THERMODYNAMICS OF SILVER–SILVER ION ELECTRODE IN ACETONITRILE–WATER MIXTURES

UPENDRA NATH DASH and ELLARANI PATTANAIK

Department of Chemistry, Utkal University, Bhubaneswar-751 004 (India)

(Received 6 September 1988)

ABSTRACT

From the electromotive force (e.m.f.) measurements of cells with liquid-junction potentials, the standard potentials of the silver electrode were obtained in 5%, 10% and 15% (w/w) acetonitrile–water mixtures at five different temperatures ranging from 15 to 35°C. Standard thermodynamic quantities for the cell reaction were estimated. Thermodynamic solubility product constants of silver halides were computed. The results are discussed in terms of ion solvation.

INTRODUCTION

Standard potentials of the silver electrodes in a wide variety of aquo–organic solvent media (comprising polar, dipolar and non-polar, protic and aprotic organic co-solvents) are known [1] over a range of temperatures. However, no work seems to have been carried out on the determination of the standard e.m.f of the silver electrode in binary aqueous media containing a highly polar organic co-solvent with a high dielectric constant and a higher dipole moment than that of water. In this paper we describe the determination of the standard e.m.f. of the silver electrode at different temperatures in acetonitrile–water mixtures containing 5%, 10% and 15% (w/w) acetonitrile. The object is to determine the standard potentials of the silver electrode and the thermodynamic solubility product constants of silver halides in solvent mixtures containing acetonitrile (a highly polar organic co-solvent with a high dielectric constant).

As described previously [1], the e.m.f. measurements on the cells of the type

$$Ag(s),AgCl(s),NaCl(c),NaNO_3(c) \parallel NaNO_3(c),AgNO_3(c),Ag(s) \qquad (A)$$

were made in various acetonitrile–water mixtures over a range of temperatures.

EXPERIMENTAL

The following chemicals were obtained in the best grade available and were used without further purification: sodium chloride (E. Merck, G.R.), sodium nitrate (BDH, AnalaR) and silver nitrate (BDH, AnalaR). Acetonitrile (BDH) was purified as described by Vogel [2] (specific conductance, $< 1.0 \times 10^{-7}$ S cm^{-1}). Silver–silver chloride and silver electrodes were prepared as described earlier [1]. The solvent mixtures of various weight percentages were prepared by weight in conductivity water. The acetonitrile contents of the solutions were 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 earlier [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 the appropriate temperatures to within $\pm 0.1°$C.

RESULTS AND DISCUSSION

The results of the e.m.f. measurements for cell (A) are presented in Table 1.

The values of E_c were calculated with the help of the equation

$$E_c^{\ominus\,'} = E + E_{Ag,AgCl}^{\ominus} - 2k\log c + 2kA(2c)^{1/2}/1 + (2c)^{1/2} - E_j$$

$$= E_{Ag,Ag^+}^{\ominus} + bc \tag{1}$$

where $k = 2.3026\,(RT/F)$, c is the molar concentration, $2c$ is the ionic strength of the solution, E_j is the liquid-junction potential of the cell and $E_{Ag,AgCl}^{\ominus}$ is the standard molar potential of the silver–silver chloride electrode (on the hydrogen scale) and is calculated from the molal potential values [3] at the experimental temperatures using the density values [3] for various acetonitrile–water mixtures. The values of E_j were calculated [1] and found to vary in the range 0.1–0.3 mV in all solvents at different temperatures.

Extrapolation of the calculated values of $E_c^{\ominus\,'}$ to zero molarity yields the standard molar e.m.f. of the cell $E_c^{\ominus}$, H$_2$ (1 atm)/Ag(s). The $E_c^{\ominus}$ values are presented in Table 1 together with their standard deviations obtained from the least-squares fit. The standard e.m.f.s on the molal ($E_m^{\ominus}$) and mole-fraction ($E_N^{\ominus}$) scales computed from $E_c^{\ominus}$ by the usual equations [4] were fitted by the method of least-squares to the equation

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

where x is m or N and t is any temperature in degrees Celsius. The constants a, b and c, and the mean deviation of fit σ in eqn. (2) for the various acetonitrile–water mixtures are recorded in Table 2.

TABLE 1

Summary of e.m.f. data (in absolute volts) of cell (A) in various acetonitrile–water mixtures at different temperatures

c (mol dm^{-3})	t (°C)				
	15	20	25	30	35
5 wt.% CH$_3$CN					
0.005	0.31264	0.30582	0.29908	0.29232	0.28558
0.0075	0.33168	0.32488	0.31818	0.31250	–
0.0125	0.35546	0.34864	0.34188	0.33568	0.33088
0.0250	0.38705	0.38125	0.37582	–	0.36494
0.0425	0.41068	0.40508	0.39965	0.39418	0.39038
0.0650	–	0.42416	0.41876	0.41328	0.40998
0.0825	0.44022	0.43492	0.42963	0.42412	0.42154
0.0950	0.44608	0.44082	0.43560	0.43032	0.42782
$E_c^{\ominus}$	0.80500	0.79936	0.79405	0.78824	0.78306
$\pm \sigma$	0.00014	0.00030	0.00057	0.00099	0.00018
10 wt.% CH$_3$CN					
0.005	0.31218	0.30558	0.29885	0.29186	0.28468
0.0075	0.33158	0.32514	0.31841	0.31156	0.30426
0.0125	0.35576	0.34932	0.34266	0.33596	0.32876
0.0250	0.38745	0.38158	0.37508	0.36921	0.36235
0.0425	0.41106	0.40542	0.39938	0.39418	0.38752
0.0650	0.42972	0.42424	0.41856	0.41370	0.40692
0.0825	0.43944	0.43455	0.42916	–	–
0.0950	0.44538	0.44070	0.43551	0.43102	0.42422
$E_c^{\ominus}$	0.90249	0.79628	0.79024	0.78397	0.77747
$\pm \sigma$	0.00042	0.00027	0.00038	0.00027	0.00082
15 wt.% CH$_3$CN					
0.005	0.31186	0.30536	0.29864	0.29138	0.28476
0.0075	0.33080	0.32478	0.31816	0.31128	0.30504
0.0125	0.35442	0.34868	0.34252	–	–
0.0250	0.38588	0.38078	0.37500	0.36906	0.36376
0.0425	0.40944	0.40476	0.39928	0.39378	0.38892
0.0650	0.42798	0.42358	0.41836	0.41325	0.40875
0.0825	0.43836	0.43406	0.42868	0.42416	0.41966
$E_c^{\ominus}$	0.79682	0.79110	0.78496	0.77826	0.77179
$\pm \sigma$	0.00008	0.00006	0.00025	0.00005	0.00003

The standard thermodynamic functions $\Delta G_m^{\ominus}$, $\Delta H_m^{\ominus}$ and $\Delta S_m^{\ominus}$ on the molal scale for the cell reaction

$$Ag^+(\text{solvated}) + 0.5H_2(1 \text{ atm}) = Ag(s) + H^+(\text{solvated}) \qquad (3)$$
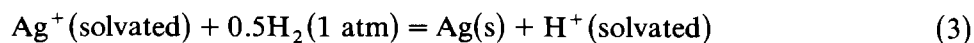
were determined from the $E_m^{\ominus}$ values by the usual relations.

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

$$\left(Ag^+ - H^+\right) \text{ in water} \rightarrow \left(Ag^+ - H^+\right) \text{ in mixed solvent} \qquad (4)$$
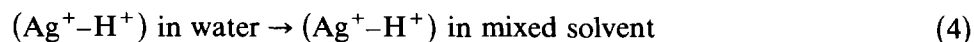
TABLE 2

Constants of eqn. (2) on molal (m) and mole-fraction (N) scales, the mean deviation of fit σ and the standard thermodynamic functions at $25\,^{\circ}$C for reaction (3)

x		CH$_3$CN (wt.%)		
		5	10	15
m	$a\ (= E_{\mathrm{m}}^{\ominus}/V$ at $25\,^{\circ}$C$)$	0.79462	0.79123	0.78651
	$-b \times 10^3$	1.0835	1.2133	1.2338
	$-c \times 10^6$	1.0	2.0	7.0
	σ	0.00013	0.00013	0.00010
N	$a\ (= E_{\mathrm{N}}^{\ominus}/V$ at $25\,^{\circ}$C$)$	0.58959	0.58785	0.58465
	$-b \times 10^3$	1.7707	1.8953	1.9108
	$-c \times 10^6$	1.0	2.0	7.0
	σ	0.00013	0.00013	0.00010
	$-\Delta G_{\mathrm{m}}^{\ominus}$ (kJ mol^{-1})	76.67 ± 0.06	76.35 ± 0.04	75.89 ± 0.03
	$-\Delta H_{\mathrm{m}}^{\ominus}$ (kJ mol^{-1})	107.7 ± 1.3	111.3 ± 1.2	111.4 ± 10.6
	$-\Delta S_{\mathrm{m}}^{\ominus}$ (kJ mol^{-1})	0.104± 0.004	0.117± 0.004	0.119± 0.002

were evaluated for various solvent mixtures by the customary thermodynamic relations on the basis of mole fraction. All the calculated thermodynamic quantities are collected in Table 3 for $25\,^{\circ}$C only.

It is of interest to compute the $\Delta G_{\mathrm{t}}^{\ominus}$ values for transfer of halogen acids from water to acetonitrile–water mixtures from the corresponding $E_{\mathrm{N}}^{\ominus}$ values available in these solvents [5]. The $\Delta G_{\mathrm{t}}^{\ominus}$(HX) values, where X is Cl, Br or I, were calculated by the usual equation. By applying the extrathermodynamic assumptions of Feakins and Watson [6], which relate the free energy of transfer of halogen acids $\Delta G_{\mathrm{t}}^{\ominus}$(HX) linearly to the reciprocal of Pauling's anodic radii $r_{\mathrm{X}^{-}}^{-1}$ [7], we obtain

$$\Delta G_{\mathrm{t}}^{\ominus}(\mathrm{HX}) = \Delta G_{\mathrm{t}}^{\ominus}(\mathrm{H}^{+}) + \alpha r_{\mathrm{X}^{-}}^{-1} \tag{5}$$

$\Delta G_{\mathrm{t}}^{\ominus}(\mathrm{H}^{+})$ is the free energy of transfer of the proton and α is a constant which can be identified with the quantity $0.5\ Ne^2\ (\epsilon_{\mathrm{s}}^{-1} - \epsilon_{\mathrm{w}}^{-1})$ from Born's

TABLE 3

Transfer thermodynamic quantities for reaction (4), single-ion free energies of transfer from water to acetonitrile–water mixtures and primary medium effect of acetonitrile–water media on Ag$^+$ ion at $25\,^{\circ}$C

CH$_3$CN (wt.%)	$\Delta G_{\mathrm{t}}^{\ominus\mathrm{N}}$ (kJ mol^{-1})	$-\Delta H_{\mathrm{t}}^{\ominus\mathrm{N}}$ (kJ mol^{-1})	$-\Delta S_{\mathrm{t}}^{\ominus\mathrm{N}}$ (kJ mol^{-1} K^{-1})	$\Delta G_{\mathrm{t}}^{\ominus\mathrm{N}}(\mathrm{H}^{+})$ (kJ g-ion^{-1})	$\Delta G_{\mathrm{t}}^{\ominus\mathrm{N}}(\mathrm{Ag}^{+})$ (kJ g-ion^{-1})	$\lim(\log{}^{\mathrm{s}}\gamma_{\mathrm{w}})_{\mathrm{Ag}^{+}}$ N $\rightarrow$ 0
5	0.301	1.82	0.008	-2.801	-2.500	-0.193
10	0.469	5.40	0.020	-5.482	-5.013	-0.399
15	0.777	5.50	0.021	-8.803	-8.026	-0.637

equation in which ϵ_s and ϵ_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, gives a measure of the free energy of transfer of the proton, since $\Delta G_t^{\ominus}(X^-)$ for an ion of infinite radius should approach a value of negligible magnitude when $r_X^{-1} = 0$. The extrapolatéd values of $\Delta G_t^{\ominus}(H^+)$ are collected in Table 3. Single-ion values of $\Delta G_t^{\ominus}(Ag^+)$ derived from eqn. (4) are also shown in the table.

The primary medium effect is a measure of the change in Gibbs free energy which accompanies the transfer process in eqn. (4) from the standard state in water to the standard state in the mixed solvent. The values of primary medium effect (mole-fraction scale) of acetonitrile–water mixtures on the $(Ag^+–H^+)$ ion at $25°C$ were computed by the equation.

$$\lim_{N \to 0} (\log {}^s\gamma_w) = \left({}^wE_N^{\ominus} - {}^sE_N^{\ominus}\right)/2.3026(RT/F) \tag{6}$$

where the limit term indicates the primary medium effect. If we now tentatively accept a first approximation that the primary medium effect, $\lim(\log {}^s\gamma_w)_{HX}(N \to 0)$, is a linear function of r_X^{-1}, the limiting value of the primary medium effect of the mixed media on HX as r_X^{-1} tends to zero will give the primary medium effect for the hydrogen ion. Accordingly, the values of the primary medium effect of various acetonitrile–water mixtures on HX were evaluated [5] at $25°C$ by the equation

$$\lim_{N \to 0} (\log {}^s\gamma_w)_{HX} = \left({}^wE_N^{\ominus} - {}^sE_N^{\ominus}\right)F/4.6052RT \tag{7}$$

and were extrapolated to $r_X^{-1} = 0$, yielding the primary medium effect for the H^+ ion. The values of the primary medium effect of the mixed solvents on the Ag^+ ion derived from the extrapolated value for the H^+ ion are also presented in Table 3.

The thermodynamic solubility product constants $K_{so}^{\ominus}$ (mol^2 dm^{-6}) of AgX (where X is Cl, Br or I) in acetonitrile–water mixtures were evaluated

TABLE 4

Solubility product constants $K_{so}^{\ominus}$ (mol^2 dm^{-6}) of silver halides at $25°C$, constants of eqn. (9) on the molar scale for AgCl, the mean deviation of fit σ and the molar heat of solution ΔH_{so} (kJ mol^{-1}) for the reaction, AgCl(s) = $Ag^+ + Cl^-$

	CH$_3$CN (wt.%)		
	5	10	15
$K_{so}^{\ominus}$ (AgCl) $\times 10^{10}$	1.798	1.777	1.766
$K_{so}^{\ominus}$ (AgBr) $\times 10^{13}$	5.468	6.019	6.809
$K_{so}^{\ominus}$ (AgI) $\times 10^{16}$	1.016	1.211	1.530
$-A$	3525.025	3647.44	3513.457
B	2.08001	2.4916	2.04099
σ	0.003	0.002	0.003
ΔH_{so} (kJ mol^{-1})	67.5	69.8	67.3

from the values of standard molar potentials by means of the equation

$$\ln K_{so}^{\ominus}(\text{AgX}) = \left[E_c^{\ominus}(\text{Ag,AgX}) - E_c^{\ominus}(\text{Ag,Ag}^+)\right](F/RT) \tag{8}$$

where $E_c^{\ominus}(\text{Ag,AgX})$ is the standard molar potential of the Ag(s), AgX(s), X^- electrode and is obtained from the literature [3,5]. The values for $K_{so}^{\ominus}$ (molar scale) are given in Table 4 at $25°C$ for the silver halides. The solubility data for AgCl in all solvents were fitted by the least-squares method to the equation.

$$\log K_{so}^{\ominus}(\text{mol}^2\,\text{dm}^{-6}) = A/T + B \pm \sigma \tag{9}$$

where T is any temperature in kelvin. The constants A and B of eqn. (9) are shown in Table 4 together with the standard deviation of the least-squares fit σ; the correlation coefficient for these relations is 0.999 for all solvents. From the equations, the heat of solution ΔH_{so} for the reaction AgCl(s) = $Ag^+ + Cl^-$ was evaluated.

A perusal of Table 3 shows that the $\Delta G_t^{\ominus}$ values for transfer of Ag^+ ion from water to the mixed solvents are negative, and become increasingly negative as the acetonitrile content increases in the mixed solvent. This indicates that the combined effects of the solvent and solute properties favour the transfer of Ag^+ ion. Furthermore it can be seen that the addition of small amounts of acetonitrile appreciably changes the effect of the solvent medium on the ions at infinite dilution. The medium has a greater effect on the silver ions as the acetonitrile content of the solvent system increases. This indicates that the escaping tendency of the Ag^+ ion is greater in water than in the mixed media. This conclusion is consistent with the $\Delta G_t^{\ominus}(Ag^+)$ values in the mixed media.

Silver halides were observed to be more soluble in acetonitrile–water mixtures than in pure water. The higher solubility is probably due to the non-solvation of halide ion by aprotic acetonitrile. The high solubility value may also be due to strong π bonding, which according to Pearson is a typical soft–soft interaction, and according to Ahrland et al. [8] is typical of π-bonding effects; for example, the centre $C \equiv N$ in CH_3CN is well characterized as a π acceptor which should be expected to react strongly with good donors such as the 'soft' Ag^+ ion, forming a bulky solvated sphere which, in turn, keeps away the halide ion. Several workers [9] have shown that silver ion is preferentially solvated by CH_3CN molecules rather than by water. This preferential solvation of Ag^+ ion by CH_3CN results in higher solubility of silver halides with an increased proportion of acetonitrile in mixed solvents. This is reflected in the increased solubility values of AgBr and AgI with increasing CH_3CN content of the solvent. However, this trend is opposite in the case of AgCl and the solubility decreases (although not markedly) with increasing concentration of acetonitrile in water; the decrease in dielectric constant of the medium dominates the solvation. This probably involves association between water and CH_3CN in the presence of

the smaller anion Cl^- ($r_{Cl^-} = 1.81$ Å) [7] as compared with larger anions such as Br^- ($r_{Br^-} = 1.95$ Å) [7] and I^- ($r_{I^-} = 2.16$ Å) [7]; hence solvation of Ag^+ ion by CH_3CN is slightly lowered with increasing CH_3CN concentration. However, it appears from the decreasing trend of AgCl solubility with increasing CH_3CN content in water that preferential solvation of Ag^+ ion by CH_3CN would be expected at higher concentrations of CH_3CN (> 20 wt.%).

REFERENCES

1 U.N. Dash, B.B. Das, U.K. Biswal, T. Panda, N.K. Purohit, D.K. Rath and S. Bhat-tacharya, Thermochim. Acta, 61 (1983) 379; 63 (1983) 261; 71 (1983) 199.
  U.N. Dash, B.B. Das, U.K. Biswal and T. Panda, Thermochim. Acta, 70 (1983) 383; 80 (1984) 331; 95 (1985) 213; 121 (1987) 353.
  U.N. Dash, B.B. Das, U.K. Biswal and T. Panda, Electrochim. Acta, 28 (1983) 1273.
  U.N. Dash and P.K. Samanta, Thermochim. Acta, 115 (1987) 111; 119 (1987) 337.
2 A.I. Vogel, A Text Book of Practical Organic Chemistry, Longmans, London, 1955, p. 407.
3 T. Mussini, P. Longhi and P. Giammario, Chim. Ind. (Milan), 53 (1971) 1124.
4 U.N. Dash and M.C. Padhi, Thermochim. Acta, 39 (1980) 335.
5 T. Mussini, P. Longhi and P. Giammario, Chim. Ind. (Milan), 54 (1972) 3.
6 D. Feakins and P. Watson, J. Chem. Soc., (1963) 4734.
7 L. Pauling, The Nature of the Chemical Bond, 3rd edn., Oxford University Press, London, 1960, p. 519.
8 S. Ahrland, J. Chatt and N.R. Davies, Q. Rev., Chem. Soc., 12 (1968) 265.
9 H. Strehlow and H.M. Koepp, Z. Electrochem. Busenges. Phys. Chem., 62 (1958) 373.
  C.B. Baddiel, M.J. Tait and G.J. Janz, J. Phys. Chem., 69 (1965) 3634.
  G.J. Janz, M.J. Tait and J. Meier, J. Phys. Chem., 71 (1967) 963.