Selective Solvation of Silver(I) Acetate and Sulfate in Acetone – DMF Mixtures at 30 °C**

By

V. V. Giridhar and C. Kalidas*

Department of Chemistry, Indian Institute of Technology, Madras-600036, India

Selective solvation / Solvent transference number / Solubility / Emf measurements

The selective solvation of silver(I) sulfate and acetate has been investigated in the binary mixtures of N,N-dimethylformamide (DMF) and acetone at 30 °C by Gibbs energies of transfer and solvent transport number measurements. The Gibbs transfer energy of silver acetate from acetone to acetone + DMF mixtures increases upto $x_{DMF} = 0.1$ and thereafter decreases continuously upto pure DMF. The transfer energy of silver sulfate under the same conditions is negative and continuously decreases with the addition of DMF. While the Gibbs energy of transfer of silver(I) ion is negative and decreases continuously with the addition of DMF (on the basis of negligible liquid junction potential method) the transfer energies of both the anions are positive and continuously increase upto $x_{DMF} = 0.5$. At $x_{DMF} > 0.6$, however, the transfer energy of the sulfate ion is nearly constant till $x_{DMF} = 0.8$ and then decreases somewhat whereas that of the acetate ion is almost constant.

The solvent transport number Δ, of DMF for both the salts passes through a maximum at $x_{DMF} = 0.35$ with $\Delta_{max} = 7.2$ for silver acetate and $\Delta_{max} = 11.5$ for silver sulfate. These results suggest that both the salts are heteroselectively solvated in these mixtures with the silver ion being preferentially solvated by DMF and the anions by acetone.

Die auswählende Solvatation von Silber(I)-sulfat und -acetat wurde bei 30 °C in Gemischen von N,N-dimethylformamid (DMF) und Aceton mit Hilfe der Gibbs-Überführungsenergie und der Solvens-Überführungszahl untersucht. Die Gibbs-Überführungsenergien ΔG_t^0 von Aceton zu Aceton-DMF-Mischungen des Molenbruchs x_{DMF} besitzen für Silberacetat bei $x_{DMF} = 0,1$ ein positives Maximum, für Silbersulfat sind sie stets negativ. Für beide Salze fallen sie bis zu $x_{DMF} = 1$ auf stark negative Werte. ΔG_t^0 von Ag-Ionen (gemessen mit vernachlässigtem Potential an der Flüssigkeitsphasengrenze) ist stets negativ und sinkt mit wachsendem Gehalt an DMF.

---

* To whom correspondence should be addressed
** Dedicated to Prof. H. Strehlow on the occasion of his 65th birthday

Dagegen sind die ΔG_t^0 beider Anionen positiv und steigen bis $x_{DMF} = 0,5$. Zwischen $x_{DMF} = 0,6$ und 0,8 bleibt ΔG_t^0 des Sulfations konstant und sinkt darüber hinaus wieder ab, während ΔG_t^0 des Acetations sich nicht mehr ändert.

Die Solvens-Überführungszahl Δ von DMF besitzt bei beiden Salzen ein Maximum bei $x_{DMF} = 0,35$. Δ_{max} beträgt für Silberacetat 7,2, für Silbersulfat 11,5. Die Resultate legen eine heteroselektive Solvatation beider Salze in diesen Gemischen nahe, wobei Silberionen bevorzugt durch DMF, die Anionen bevorzugt durch Aceton solvatisiert sind.

Introduction

The importance of selective solvation studies of electrolytes in binary mixed solvents has been well recognised [1-4]. Such investigations have frequently been carried out in solvent mixtures consisting of a dipolar aprotic solvent and a protic solvent [5-9]. Binary mixtures of dipolar aprotic solvents have some advantages [10] from a theoretical view point in these studies and Cox and Waghorne [11] have discussed this aspect in considerable detail in a recent review.

Gill and Schneider [12] have made an exhaustive study of the physico-chemical properties of the binary dipolar aprotic DMF-acetone mixtures and concluded that they are nearly ideal. In the present work, we have undertaken a study of the selective solvation behaviour of two silver(I) salts *viz.*, silver sulfate and acetate in DMF + acetone mixtures and the results are compared with those obtained earlier [13-15] in the related DMF + water and DMF + methanol mixtures which are known to possess strong solvent-solvent interactions in order to consider the effect of replacement of a protic by a dipolar aprotic component.

Experimental

Solvents and salts

DMF (BDH, LR)* after a preliminary vacuum distillation was dried over anhydrous copper sulfate for a week and again distilled under vacuum following the procedure of Faulkner and Bard [16]. The fraction boiling at 45 °C under 15 mm Hg pressure was collected and stored out of contact with air. It had $d^{25} = 0.9441$ g cm^{-3}, $n_D^{25} = 1.4269$, Sp. conductivity $= 1.05 \times 10^{-7}$ ohm^{-1} cm^{-1} at 25 °C in good agreement with literature values [17]. Acetone (BDH, AR)* was refluxed with KMnO$_4$ for 5 hrs. and then distilled onto dried molecular sieves (5 Å). A further distillation followed and the fraction boiling at 56.2 °C was collected following the method of Salomon [18].

---

* British Drug House, Ltd; laboratory reagents resp. analytical reagents.

Silver sulfate and acetate (S. Merck, Baroda) were dried over P_2O_5 under vacuum before use.

Results and discussion

Solubility measurements

The solubility of silver acetate over the whole range of solvent compositions and that of silver sulfate at $x_{DMF} \geq 0.6$ was determined potentiometrically exactly as described previously [19]. Since the solubility of silver sulfate in the composition range $0 \leq x_{DMF} \leq 0.5$ was found to be low, its solubility in the range upto $x_{DMF} = 0.5$ was determined by employing the concentration cell similar to that used by Kalidas and Schneider [20].

| Ag | Ag₂SO₄ (saturated) in solvent 'S' | TEAP 0.1 m in solvent 'S' | AgNO₃ 0.005 m in solvent 'S' | Ag |
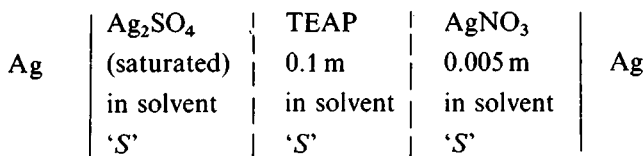
Scheme I

in which a 0.1 m solution of tetraethylammonium picrate (TEAP) was used as a bridge electrolyte. The emf of cell(I) is related to the activity of silver ions in the saturated solution of the salt by

$$E = \frac{RT}{F} \ln \left[\frac{(a_{Ag^+})_{ref}}{(a_{Ag^+})_{satd.\ solution}} \right]. \tag{1}$$

Using the solubility data, the Gibbs transfer free energies of the salts (from acetone to its mixtures with DMF) in different solvent mixtures (S) were calculated by employing the equation

$$\Delta G_t^0 (Salt) = -2.303\ RT \log \left[\frac{K_{sp}(S)}{K_{sp}(R)} \right] \tag{2}$$

where (R = acetone).

The solubilities (C) of silver acetate and silver sulfate are related to the respective thermodynamic solubility products by

$$K_{sp}(AgOAc) = \gamma_\pm^2 C^2 \tag{3}$$

and

$$K_{sp}(Ag_2SO_4) = 4\gamma_\pm^3 C^3 \tag{4}$$

where $\gamma_\pm$ is the mean molal activity coefficient of the electrolyte calculated from the extended Debye-Hückel equation with ion-size parameter $a = 7.0$ Å for silver sulfate and silver acetate.

The transfer energies of the salts were split into their ionic contributions by using the transfer energy data on silver ion in these mixtures as determined by the negligible liquid junction potential (nLJP) method of Alexander et al. [21]. The cell

$$
\text{Ag} \quad \left| \begin{array}{c} \text{AgClO}_4 \\ 0.01 \text{ m} \\ (\text{AN}) \end{array} \right| \begin{array}{c} \text{TEAP} \\ 0.1 \text{ m} \\ (\text{AN}) \end{array} \left| \begin{array}{c} \text{AgClO}_4 \\ 0.01 \text{ m} \\ R \text{ or } S \end{array} \right| \quad \text{Ag}
$$
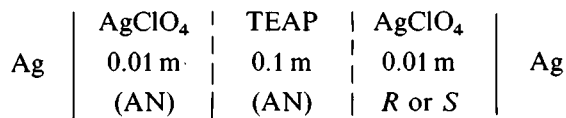
Scheme II

was employed for this purpose where R and S have the same significance as mentioned earlier.

The Gibbs transfer energy of silver ion from acetone to its mixtures with DMF is given by

$$\Delta G_t^0(\text{Ag}^+) = F(E_S - E_R) - RT \ln \left[\frac{a_{\text{Ag}^+}(S)}{a_{\text{Ag}^+}(R)} \right] \tag{5}$$

where E_R and E_S refer to the emf of cell (II) in acetone and solvent mixtures respectively.

The transfer energies of the anions were then computed from the relations
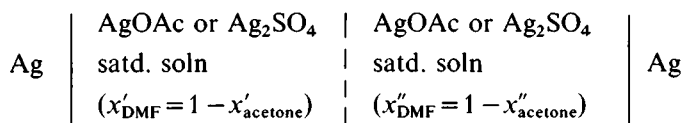
$$\Delta G_t^0(\text{AgOAc}) = \Delta G_t^0(\text{Ag}^+) + \Delta G_t^0(\text{OAc}^-) \tag{6}$$

and

$$\Delta G_t^0(\text{Ag}_2\text{SO}_4) = 2\Delta G_t^0(\text{Ag}^+) + \Delta G_t^0(\text{SO}_4^{2-}) \tag{7}$$

The transfer energies of the salts and respective ions are given in Table 2.

The solvent transport number (Δ) of DMF was determined according to the method of Wagner [22] using the following cell with transference

$$
\text{Ag} \quad \left| \begin{array}{c} \text{AgOAc or Ag}_2\text{SO}_4 \\ \text{satd. soln} \\ (x'_{\text{DMF}} = 1 - x'_{\text{acetone}}) \end{array} \right| \begin{array}{c} \text{AgOAc or Ag}_2\text{SO}_4 \\ \text{satd. soln} \\ (x''_{\text{DMF}} = 1 - x''_{\text{acetone}}) \end{array} \quad \left| \quad \text{Ag} \right.
$$

Scheme III

The emf of this cell is related to Δ by

$$E = -\left(\frac{RT}{F} \right) \frac{(x''_{\text{DMF}} - x'_{\text{DMF}})}{x_{\text{DMF}}(1 - x_{\text{DMF}})} \cdot \Delta \cdot \left[1 + \frac{\partial \ln f_{\text{DMF}}}{\partial \ln x_{\text{DMF}}} \right] \tag{8}$$

where the various terms have their usual significance. The activity coefficient term in equation (8) was calculated from the vapour pressure data of acetone-

Table 1. Solubilities 'C', mean molal activity coefficients, $\gamma_\pm$, and thermodynamic solubility product, K_{sp}, for silver sulfate and acetate in acetone-DMF mixtures at 30 °C

x_{DMF}	Dielectric constant 'D' of the solvent mixture	Solubility of Ag_2SO_4[a] $\times 10^6$/mol Kg^{-1} C	$\gamma_\pm$	K_{sp}	Solubility of AgOAc[a] $\times 10^4$/mol Kg^{-1} C	$\gamma_\pm$	K_{sp}
0	20.3	0.65	0.976	1.02×10^{-18}	0.63	0.935	3.47×10^{-9}
0.1	22.0	1.05	0.973	4.27×10^{-18}	0.45	0.951	1.83×10^{-9}
0.2	23.5	1.50	0.971	1.24×10^{-17}	0.76	0.943	5.14×10^{-9}
0.3	25.1	1.70	0.972	1.80×10^{-17}	0.91	0.943	7.36×10^{-9}
0.4	26.8	2.35	0.970	4.74×10^{-17}	0.95	0.948	8.11×10^{-9}
0.5	28.4	3.00	0.969	9.84×10^{-17}	1.51	0.940	2.01×10^{-8}
0.6	30.1	7.20	0.957	1.31×10^{-15}	2.30	0.933	4.60×10^{-8}
0.7	31.8	9.60	0.954	3.07×10^{-15}	2.77	0.933	6.68×10^{-8}
0.8	33.3	13.0	0.951	7.55×10^{-15}	2.88	0.936	7.27×10^{-8}
0.9	35.0	27.0	0.935	6.44×10^{-14}	3.47	0.935	1.05×10^{-7}
1.0	36.5	41.0	0.926	2.19×10^{-13}	6.15	0.921	3.21×10^{-7}

[a] Solubilities accurate to ±1%

DMF mixtures reported in the literature [23]. These data together with the emfs of the cell (III) and the calculated Δ values for the two salts are given in Table 3.

Discussion

The solubilities of both silver sulfate and silver acetate increase continuously with the addition of DMF except for silver acetate at $x_{DMF} = 0.1$ where it shows a slight decrease initially (Table 1). Thus the Gibbs transfer energy of silver acetate shows a small positive value at $x_{DMF} = 0.1$ and thereafter is negative and decreases continuously with the addition of DMF (Table 2). But for silver sulfate, the transfer energy is negative and decreases continuously with the addition of DMF (Table 2). In the related $DMF - H_2O$-mixtures [13], also in $DMSO - H_2O$-mixtures [5, 24] an opposite variation is observed. This is most presumably due to the strong solvent-solvent interactions in the latter two systems [25 − 27].

It is seen that the transfer energy of the silver ion, (Table 2), is negative throughout and decreases with the addition of DMF indicating that its transfer from acetone to acetone-DMF mixtures is favourable and thus it is preferentially solvated by DMF. The transfer energies of acetate and sulfate ions are however, positive and increase gradually till $x_{DMF} = 0.5$ and remain nearly constant although a slight decrease is noted for sulfate ion beyond $x_{DMF} = 0.8$. It may be mentioned that the transfer energies of some anions such as chloride, bromide and iodide ions from acetone to DMF obtained by the tetraphenylarsonium tetraphenylborate (TATB) method have been reported to be negative whereas the values for sulfate and acetate ions in this work are seen to be positive. A direct comparison of the results of transfer energies of anions in this work with literature values is rendered difficult because of nonavailability of other data on these ions. However, the conclusions based on transfer energy variation of silver ion and the anions in the present case derive independent support from solvent transport number measurements as shown subsequently. Thus the transfer of anions from acetone to acetone-DMF mixtures is disfavoured which suggests that they are preferentially solvated by acetone in these mixtures. A heteroselective solvation of both the salts may, therefore, be inferred in these mixtures. The preferential solvation of silver ion by DMF in these mixtures may be explained in terms of specific backbonding interactions between the d^{10} cation and π^* orbitals of the carbonyl group in DMF. The specific solvation of the anions by acetone possibly arises through the H-bond formation between these ions and the H atom of the enolic form of acetone molecule. Table 3 shows that the Δ values are positive throughout and pass through a maxima at $x_{DMF} = 0.35$ for both the salts with $\Delta_{max} = 11.5$ for silver sulfate and $\Delta_{max} = 7.2$ for silver acetate. Thus there is an increase of 7.2 and 11.5 moles of DMF for silver acetate and sulfate respectively per faraday relative to the mean molar velocity of solvent

Table 2. *Gibbs transfer free energies, ΔG_t^0, of Ag_2SO_4, $AgOAc$, Ag^+, SO_4^{2-} and OAc^- from acetone to acetone-DMF mixtures at 30 °C*

x_{DMF}	$\Delta G_t^0(Ag_2SO_4)$**/ kJ mol^{-1}	$\Delta G_t^0(AgOAc)$**/ kJ mol^{-1}	$\Delta G_t^0(Ag^+)$*/ kJ mol^{-1}	$\Delta G_t^0(SO_4^{2-})$/ kJ mol^{-1}	$\Delta G_t^0(OAc^-)$/ kJ mol^{-1}
0	0	0	0	0	0
0.1	− 3.61	− + 1.61	− 5.91	8.21	7.52
0.2	− 6.30	− 0.99	−10.14	13.98	9.15
0.3	− 7.25	− 1.90	−13.05	18.85	11.15
0.4	− 9.68	− 2.14	−14.70	19.72	12.56
0.5	−11.52	− 4.43	−17.67	23.82	13.24
0.6	−18.04	− 6.52	−18.94	19.84	12.42
0.7	−20.19	− 7.46	−21.03	21.86	13.57
0.8	−22.46	− 7.67	−21.72	20.98	14.05
0.9	−27.86	− 8.60	−22.89	17.92	14.29
1.0	−30.95	−11.41	−24.48	18.01	13.07

** Accurate to ± 0.08 kJ mol^{-1}
* Accurate to ± 0.2 kJ mol^{-1}

Table 3. *Solvent transport numbers Δ, of DMF in Ag_2SO_4 and $AgOAc$ in the acetone-DMF system at 30 °C*

x_{DMF}	$\dfrac{\partial \ln f_{DMF}}{\partial \ln x_{DMF}}$	Ag_2SO_4		$AgOAc$	
		$-E$(mV)	Δ	$-E$(mV)	Δ
0.05	0.0	105±2	1.9±0.03	20.5±0.5	0.4±0.01
0.25	−0.104	75±2	6.0±0.15	37.0±2	3.0±0.15
0.35	−0.125	115±2	11.5±0.20	72.0±2	7.2±0.20
0.45	−0.117			53.0±1	5.7±0.11
0.55	−0.084	45±1	4.8±0.11	47.0±1	4.9±0.11
0.65	−0.061	42±1	3.8±0.10		
0.75	−0.047			27.5±0.5	2.1±0.04
0.85	−0.021	19±0.5	0.9±0.03	31.0±1	1.5±0.05
0.95	0.0	20±0.5	0.4±0.01		

mixture as reference in the cathode compartment, when solutions of these salts are electrolysed in acetone-DMF mixtures at the given composition.

Δ can be represented in terms of the solvation numbers of the cation and anions (n_{1+}, n_{2+}, n_1n_{2-}) and the transport number of ions as

$$\Delta = (x_1 n_{2+} - x_2 n_{1+})t_+ - (x_1 n_{2-} - x_2 n_{1-})t_- \qquad (9)$$

where subscript 1 refers to acetone and 2 refers to DMF. Detailed interpretation of Δ on the basis of equation (9) is difficult in view of the non-availability of data on ionic transport numbers as well as of ion association in these solvent mixtures. It is assumed that the effect of ion association on Δ is

small and that the variation of Δ with solvent composition is governed mainly by changes of ion-solvation rather than by the transport numbers of the ions. The large positive Δ values for both salts can be explained on the basis that n_{2+} and n_{1-} are large while n_{2-} and n_{1+} are small for such electrolytes. However, the larger Δ values in the case of Ag_2SO_4 as compared to AgOAc are possibly due to a larger contribution of n_{1-} in the case of sulfate ion than acetate ostensibly due to the higher charge on the former. The large increase of DMF in the cathode compartment may be explained as arising due to its transport by silver ion to the cathode while the anion transports acetone in the opposite direction, i.e., towards the anode. The cumulative effect of these two processes leads to large Δ values which can only be due to a heteroselective solvation of the salts. These results therefore support the conclusions based on the transfer energy variation of the ions obtained earlier.

References

1. A. J. Parker, Pure Appl. Chem. **53** (1981) 1437.
2. A. J. Parker and J. Avraamides, Aust. J. Chem. **27** (1974) 477.
3. S. Jayasurya, J. Avraamides and A. J. Parker, Aust. J. Chem. **36** (1983) 1695.
4. I. D. MacLeod, D. M. Muir, A. J. Parker and P. Singh, Aust. J. Chem. **30** (1977) 1423.
5. H. Schneider and A. A. El Harakany, J. Electroanal. Chem. **46** (1973) 255.
6. L. Rodehuser and H. Schneider, Z. Phys. Chem. Neue Folge **200** (1976) 119.
7. S. Janardhanan and C. Kalidas, Bull. Chem. Soc. Japan **53** (1980) 2363.
8. S. Subramanian and C. Kalidas, Electrochim. Acta **29** (1984) 753.
9. V. V. Giridhar and C. Kalidas, J. Solution Chem. **11** (1982) 539.
10. B. G. Cox, A. J. Parker and W. E. Waghorne, J. Phys. Chem. **78** (1974) 1731.
11. B. G. Cox and W. E. Waghorne, Chem. Soc. Rev. **9** (1980) 381.
12. D. S. Gill and H. Schneider, Indian J. Chem. **19A** (1980) 313.
13. V. V. Giridhar and C. Kalidas, Proc. Indian Acad. Sci. (Chemical Sciences) **93** (1984) 795.
14. V. V. Giridhar and C. Kalidas, Indian J. Chem. **22A** (1983) 224.
15. J. Stroka and H. Schneider, Polish J. Chem. **54** (1980) 1805.
16. L. R. Faulkner and A. J. Bard, J. Am. Chem. Soc. **51** (1968) 2901.
17. B. E. Geller, Russ. J. Phys. Chem. **35** (1961) 1090.
18. M. Salomon, J. Electrochem. Soc. **121** (1974) 1584.
19. C. Kalidas and H. Schneider, Z. Phys. Chem. Neue Folge **120** (1980) 1457.
20. C. Kalidas and H. Schneider, Electrochim. Acta **27** (1982) 477.
21. R. Alexander, A. J. Parker and W. E. Waghorne, J. Am. Chem. Soc. **94** (1972) 1148.
22. C. Wagner, *Advances in Electrochemistry and Electrochemical Engg.*, Vol. 4 (Eds. P. Delahay and C. W. Tobias), Wiley Interscience, New York, 1966, pp. 1 –46.
23. K. Quitzch, H. P. Hoffmann, R. Pfestorf and G. Geiseller, J. Prakt. Chem. **34** (1966) 145.
24. S. Janardhanan and C. Kalidas, Monatsh. Chem. **113** (1982) 691.
25. J. Kentamaa and J. J. Lindberg, Suom. Kemistil. **B33** (1960) 3288.
26. G. J. Safford, P. C. Shaffer, P. S. Leung, G. F. Doebbler, G. W. Brady and E. F. X. Lyndon, J. Chem. Phys. **50** (1969) 2140.
27. D. Singh, Lal Bahadur and M. V. Ramana Murti, J. Solution Chem. **6** (1977) 703.