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STANDARD THERMODYNAMICS OF TRANSFER
V. THE SILVER AND SILVER SALT ELECTRODES IN *t*-BUTYL ALCOHOL–WATER MIXTURES AT VARIOUS TEMPERATURES

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ABSTRACT

From the electromotive force measurements of cells with liquid-junction potentials, the standard potentials of the silver, silver–silver halide, silver–silver pseudohalide and silver–silver oxyhalide electrodes have been determined in 10 and 20 wt.% *t*-butyl alcohol–water mixtures at 5, 15, 25 and 35 °C. The values of the standard potentials have been used to evaluate the primary medium effects and the standard thermodynamic functions for the transfer of the ion from water to the respective solvent media. The results have been discussed in relation to the breakdown of the structure of water on the addition of *t*-butyl alcohol.

INTRODUCTION

In recent years, attention has been directed towards the physico-chemical studies in aqueous binary solvent mixtures with a view to studying the ion–solvent interactions in these mixed solvent media. The results in the mixed solvent media offer some understanding of the acid–base properties and the structural aspects of the solvents. Dash and coworkers [1–9], in their studies on ion–solvent interactions in a wide variety of aqueous–organic solvent mixtures, discussed the results in relation to the breakdown of water structure on the addition of an organic cosolvent. In continuation of our work on the potentiometric investigations in alcohol–water mixtures [3,4,6], this paper reports the results of potentiometric measurements of dilute solutions of bromide, iodide, oxide, thiocyanate, iodate, bromate and silver ions in *t*-butyl alcohol–water mixtures (10 and 20 wt.% *t*-butanol) at temperatures from 5 to 35 °C at intervals of 10 °C. Measurements of the EMF of the cells of the type,

$$\mathrm{Ag(s),\ AgCl(s),\ MCl(c)\ \|\ MX(c),\ AgX(s),\ Ag(s)} \qquad \text{(A)}$$

and

$$\mathrm{Ag(s), AgCl(s), NaCl(c), NaNO_3(c) \,||\, NaNO_3(c), AgNO_3(c), Ag(s)} \qquad \text{(B)}$$

where (s) and (c) represent the solid and molar solutions, respectively, and || represents the liquid junction ($M \equiv Na$ or K and $X \equiv Br$, I, N_3, CNS, BrO_3 or IO_3).

EXPERIMENTAL

Sodium chloride, sodium nitrate, silver nitrate, potassium chloride, sodium azide, potasium thiocyanate, potassium bromate and potassium iodate were either of reagent grade or E. Merck samples as used in earlier studies [1–8]. *t*-Butyl alcohol (BDH, laboratory reagent grade) was treated with a 4A molecular sieve and distilled. The solvent mixtures of various mass percentages were prepared by weight from deionized water and the purified solvent. The *t*-butyl alcohol contents of the mixed solvent were accurate to within ±0.2%.

Preparation of the electrodes and of the cell solutions, setting up the cells, e.m.f. and conductance measurements were similar to the procedures described earlier [1–9]. All measurements were made in water baths at the required temperature with a precision of ±0.1°C. The reproducibility of EMF measurements was of the order of ±0.2 mV.

RESULTS AND DISCUSSION

The evaluation of the standard potentials of the electrodes involves the graphical extrapolation of a linear plot of e.m.f. data against the molarity of the electrolyte solution. As usual [1–9] the e.m.f., *E*, of the cell (A) is given by

$$E = E^{\circ}_{\mathrm{Ag,AgX}} - E^{\circ}_{\mathrm{Ag,AgCl}} - \frac{RT}{F}\ln([\mathrm{X}^-]\gamma\mathrm{X}^-/([\mathrm{Cl}^-]\gamma\mathrm{Cl}^-) + E_{\mathrm{j}}\ldots \qquad (1)$$

where $X \equiv N_3$, BrO_3 or IO_3
and

$$E = E^{\circ}_{\mathrm{Ag,AgCl}} - E^{\circ}_{\mathrm{Ag,AgX}} - (RT/F)\ln([\mathrm{Cl}^-]\gamma\mathrm{Cl}^-/[\mathrm{X}^-]\gamma\mathrm{X}^-) + E_{\mathrm{j}}\ldots \qquad (1a)$$

where $X \equiv Br$, I or CNS.
E for cell (B) is given by

$$E = E^{\circ}_{\mathrm{Ag,Ag^+}} - E^{\circ}_{\mathrm{Ag,AgCl}} + (RT/F)\ln[\mathrm{Ag}^+][\mathrm{Cl}^-]\gamma^2_{\pm} + E_{\mathrm{j}}\ldots \qquad (2)$$

where brackets denote molar concentration, γ represents the activity coefficient of the designated species and E_{j} is the liquid junction potential.

Using the molar concentrations of the corresponding electrolyte solutions and expressing the mean molar activity coefficients by the Debye–Huckel expression, the standard molar potentials, E_c° of the Ag(s), AgX(s), X^- and Ag,Ag^+ electrodes were obtained by extrapolating [1–9] the corresponding auxiliary functions to molarity $c = 0$.

The values of the liquid junction potentials E_j were calculated from the equivalent conductivity values of the corresponding cell solutions by means of the Lewis–Sargent equation [1–9]. It was found that the values of E_j varied in the range 0.1–0.3 mV for the cells (A) and (B) in all solvents for all temperatures. The values of $E^\circ_{\mathrm{Ag,AgCl}}$ (molar scale) needed for the calculation of E_c° of the electrodes at various temperatures in 10 and 20 wt.% *t*-butyl alcohol–water mixtures were evaluated from the E°_m (molal scale) values available in the literature [10] using the density values of the solvent concerned [11]. The Debye–Huckel constant, A needed for the calculation of E_c° of the silver electrode in eqn. (2) was obtained using the dielectric constant values of the solvents available in the literature [12] and the viscosity of the solvent [11].

The standard potentials on the molar scale E_c° were converted into the molal, E°_m, and mole-fraction, E°_N, scales by means of the usual equations [1] using the density values [11] and the average molecular weights of the solvents concerned. The E° values can be represented as a function of temperature, T (°C) by eqn. (3).

$$E_p^\circ = a + b(T - 25) + c(T - 25)^2 \tag{3}$$

where p is c, m or N, and a, b and c are the empirical constants; these are shown in Table 1. The average difference between the observed values of E° and those calculated from the above equation agree within ± 0.3 mV.

The standard thermodynamic quantities (ΔG°, ΔH° and ΔS°) on the molal scale for the corresponding electrode reactions at different temperatures in the mixed solvents have been computed by the usual equations [1]. These values at 25 °C are presented in Table 2.

The standard thermodynamic quantities (ΔG_t°, ΔH_t° and ΔS_t°) for the transfer process, Ag^+ or X^- (in water) $\rightarrow$ Ag^+ or X^- (in mixed solvent) were evaluated at different temperatures for the mixed solvents by the usual equations [1]. These transfer thermodynamic quantities were obtained on the mole-fraction scale since that eliminates the free energy changes due to concentration changes [13]. They are recorded in Table 2 for 25 °C only.

Since the transfer process involves the transfer of charged particles from water to another solvent having a different dielectric constant, the related thermodynamic quantities consist of two parts: electrostatic (el) and non-electrostatic or chemical (ch). The electrostatic effect is caused by the change in the dielectric constant of the medium, whereas the chemical contribution reflects the solvating capacity as well as specific chemical interaction (basic-

TABLE 1

Constants of eqn. (3) on the molar (c), molal (m) and mole-fraction (N) scales

Electrode Ag(s), Agx(s), X^-	Wt.% *t*-butyl alcohol	p	a ($= E^\circ_{25^\circ C}$)	$-b \times 10^4$	$c \times 10^6$
X ≡ Br	10	c	0.07931	7.207	1.240
		m	0.08003	7.016	1.607
		N	−0.12231	13.806	1.583
	20	c	0.07609	6.650	1.257
		m	0.07763	6.314	1.440
		N	−0.12032	12.949	1.467
I	10	c	−0.15968	2.700	0.627
		m	−0.15895	2.509	0.960
		N	−0.36129	9.299	0.940
	20	c	−0.15779	2.758	−0.127
		m	−0.15627	2.440	0.056
		N	−0.35422	9.074	0.083
N_3	10	c	0.28184	1.516	0.39
		m	0.28257	1.325	0.722
		N	0.08023	8.115	0.700
	20	c	0.27884	2.380	−0.678
		m	0.28035	2.077	−0.494
		N	0.08242	8.679	−0.467
CNS	10	c	0.07968	−1.393	0.367
		m	0.08041	−1.583	0.700
		N	−0.12193	5.201	0.706
	20	c	0.08124	−0.409	−0.417
		m	0.08277	−0.744	−0.233
		N	−0.11524	5.890	−0.205
BrO_3	10	c	0.52329	1.130	0.077
		m	0.52403	0.939	0.411
		N	0.32169	7.729	0.389
	20	c	0.51776	2.760	0.280
		m	0.51930	2.424	0.461
		N	0.32135	9.059	0.489
IO_3	10	c	0.31591	2.425	−0.144
		m	0.31664	2.234	0.189
		N	0.11421	9.017	0.567
	20	c	0.30058	1.825	0.330
		m	0.30212	1.489	0.511
		N	0.10417	8.126	0.530
Ag, Ag^+	10	c	0.78654	10.370	3.100
		m	0.78727	10.179	3.433
		N	0.58493	16.969	3.410
	20	c	0.79906	11.208	0.360
		m	0.80059	10.872	0.544
		N	0.60264	17.507	0.572

TABLE 2

Standard thermodynamic quantities [a] (on the molal scale); transfer thermodynamic quantities [b] (on the mole-fraction scale) and the primary medium effect in *t*-butyl alcohol–water mixtures at 25°C ($\Delta G°$ and $\Delta H°$ in kJ mol^{-1} and $\Delta S°$ in J mol^{-1} K^{-1})

Parameter	Electrode						
	Ag,Ag$^+$	Ag,AgX,X$^-$					
		Br	I	N_3	CNS	BrO_3	IO_3
10 wt.% *t*-butyl alcohol–water							
$-\Delta G°$	75.96	7.72	−15.34	27.26	7.76	50.56	30.56
$-\Delta H°$	105.39	28.05	−8.04	31.15	3.10	53.29	36.92
$-\Delta S°$	98.8	68.3	24.5	13.1	15.7	9.15	21.3
$\Delta G_t°$	0.771	18.64	20.13	0.665	0.357	−0.181	0.811
$\Delta G_{t,el}°$	15.895	105.516	126.150	132.043	94.625	105.516	107.590
$-\Delta G_{t,ch}°$	15.124	86.872	106.020	131.378	94.268	105.698	106.779
$-\Delta H_t°$	76.43	23.07	8.62	24.68	16.61	24.42	27.13
$-\Delta H_{t,el}°$	24.72	164.12	130.73	205.38	147.18	164.12	167.35
$\Delta H_{t,ch}°$	−51.72	141.05	122.11	180.70	130.57	139.70	140.22
$-\Delta S_t°$	259.07	139.97	96.48	85.06	56.94	81.33	93.76
$-\Delta S_{t,el}°$	0.137	0.905	0.862	1.132	0.811	0.905	0.923
$\Delta S_{t,ch}°$	−0.123	0.765	0.766	1.047	0.755	0.824	0.829
$\lim_{N\to 0} (\log {}^s\gamma_w)$	0.135	3.266	3.526	0.117	0.063	−0.032	0.142
20 wt.% *t*-butyl alcohol–water							
$-\Delta G°$	77.25	7.45	−15.08	27.05	7.99	50.11	29.15
$-\Delta H°$	108.48	25.66	−8.05	33.09	5.91	57.08	33.44
$-\Delta S°$	105.00	61.01	23.60	20.03	6.95	23.40	14.40
$\Delta G_t°$	−0.944	18.449	19.445	0.456	−0.290	−0.149	1.779
$\Delta G_{t,el}°$	37.04	245.87	234.24	307.68	220.49	245.87	250.71
$-\Delta G_{t,ch}°$	37.98	227.42	214.80	307.22	220.78	246.02	248.93
$-\Delta H_t°$	79.69	20.80	8.66	26.51	19.24	28.21	23.60
$-\Delta H_{t,el}°$	53.82	357.28	340.30	447.16	132.64	357.28	364.29
$\Delta H_{t,ch}°$	−25.88	336.48	331.64	420.65	113.40	329.07	340.69
$-\Delta S_t°$	264.26	131.69	94.31	90.50	63.59	94.17	85.16
$-\Delta S_{t,el}°$	0.305	2.024	1.928	2.532	1.815	2.024	2.064
$\Delta S_{t,ch}°$	0.041	1.892	1.834	2.443	1.751	1.930	1.979
$\lim_{N\to 0} (\log {}^s\gamma_w)$	−0.165	3.232	3.406	0.080	0.051	−0.026	0.312

[a] Uncertainties in $\Delta G°$, 0.03 kJ mol^{-1}; $\Delta H°$, 0.04 kJ mol^{-1} and $\Delta S°$, 15 J mol^{-1} K^{-1}.
[b] Uncertainties in $\Delta G_t°$, 0.01 kJ mol^{-1}, $\Delta H_t°$, 0.02 kJ mol^{-1} and $\Delta S_t°$, 10 J mol^{-1} K^{-1}.

ity), which involves the destruction of one type of solvation shell and the creation of another. Thus for the Gibbs free energy transfer, we obtain

$$\Delta G_t° = \Delta G_{t,el}° + \Delta G_{t,ch}° \tag{4}$$

and similarly for the other thermodynamic functions $\Delta S_t°$ and $\Delta H_t°$. As usual [4] the values of $\Delta G_{t,el}°$ and $\Delta S_{t,el}°$ have been computed from the well-known Born equations

$$\Delta G_{t,el}° = \left(Ne^2/2\right)\left(D_s^{-1} - D_w^{-1}\right)\left(r_+^{-1} + r_-^{-1}\right) \tag{5}$$

and

$$\Delta S^{\circ}_{\mathrm{t,el}} = \left(-Ne^2/2\right)\left(D_{\mathrm{s}}^{-1}\theta_{\mathrm{s}}^{-1} - D_{\mathrm{w}}^{-1}\theta_{\mathrm{w}}^{-1}\right)\left(r_{+}^{-1} + r_{-}^{-1}\right) \qquad (6)$$

where N is Avogadro's number, e is the electronic charge, γ_+ and γ_- are the effective radii of the cation and anion respectively, D_{s} and D_{w} are the dielectric constants of the mixed solvent and water respectively and θ_{s} and θ_{w} are the temperature coefficients of the dielectric constants of the mixed solvent and water, respectively. The ionic radii of Ag^+ (r_-) and various anions (r_-) were obtained from the literature [5]. The values of the dielectric constant of water and water–*t*-butyl alcohol mixtures were taken from the literature [12] and those of θ_{w} and θ_{s} from the slopes of Akerlof's equations reported elsewhere [10]. The values of $\Delta H^{\circ}_{\mathrm{t,el}}$ were computed from a knowledge of $\Delta G^{\circ}_{\mathrm{t,el}}$ and $\Delta S^{\circ}_{\mathrm{t,el}}$. The chemical parts of these parameters were obtained from eqn. (4). These quantities at 25 °C are also given in Table 2.

The primary medium effect ($\log {}^{\mathrm{s}}\gamma_{\mathrm{w}}$) is a measure of the change in free energy in transferring one mole of Ag^+ or X^- ion from infinite dilution in the aqueous state to infinite dilution in the respective solvent mixture and has been evaluated by the equation

$$\lim_{N \to 0} \left(\log {}^{\mathrm{s}}\gamma_{\mathrm{w}}\right) = \frac{\left(E^{\circ}_{\mathrm{N}}\right)_{\mathrm{w}} - \left(E^{\circ}_{\mathrm{N}}\right)_{\mathrm{s}}}{2.3026(RT/F)} \qquad (7)$$

in the mixed solvents at different temperatures. The values of this quantity are recorded in Table 2 for 25 °C only.

The thermodynamic solubility products, K_{s}° (on the molar scale) of AgX ($\mathrm{X} \equiv \mathrm{Cl}$, Br, I, $\mathrm{N_3}$, CNS, $\mathrm{BrO_3}$ or $\mathrm{IO_3}$) in the mixed solvents have been calculated at different temperatures from the value of standard potentials by means of the equation

$$\log K_{\mathrm{s}}^{\circ}(\mathrm{AgX}) = \left[E_{\mathrm{c}}^{\circ}(\mathrm{Ag/AgX}) - E_{\mathrm{c}}^{\circ}(\mathrm{Ag/Ag^+})\right]\frac{2.3026RT}{F} \qquad (8)$$

where $E_{\mathrm{c}}^{\circ}(\mathrm{Ag/AgX})$ is the standard molar potential of the Ag, AgX, X^- and $E_{\mathrm{c}}^{\circ}(\mathrm{Ag/Ag^+})$ is the standard molar potential of the silver electrode in the solvent concerned. These were obtained in the present study. The values for K_{s}° (on the molar scale) for the various silver salts are presented in Table 3. The data for K_{s}° (on the molal scale) were calculated from K_{s}° $(\mathrm{mol^2\ dm^{-6}})/\rho^2$ where ρ is the density of the mixed solvent.

A comparison of the E° values of the $\mathrm{Ag/Ag^+}$ and Ag, AgX, X^- electrodes in the *t*-butyl alcohol–water mixture with those in water [5] shows that the E° values are less in the mixed solvents than in water and decrease (excepting the $\mathrm{Ag/Ag^+}$ and Ag, AgX, X^- ($\mathrm{X} \equiv \mathrm{I}$ or CNS) with increasing the *t*-butyl alcohol content in water. The higher E° values of the $\mathrm{Ag/Ag^+}$, Ag, AgI, I^- and Ag, AgCNS, CNS^- electrodes in 20 wt.% *t*-butyl alcohol–water mixtures in comparison with the 10 wt.% mixture might be due to the fact that the Ag^+, I^- or CNS^- ions are more solvated in the

TABLE 3

Solubility product values K_s° ($\text{mol}^2\ \text{dm}^{-6}$) of AgX (X ≡ Cl, Br, I, N_3, CNS, BrO_3 or IO_3) in *t*-butyl alcohol–water mixtures at different temperatures

X	$K_s^\circ \times$	T (°C)			
		5	15	25	35
10 wt.% *t*-butyl alcohol–water					
Cl	10^9	0.112	0.353	1.028	2.707
Br	10^{12}	0.114	0.372	1.110	3.028
I	10^{16}	0.036	0.204	1.013	4.413
N_3	10^9	0.328	1.028	2.945	7.675
CNS	10^{13}	0.560	2.651	11.287	42.161
BrO_3	10^5	0.750	1.688	3.555	6.912
IO_3	10^8	0.146	0.418	1.111	2.665
20 wt.% *t*-butyl alcohol–water					
Cl	10^9	0.045	0.143	0.423	1.206
Br	10^{12}	0.055	0.189	0.601	1.785
I	10^{16}	0.0223	0.131	0.375	3.071
N_3	10^9	0.176	0.558	1.604	4.319
CNS	10^{13}	0.368	1.742	7.736	28.114
BrO_3	10^5	0.394	0.856	1.757	3.447
IO_3	10^8	0.042	0.131	0.375	1.002

former solvent than in the latter. Similar observations have been made for these electrodes in water–monohydric alcohol mixtures [6]. Since the standard potential of the electrode is a measure of the decrease in free energy of solvation of the ion derived from the electrode material, the relative magnitude of the E° values of the halide, pseudohalide and oxyhalide electrodes gives an indication of the extent of solvation of the ions in these mixed solvents. The E° values of the electrodes follow the order: $E^\circ_{BrO_3} > E^\circ_{IO_3} > E^\circ_{N_3} > E^\circ_{Cl} > E^\circ_{CNS} > E^\circ_{Br} > E^\circ_{I}$, where BrO_3, IO_3 etc. represent the ions derived from the corresponding electrode materials. And this is the relative order of the free energies of solvation of the ions.

Table 2 shows that the transfer free energy appears to be positive (except in 20 wt.% for CNS^- and Ag^+, and in 10 and 20 wt.% for BrO_3^-) for all weight percentages of *t*-butyl alcohol. The positive ΔG_t° values thus indicate that the transfer of the ions concerned from water to the mixed solvents is not favourable and the ions in question are in higher free energy states in the mixed solvent than in water. The chemical part of the free energy change is fairly uniform and negative, which suggests that the transfer process from water to the mixed solvents is favoured insofar as the chemical interaction is concerned, but electrostatic effects predominate over the chemical interaction causing an unfavourable effect in the overall transfer process. The negative $\Delta G^\circ_{t,ch}$ values also suggest that *t*-butyl alcohol–water mixtures are stronger bases than water. Similar observations were also made in case of Cl^- ions in *t*-butyl alcohol–water mixtures [2].

The values of ΔH_t° and ΔS_t° listed in Table 2 appear to be negative. Since the structure forming process is exothermic accompanied by a decrease in entropy, the negative values of ΔH_t° and ΔS_t° indicate that as a result of transfer from water to *t*-butyl alcohol–water mixtures the ions are involved in the structure forming process (*i.e.* solvation) and thereby lead to an increase in the degree of order in the system as well as in the degree of structure of the system. The decreasing and negative values of ΔH_t° and ΔS_t° with increasing *t*-butyl alcohol content support the view that the mixed solvent becomes less associated than pure water. Thus the Ag^+ or X^- ions break more structure in water than in the mixed solvent. Similar behaviour was also observed in case of Cl^- ion in these solvents [10].

A perusal of Table 2 shows that the values of the primary medium effect appear to be positive (except for the BrO_3^- in all solvents and for Ag^+ in 20 wt.%) and to decrease with increasing proportion of *t*-butyl alcohol in water. The positive magnitude of this quantity suggests that the escaping tendency of the ions concerned is greater in the mixed solvent than in the pure aqueous medium.

An inspection of Table 3 shows that the solubility of the silver salts decreases with increasing proportion of *t*-butyl alcohol. As observed, the solubilities of silver chloride, silver bromide and silver thiocyanate are greater in *t*-butyl alcohol–water mixtures than in water, whereas that of silver azide, silver iodide, silver bromate and silver iodate are less in the mixed solvents. The higher solubility of the silver salts in question may be due to the fact that these silver salts are more strongly solvated in the mixed solvents than in water. In any solvent, the solubility of the silver salts follows the order: $AgBrO_3 > AgIO_3 > AgN_3 > AgCl > AgBr > AgCNS > AgI$.

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