two different solvent components of the mixture, *viz.* heteroselective solvation. The sorting out of the solvent components by the ions of the electrolyte as mentioned above is important both from a fundamental as well as a technological view point [3] and finds many applications.

Macrocyclic ligands such as crown ethers, which have the capacity to partially or completely encapsulate cations on complexation, offer an interesting possibility for the study of ionic solvation [4–6]. Although considerable work involving the selective solvation of Ag(I) and copper(II) salts in protic-dipolar aprotic solvent mixtures has been reported in recent years [7, 8], practically no report is available on the selective solvation of the metal complexes of crown ethers or cryptands.

The present work, which deals with the preferential solvation of the [Ag(I)-18-crown-6]perchlorate complex in methanol–acetonitrile (M–AN) mixtures, was therefore undertaken with a view to understanding the effect of ligand encapsulation of cations on the nature of solvation of the silver ions in these mixtures.

TABLE I. Solubility ( $S$ ) and Gibbs transfer energies ( $\Delta G_t^0$ ) of the complex salt in methanol-acetonitrile mixtures at 30°C.

$X_{AN}$	$S$ (mol kg <sup>-1</sup> )	$K_A$	$pK_{sp}$	$\Delta G_t^0(\text{salt})$ (kJ mol <sup>-1</sup> )	$\Delta G_t^0(\text{Ag-18C6})^+$ (kJ mol <sup>-1</sup> )	$\Delta G_t^0(\text{ClO}_4^-)$ (kJ mol <sup>-1</sup> )
0.0	6.89	17.60	1.09	0.00	0.00	0.00
0.1	3.78	16.20	1.30	1.22	-11.97	13.19
0.3	2.65	21.10	1.54	2.58	-16.55	19.13
0.5	2.27	8.01	1.24	0.88	-21.14	22.02
0.7	2.03	9.28	1.33	1.37	-22.85	24.22
0.9	1.70	18.00	1.63	3.12	-23.61	26.73
1.0	0.875	24.70	2.02	5.39	-22.72	28.11

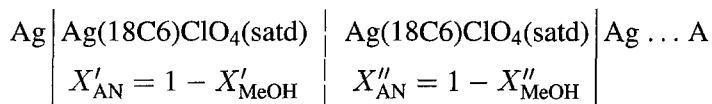
## 2. Experimental

18-Crown-6 (E. Merck) was used throughout. Methanol and AN were purified as described previously [9]. The complex [Ag(18-crown-6)]ClO<sub>4</sub> was prepared [10] by mixing stoichiometric amounts of silver perchlorate and 18-crown-6 dissolved in methanol. The resulting solid was recrystallised twice from methanol and was subjected to elemental analysis: C = 31.26% (calculated 30.57%) and H = 5.52% (calculated 5.10%).

### 2.1. DETERMINATION OF $\Delta G_t^0(\text{SALT})$

The solubility of [Ag[(18-crown-6)]ClO<sub>4</sub> in various methanol-AN mixtures was determined by evaporating a known weight of saturated solution at the desired temperature and weighing the resultant solid. All the measurements were carried out at least twice and are accurate to  $\pm 0.5\%$ .

The solvent transport number of acetonitrile,  $\Delta_{AN}$ , for the complex salt was determined by employing a concentration cell with transference of the type



in which the two half cells contain saturated solutions of the salt in solvent mixtures differing by 0.1 mole fraction (i.e.  $X''_{AN} - X'_{AN} = 0.1$ ) throughout. Further details are given elsewhere [11]. All the measurements were carried out at  $30 \pm 0.1^\circ\text{C}$ .

## 3. Results

The solubility and solubility products of the complex salt in various compositions of methanol-AN mixtures are given in Table I.

The Gibbs free energy of transfer  $\Delta G_t^0$ , of the salt from methanol to methanol-AN mixtures was calculated [12] from

TABLE II. EMF data and solvent transport number,  $\Delta_{AN}$ , of acetonitrile for the silver(I)-18-Crown-6 perchlorate complex in methanol-AN mixtures at 30°C.

$X_{AN}$	$-\frac{d \ln f_{AN}}{d \ln X_{AN}}$	$-E$ (mV)	$\Delta_{AN}$
0.05	0.110	$29.0 \pm 1.0$	$0.59 \pm 0.02$
0.15	0.246	$11.0 \pm 1.0$	$0.71 \pm 0.07$
0.25	0.367	$8.0 \pm 0.5$	$0.91 \pm 0.05$
0.35	0.486	$9.5 \pm 1.0$	$1.61 \pm 0.16$
0.45	0.625	$10.6 \pm 1.0$	$2.68 \pm 0.24$
0.55	0.770	$13.3 \pm 0.5$	$5.48 \pm 0.21$
0.65	0.792	$9.2 \pm 1.0$	$3.85 \pm 0.42$
0.75	0.600	$11.2 \pm 1.0$	$2.01 \pm 0.18$
0.85	0.430	$18.3 \pm 1.0$	$1.57 \pm 0.08$
0.95	0.260	$10.0 \pm 1.0$	$0.25 \pm 0.02$

$$\Delta G_t^0(\text{salt}) = -RT \ln \frac{K_{sp}(\text{methanol-AN})}{K_{sp}(\text{methanol})} \quad (1)$$

where  $K_{sp}$  refers to the thermodynamic solubility product of the salt. In evaluating  $K_{sp}$  in Equation 1, the extended Debye-Hückel limiting equation with  $a = 9.16 \text{ \AA}$  was used. The Gibbs transfer energy,  $\Delta G_t^0$ , of the salt was corrected for ion association by using the experimentally determined  $K_A$  of the salt in these mixtures and they are incorporated in Table I.

The solvent transport number,  $\Delta_{AN}$ , of acetonitrile was calculated from the EMF data of cell A using the relation

$$E = -\frac{RT}{F} \cdot \frac{X''_{AN} - X'_{AN}}{X_{AN}(1 - X_{AN})} \cdot \Delta \cdot \left(1 + \frac{d \ln f_{AN}}{d \ln X_{AN}}\right) \quad (2)$$

where the various terms have their usual significance [13]. The activity coefficient of the dipolar aprotic component,  $f_{AN}$  (standard state : methanol) was evaluated from the vapour pressure data of methanol-AN mixtures [14] and these data were used to calculate the last term of Equation 2.

The EMF of the cell A and  $\Delta_{AN}$  calculated from Equation 2 are given in Table II.

#### 4. Discussion and Conclusions

The results (Table I) show the solubility of the salt decreases continuously with the addition of AN. The Gibbs transfer energy of the salt is positive throughout, indicating that its transfer from methanol to methanol-AN mixtures is not thermodynamically favoured.

The  $\Delta G_t^0(\text{salt})$  in various mixtures was split into its ionic components by employing  $\Delta G_t^0(\text{ClO}_4^-)$  data obtained from solubility measurements on silver per-

chlorate and the so derived  $\Delta G_t^0(\text{ClO}_4^-)$  in various solvent compositions. The Gibbs transfer energies of silver perchlorate were combined with the transfer energy of silver ion in these mixtures determined on the basis of the nLJP method of Parker *et al.* [15] to obtain  $\Delta G_t^0(\text{ClO}_4^-)$ . The transfer energy of the  $[\text{Ag}-(18\text{C}6)]^+$  ion was then calculated using the relationship

$$\Delta G_t^0([\text{Ag}-18\text{C}6]\text{ClO}_4) = \Delta G_t^0([\text{Ag}-18\text{C}6])^+ + \Delta G_t^0(\text{ClO}_4^-) \quad (3)$$

The transfer energies of these ions are also given in Table I. The Gibbs transfer energy of the  $[\text{Ag}-18\text{C}6]^+$  ion is negative throughout and decreases continuously (except  $X_{\text{AN}} = 1.0$ ) with the addition of AN. Thus its transfer from methanol to methanol-AN mixtures is thermodynamically favourable and a preferential solvation of this ion by AN may be inferred. The preferential solvation of the  $[\text{Ag}-18\text{C}6]^+$  ion by AN, which is similar to that of uncomplexed silver ion by AN in these mixtures, is somewhat surprising as one would expect that the shielding by the ligand in the case of  $[\text{Ag}-18\text{C}6]^+$  will hinder  $\text{Ag}^+$ -AN interactions somewhat, or at least reduce them to a large extent. Silver ion has much stronger and partially covalent interactions with the lone pairs on oxygen of 18C6 apart from the ion-dipole type interactions, leading to a large stability constant ( $\log K_s = 4.8$  at  $25^\circ\text{C}$ ) [16] in methanol. It is also preferentially solvated by AN in methanol-AN mixtures ( $\Delta G_t^0(\text{methanol} \rightarrow \text{AN}) = -28.0 \text{ kJ mol}^{-1}$  at  $30^\circ\text{C}$ ) [9] due to specific back-bonding interactions of this cation with  $\pi^*$  orbitals of the nitrile [17] group, and even a silver ion-AN complex with two molecules of AN in dilute methanolic solutions of AN has been reported [18]. The transfer of the  $[\text{Ag}-18\text{C}6]^+$  ion from methanol to methanol-AN mixtures presumably results in a weakening of silver-18C6 interactions and thereby facilitates the enrichment of AN in the solvation shell of the complex ion due to the specific interactions mentioned above.

A comparison of the Gibbs free energies of transfer of complexed and uncomplexed silver ion shows that the difference between them at any given mole fraction is not large although the values are slightly more negative for the uncomplexed  $\text{Ag}^+$  ion as they were to be expected.

For  $\text{ClO}_4^-$  ion, the  $\Delta G_t^0$ , is positive and increases with the addition of AN. This ion is preferentially solvated by methanol and may be explained as arising from H-bonded interactions between the negative charge of the anion and the positive H atoms of the methanol.

$\Delta_{\text{AN}}$  is positive (Table II) throughout and passes through a maximum  $\Delta_{\text{AN}} = 5.48$  at  $X_{\text{AN}} = 0.55$  for the complex salt. Thus there is an enrichment of 5.48 moles of AN per Faraday relative to the mean molar velocity of the solvent mixture as reference when a saturated solution of the salt is electrolysed in methanol-AN mixtures at a given composition.

$\Delta_{\text{AN}}$  is a composite quantity involving the solvation numbers,  $n$ , of the cation and anion by the two solvent components methanol and AN, their mole fraction,  $X$  and the ionic transport numbers,  $t$  of the salt and is given by

$$\Delta_{\text{AN}} = (X_{\text{M}}n_{\text{AN}}^+ - X_{\text{AN}}n_{\text{M}}^+)t_+ - (X_{\text{M}}n_{\text{AN}}^- - X_{\text{AN}}n_{\text{M}}^-)t_- \quad (4)$$

For heteroselectively solvated salts,  $n_{AN}^+$  and  $n_M^-$  are large while  $n_M^+$  and  $n_{AN}^-$  are small, resulting in a large  $\Delta_{AN}$  value, as observed in this case.

A comparison of the  $\Delta_{AN}$  maximum value with other 1 : 1 silver salts like Ag(I) bromate or Ag(I) acetate in these mixtures shows [19] that  $\Delta_{AN}$  max for the complex salt is somewhat higher than in the case of salts mentioned above.

The large positive  $\Delta_{AN}$  indicates clearly that the  $[Ag(18C6)]ClO_4$  salt is also heteroselectively solvated in these mixtures with the complex cation being preferred by AN and the anion by methanol. This result is similar to that in the case of uncomplexed 1 : 1 silver salts like Ag(I) bromate or acetate. Obviously, the ligand encapsulation of silver cation does not affect significantly the solvation behaviour of the complex salt. These conclusions are similar to those based on  $\Delta G_t^0$  measurements discussed earlier.

## References

1. (a) H. Schneider: in *Solute-Solvent Interactions*, Eds., J.F. Coetzee and C.D. Ritchie, Marcel Dekker, New York (1976). (b) *Electrochim. Acta* **21**, 711 (1976).
2. S. Janardhanan and C. Kalidas: *Rev. Inorg. Chem.* **6**, 101 (1984).
3. A.J. Parker: *Pure Appl. Chem.* **53**, 1445 (1981).
4. J. Gutknecht, H. Schneider, and J. Stroka: *Inorg. Chem.* **17**, 3326 (1978).
5. M.H. Abraham, A.F. Danil de Namor, and R.A. Schulz: *J. Chem. Soc. Faraday Trans. 1* **76**, 869 (1980).
6. I.M. Kolthoff and M.K. Chantooni: *Anal. Chem.* **52**, 1039 (1980).
7. S. Subramanian and C. Kalidas: *Fluid Phase Equilibria* **32**, 205 (1987).
8. G. Rajendran, T.K. Sreekumar, and C. Kalidas: *Fluid Phase Equilibria* **46**, 249 (1989).
9. S. Subramanian and C. Kalidas: *Electrochim. Acta* **29**, 753 (1984).
10. A.K. Srivastava and B. Tiwari: *J. Electroanal. Chem.* **325**, 301 (1992).
11. C. Kalidas and H. Schneider: *Z. Phys. Chem. (N.F.)* **10**, 8479 (1981).
12. O. Popovych: *Crit. Rev. Anal. Chem.* **1**, 73 (1970).
13. G. Rajendran and C. Kalidas: *J. Chem. Eng. Data* **31**, 226 (1986).
14. J. Timmermanns: in *The Physicochemical Constants of Binary Systems in Concentrated Solutions*, Vol. II, Interscience, New York, p. 688 (1960).
15. R. Alexander, A.J. Parker, J.H. Sharp, and W.E. Waghorne: *J. Am. Chem. Soc.* **23**, 1148 (1972).
16. J.D. Lamb, R.M. Izatt, S.W. Swain, and J.J. Christensen: *J. Am. Chem. Soc.* **102**, 475 (1980).
17. A.J. Parker, J.W. Diggle, and J. Avraamides: *Aust. J. Chem.* **27**, 721 (1974).
18. S.E. Manahan and R.T. Iwamoto: *J. Electroanal. Chem.* **14**, 213 (1967).
19. S. Subramanian, G. Sasikumar, and C. Kalidas: *Trans. SAEST* **17**, 23 (1982).