Studies in Isodielectric Media. The Standard Potentials of Ag–AgCl and Ag–AgBr Electrodes in 1,2-Ethanediol–2,2'-Oxydiethanol Mixtures at 25 °C

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Standard potentials of Ag–AgCl and Ag–AgBr electrodes in various compositions of 1,2-ethanediol–2,2'-oxydiethanol (ethylene glycol–diethylene glycol) mixtures at 25 °C are reported. The free energies of transfer of the hydrogen halides from ethylene glycol to the mixtures were evaluated on mole fraction scale. The transfer free energies of H^+ and the halide ions were determined employing the ferrocene reference method. The results suggest that the basicity of the mixtures increases with the addition of diethylene glycol and that it is more basic than ethylene glycol.

Studies in isodielectric solvent mixtures have provided valuable information[1,2] on solute-solvent interactions in mixed solvents in recent years. In particular, such investigations enable one to study the influence of the chemical effect of the solvents on the thermodynamics of transfer between different solvents, for the electrostatic effects arising out of the difference in the dielectric constants of the solvent components are expected to be small in these media. Although a few emf studies in isodielectric media have been made,[3,4] no measurements have been reported in the binary mixtures of glycols. Since the dielectric constants of ethylene glycol (EG) and diethylene glycol (DEG) at 25 °C are 41.20 and 31.20 respectively and those of their mixtures are expected to be between these limits, all these solvents should serve approximately as isodielectric media. In continuation of our earlier work on the thermodynamic behaviour of electrolytes and ions in glycolic solvents,[5,6,7] the present work therefore deals with the determination of standard potentials of the silver–silver chloride and silver–silver bromide electrodes in 20 to 80 wt % EG–DEG mixtures at 25 °C. The cell (1) was used for the determination of the standard potential of the Ag–AgCl electrodes.

$$\text{Pt, } H_2(\text{g, 1 atm})/\text{HCl(m) solvent/AgCl, Ag} \qquad (1)$$

and the buffered cell (2)

$$\text{Pt, } H_2(\text{g, 1 atm})/\text{HOAc(m1), NaOAc(m2), KX(m3) solvent/AgX, Ag} \qquad (2)$$

containing acetic acid (HOAc), sodium acetate (NaOAc) and potassium bromide (KBr) with X=Br was used for determining the standard potentials of Ag–AgBr electrode. The dissociation constant of acetic acid required in the evaluation of the standard potentials of Ag–AgBr electrode in these solvents was determined as described later.

Experimental

EG (LR, BDH) and DEG (LR, BDH) were purified by the methods described earlier.[5,8] The preparation of the stock acid solutions was as described elsewhere.[8]

Ag–AgCl and Ag–AgBr electrodes were of the thermal electrolytic type and were prepared according to the method of Janz and Ives.[9] The preparation of the hydrogen electrode and the experimental set up employed in EMF measurements are similar to those described in detail in earlier work.[5] The cells were thermostated with an accuracy of ±0.05 °C during equilibration. The cells normally attained equilibrium 5—6 h after the start of hydrogen bubbling in all the mixtures and constancy of emf values to ±0.1 mV over a period of half an hour was considered as an adequate criterion of equilibrium. The vapour pressures of the solvents being very small, no vapour pressure correction was applied to the emf data. The transfer free energy of proton in these mixtures was determined by employing the ferrocene reference method according to the procedure described earlier.[10]

Results and Discussion

The standard molal potentials ${}_{\text{s}}E^{\circ}_{\text{m}}$ of the cell (1) in different solvent mixtures were obtained by extrapolation of the function

$$\begin{aligned} E^{\circ\prime} &= E + 2k\log m - 2kA'm^{1/2}/(1+aB'm^{1/2}) \\ &\quad - 2k\log(1+0.002\,mM_{\text{xy}}) \\ &= {}_{\text{s}}E^{\circ}_{\text{m}} - 2k\,b\,m \end{aligned} \qquad (3)$$

to zero molality. In the above equation,

$$k = 2.303\,RT/F, \qquad (4)$$

m is the molality of HCl, A' and B' are the Debye-Hückel constants on the molality scale, a is the ion size parameter, b is the coefficient occurring in the activity coefficient expression as a function of molality and M_{xy} is the mean molar mass of the mixed solvent as defined earlier.[5] In determining ${}_{\text{s}}E^{\circ}_{\text{m}}$, $a=5$ Å was used as this was found to give good linear plots with the least slope. The standard potentials of the Ag–AgCl electrode on molar (${}_{\text{s}}E^{\circ}_{\text{c}}$) and mole fraction scales (${}_{\text{s}}E^{\circ}_{\text{N}}$) were calculated from (${}_{\text{s}}E^{\circ}_{\text{m}}$) with the help of usual relationships given earlier.[5] All these values at 25 °C are given in Table 1.

The standard potentials (${}_{\text{s}}E^{\circ}_{\text{m}}$) of the Ag–AgBr electrode at 25 °C in different solvent mixtures were obtained from a plot of the function $E^{\circ\prime}$ defined by

$$\begin{aligned} E^{\circ\prime} &= E - 2.303\frac{RT}{F}\text{p}K_{(\text{HOAC})} + 2.303\frac{RT}{F}\log\frac{m\,\text{HOAC}\,m\,\text{Br}^-}{m\,\text{OAC}^-} \\ &= {}_{\text{s}}E^{\circ}_{\text{m}} - 2.303\frac{RT}{F}\log\frac{\gamma\text{HOAC}\,\gamma\text{Br}^-}{\gamma\text{OAC}^-} \\ &= {}_{\text{s}}E^{\circ}_{\text{m}} + f(\mu) \end{aligned} \qquad (5)$$

against μ, the ionic strength, by extrapolating to $\mu=0$. $E^{\circ\prime}$ values were computed by using the values of $\text{p}K_{(\text{HOAC})}$ and the measured EMF values of cell (2) with X=Br for various buffer compositions. $\text{p}K_{(\text{HOAC})}$ values required in Eq. 5 were obtained from measurements

Table 1. Standard potentials of the Ag–AgCl and Ag–AgBr electrodes (V) in ethylene glycol–diethylene glycol mixtures at 25 °C

DEG wt %	Ag–AgCl electrode			Ag–AgBr electrode		
	E°_m	E°_c	E°_N	E°_m	E°_c	E°_N
0	0.0240[a]	0.0294	−0.1188	−0.0991[b]	−0.0938	−0.2419
20	0.0242	0.0298	−0.1142	−0.0932	−0.0876	−0.2316
40	0.0190	0.0246	−0.1145	−0.0987	−0.0931	−0.2322
60	−0.0034	0.0022	−0.1247	−0.1091	−0.1035	−0.2372
80	−0.0191	−0.0135	−0.1412	−0.1257	−0.1200	−0.2478
100[c]	−0.0308	−0.0251	−0.1461	−0.1451	−0.1395	−0.2604

a) *J. Chem. Soc., Faraday Trans. 1*, **73**, 284 (1977). b) *J. Chem. Eng. Data*, **15**, 209 (1970). c) Our unpublished work.

Table 2. Standard free energies of transfer of HCl, HBr, H^+ and halide ions from ethylene glycol to ethylene glycol–diethylene glycol mixtures (mole fraction scale) at 25 °C ($J\ mol^{-1}$)

DEG wt %	$\Delta G^\circ_{t(HCl)}$	$\Delta G_{t(HBr)}$	$\Delta G^\circ_{t(H^+)}$	$\Delta G^\circ_{t(Cl^-)}$	$\Delta G^\circ_{t(Br^-)}$
0	0	0	0	0	0
20	−444	−994	25	−469	−1019
40	−415	−936	−39	−376	−897
60	569	−454	−268	837	−186
80	2162	569	−922	3084	1491
100	2635	1785	−1267	3902	3052

on cell 2 with X=Cl and utilizing the ${}_sE^\circ_m$ values of Ag–AgCl electrode in these solvents obtained with cell (1). In calculating $E^{\circ\prime}$, it was assumed that KBr and NaOAc are completely dissociated in all the solvents, and that the dissociation of HOAc is so small that it does not affect the effective concentration of HOAc and OAc^-. The ${}_sE^\circ$ values on different scales are also presented in Table 1.

The transfer free energy of proton, $\Delta G^\circ_{H^+}$ in these mixtures was determined as described earlier from the relation

$$\Delta G^\circ_{\text{cell}} = F({}_{\text{s}}E^\circ_{\text{N}} - {}_{\text{EG}}E^\circ_{\text{N}}) = \Delta G^\circ_{\text{FiC}^+(\text{el})} - \Delta G^\circ_{\text{H}^+}, \qquad (6)$$

where ${}_sE^\circ_N$ and ${}_{EG}E^\circ_N$ represent the standard potentials of the cell

$$\frac{\text{Pt, H}_2\text{(g, 1 atm)}}{\text{H}^+\text{ in the solvent}} \;\vdots\; \frac{\text{FiC}^+\text{, FOC 1 : 1 in the solvent}}{\text{Pt}} \qquad (7)$$

in the solvent and EG respectively on the mole fraction scale.

$\Delta G^\circ_{FiC^+(el)}$ which represents the electrostatic transfer free energy of the ferricinium ion from EG to the solvent was determined from the Born equation using the dielectric constants of the solvent mixtures (our unpublished results) determined by us.

The standard free energy change, ΔG°_t, for the transfer of one mole of HX from the standard state in one reference solvent to the standard state in another can be calculated from the standard potential data of the Ag–AgX electrodes in different solvents. Considering EG as the reference solvent, $\Delta G^\circ_{t(HX)}$ for HCl and HBr were computed by

$$\Delta G^\circ_t = F({}_{\text{EG}}E^\circ_{\text{N}} - {}_{\text{s}}E^\circ_{\text{N}}), \qquad (8)$$

where ${}_{EG}E^\circ_N$ and ${}_sE^\circ_N$ are the standard potentials in EG and the solvent mixtures respectively. They are recorded in Table 2 and are accurate to ±90 J. The free energies of transfer of H^+, and the halide ions are also given in Table 2. The ΔG°_t values for both acids are found to have small negative values initially, pass through a minimum at about 20 wt % DEG and then increase (become positive) with the further addition of DEG. Thus while the transfer of HCl and HBr from EG to the mixed solvents is thermodynamically favourable upto about 40 wt % DEG, the transfer process is not favoured at higher compositions of DEG. For any solvent the values for HBr are more negative than for HCl indicating that the transfer is relatively easier for HBr than for HCl. The nature of the variation of ΔG°_t with solvent composition suggests that two opposing factors must operate so as to give the observed minimum in the EG rich region. The transfer free energies of the proton together with the data for the halide ions (Table 2) in these solvent mixtures lend support to the above conclusion because $\Delta G^\circ_{t(H^+)}$ and $\Delta G^\circ_{t(Cl^-)}$ clearly vary in opposite directions. However, it is seen that the changes in $\Delta G^\circ_{t(X^-)}$ predominate over that of $\Delta G^\circ_{t(H^+)}$ and thus govern the overall variation of $\Delta G^\circ_{t(HX)}$ with the solvent composition.

In general, the basicity of the solvent mixtures increases with increasing proportion of DEG and also DEG is more basic than EG. These results are in agreement[10] with the conclusions arrived on the basis of proton medium effects determined by the ferrocene reference method in DEG–water and EG–water mixtures earlier.

References

1) K. K. Kundu, A. L. De, and M. N. Das, *J. Chem. Soc., Dalton Trans.*, **1972**, 373.

2) H. P. Bennetto and J. J. Spitzer., *J. Chem. Soc., Faraday Trans.*, **69**, 1491 (1973).

3) K. K. Kundu and A. K. Das, *Indian J. Chem.*, **11**, 952 (1973).

4) C. Kalidas, P. Sivaprasad, and U. V. Venkatram, *Z. Naturforsch.*, **32a**, 791 (1977).

5) C. Kalidas and V. Srinivas Rao, *J. Chem. Eng. Data*, **19**, 201 (1974).

6) V. Srinivas Rao and C. Kalidas, *J. Chem. Eng. Data*, **21**, 314 (1976).

7) V. Srinivas Rao and C. Kalidas, *Bull. Chem. Soc. Jpn.*, **48**, 2957 (1975).

8) C. Kalidas and S. R. Palit, *J. Chem. Soc.*, **1961**, 3998.

9) G. J. Hills and D. J. G. Ives, "Reference Electrodes," D. J. G. Ives and G. J. Janz, Es., Academic Press, New York, N. Y. (1961), p. 190.

10) V. Srinivas Rao and C. Kalidas, *Indian J. Chem.*, **13**, 1303 (1975).