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Preferential Solvation of Ag(I) Bromate and Iodate in Dimethyl Sulfoxide-Water Mixtures

Sivasankaran nair JANARDHANAN and Chatty KALIDAS*
Department of Chemistry, Indian Institute of Technology, Madras 600 036, India

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The selective solvation of Ag(I) bromate and iodate was studied in dimethyl sulfoxide–water mixtures at 30 °C by solubility and EMF measurements. The solubility of silver bromate decreases down to $X_{\mathrm{DMSO}}=0.2$ and thereafter increases with addition of dimethyl sulfoxide, the solubility of silver iodate continuously decreasing under the same conditions. The transfer free energy of silver cation decreases while that of halate ions increases with the addition of dimethyl sulfoxide. The solvent transport number, Δ, passes through a maximum around $X_{\mathrm{DMSO}}=0.5$ in both cases. These results were interpreted in terms of a heteroselective solvation of both the salts, the silver ion being preferentially solvated by dimethyl sulfoxide and the halate ions selectively hydrated by water in the mixtures.

Investigations on ion solvation have largely been confined to aqueous[1)] and pure non-aqueous solvents,[2)] only few studies being carried out[3—5)] in binary mixed solvents. In mixed solvents containing an electrolyte, there are two possibilities[6)] depending on whether (a) both the ions of the electrolyte are solvated by the same solvent component, *i.e.*, a homoselective solvation or (b) one ion is bound more strongly by one solvent component while the other ion prefers the second solvent, *i.e.*, a heteroselective solvation. The present work deals with the selective solvation of two salts. The behavior of silver bromate and silver iodate in DMSO–water mixtures of varying composition was studied by means of electromotive force and solubility measurements in order to study the solvation of these salts and also the effect of solvent-solvent interactions on ion solvation.

Experimental

Materials. Dimethyl sulfoxide (BDH, LR Grade) was purified by the method of Maricle and Hodgson.[7)] The middle fraction boiling at 60 °C under a pressure of 12 mm of Hg was collected and stored out of contact with air. Doubly distilled water was used in the preparation of DMSO–water mixtures. Ferrocene (E. Merck) was purified by sublimation in a vacuum. Silver bromate and silver iodate were prepared by the reaction of silver nitrate with the corresponding potassium salt. The precipitated silver halates were first thoroughly washed with water and then with acetone, and dried in a vacuum at 70—80 °C for several hours. The purity of the salts was checked by estimation of their silver content.

Solubility Measurements. The solubility measurements on the salts were performed at 30±0.1 °C in accordance with the general procedure.[4)] The silver content of the saturated solution was determined by the addition of excess standard aqueous potassium iodide, the remaining potassium iodide being estimated by potentiometric titration with a standard solution of silver nitrate. A Metrohm Multidosimat (Type E 415) automatic titrator in conjunction with a Knick pH meter (for recording the EMF data) was employed. Oxidation of the iodide ion by iodate was found to be negligible.

Electromotive Force Measurements. The concentration cell was of the following type:[8)]

$$\mathrm{Ag}\left|\begin{array}{l:l} x_1'\ \mathrm{H_2O} & x_1''\ \mathrm{H_2O} \\ x_2'\ \mathrm{DMSO} & x_2''\ \mathrm{DMSO} \\ \text{saturated with} & \text{saturated with} \\ \mathrm{AgXO_3} & \mathrm{AgXO_3} \end{array}\right|\mathrm{Ag} \qquad (1)$$

$$\mathrm{X}=\mathrm{Br\ or\ I}$$

EMF measurements were carried out over the complete range of DMSO–water mixtures keeping the mole fraction difference $x_2''-x_2'$ at 0.1. A U-type cell fitted with ground joints at the top and a $\mathrm{G_3}$ frit in the middle to avoid direct contact of the solution was used in the EMF measurements. Silver electrodes freshly prepared according to the method of Carmody[9)] were used. The EMF of cell 1 was measured at 30 °C with a Keithley (Model 602) Solid State Electrometer having an input impedence $>10^{14}\ \Omega$, reproducible with accuracy better than ±1 mV.

Results and Discussion

Solubility Measurements. The solubility and the transfer free energies of the salt (for transfer from water to DMSO–water mixtures) was calculated from the relation

$$\Delta G^{\circ}_{\mathrm{t(salt)}} = 2.303RT\log\frac{K_{\mathrm{sp(water)}}}{K_{\mathrm{sp(solvent)}}} \qquad (2)$$

in different compositions of DMSO–water mixtures for both the salts. The results are given in Table 1, together with the free energy of transfer of silver ion in these mixtures.[11)] The transfer free energy of the salts is related to that of the corresponding ions by

$$\Delta G^{\circ}_{\mathrm{t(AgXO_3)}} = \Delta G^{\circ}_{\mathrm{t(Ag^+)}} + \Delta G^{\circ}_{\mathrm{t(XO_3^-)}}. \qquad (3)$$

The transfer free energies of the anions calculated from Eq. 3 are given in Table 1, the results being plotted in Fig. 1. K_{sp} in Eq. 2 represents the thermodynamic solubility product of the salt in water or the solvent mixtures and the mean activity coefficients required in these calculations were obtained from the extended Debye-Hückel equation with $a=6.5$ Å. The solubility of silver bromate decreases down to $X_{\mathrm{DMSO}}=0.2$ and subsequently increases with the addition of DMSO, the solubility of silver iodate decreasing continuously under the same conditions. Thus $\Delta G^{\circ}_{\mathrm{t(salt)}}$ increases up to $X_{\mathrm{DMSO}}=0.2$ and thereafter decreases down to $X_{\mathrm{DMSO(pure)}}$ in the case of silver bromate; it increases continuously in the case of silver iodate. However, the transfer free energy of silver ion (on the basis of ferrocene reference method, Table 1) shows a continuous decrease with the addition of DMSO, indicating that silver ion is preferentially solvated by DMSO. On the contrary, the transfer free energy of the anions is positive and continuously increases with the addition of DMSO indicating that they are selectively hydrated. Thus a

TABLE 1. SOLUBILITY AND TRANSFER FREE ENERGY DATA FOR $AgBrO_3$ AND $AgIO_3$ IN DMSO–WATER MIXTURES

Mole fraction of DMSO	Solubility of $AgBrO_3$ mol kg^{-1} × 10^2	Solubility of $AgIO_3$ mol kg^{-1} × 10^4	$\Delta G^\circ_{t(AgBrO_3)}$ kcal mol^{-1}	$\Delta G^\circ_{t(AgIO_3)}$ kcal mol^{-1}	$\Delta G^\circ_{t(Ag^+)}$ kcal g-ion^{-1}	$\Delta G^\circ_{t(BrO_3^-)}$ kcal g-ion^{-1}	$\Delta G^\circ_{t(IO_3^-)}$ kcal g-ion^{-1}
0.0	0.98	3.3	0	0	0	0	0
0.1	0.80	3.0	0.24	0.08	−0.61	0.85	0.69
0.2	0.71	2.8	0.37	0.18	−2.52	2.89	2.70
0.3	0.87	2.4	0.15	0.34	−4.30	4.45	4.64
0.4	1.14	2.1	−0.13	0.53	−5.75	5.62	6.28
0.5	1.40	0.73	−0.38	1.78	−7.09	6.71	8.87
0.6	1.84	0.46	−0.68	2.33	−8.00	7.33	10.33
0.7	2.27	0.40	−0.89	2.51	−8.80	7.91	11.31
0.8	2.77	0.25	−1.09	3.05	−9.55	8.41	12.60
0.9	3.33	0.18	−1.27	3.49	−10.10	8.83	13.59
1.0	3.79	0.08	−1.36	4.36	−10.57	9.23	14.92

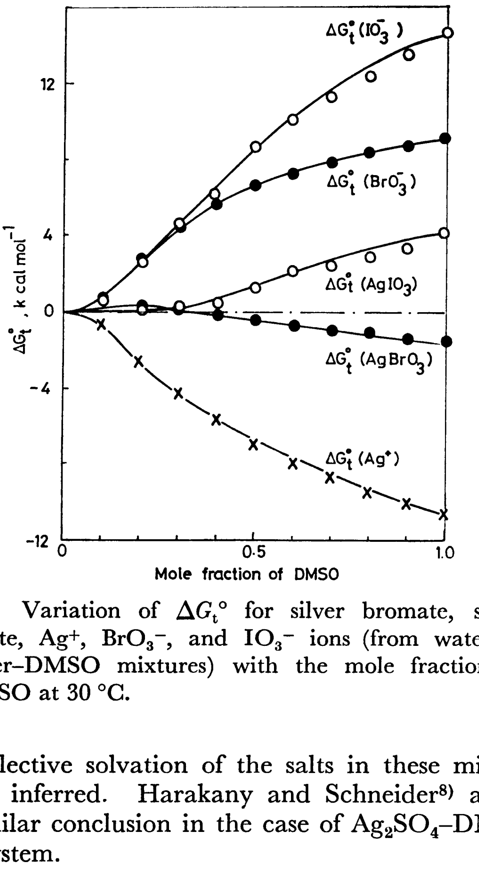

Fig. 1. Variation of ΔG_t° for silver bromate, silver iodate, Ag^+, BrO_3^-, and IO_3^- ions (from water to water–DMSO mixtures) with the mole fraction of DMSO at 30 °C.

heteroselective solvation of the salts in these mixtures may be inferred. Harakany and Schneider[8] arrived at a similar conclusion in the case of Ag_2SO_4–DMSO–water system.

We see from Table 1 that in aqueous solutions containing small amounts of DMSO ($X_{DMSO} \approx 0.1$), $\Delta G^\circ_{t(Ag^+)}$ is nearly equal to zero or slightly negative indicating that Ag^+ ion behaves as if it were in pure aqueous solution because of the strong interactions of DMSO with water molecules at low mole fractions of DMSO.[12,13] These strong solvent-solvent interactions result in a decrease of solubility of both salts at low mole fractions of DMSO. At higher mole fractions of DMSO, the relatively strong hydration of IO_3^- over that of BrO_3^- has a profound effect on the observed solubility of the two salts. The large positive ΔG_t° values of the bromate and iodate ions agree with earlier results,[14] the unusually strong hydration of these ions being attributed to their pyramidal structure with the halogen at the apex.

Solvent-transport Number Δ, from EMF Measurements. The emf data obtained from cell (1) utilised to calculate the solvent transport number, Δ of DMSO in these mixtures is expressed[12] by

$$E = \frac{-RT}{F}\,\frac{(x_2''-x_2')\Delta}{X_2(1-X_2)}\left(1+\frac{\partial \ln f_2}{\partial \ln X_2}\right), \qquad (4)$$

where $X_2=(x_2''+x_2')/2$ and $\partial \ln f_2/\partial \ln X_2$ represents the variation of the activity coefficient of DMSO with the mole fraction in these mixtures, taken from the work of Cox and Mctigue[15] for the calculation of Δ. The other terms have their usual meanings. Δ may be defined as the net increase in the number of moles of DMSO in the cathode compartment, with the mean molar velocity of the solvent mixtures as a reference, when one faraday of electricity is passed through the cell during the course of electrolysis at the given solvent composition. The EMF data, values of $\partial \ln f_2/\partial \ln X_2$ and the calculated Δ values of DMSO in the case of the two salts are given in Table 2 and Fig. 2. The values are positive throughout, passing through a maximum at $X_{DMSO}=0.45$ ($\Delta=1.6$) in the case of silver bromate and at $X_{DMSO}=0.55$ ($\Delta=2.1$) in the case of silver iodate. The Δ_{max} values provide direct information on ion solvation. The considerable positive values of Δ for both salts is in line with the conclusion arrived at from the transfer

TABLE 2. EMF DATA ON CELL (1) AND SOLVENT TRANSPORT NUMBER FOR $AgBrO_3$ AND $AgIO_3$ IN DMSO–WATER MIXTURES AT 30 °C

Mole fraction of DMSO (X_2)	$\frac{\partial \ln f_2}{\partial \ln X_2}$	Silver bromate		Silver iodate	
		$-E$(mV)	Δ	$-E$(mV)	Δ
0.05	1.175	5	0.08	17	0.26
0.15	1.245	20	0.78	20	0.78
0.25	1.365	22	1.16	18	0.95
0.35	1.515	24	1.38	23	1.32
0.45	1.705	29	1.61	30	1.70
0.55	1.920	15	0.74	43	2.12
0.65	2.155	14	0.57	41	1.66
0.75	2.235	9	0.30	36	1.16
0.85	2.235	8	0.18	26	0.57
0.95	2.235	5	0.04	20	0.16

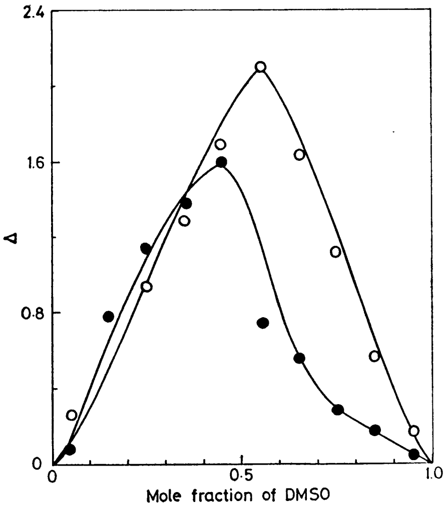

Fig. 2. Variation of solvent transport number, Δ for $AgBrO_3$ (●—●) and $AgIO_3$ (○—○) in water–DMSO mixtures at 30 °C.

free energy data of the two salts in the mixtures. The transport of DMSO into the cathode compartment occurs largely through the silver ion while the anions transport water into the anode compartment. The two effects are combined, characterising the heteroselective solvation with significantly large Δ.

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