

Ion-solvent interactions of some silver salts in N,N-dimethyl formamide-water mixtures at 30°C

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Abstract. The solvation behaviour of the salts, silver bromate, silver acetate and silver sulphate has been investigated in the binary mixtures of N,N-dimethyl formamide (DMF) and water. The Gibbs energies of transfer of these salts from water to water-DMF mixtures have been calculated from the solubilities of the salts in these mixtures. The transfer free energies of the salts were split into their ionic contributions by using the transfer-free energy of the silver ion in these mixtures obtained on the basis of negligible liquid junction potential (nLJP) method from independent EMF measurements. The solvent transference number, Δ of DMF, was determined by EMF measurements using a suitable galvanic cell with transference. The results have been interpreted in terms of a heteroselective solvation of the salts with the silver ion selectively solvated by DMF and the anions by water.

Keywords. Selective solvation; water-dimethyl formamide mixtures; solubility; EMF method; silver bromate; silver acetate; silver sulphate.

1. Introduction

The determination of solvent transport number, Δ is an important approach to obtain information (Schneider 1976) on the composition of solvation shells of ions in mixed solvents. Δ is defined as the change in the number of moles of one solvent component in the cathode compartment relative to the mean molar velocity of the solvent mixture as reference when one Faraday of electricity is passed through a cell during electrolysis. Δ will be small (usually < 1) for homoselectively solvated electrolytes whereas it will be large (usually > 1) for heteroselectively solvated electrolytes. Further its sign will also indicate the solvent component that preferentially solvates the ions.

Despite the fact that selective solvation of ions in some binary amphiprotic dipolar aprotic solvent mixtures has been studied (Subramanian *et al* 1981; Giridhar and Kalidas 1982), very few results have been reported (Stroka and Schneider 1980; Giridhar and Kalidas 1983) dealing with N,N-dimethyl formamide (DMF) as one of the dipolar aprotic components. Both DMF and water are associated liquids and their heat of mixing is exothermic indicating strong inter component interactions. Although no data on excess thermodynamic quantities such as Gibbs energy or entropy of mixing are available, hydrogen bonded complexes (Singh *et al* 1977) between DMF and water molecules of the type $\text{DMF} \cdot n\text{H}_2\text{O}$ where $n = 2$ to 4 have been suggested. Despite such strong solvent-solvent interactions, DMF-water mixtures conform to Raoult's law at temperatures around 90°C (Ivanova and Geller 1961) and presumably this behaviour is also valid at lower temperatures. The present paper reports the effect of such solvent

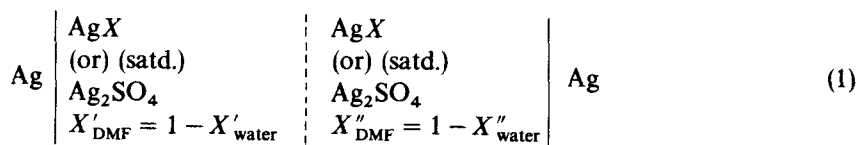
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mixtures having strong interactions among themselves on ion solvation *vis a vis* the solvent mixtures possessing weak interactions among the components. The results of the solvation behaviour of some silver salts such as silver sulphate, bromate and acetate in DMF-water mixtures at 30°C by solvent transport number measurements and by determination of Gibbs energies of transfer of the ions in these mixtures are reported.

2. Experimental

DMF (BDH, LR) after a preliminary distillation under vacuum was dried over anhydrous copper sulphate for a week and distilled under vacuum following the procedure of Faulkner and Bard (1968). It has a boiling point of 45°C at 15 mm Hg pressure, $d^{25} = 0.9441 \text{ g cm}^{-3}$, $n_D^{25} = 1.4269$, sp. conductivity = $1.05 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ in agreement with literature values (Geller 1961).

Doubly-distilled conductivity water was used in the preparation of solvent mixtures. Silver acetate and silver sulphate (S. Merck, Baroda) were dried over P_2O_5 under vacuum before use. Their purity was checked by estimation of their silver content by potentiometry. Silver bromate prepared as described earlier (Janardhanan and Kalidas 1980) was used. The solubility of the salts in various compositions of solvent mixtures was determined potentiometrically as described previously (Kalidas and Sivaprasad 1979). The solvent transport number, Δ has been determined by employing a galvanic cell with transference according to the method of Wagner (1966).



(where $X = \text{BrO}_3$ (or) OAc) and EMF measurements on cell (1) were carried out with a solid state electrometer (Keithley Model 602) over the complete range of water-DMF mixtures keeping the molefraction difference, $(X''_{\text{DMF}} - X'_{\text{DMF}})$ constant throughout. The silver electrodes required for EMF measurements were always prepared afresh according to Carmody (1928). All measurements were carried out at $30 \pm 0.1^\circ\text{C}$.

3. Results and discussion

The Gibbs transfer energy of the salt (from water to its mixtures with DMF) can be calculated from the solubility data by using the relation

$$\Delta G_t^0(\text{salt}) = -2.303 RT \log \frac{K_{SP}(\text{solvent})}{K_{SP}(\text{water})}, \quad (1)$$

and the results are given in tables 1-3. The solubilities of silver bromate and silver acetate are related to the respective thermodynamic solubility products by

$$K_{SP} = S^2 \gamma_{\pm}^2, \quad (2)$$

and for silver sulphate,

$$K_{SP} = 4S^3 \gamma_{\pm}^3, \quad (3)$$

Table 1. Solubility of silver (I) bromate and Gibbs transfer free energies of AgBrO_3 , Ag^+ and BrO_3^- from water to water-DMF mixtures at 30°C (molal scale).*

Mole fraction of DMF (X_{DMF})	Solubility of $\text{AgBrO}_3 \times 10^3$ (mol kg ⁻¹)	$\Delta G_f^\circ(\text{AgBrO}_3)$ (kJ mol ⁻¹)	$\Delta G_f^\circ(\text{Ag}^+)$ (kJ mol ⁻¹)	$\Delta G_f^\circ(\text{BrO}_3^-)$ (kJ mol ⁻¹)
0	10.2	0	0	0
0.1	5.26	3.2 ± 0.02	-2.3 ± 0.01 (-3.5)	5.5 ± 0.03
0.2	3.68	5.1 ± 0.05	-4.4 ± 0.01 (-8.6)	9.5 ± 0.06
0.3	2.19	7.7 ± 0.04	-6.2 ± 0.01 (-12.6)	13.9 ± 0.05
0.4	1.83	8.6 ± 0.04	-7.8 ± 0.01 (-14.4)	16.4 ± 0.05
0.5	1.31	10.2 ± 0.04	-9.1 ± 0.01 (-15.4)	19.3 ± 0.05
0.6	0.90	12.1 ± 0.01	-10.2 ± 0.01 (-16.4)	22.3 ± 0.02
0.7	0.62	14.0 ± 0.01	-11.1 ± 0.01 (-17.4)	25.1 ± 0.02
0.8	0.52	14.9 ± 0.01	-11.6 ± 0.01 (-18.6)	26.5 ± 0.02
0.9	0.34	17.0 ± 0.01	-12.1 ± 0.01 (-19.6)	29.1 ± 0.02
1.0	0.21	19.5 ± 0.01	-11.7 ± 0.01 (-20.6)	31.2 ± 0.02

* The values in parenthesis in tables 1-3 correspond to the one determined on the basis of reference electrolyte method by Kundu and Parker (1981).

Table 2. Solubility of silver(I) acetate and Gibbs transfer free energies of AgOAc , Ag^+ and OAc^- from water to water-DMF mixtures at 30°C (molal scale).*

Mole fraction of DMF (X_{DMF})	Solubility of $\text{AgOAc} \times 10^3$ (mol kg ⁻¹)	$\Delta G_f^\circ(\text{AgOAc})$ (kJ mol ⁻¹)	$\Delta G_f^\circ(\text{Ag}^+)$ (kJ mol ⁻¹)	$\Delta G_f^\circ(\text{OAc}^-)$ (kJ mol ⁻¹)
0	72.0	0	0	0
0.1	29.4	4.3 ± 0.01	-2.3 ± 0.01 (-3.5)	6.6 ± 0.02
0.2	12.5	8.5 ± 0.01	-4.4 ± 0.01 (-8.6)	12.9 ± 0.02
0.3	5.88	12.1 ± 0.03	-6.2 ± 0.01 (-12.6)	18.3 ± 0.04
0.4	3.05	15.4 ± 0.01	-7.8 ± 0.01 (-14.4)	23.2 ± 0.02
0.5	1.58	18.7 ± 0.01	-9.1 ± 0.01 (-15.4)	27.8 ± 0.02
0.6	1.44	19.2 ± 0.02	-10.2 ± 0.01 (-16.4)	29.4 ± 0.03
0.7	1.32	19.6 ± 0.03	-11.1 ± 0.01 (-17.4)	30.7 ± 0.04
0.8	0.72	22.6 ± 0.01	-11.6 ± 0.01 (-18.6)	34.2 ± 0.02
0.9	0.48	24.6 ± 0.05	-12.1 ± 0.01 (-19.6)	36.7 ± 0.06
1.0	0.62	23.4 ± 0.01	-11.7 ± 0.01 (-20.6)	35.1 ± 0.02

*

where γ_{\pm} is the mean molal activity coefficient of the electrolyte under consideration calculated from the extended Debye-Hückel equation with $a = 6.5 \text{ \AA}$ for silver bromate and silver sulphate and $a = 7 \text{ \AA}$ for silver acetate. The Gibbs transfer energy of silver ion from water to water-DMF mixtures was determined on the basis of negligible liquid junction potential method proposed by Alexander *et al* (1972). The same quantity reported (Kundu and Parker 1981) on the basis of reference electrolyte method at 25°C is also given in tables 1-3 for comparison. The transfer-free energy of

Table 3. Solubility of silver(I) sulphate and Gibbs transfer free energies of Ag_2SO_4 , Ag^+ and SO_4^{2-} from water to water-DMF mixtures at 30°C (molal scale).*

Molefraction of DMF (X_{DMF})	Solubility of $\text{Ag}_2\text{SO}_4 \times 10^3$ (mol kg^{-1})	$\Delta G_r^0(\text{Ag}_2\text{SO}_4)$ (kJ mol^{-1})	$\Delta G_r^0(\text{Ag}^+)$ (kJ mol^{-1})	$\Delta G_r^0(\text{SO}_4^{2-})$ (kJ mol^{-1})
0	29.3	0	0	0
0.1	6.4	11.0 ± 0.02	-2.3 ± 0.01 (-3.5)	15.6 ± 0.04
0.2	1.4	22.3 ± 0.02	-4.4 ± 0.01 (-8.6)	31.1 ± 0.04
0.3	0.64	28.1 ± 0.02	-6.2 ± 0.01 (-12.6)	40.5 ± 0.04
0.4	0.19	37.2 ± 0.02	-7.8 ± 0.01 (-14.4)	52.8 ± 0.04
0.5	0.13	40.1 ± 0.08	-9.1 ± 0.01 (-15.4)	58.3 ± 0.10
0.6	0.08	43.6 ± 0.02	-10.2 ± 0.01 (-16.4)	64.0 ± 0.04
0.7	0.06	45.7 ± 0.02	-11.1 ± 0.01 (-17.4)	67.9 ± 0.04
0.8	0.053	46.8 ± 0.02	-11.6 ± 0.01 (-18.6)	70.0 ± 0.04
0.9	0.048	47.5 ± 0.02	-12.1 ± 0.01 (-19.6)	71.7 ± 0.04
1.0	0.041	48.7 ± 0.02	-11.7 ± 0.01 (-20.6)	72.1 ± 0.04

the salt is related to the transfer energies of the corresponding ions by

$$\Delta G_r^0(\text{Ag}X) = \Delta G_r^0(\text{Ag}^+) + \Delta G_r^0(X^-), \quad (4)$$

where $X^- = \text{BrO}_3^-$ and OAc^- in the case of silver bromate and acetate and for silver sulphate, it is given by

$$\Delta G_r^0(\text{Ag}_2\text{SO}_4) = 2\Delta G_r^0(\text{Ag}^+) + \Delta G_r^0(\text{SO}_4^{2-}). \quad (5)$$

It is seen (tables 1–3) that the solubility of all the three salts decreases continuously with the addition of DMF excepting for silver acetate where there is a slight rise in pure DMF. A comparison of these results with those obtained in the related DMF-methanol system shows a completely different behaviour for the three salts. Whereas the solubility of silver bromate increases continuously up to $X_{\text{DMF}} = 0.9$ and then shows a slight decrease in the pure solvent, an exactly opposite variation is observed (Giridhar and Kalidas 1983) for silver acetate in DMF-methanol mixtures. In silver sulphate the solubility passes (Stroka and Schneider 1980) through a maximum at $X_{\text{DMF}} = 0.6$ and then decreases. In acetonitrile-water mixtures where the solvent-solvent interactions are weak and the system shows positive deviation from Raoult's law (Vierk 1950), the solubility of silver sulphate, silver bromate and silver acetate passes through a maximum on the addition of acetonitrile and then decreases. The transfer-free energy of all the three salts continuously increases with the addition of DMF in water-DMF mixtures. The transfer-free energy of the silver ion, is, however negative and continuously decreases down to $X_{\text{DMF}} = 0.9$ and then shows a slight increase in pure DMF, with the sign remaining unaffected. A similar observation is noted for the variation of the free energy of transfer of silver ion from methanol to methanol-DMF mixtures (Giridhar and Kalidas 1983). Thus the transfer of silver ion from water to water-DMF mixtures is a favourable process indicating that the silver ion is preferentially solvated by DMF. The preferential solvation of silver ion by DMF in these mixtures can be rationalised on the basis of the specific backbonding interactions between the d^{10} cation and the π^* orbitals of the carbonyl double bond in DMF. On the other hand, the transfer-free energies of all the anions are seen to be positive and increase continuously

with the addition of DMF. The large ΔG_t^0 values in sulphate compared to the bromate and acetate reflect the stronger ion-solvent interactions of this doubly-charged ion with water compared to that of singly-charged ions. Thus the transfer of anions from water to water-DMF mixtures is not favoured and points to a preferential hydration of the anions by water. This may be attributed to the strong H-bonding interactions between the anions and water molecules. A comparison of the transfer-free energies of the silver ion and the anions on the nLJP and reference electrolyte method (tables 1-3) shows that silver ion is more strongly solvated by DMF and the anions by water with respect to reference electrolyte method.

If, however, the transfer-free energies of the ions on the basis of ferrocene reference method are considered (Barraqué *et al* 1968), an even stronger solvation of cations by DMF and anions by water may be inferred. Thus a heteroselective solvation of the salts in these mixtures is indicated irrespective of whatever extra thermodynamic assumption is used for comparing the transfer energies of single ions.

The solvent transport number, Δ of DMF in these mixtures was calculated from the EMF data on the cell (1) using the expression,

$$E = -(RT/F) [(X''_{DMF} - X'_{DMF})/X_{DMF}(1 - X_{DMF})] \cdot \Delta \cdot (1 + \partial \ln f_{DMF} / \partial \ln X_{DMF}), \tag{6}$$

where the various terms have their usual significance (Janardhanan and Kalidas 1982). The last term in (6) represents the variation of the rational activity coefficient of DMF with solvent composition. Since the water-DMF system behaves ideally at 90°C (Ivanova and Geller 1961) and since no vapour pressure data for this system are available in literature it has been tacitly assumed that no significant departures from ideality arise for this system at 30°C and hence the activity coefficient term has been taken to be zero at all compositions in these mixtures. The EMF data of cell (1) and the calculated Δ values of DMF for the three salts are given in table 4. It is seen that the Δ values for all the three salts are positive throughout and pass through a maximum ($\Delta_{max} = 3$ at $X_{DMF} \approx 0.55$) for silver sulphate, ($\Delta_{max} = 2.5$ at $X_{DMF} \approx 0.35$) for silver bromate ($\Delta_{max} = 2.1$ at $X_{DMF} \approx 0.55$) for silver acetate respectively. Δ is given by

$$\Delta = [(X_w n_D^+ - X_D \cdot n_w^+)t_+ - (X_w n_D^- - X_D n_w^-)t_-], \tag{7}$$

Table 4. EMF data and solvent transference number, Δ of DMF for AgBrO₃, AgOAc and Ag₂SO₄ in water-DMF mixtures at 30°C.

X_{DMF}	AgBrO ₃		AgOAc		Ag ₂ SO ₄	
	$-E^*$ (mV)	Δ	$-E^*$ (mV)	Δ	$-E^*$ (mV)	Δ
0.15	2.5	0.1	10.4	0.5	4.1	0.2
0.25	7.8	0.6	8.3	0.6	10.3	0.7
0.35	28.5	2.5	9.5	0.8	13.5	1.1
0.45	25.5	2.4	10.8	1.0	23.8	2.3
0.55	7.8	0.8	22.3	2.1	32.0	3.0
0.65	7.3	0.7	16.5	1.4	14.0	1.2
0.75	5.6	0.4	13.8	1.0	9.3	0.7
0.85	4.2	0.2	6.2	0.3	9.6	0.5
0.95	2.2	0.0	2.6	0.1	4.0	0.1

* Accurate up to ± 1 mV.

where X refers to the molefractions, n the solvation numbers of water (W) and DMF (D) and t the Hittorf transport numbers of cation and anion. In heteroselective solvation n_D^+ and n_W^- are large while the other two solvation numbers are small resulting in large positive Δ values as described earlier. Thus there is an increase of 3, 2.5 and 2.1 moles of DMF for silver sulphate, silver bromate and silver acetate respectively per Faraday relative to the mean molar velocity of solvent mixture as reference in the cathode compartment when solutions of these salts are electrolysed in water-DMF mixtures at the given composition. The enrichment of DMF in the cathode compartment arises largely through its transport by the silver ion while the anion transports water in the opposite direction, *i.e.* towards anode. These two effects add together and thus a heteroselective solvation results in large Δ values. These results support the conclusion based on the transfer energy variation of the ions obtained earlier.

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