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The thermodynamics of a silver–silver ion electrode in dioxan–water and mannitol–water systems at different temperatures

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Abstract

From the electromotive force (e.m.f.) measurements of cells with liquid junction potentials, the standard potentials of a silver electrode were obtained in 5% and 15% (w/w) dioxan–water mixtures at 20, 25, 30 and 35°C, and in 5% (w/w) mannitol–water mixture at 5, 15, 25, and 35°C. The data were used to derive (a) the equation of standard potential for the silver electrode as a function of temperature, (b) the standard thermodynamic quantities for the cell reaction, (c) the standard Gibbs free energy of transfer of Ag^+ ion from water to the mixed solvent, and (d) the primary medium effect of the mixed solvent on the Ag^+ ion The results are discussed in terms of ion solvation in these mixed solvents.

INTRODUCTION

Aqueous–organic solvent systems are of great importance as reaction media. These solvents have an influence on chemical equilibria as well as on the rates and mechanisms of reactions in solution. The study of the effect of the solvent on the electrode reactions in mixed solvents is very interesting.

As part of our studies on ion solvation in aqueous–organic solvents [1] we have determined the standard molar e.m.f.s of the cell (A)

$$\mathrm{Ag(s),AgBr(s),KBr(c),KNO_3(c)} \parallel \mathrm{KNO_3(c),AgNO_3(c),Ag(s)} \qquad (A)$$

in dioxan–water mixtures containing 5 and 15 wt.% dioxan at 20, 25, 30, and 35°C, and of the cell (B)

$$\mathrm{Ag(s),AgCl(s),KCl(c),KNO_3(c)} \parallel \mathrm{KNO_3(c),AgNO_3(c),Ag(s)} \qquad (B)$$

in 5% (w/w) mannitol–water mixture at 5, 15, 25, and 35°C. From these data it is possible to determine the thermodynamic functions of the cell reactions and the thermodynamic solubility product constants of silver halides in these mixed solvents.

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EXPERIMENTAL

The following chemicals were obtained in the best grade available and were used without further purification: potassium chloride, potassium bromide, and potassium nitrate (E. Merck, G.R. samples); silver nitrate and mannitol (B.D.H. AnalaR); the dioxan (E. Merck) was purified as described earlier [2]. Silver–silver chloride, silver–silver bromide and silver electrodes were prepared as described earlier [1]. Solvent mixtures of the various mass percentages were prepared by weight in conductivity water. The organic co-solvent contents of the mixed solvent are accurate to within ±0.02%.

The preparation of the cell solutions, the setting up of the cells, and the e.m.f. and conductance measurements were essentially the same as described elsewhere [1]. The reproducibility of the e.m.f. measurements was of the order of ±0.2 mV. All measurements were made in water thermostats maintained at appropriate temperatures varying within ±0.1°C.

RESULTS AND DISCUSSION

The results of the e.m.f. measurements for cells (A) and (B) are shown in Table 1.

As before [1], the standard molar e.m.f. $E_c^\ominus$ was obtained by extrapolating the auxiliary function $E_c^{\ominus\prime}$, as defined by

$$\begin{aligned} E_c^{\ominus\prime} &= E + E^\ominus_{\mathrm{Ag,AgX}} - 2k \log c + 2kA\sqrt{2c}/l + \sqrt{2c} - E_j \\ &= E_c^\ominus + bc \end{aligned} \tag{1}$$

to zero molarity ($c = 0$), where E is the observed e.m.f. of the cell (A) or (B), $E^\ominus_{\mathrm{Ag,AgX}}$ is the standard molar potential of the Ag(s), AgX(s),X$^-$ (X is Cl or Br) electrode obtained from the corresponding standard molal potential values in the hydrogen scale in dioxan–water [3a] and mannitol–water [4] solutions, $k = 2.3026\ (RT/F)$, c is the molar concentration, $2c$ is the ionic strength of the solution, A is the Debye–Hückel constant calculated for the respective mixed solvents from their dielectric constant values [5] at the required temperatures, and E_j is the liquid junction potential of the cell concerned and evaluated by the usual method, as described earlier [2].

The values of the standard molar e.m.f. $E_c^\ominus$ of the silver–silver ion electrode obtained by the method of extrapolation are recorded in Table 1 along with their standard deviations obtained by the least-squares fit. The values for the standard e.m.f. on the molal scale $E_m^\ominus$ and on the molar fraction scale $E_N^\ominus$, calculated from $E_c^\ominus$ according to the equations

$$\begin{aligned} E_m^\ominus &= E_c^\ominus - 2k \log d_0 \\ E_N^\ominus &= E_m^\ominus - 2k \log(1000/M_{\mathrm{av}}) \end{aligned} \tag{2}$$

where d_0 and M_{av} are the density and average molecular weight of the mixed solvent, respectively, were fitted by the method of least-squares to the equation

$$E_x^\ominus = a + b(t-25) + c(t-25)^2 \pm \sigma \tag{3}$$

where x is m or N, and t is any temperature in °C. The constants a, b, and c and the mean deviation of fit, σ in eqn. (3), for various solvents are presented in Table 2.

TABLE 1

Values of the observed e.m.f. (in V) of cells (A) and (B) in various dioxan–water and mannitol–water mixtures at different temperatures

c in mol dm^{-3}	5°C	15°C	20°C	25°C	30°C	35°C
5 wt.% dioxan						
0.01	–	–	0.47341	0.46584	0.45804	0.45074
0.02	–	–	0.50580	0.49850	0.49142	0.48466
0.03	–	–	0.52424	0.51724	0.51062	0.50416
0.04	–	–	0.53743	0.53044	0.52414	0.51788
0.05	–	–	0.54736	0.54070	0.53456	0.52842
0.06	–	–	0.55552	0.54912	0.54278	0.53696
0.08	–	–	0.56825	0.56210	0.55585	–
0.10	–	–	0.57812	0.57212	0.566600	–
$E_c^\ominus$	–	–	0.78421	0.77816	0.77205	0.76623
$\pm\sigma$		–	0.00007	0.00015	0.00008	0.00014
15 wt.% dioxan						
0.01	–	–	0.47398	0.46655	0.45940	0.45258
0.02	–	–	0.50578	0.49885	0.49228	0.48508
0.03	–	–	0.52404	0.51734	0.51092	0.50482
0.04	–	–	0.53680	0.53034	0.52402	0.51802
0.05	–	–	0.54664	0.54028	0.53400	0.52826
0.06	–	–	0.55462	0.54836	0.54210	0.53658
0.08	–	–	0.56712	0.56102	0.55492	0.54934
$E_c^\ominus$	–	–	0.78211	0.77618	0.77038	0.76452
$\pm\sigma$	–	–	0.00019	0.00016	0.00006	0.00006
5 wt.% mannitol						
0.01	0.25721	0.23928	–	0.22142	–	0.20356
0.02	0.28814	0.27129	–	0.25452	–	0.23763
0.03	0.30595	0.28977	–	0.27360	–	0.26870
0.04	0.31851	0.30277	–	0.28705	–	0.27103
0.05	0.32821	0.31284	–	0.29740	–	0.28167
0.06	0.33608	0.32103	–	0.30585	–	0.29032
0.08	0.34846	0.33385	–	–	–	–
0.10	0.35802	0.34380	–	0.32925	–	0.31419
$E_c^\ominus$	0.71693	0.70142	–	0.68573	–	0.66940
$\pm\sigma$	0.00023	0.00032	–	0.00028	–	0.00010

TABLE 2

Values of constants of eqn. (1) on molal and mole fraction scales with the mean deviation of fit σ, and the standard thermodynamic functions at 25°C for reaction (4)

Constants	Wt.% dioxan		5 wt.% mannitol
	5	15	
$a(=E_m^\ominus/\mathrm{V}$ at 25°C)	0.77809	0.77567	0.68499
$-b \times 10^3$	1.18	1.212	1.5926
$-c \times 10^6$	3.6	−4.44	2.825
σ	0.00015	0 00008	0.00007
$a(=E_N^\ominus/\mathrm{V}$ at 25°C)	0.57374	0.57582	0.48096
$-b \times 10^3$	1.18	1.212	2.2765
$-c \times 10^6$	3.6	−4.44	2.75
σ	0.00015	0.00008	0.00007
$-\Delta G_m^\ominus/\mathrm{kJ\ mol^{-1}}$	75.08 ±0.02	74.85 ±0.02	66.10 ±0.03
$-\Delta S_m^\ominus/\mathrm{kJ\ mol^{-1}\ K^{-1}}$	0.114 ±0.001	0.117 ±0 002	0.154 ±0.002
$-\Delta H_m^\ominus/\mathrm{kJ\ mol^{-1}}$	109.07 ±0.32	109.73 ±0.62	112.00 ±0.62

The standard thermodynamic functions $\Delta G_m^\ominus$, $\Delta S_m^\ominus$ and $\Delta H_m^\ominus$ for the reaction

$$\mathrm{Ag^+(solvated) + 0.5H_2(1\ atm) = Ag(s) + H^+(solvated)} \tag{4}$$

have been determined from the $E_m^\ominus$ values and from the corresponding temperature coefficient, $\mathrm{d}E_m^\ominus/\mathrm{d}T$ (obtained as the first derivative of eqn. (3)), the relevant expressions being interrelated by the Gibbs–Helmholtz equation. All the calculated thermodynamic functions are shown in Table 2 for 25°C only.

The standard thermodynamic quantities $\Delta G_t^\ominus$, $\Delta S_t^\ominus$ and $\Delta H_t^\ominus$ for the transfer process

$$\mathrm{Ag^+(w)-H^+(w) \rightarrow Ag^+(s)-H^+(s)} \tag{5}$$

where w and s denote water and mixed solvent, respectively, were evaluated by the customary thermodynamic relations on the mole fraction scale and are listed in Table 3 for 25°C only. The single-ion thermodynamic quantities for the transfer of $\mathrm{Ag^+}$ ion from water to the mixed solvent concerned may be computed from eqn. (5) from the values for the $\mathrm{H^+}$ ion, which can be evaluated from a knowledge of the thermodynamic quantities for transfer of halogen acids from water to the respective mixed solvent. The $\Delta G_t^\ominus$ values for transfer of halogen acids (HCl, HBr and HI) from water to dioxan–water mixtures have been computed from the $E_N^\ominus$ values of the correspond-

TABLE 3

Transfer thermodynamic quantities for reaction (5), single-ion free energies of transfer from water to dioxan–water mixtures, and the primary medium effect of dioxan–water media on Ag^+ ion at 25°C

Wt % dioxan	$\Delta G_t^{\ominus N}$ in kJ mol^{-1}	$\Delta H_t^{\ominus N}$ in kJ mol^{-1}	$\Delta S_t^{\ominus N}$ in kJ mol^{-1} K^{-1}	$\Delta G_t^{\ominus N}(H^+)$ in kJ (g ion)	$\Delta G_t^{\ominus N}(Ag^+)$ in kJ (g ion)$^{-1}$	$\lim_{N\to 0}(\log {}^s\nu_w)_{Ag^+}$
5	1.83	−3.22	0.049	−2.67	−0.84	0.087
15	1.63	−3.88	0.046	−6.65	−5.02	−0.297

ing electrodes available in these solvents [3b] at 25°C only, and are also collected in Table 3. Applying the extra-thermodynamic assumptions of Feakins and Watson [6], which relate the free energy of transfer of halogen acids $\Delta G_t^{\ominus}(HX)$, where X is Cl, Br, or I, linearly with the reciprocal of Pauling's anionic radii [7], r_{X^-}, we obtain the equation

$$\Delta G_t^{\ominus}(HX) = \Delta G_t^{\ominus}(H^+) + \alpha(r_{X^-})^{-1} \tag{6}$$

where $\Delta G_t^{\ominus}(H^+)$ is the free energy of transfer of the proton, and α is a constant which can be identified with the quantity, $0.5Ne^2(D_s^{-1} - D_w^{-1})$ from Born's equation in which D_s and D_w are the dielectric constants of the mixed solvent and water, respectively. The limiting value of $\Delta G_t^{\ominus}(HX)$, as $(r_{X^-})^{-1}$ tends to zero, would provide a measure of the free energy of transfer of the proton, because $\Delta G_t^{\ominus}(X^-)$ for an ion of infinite radius, when $(r_{X^-})^{-1} = 0$, should approach a value of negligible magnitude. The extrapolated values of $\Delta G_t^{\ominus}(H^+)$ are collected in Table 3. Single-ion values of $\Delta G_t^{\ominus}(Ag^+)$ derived from eqn. (5) are also presented in Table 3.

The primary medium effect represents the difference in ion–solvent interaction for the ions involved in the transfer process in eqn. (5) from the standard state in water to the standard state in the mixed solvent. The values of the primary medium effect (mole fraction scale) of dioxan–water and mannitol–water mixtures on the $(Ag^+–H^+)$ ion at 25°C were computed using the equation

$$\lim_{N\to 0}(\log {}^s\nu_w) = ({}^wE_N^{\ominus} - {}^sE_w^{\ominus})/2.3026(RT/F) \tag{7}$$

where the limit term indicates the primary medium effect. If we now tentatively accept to a first approximation that the primary medium effect, $\lim_{N\to 0}(\log {}^s\nu_w)$ is a linear function of $(r_{X^-})^{-1}$, the limiting value of the primary medium effect of the mixed solvent media on HX, as $(r_{X^-})^{-1}$ tends to zero, would provide the primary medium effect for the H^+ ion. Accordingly, the values of the primary medium effect of various dioxan–water mixtures on HX were evaluated at 25°C by the equation

$$\lim_{N\to 0}(\log {}^s\nu_w)_{HX} = ({}^wE_N^{\ominus} - {}^sE_N^{\ominus})/4.6052(RT/F) \tag{8}$$

TABLE 4

Solubility product constants $K_{so}^{\ominus}$ (in $mol^2\,dm^{-6}$) of silver halides at 25°C, constants of eqn. (10) on the molar scale, the mean deviation of fit σ, and the molar heat of solution ΔH_{so} (in $kJ\,mol^{-1}$) for the reaction $AgX(s) = Ag^+ + X^-$

$K_{so}^{\ominus}$ (AgX)	Wt.% dioxan		5 wt.% mannitol
	5	15	
$K_{so}^{\ominus}$ (AgCl) × 10^{10}	3.280	2.547	135.28
$K_{so}^{\ominus}$ (AgBr) × 10^{13}	9.863	8.872	
$K_{so}^{\ominus}$ (AgI) × 10^{16}	1.842	1.907	
AgBr			
$-A$	4551.7363	4440.1409	
B	3.2576	2.8376	
σ	0.003	0.002	
$\Delta H_{so}/kJ\,mol^{-1}$	87.1	85.0	
AgCl			
$-A$	–	–	3769.3493
B	–	–	4.7802
σ	–	–	0.0014
$\Delta H_{so}/kJ\,mol^{-1}$	–	–	72.2

and extrapolated to $(r_{X^-})^{-1} = 0$, yielding the value for the H^+ ion. The values of the primary medium effect of dioxan–water mixtures on the Ag^+ ion derived from the extrapolated value of the H^+ ion are also recorded in Table 3.

The thermodynamic solubility product constants $K_{so}^{\ominus}$ (in $mol^2\,dm^{-6}$) of AgX where X is Cl, Br, or I in dioxan–water and in mannitol–water mixtures were evaluated at a single temperature, 25°C, or over a range of temperatures, from the values of the standard molar potentials using the equation

$$\ln K_{so}^{\ominus}(AgX) = [E_c^{\ominus}(Ag,AgX) - E_c^{\ominus}(Ag,Ag^+)](F/RT) \qquad (9)$$

where $E_c^{\ominus}(Ag,AgX)$ is the standard molar potential of the Ag(s), AgX(s), X^- electrode and is obtained from the literature [3, 4, 6]. The values of $K_{so}^{\ominus}$ (molar scale) are given in Table 4 for AgX at 25°C. The solubility data for AgCl and AgBr in any solvent were fitted by least-squares to the equation

$$\log(K_{so}^{\ominus}/mol^2\,dm^{-6}) = A/T + B \pm \sigma \qquad (10)$$

where T is any temperature in kelvin. The constants A and B of eqn. (10) are shown in Table 4 along with the values of σ, the standard deviation of the least-squares fit; the correlation coefficient for these relations is 0.9999 for all solvents. The heats of solution ΔH_{so} for the reaction $AgX(s) = Ag^+ + X^-$ were evaluated from the smoothing equations and are collected in Table 4.

As observed (Table 3), the $\Delta G_t^{\ominus}$ values for transfer of Ag^+ ion from water to dioxan–water mixtures are negative, and become increasingly negative with increasing dioxan content in water. This indicates that the combined effects of the solvent and solute properties favour the transfer of Ag^+ ion. It is seen that the medium has a greater effect on the silver ion as the dioxan content of the solvent system rises. This implies that the escaping tendency of the Ag^+ ion is greater in water than in the dioxan–water system. This conclusion is in agreement with the $\Delta G_t^{\ominus N}(Ag^+)$ values in the mixed solvents.

It has been observed that the solubility of the silver halides is greater in aqueous dioxan and mannitol systems than in pure water. The higher solubility is probably due to strong π-bonding which is a typical soft–soft interaction, and according to Ahrland et al. [8] is typical of π-bonding effects, e.g. the central –O– moiety in dioxan is characterized as a π-acceptor which would be expected to react strongly with good donors such as the 'soft' Ag^+ ion. This agrees with the fact that the addition of relatively small amounts of dioxan to water promotes its 'three-dimensional structure' so that a mixture of dioxan and water becomes a more highly structured solvent than water, and hence, the Ag^+ and halide ions break more structure in the mixed solvent than in water. These effects can be connected with the structure-breaking process which is endothermic and leads to an increase in ion–solvent interaction and solvation. This is reflected in the increase in solubility product values of silver halides in 5 wt.% dioxan–water mixture. When the dioxan content of the solvent increases, more dioxan molecules take part in constituting the diffused layer and replace the loosely oriented water molecules held in the solvation sphere in dioxan-poor solvent mixtures. Thus, the replacement of aqueous solvates by dioxan solvates promotes a sort of ordering effect in the solvation shell and leads to a decrease in ion–solvent interaction. This is amply confirmed by the lower solubility value of silver halides in 15 wt.% dioxan mixture. However, the case is reversed in silver iodide where the solubility increases with increasing dioxan content of the solvent. The increase in solubility might be due to the preferential solvation of I^- ion by water molecules in dioxan-rich solvent.

The higher solubility of silver chloride in 5 wt.% mannitol than in water or in 5 wt.% dioxan might be due to the more basic nature of the former compared with the latter solvents. Because of the presence of an active methylene group ($-CH_2-$) in the mannitol molecule (a polyhydroxy compound), the negative charge on the oxygen atom is somewhat higher than in the water molecule, and the positive charge of the hydrogen atom in the –OH group is lower in mannitol than in water. In other words, mannitol–water mixture is more basic than water. Moreover, in a mannitol–water mixture, which is extensively hydrogen bonded, one might expect that a mannitol molecule induces a change in charge density in a water molecule adjacent to it as well as in other water molecules at some distance. Due to these changes, the water molecules in the mixture are also more basic than those in pure water. Therefore, the mixture of mannitol and water (5 wt.%) acts as a stronger base than water and also than dioxan–water mixture. This higher basicity leads to greater ion–solvent interaction and solvation, and causes an increase in the dissolution of silver chloride.

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