Standard Potentials of Ag-AgCl and Ag-AgBr Electrodes in Ethylene Glycol and Propylene Glycol at 30°C. and Related Thermodynamic Quantities

KIRON KUMAR KUNDU and MIHIR NATH DAS
Jadavpur University, Calcutta, India

Standard potentials ($E°$) of Ag-AgCl and Ag-AgBr electrodes in ethylene glycol and propylene glycol at 30° C. have been determined from e.m.f. measurements of the cell H_2| HX, (glycol) | AgX-Ag, where X is Cl or Br. The $E°$ values of the molal scale for Ag-AgCl in the two glycols are +0.022 and −0.029 volt, respectively, the corresponding values for Ag-AgBr are −0.104 and −0.152 volt. Mean activity coefficients of HCl and HBr (${}^s_s\gamma_{HX}$) in glycol solutions at concentrations in the range 0.005 to 0.01m were evaluated using an infinitely dilute solution in the particular solvent as the reference state. The medium effects, primary and secondary, of several solvents on HCl and HBr were computed.

GLYCOLIC SOLVENTS have been extensively used as media for acid-base titrations (*7*), but little attempt has been made to study quantitatively acid-base equilibria or ionic processes occurring in glycolic solvents. As a prelude to such studies, the authors have determined the standard potentials of silver-silver chloride and bromide electrodes in ethylene glycol and propylene glycol, and related thermodynamic quantities have been evaluated. A cell of the following type, without liquid junction, has been used for the purpose:

$$\text{(Pt) } H_2\text{(gas, 1 atm.)} \mid HX(m)\text{, glycol} \mid AgX\text{-}Ag,$$

where X represents Cl or Br.

EXPERIMENTAL

Materials. Pure ethylene glycol (Merck) was refluxed with 2% NaOH 3 to 4 hours and distilled. The distilled samples were dried with anhydrous Na_2SO_4 5 to 6 days, decanted and fractionally distilled twice through a Vigreaux column of 1 meter in length. Only middle fractions were collected. The distilled samples were preserved in a disiccator and small portions, as required, were again fractionally distilled before final use. The solvent's properties were boiling point (1 atm.) 196–197° C.; density (30° C.), 1.1063; ($n_D^{30°}$), 1.4288.

Propylene glycol (B.D.H.) was similarly treated and the purified samples had boiling point (1 atm.), 185–186° C.; $d_{30°}$, 1.0288; $n_D^{30°}$, 1.4293.

Concentrated hydrochloric acid (pro-analysi, Merck) was distilled and the constant boiling fraction collected. Hydrogen chloride gas was generated by dropping concentrated sulfuric acid on the distilled sample of hydrochloric acid, and dried by passing through a bubbler containing concentrated sulfuric acid and through a U-tube filled with fused calcium chloride.

Dry, gaseous, hydrobromic acid was obtained by treating analytical reagent grade bromine (Merck) with moist red phosphorus. Before absorption in the solvent kept in a Jena bottle. The gas dried by being passed through two U-tubes containing moist red phosphorus and two U-tubes containing fused $CaBr_2$.

The dried gases were passed into the respective solvents and formed approximately 0.2m solutions. Cell solutions of desired strengths were prepared by proper dilution. The acid solutions were standardized by titrating weighed amounts dissolved in water against standard aqueous alkali with phenolphthalein as the indicator. As a check, after potentiometric measurements were taken, a portion was withdrawn from the cell vessel and titrated. No significant difference was observed.

Electrodes. The silver-silver chloride electrodes were the thermoelectrolytic type and the method of preparation was essentially similar to that of Taniguchi and Janz (*9*).

The Ag-AgBr electrodes were of thermal type, their method of preparation similar to that of Keston (*3*). The electrodes were preserved over the respective solvents when not in use. The electrodes functioned smoothly with good reproducibility in the solvents and with very little asymmetry potential.

The platinum foil hydrogen electrode was prepared by following the method of platinization of Hills and Ives (*1*) and was preserved in distilled water when not in use. The hydrogen electrodes and the Ag-AgX electrodes were provided with ground glass joints suitable for insertion in the cell vessel.

The cell. The cell vessel was a pear-shaped glass container fitted with five ground glass joint mouths which permitted the insertion of three Ag-AgX electrodes at the same time and one hydrogen electrode (Platinum foil). Hydrogen gas entered the vessel through an inlet near the bottom against the platinum foil of the hydrogen electrode, and escaped through a small bubbler containing the solution attached to the opposite and upper part of the vessel.

The hydrogen gas prepared electrolytically in the laboratory was purified through the usual train of purifiers, viz., alkaline pyrogallol, lead acetate solution, concd. NaOH solution, concd. H_2SO_4, and the solvent, interconnected with polyethylene tubings. Measurements were made at 30 ± 0.1° C. with a Leeds & Northrup K-type potentiometer and moving coil galvanometer.

Procedure. Seven to 8 ml. of the acid solution in glycol were taken in to the electrode vessel. The platinum foil electrode was washed with distilled water, wiped carefully with filter paper, washed with solvent, wiped, and after washing with the solution, was introduced into the cell. Three silver–silver halide electrodes were also rinsed with the solution before being introduced in the cell. The cell vessel was then connected to the H_2 gas inlet and was kept in the thermostat for 3 to 4 hours to attain equilibrium. Potentiometer readings were taken at intervals of 15 minutes until successive readings were constant within 0.5mv. The final readings were checked with all three electrodes. A total period of 5 to 6 hours was usually necessary for the procedure.

The e.m.f. values of acid solutions in propylene glycol were fairly constant for a considerable period, after which, a slight drift to the extent of about 0.5mv. at half hourly intervals was observed. This drift decreased with decreasing concentration of HBr. This limitation is inherent in the results presented here for propylene glycol and the E° values obtained are presumably correct within ±0.002 volt. The accuracy for the values in ethylene glycol is ±0.001 volt.

RESULTS

Assuming that HCl and HBr are completely dissociated in the two solvents, the e.m.f. of the cell, E, is given by:

$$E = E^\circ_m - 2k \log m + \frac{2kS_fC^{1/2}}{1 + a_oBC^{1/2}} + 2k \log (1 + 0.002\,Mm) \qquad (1)$$

where E°_m is the standard potential of the silver–silver halide electrode on the molal scale, $k = 2.3026\ RT/F = 0.06015$ (at 30° C.), m and C the molality and molarity of HCl or HBr, respectively, S_f and B the Debye-Hückel constants for solvent, a_o the ion-size parameter and M the molecular weight of the solvent. If the function $E^{\circ\prime}$ is defined as:

$$E^{\circ\prime} = E + 2k \log m - \frac{2kS_fC^{1/2}}{1 + a_oBC^{1/2}} - 2k \log (1 + 0.002\,Mm) \qquad (2)$$

We have, $E^{\circ\prime} = E^\circ_m + f(m)$.

Table I. Standard Potentials of Ag-AgCl Electrode in Ethylene Glycol and Propylene Glycol at 30° C.

Ethylene Glycol		Propylene Glycol	
m_{HCl}	$E_{\text{obs, volts}}$	m_{HCl}	$E_{\text{obs, volts}}$
0.0962	0.1820	0.1174	0.1375
0.0920	0.1835	0.0933	0.1450
0.0779	0.1895	0.0738	0.1535
0.0608	0.1995	0.0623	0.1595
0.0454	0.2120	0.0480	0.1690
0.0317	0.2275	0.0458	0.1700
0.0174	0.2540	0.0316	0.1845
0.0141	0.2640	0.0276	0.1895
0.00933	0.2820	0.0219	0.1995
0.00758	0.2910	0.0125	0.2230
0.00692	0.2955	0.00922	0.2350
0.00468	0.3140	0.00758	0.2450
$E^\circ_m = +\ 0.022 \pm 0.001$ volt		$E^\circ_m = -\ 0.029 \pm 0.002$ volt	

Table II. Standard Potentials of Ag-AgBr Electrode in Ethylene Glycol and Propylene Glycol at 30° C.

Ethylene Glycol		Propylene Glycol	
m_{HBr}	$E_{\text{obs, volt}}$	m_{HBr}	$E_{\text{obs, volt}}$
0.1005	0.0480	0.1129	0.0115
0.0947	0.0510	0.1031	0.0150
0.0895	0.0540	0.0885	0.0210
0.0886	0.0535	0.0714	0.0285
0.0810	0.0565	0.0646	0.0325
0.0607	0.0705	0.0628	0.0340
0.0496	0.0768	0.0480	0.0465
0.0421	0.0850	0.0448	0.0505
0.0386	0.0883	0.0384	0.0535
0.0294	0.0995	0.0255	0.0705
0.0236	0.1095	0.0186	0.0865
0.0222	0.1136	0.0117	0.1025
0.0131	0.1375	0.0113	0.1030
0.0103	0.1490	0.00455	0.1450
0.0084	0.1575		
0.0083	0.1590		
0.0054	0.1810		
0.0044	0.1900		
$E^\circ_m = -\ 0.104 \pm 0.001$ volt		$E^\circ_m = -\ 0.152 \pm 0.002$ volt	

The values of S_f and B used are 1.553 and 0.477, respectively, for ethylene glycol ($\epsilon_s = 36.73$) and 2.095 and 0.527 respectively, for propylene glycol ($\epsilon_s = 30.05$) at 30° C. Two sets of values of $E^{\circ\prime}$ for each solvent were calculated taking $a_o = 0$ and $a_o = 5$ respectively. Because the vapor pressures of the glycols at 30° C. are quite small, no correction for hydrogen pressures was necessary. Table I represents the data for Ag-AgCl in ethylene glycol and propylene glycol and Table II the corresponding data for Ag-AgBr. The values of $E^{\circ\prime}$ were plotted against m and the curves were extrapolated to $m = 0$. The value of $E^{\circ\prime}$ for $m = 0$, gives the standard molal potential E°_m of the Ag-AgX electrode in each solvent. The ion-size parameter for both HCl and HBr in the two glycols may be close to 5A, but accurate determination of its value was not feasible because of the low sensitivity of e.m.f. values to changing concentrations of HX in the glycols at high dilutions—a limitation inherent in the system itself. This uncertainty in the value of a_o does not appreciably affect the value of E°_m obtained by extrapolation.

The standard electrode potentials E°_c and E°_N on the molar and mole fraction scales for the two electrodes were calculated from:

$$E^\circ_c = E^\circ_m + 0.1203 \log d_o$$

and

$$E^\circ_N = E^\circ_m - 0.1203 \log 1000/M$$

where d_o represents the density of the pure solvent at 30° C. The values of E° in volts at 30° C. on molal, molar, and mole fraction scales for the two electrodes in the two solvents are shown in Table III.

ACTIVITY COEFFICIENTS OF HCl AND HBr IN ETHYLENE AND PROPYLENE GLYCOLS

The mean molar activity coefficient $(\gamma_\pm)_{\text{HX}}$ or ${}^{s}_{s}\gamma_{\text{HX}}$ in the two solvents at different molalities were computed from the equation:

$$\log {}^{s}_{s}\gamma_{\text{HX}} = \frac{E^\circ_m - E}{2k} - \log m \qquad (3)$$

using the respective values of E°_m evaluated above. The superscript s indicates that the activity coefficients refer to solutions in a nonaqueous solvent and the subscript s signifies that the reference state in an infinitely dilute solution in that particular solvent. The values of ${}^{s}_{s}\gamma$ are presented at concentrations of HX in Table IV for HCl and HBr in ethylene and propylene glycols. An error of ±0.5mv. in the e.m.f. values corresponds to an error of the order of ±0.005 unit in the activity coefficient.

Medium effects on the activity coefficients of HX in glycols. The activity coefficients, ${}^{s}_{s}\gamma_{\text{HX}}$, are referred to a value of unity at infinite dilution in each particular solvent. Because of different reference states, these values are not directly comparable. They become amenable to comparison only when referred to the same reference state, *e.g.*, the infinitely dilute aqueous solution. The relative influence of solvents upon the values of the activity coefficients can be computed using Owen's (*6*, *8*) concept of primary and secondary medium effects.

The primary medium effects of HCl and HBr in ethylene and propylene glycols were calculated using E°_m values. Using these values, plus the values of ${}^{s}_{s}\gamma_{\text{HX}}$ at different concentrations and the total medium effect, ${}^{s}_{w}\gamma_{\text{HX}}$, at the corresponding concentrations, has been computed for glycols. The values of ${}^{s}_{w}\gamma_{\text{HX}}$, so obtained, are presented in Table V. For comparison, the corresponding values of ${}^{s}_{w}\gamma_{\text{HX}}$ at 25° C. in methanol and ethanol were also calculated from the e.m.f. values reported in the literature (*2*, *4*, *5*, *10*) and are included in the same table. The values of ${}^{s}_{w}\gamma_{\text{HX}}$ for

Table III. Standard Potentials (Volts) of Ag-AgCl Electrodes in Ethylene Glycol and Propylene Glycol at 30° C. on Different Scales

Electrode	Solvent	E°_{m}	E°_{c}	E°_{N}
Ag-AgCl	Ethylene glycol	0.022	0.027	−0.123
	Propylene glycol	−0.029	−0.028	−0.164
Ag-AgBr	Ethylene glycol	−0.104	−0.099	−0.249
	Propylene glycol	−0.152	−0.151	−0.287

Table IV. Activity Coefficients (${}^{s}_{s}\gamma_{HX}$) in Glycols at 30° C.

	Ethylene Glycol		Propylene Glycol	
Molality	${}^{s}_{s}\gamma$ HCl	${}^{s}_{s}\gamma$ HBr	${}^{s}_{s}\gamma$ HCl	${}^{s}_{s}\gamma$ HBr
0.005	0.820	0.840	0.735	0.740
0.007	0.785	0.810	0.695	0.700
0.010	0.745	0.780	0.665	0.660
0.020	0.665	0.715	0.575	0.580
0.030	0.625	0.675	0.530	0.540
0.050	0.565	0.620	0.465	0.480
0.070	0.525	0.580	0.415	0.430
0.100	0.490	0.545	0.375	0.395

Table V. Variation of ${}^{s}_{w}\gamma_{HX}$ with Concentrations of Hcl and HBr in Different Solvents

	Ethylene Glycol 30° C.		Propylene Glycol 30° C.		Ethanol 25° C.		Methanol 25° C.	
Molality	${}^{s}_{w}\gamma$ HCl	${}^{s}_{w}\gamma$ HBr	${}^{s}_{w}\gamma$ HCl	${}^{s}_{w}\gamma$ HBr	${}^{s}_{w}\gamma$ HCl	${}^{s}_{w}\gamma$ HBr	${}^{s}_{w}\gamma$ HCl	${}^{s}_{w}\gamma$ HBr
0.0	43.4	27.2	115.3	68.4	369.8	137.1	92.3	53.1
0.005	35.7	22.9	84.7	50.6	217.3	88.9	72.1	42.8
0.007	34.1	22.1	80.7	47.9	199.5	...	68.2	...
0.010	32.4	21.2	69.8	45.2	181.1	80.9	65.8	39.6
0.020	28.9	19.5	66.4	39.6	145.2	73.6	58.1	35.8
0.030	27.2	18.4	61.1	36.9	131.5	69.5	53.7	33.1
0.050	24.6	16.9	53.7	32.8	110.9	65.0	48.0	30.8
0.070	22.8	15.8	47.9	29.4	97.3	61.9	44.4	...
0.100	21.3	14.8	43.3	27.0	85.7	59.2	41.2	...

the four solvents at any concentration decrease in the order of ethanol > propylene glycol > methanol > ethylene glycol (Table V). This is the order of increasing dielectric constants. The primary medium effect is the highest in ethanol which has the largest difference in dielectric constant from that of water. As the dielectric constant differences become smaller the primary medium effect decreases.

At infinite dilution in any medium ($m = 0$), the interionic effects are absent, and the value of ${}^{s}_{w}\gamma_{HX}$ becomes a measure of the difference of ion-solvent interactions in the solvent and in water. The influence of the chemical nature of the solvent, which includes interaction between solvent molecules and depends upon the structure of solvent molecules in bulk as well as in an isolated state, is, however, included in the medium effect computed above. The chemical nature of these solvents are similar and should not make any substantial contribution. The dielectric constant, which possibly reflects the polarity of the solvent molecules, predominates in the medium effect. As expected, the specificity of the ion-solvent interactions in different solvents is reflected to a greater degree in the primary medium effect. This is seen from the values of ${}^{s}_{w}\gamma_{HX}$ at $m = 0$ in Table V. Although the actual value of the medium effect would be a complicated function of several factors depending on physical and chemical properties of the solvent and water as well as of the solutes, evaluation of the medium effect serves the useful purpose of supplying a measure of the difference in chemical potentials of a solute in various solvents.

ACKNOWLEDGMENT

The authors thank the Council of Scientific and Industrial Research, India, for financial assistance.

LITERATURE CITED

(1) Hills, G.J., Ives, D.J.G., *J. Chem. Soc.* **1951**, 305.
(2) Kanning, E.W., Cambell, G.W., *J. Am. Chem. Soc.* **64**, 517 (1942).
(3) Keston, A.S., *Ibid.*, **57**, 1671 (1935).
(4) Nunez, L.J., Day, M.C., *J. Phys. Chem.* **65**, 164 (1961).
(5) Oiwa, I.T., *Ibid.* **60**, 754 (1956).
(6) Owen, B.B., *J. Am. Chem. Soc.* **54**, 1758 (1932).
(7) Palit, S.R., Das, M.N., Somayajulu, G.R., "Nonaqueous Titration," Indian Association for Cultivation of Science, 1954.
(8) Robinson, R.A., Stokes, R.H., "Electrolyte Solutions," p. 351, Butterworth Scientific Publications, London, 1959.
(9) Taniguchi, H., Janz, G.J., *J. Electrochem. Soc.* **104**, 123 (1957).
(10) Taniguchi, H., Janz, G.J., *J. Phys. Chem.* **61**, 688 (1957).

RECEIVED for review July 23, 1963. Accepted August 8, 1963.