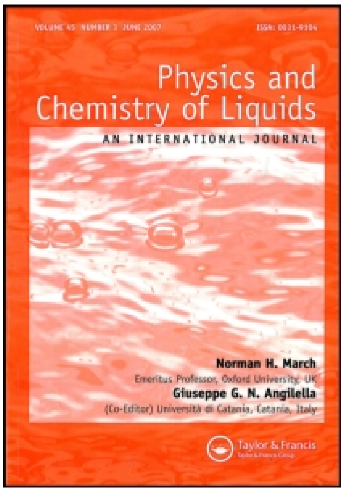

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PREFERENTIAL SOLVATION OF SILVER (I) CRYPTAND 2,2,2 PERCHLORATE COMPLEX IN WATER-PYRIDINE AND WATER-DMSO MIXTURES

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The preferential solvation of silver (I) cryptand 2,2,2 perchlorate complex has been studied in water-dimethylsulphoxide and water-pyridine mixtures by Gibbs transfer energy and solvent transport number measurements. While the Gibbs transfer energy of silver (I) cryptand 2,2,2 cation continuously decreases, that of the perchlorate ion increases with the addition of organic component in both solvent mixtures.The solvent transport number of the salt passes through a maximum, $\Delta_{Py} = 10.4$ and $\Delta_{DMSO} = 2.5$ at $X_{Py} = 0.35$ and $X_{DMSO} = 0.45$ respectively. These results indicate a heteroselective solvation of the salt with the complex cation being selectively solvated by the organic component and the perchlorate ion by water.

Keywords: Gibbs transfer energy; solvent transport number

The preferential solvation group IB salts like copper [II] [1–4] and silver (I) salts [5–8] and group II B salts like Zn (II) salts [9] in several binary solvent mixtures has been widely investigated in recent years because of their fundamental [10] and technological importance [11]. However, such studies involving metal complexes have scarcely been reported and only very few reports [12–14] are available in literature. Macrocyclic ligands such as cryptands which are capable of encapsulating cations partially or completely are of interest in this context [15, 16] to study the ion solvation characteristics of metal-cryptand complexes. This is because the shielding of the metal ions in

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the three dimensional cavity of the cryptands in the complex may significantly alter the ion-solvent interactions of the complex salt vis a vis the uncomplexed salt. The present study therefore deals with the ion solvation behaviour of a silver (I) cryptand 2,2,2 complex viz silver (I) (cryptand 2,2,2) perchlorate in the two mixed solvents, water-pyridine (Py) and water-dimethylsulfoxide (DMSO) which are known to possess strong solvent – solvent interactions [17, 18], by Gibbs transfer energy and solvent transport number measurements at 30 ± 0.1 °C. The results are compared with those on the uncomplexed salt and also the effect of strong intercomponent interactions on ion solvation of the complex has been examined.

EXPERIMENTAL

The solvents pyridine (E Merck GR) and dimethylsulfoxide (E. Merck) were purified as described previously [4, 8]. The finally distilled sample of pyridine [19] had a boiling point 115 °C and density $d^{25} = 0.9787$ g cm^{-3} and for DMSO [20] the boiling point was 60 °C at 8 mm Hg, density $d^{25} = 1.0956$ g cm^{-3}. Doubly distilled water, prepared in the presence of $KMnO_4$ and KOH, was employed in the preparation of solvent mixtures.

Cryptand 2,2,2 ($C_{18}H_{36}N_2O_6$; 4,7,13,16,21,24-Hexaoxa-1,10-diaza-bicyclo [8, 8, 8] hexacosan) supplied by Merck-Schuchardt was used as received. Silver (I) cryptand 2,2,2 perchlorate complex was prepared [21] by dissolving stoichiometric amounts of silver (I) perchlorate and cryptand 2,2,2 in acetonitrile and evaporating the solution slowly. The crude product was recrystallised twice from acetonitrile and was subjected to elemental analysis, C = 36.79% (Calculated 37.0%), H = 6.26% (Calculated = 6.17%) and N = 5.0% (Calculated = 4.79%).

DETERMINATION OF $\Delta G^0_{t(\mathrm{salt})}$

The standard Gibbs transfer energies of the complex salt in various compositions of water-pyridine and water-DMSO mixtures were determined form solubility measurements at 30 ± 0.1 °C. For this purpose, the solubility of Ag(Cryptand 2,2,2)ClO_4 in various water-pyridine and water-DMSO mixtures was determined by carefully evaporating a known weight of the saturated solution in the given composition and weighing the resultant solid. The details of preparation of the saturated solutions have been described earlier [22]. Separate experiments carried with all the salts in both mixed solvents at various compositions according to the method of Deligny *et al.* [23] showed no indication of solvate formation.

All solubility measurements were carried out twice and the results are accurate to ± 0.5%.

DETERMINATION OF SOLVENT TRANSPORT NUMBER, Δ

The solvent transport number, Δ for the complex salt in both the mixed solvent systems was determined by employing a concentration cell with transference [24] given by

$$\begin{array}{c|c}
\text{Ag}\,|\,\text{Ag(cryptand2,2,2)ClO}_4\text{(satd)} & \text{Ag(cryptand2,2,2)ClO}_4\text{(satd)}\,|\,\text{Ag} \\
X'_{\text{Py}} = 1 - X'_W \text{ or} & X''_{\text{Py}} = 1 - X''_W \text{ or} \\
\text{where } X'_{\text{DMSO}} = 1 - X'_W & X''_{\text{DMSO}} = 1 - X'_W
\end{array} \qquad \text{(I)}$$

in which the two half cells contained saturated solutions of the salt in solvent mixtures differing by 0.1 mole fraction (i.e. $X''_{\text{Py}} - X'_{\text{Py}}$ or $X''_{\text{DMSO}} - X'_{\text{DMSO}} = 0.1$) throughout. All measurements were carried out at 30 ± 0.1 °C.

RESULTS AND DISCUSSION

The solubilities and Gibbs transfer energies of the complex salt in various compositions of water-pyridine and water-DMSO mixtures are given in Table I. The standard Gibbs free energy of transfer of the salt from water to water-py and water to water-DMSO mixtures was calculated from

$$\Delta G^0_{t(\text{salt})} = -RT \ln \frac{K_{\text{sp}}(\text{water} - \text{Py or water} - \text{DMSO})}{K_{\text{sp}}(\text{water})} \qquad (1)$$

TABLE I Solubilities (S) and Gibbs transfer energies (ΔG_t^0) of the [silver (I) cryptand 2,2,2, perchlorate {complex salt} and other salts in water-DMSO and water-pyridine mixtures at 30 °C

			Water-DMSO			
	S/mol kg^{-1}				*ΔG_t^0/kJ mol^{-1}*	
X_{DMSO}	*KIO_3*	*$KClO_4$*	*Complex salt*	*KIO_3*	*$KClO_4$*	*Complex salt*
0.0	0.1470	0.0667	0.0101	0.0	0.0	0.0
0.1	0.0533	0.0523	0.0206	4.8	1.2	−3.4
0.3	0.0130	0.0676	0.0266	11.6	0.1	−4.5
0.5	0.0124	0.1990	0.0413	11.8	−4.7	−6.5
0.7	0.0126	0.3410	0.0938	12.0	−6.9	−10.0
0.9	0.0108	0.3777	0.1220	12.9	−7.0	−10.9
1.0	0.0058	0.7140	0.1350	15.9	−9.7	−11.2

			Water-Pyridine			
	S/mol kg^{-1}				*ΔG_t^0/kJ mol^{-1}*	
X_{Py}	*KIO_3*	*$KClO_4$*	*Complex salt*	*KIO_3*	*$KClO_4$*	*Complex salt*
0.0	0.1470	0.0667	0.0101	0.0	0.0	0.0
0.1	0.0350	0.0623	0.0715	7.0	0.6	−9.0
0.3	0.0070	0.0400	0.1400	15.2	3.6	−10.9
0.5	0.0050	0.0232	0.1320	17.3	7.0	−9.1
0.7	0.0040	0.0133	0.1020	19.5	11.1	−5.1
0.9	0.0033	0.0028	0.0820	21.4	18.3	−1.5
1.0	0.0027	0.0015	0.0760	22.6	21.1	0.1

where K_{sp} refers to the thermodynamic solubility product of the salt in the solvent mixture or the reference solvent (H_2O). The mean activity coefficient data required for the calculation of K_{sp} in equation (1), were obtained by means of the extended Debye-Huckel limiting equation with the ion size parameter $a = 6.2\,\text{Å}$. It is seen (Tab. I) that the solubility of [silver(cryptand 2,2,2)] perchlorate increases from pure water to $X_{Py} = 0.3$ and then decreases. Thus the Gibbs transfer energy of complex salt is negative and decreases upto $X_{Py} = 0.3$ and subsequently becomes less negative (increases) with further addition of pyridine.

In the case of water-DMSO mixtures (Tab. I) the solubility increases continuously with the addition of DMSO. Thus the Gibbs transfer energy of the complex salt is negative and decreases further with addition of DMSO.

The ΔG_t^0 (complex salt) in the two solvent mixtures was split into its respective ionic values by combining with the $\Delta G^0_{t(\mathrm{ClO}_4^-)}$ in various compositions of pyridine and DMSO. The $\Delta G^0_{t(\mathrm{ClO}_4^-)}$ was obtained in both cases from the solubility and Gibbs transfer energy data of potassium iodate and potassium perchlorate at different compositions of pyridine and DMSO which are also recorded in Table I. By combining the $\Delta G^0_{t(KIO_3)}$ with the $\Delta G^0_{t(IO_3^-)}$ data in the two mixed solvents reported earlier [7, 10, 25] on the basis of nLJP method [26], $\Delta G^0_{t(K^+)}$ was calculated which in turn was used with $\Delta G^0_{t(KClO_4)}$ to obtain $\Delta G^0_{t(ClO_4^-)}$. The transfer energy of the [silver(cryptand 2, 2, 2)]$^+$ ion was then calculated using the relation

$$\Delta G^0_t(\text{Ag [cryptand 2, 2, 2]ClO}_4) = \Delta G^0_t(\text{Ag[cryptand 2, 2, 2]}^+) + \Delta G^0_{t(ClO_4^-)} \tag{2}$$

The transfer energy data of all the ions (based on nLJP method) are given in Table II. The ΔG^0_t (Ag[cryptand 2, 2, 2])$^+$ from water to

TABLE II Gibbs transfer energies (ΔG^0_t) of various ions in water-DMSO and water-pyridine mixtures at 30°C

			Water-DMSO $\Delta G^0_t/kJ\ mol^{-1}$		
X_{DMSO}	IO_3^-**	K^+	ClO_4^-	[(*Ag*(*I*) *cryptand* 2, 2, 2)]$^+$	Ag^+
0.0	0.0	0.0	0.0	0.0	0.0
0.1	4.6	0.2	1.0	−4.4	−4.3
0.3	13.9	−2.3	2.4	−6.9	−12.5
0.5	27.7	−15.9	11.2	−17.7	−20.2
0.7	37.7	−25.0	18.1	−28.1	−26.5
0.9	44.6	−31.7	24.7	−35.6	−30.0
1.0	49.4	−33.5	23.8	−35.0	−31.2

			Water-Pyridine $\Delta G^0_t/kJ\ mol^{-1}$		
X_{Py}	IO_3^-***	K^+	ClO_4^-	[(*Ag*(*I*) *cryptand* 2, 2, 2)]$^+$	Ag^+
0.0	0.0	0.0	0.0	0.0	0.0
0.1	8.4	−1.4	2.0	−11.0	−33.4
0.3	20.8	−5.6	9.2	−20.1	−41.4
0.5	32.7	−15.4	22.4	−31.5	−47.6
0.7	43.0	−23.5	34.6	−39.7	−51.3
0.9	51.3	−29.9	48.2	−49.7	−52.6
1.0	55.2	−32.6	53.7	−53.6	−52.8

** Ref. [10].
*** Ref. [4].

water + pyridine mixtures is negative and decreases with the addition of pyridine upto pure pyridine indicating that its transfer from water to aqueous pyridine mixtures is thermodynamically favoured. Thus a preferential solvation of Ag(cryptand 2, 2, 2)$^+$ by pyridine in these mixtures is inferred. The $\Delta G^0_{t(\mathrm{ClO}_4^-)}$ is positive and increases with the addition of pyridine indicating that the perchlorate ion is preferentially hydrated.

Similar results are obtained for the complex silver cation and perchlorate anion in water-DMSO mixtures. Thus a heteroselective solvation of the complex salt with Ag(cryptand 2, 2, 2)$^+$ being selectively solvated by pyridine or DMSO and the anion by water is indicated.

The preferential solvation of Ag(cryptand 2, 2, 2)$^+$ ion by DMSO or Pyridine which is similar to that of the uncomplexed silver cation in both mixed solvents is surprising as one would expect that the effective shielding by the cryptand 2, 2, 2 in the complex cation will hinder [8] Ag$^+$-DMSO or Ag$^+$-Pyridine interactions considerably. Silver ion has strong partially covalent interactions with the nitrogen lone pairs of electrons of cryptand 2, 2, 2 apart from charge-dipole type interactions between the cation and oxygens and nitrogens of cryptand 2, 2, 2 [21].

The transfer of the complex silver cation from water to water-DMSO or water-pyridine results in a weakening of silver cryptand 2, 2, 2 interactions and also enhances Ag$^+$-Py (or DMSO) interactions. This facilitates the enrichment of DMSO or pyridine in the solvation shell of the complex cation. The preferential solvation of [Ag (cryptand 2, 2, 2)]$^+$ by DMSO or pyridine may be explained on the basis that DMSO or pyridine interacts with silver ion through Lewis acid-base interactions and hence is capable of forming strong coordinate bonds. The selective solvation of perchlorate anion by water may be explained on the basis of H-bonded interactions between the anion and the hydrogen atoms of water.

A comparision of ΔG^0_t of the complex cation in water – pyridine mixtures with those in water + DMSO mixtures at any given composition (Tab. II) shows that the values in the former mixtures are more negative than in the latter. Thus the interactions of the complex cation are some what stronger with pyridine than with DMSO. This is presumably due to the much stronger solvent – solvent interactions in water – DMSO [27] than in water – pyridine [18, 28] mixtures as shown by the excess thermodynamic functions of mixing. Further, just as in the case of the uncomplexed cation, the $\Delta G_t^0[\mathrm{Ag(cryptand\ 2,2,2)}]^+$ is quite low and nearly equal to zero around $X_{\mathrm{DMSO}} = 0.1$ indicating that the cation is solvated by water rather than DMSO at low compositions of DMSO which substantiates the above arguments.

Another aspect of the strong water–DMSO interactions is reflected in the observation that the ΔG_t^0's of the cryptand complexed silver cation and the uncomplexed silver ion (Tab. II) do not differ significantly from each other in all compositions of water–DMSO mixtures. On the other hand, the $\Delta G_t^0(\mathrm{Ag}^+)$ is more negative upto $X_{\mathrm{PY}} = 0.7$ in water + pyridine mixtures and subsequently the difference between $\Delta G_t^0[\mathrm{Ag(cryptand\ 2,2,2)}]^+$ and $\Delta G_t^0(\mathrm{Ag}^+)$ is not large at higher compositions. Presumably the strong organic(Py) – organic (cryptand 2, 2, 2 part of the complex cation) interactions at higher compositions of pyridine account for this observation [14].

The solvent transport number Δ of Pyridine or DMSO in these solvent mixtures was calculated from the emf data of the cell (I) described earlier using the expression

$$E = -\frac{RT}{F}\frac{X_A'' - X_A'}{X_A(1 - X_A)}\Delta\left[1 + \frac{\partial \ln f_A}{\partial \ln X_A}\right] \qquad (3)$$

$$(A = \mathrm{DMSO\ or\ Py})$$

where the various terms have their usual meaning [24]. f_A is the activity coefficient of the component A which accounts for the deviation of the solvent mixtures from ideal behaviour and is referred to pure water as the standard state. It was evaluated from the vapor pressure data of water–Pyridine [29] and water–DMSO mixtures [30] reported earlier. The emf of cell (I) and Δ values of DMSO and pyridine for the complex salt in the two solvent systems are given in Table III.

It is observed (Tab. III) that Δ_{PY} is a positive and passes through a maximum $\Delta_{\max} = 10.4$ at $X_{\mathrm{PY}} = 0.35$. In the case of water–DMSO mixtures, the Δ_{DMSO} values are also positive and pass through a maximum $\Delta_{\max} = 2.5$ at $X_{\mathrm{DMSO}} = 0.45$. Thus there is an increase of 10.4 moles of pyridine and 2.5 moles of DMSO for Ag(cryptand 2, 2, 2) perchlorate per Faraday relative to the mean molar velocity of

TABLE III EMF data (cell I) and solvent transport number of Py and DMSO for [silver (I) cryptand 2, 2, 2] perchlorate at 30 °C

	Water-DMSO			*Water-Py*		
X_{DMSO}/Py	$-(\partial \ln f_A/\partial \ln X_A)$	$-E(mv)$	Δ_{DMSO}	$-(\partial \ln f_A/\partial \ln X_A)$	$-E\ (mv)$	Δ_{PY}
0.05	0.175	32.0	0.5	0.667	–	–
0.15	0.245	20.0	0.8	0.667	43.5	6.4
0.25	0.365	27.5	1.4	0.637	50.0	10.0
0.35	0.515	40.6	2.3	0.556	55.0	10.4
0.45	0.705	45.0	2.5	0.556	47.0	10.1
0.55	0.920	44.3	2.2	0.444	55.0	9.3
0.65	1.155	50.0	2.0	0.421	27.0	4.1
0.75	1.235	37.2	1.2	0.316	–	–
0.85	1.235	37.0	0.8	0.250	24.0	1.6
0.95	1.235	42.0	0.3	0.100	38.0	0.8

the respective solvent mixtures as reference [31] in the cathode compartment when solutions of the complex salt are electrolysed in water–pyridine and water–DMSO mixtures at the above compositions.

The transport of pyridine or DMSO into the cathode compartment occurs through the transport of $[\mathrm{Ag(cryptand\ 2,2,2)}]^+$ ions along with their solvation shells into the cathode while the anions transport water into the anode. These two effects add together and large positive Δ values arise. This observation clearly indicates that the silver (cryptand 2, 2, 2) perchlorate is also heteroselectively solvated in these mixtures with the complex cation being preferred by pyridine or DMSO and the perchlorate ion by water.

Δ is a composite quantity due the cation and anion and is given by

$$\Delta = \Delta_+ - \Delta_- = (X_W n_A^+ - X_A n_W^+)t_+ - (X_W n_A^- - X_A n_W^-)t_- \qquad (4)$$

where X's are the mole fractions of solvent components (W = water, A = Pyridine or DMSO), n's are solvation numbers of cation and anion due to the two solvent components and t's the respective transport numbers of cation and anion. For heteroselectively solvated salts n_A^+ and n_W^- are large while n_A^- and n_W^+ are small thus giving large Δ values as observed in the present experiments.

A comparison of Δ_{DMSO} and Δ_{Py} in the two solvent mixtures shows that Δ_{Py} is much larger than Δ_{DMSO} at any given composition. Similarly, the Δ for the complex salt in water–pyridine mixtures is much higher than that of an uncomplexed salt like silver bromate while the difference in Δ's between them in water – DMSO mixtures is quite small.

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