Studies in ' Isodielectric ' Media. Part I. Standard Potentials of Ag–AgX (X = Cl or Br) Electrodes in Methanol–Propylene Glycol at 25 °C

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Standard potentials ($_sE°$) of the Ag–AgCl and Ag–AgBr electrodes have been determined in a series of approximately ' isodielectric ' media, formed by mixing methanol (D_s = 32·63) and propylene glycol (D_s = 31·0) in various proportions at 25°, from the e.m.f. measurements of the cell: Pt, H_2(g, 1 atm)|HCl(m), solvent|AgCl–Ag and Pt, H_2(g, 1 atm)|HOAc(m_1), NaOAc(m_2), NaX(m_3), solvent|AgX–Ag, where X = Br. The required p($_sK_a$)$_{HOAc}$ values for the latter were determined from the same type of cell with X = Cl. The molal activity coefficients ($^s_s\gamma$)$_{HCl}$ of HCl, referred to the standard state in each solvent mixture, have been evaluated at different concentrations (0·005—0·07m), and are found to vary only slightly from solvent to solvent at any concentration, as expected from the small difference in dielectric constants of the solvents. The standard free-energy changes $\Delta G_t°$(HX) accompanying the transfer of 1 mole of HX from methanol to the other solvent have been computed, and are found to decrease somewhat sharply at first but less so as the proportion of propylene glycol increases. The relative magnitudes of $\Delta G_t°$(HX) for both HCl and HBr indicate that anions are glycophilic and that H^+ is methanophilic, suggesting that methanol is more ' basic ' than propylene glycol.

ISODIELECTRIC media constitute a distinct class of solvents which should be particularly useful for the studies of proton- or ion-transfer equilibria. The ' electrostatic effects '[1] arising from the difference of permittivity of the solvents, usually difficult to assess, are expected to be negligible in these solvents. Consequently, the ' chemical effects '[1] of the solvents are expected to be directly reflected in the observed free-energy change accompanying the transfer process.

Since the dielectric constants of methanol and propylene glycol (PG) at 25° are 32·63 [2] and 31·0 [3] respectively and those of their mixtures are expected to lie within these extreme values, all these solvents should essentially serve as ' isodielectric ' media. As an essential prerequisite for the studies of acid–base equilibria or ion-transfer processes [4,5] in this solvent system, the standard potentials ($_sE°$) of the Ag–AgCl and Ag–AgBr electrodes have been determined. The cell A has been used in the

$$\text{Pt, H}_2\text{(g, 1 atm.)|HCl}(m)\text{, solvent|AgCl–Ag} \qquad \text{A}$$

case of the AgCl–Ag electrode. Since the cell of the type A with HBr was not found suitable for this solvent system,[6] a method essentially similar to Owen's method,[7]

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[1] R. G. Bates, ' Hydrogen Bonded Solvent Systems,' eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968.

[2] J. Timmermans, ' Physico-Chemical Constants of Pure Organic Compounds,' Elsevier, Amsterdam, 1950.

[3] G. O. Curme and F. Johnston, ' Glycols,' Reinhold, New York, 1952.

[4] D. Feakins, ' Physico-Chemical Processes in Mixed Aqueous Solvents,' ed. F. Franks, Heinemann, London, 1967.

[5] H. Strehlow, ' The Chemistry of Non-Aqueous Solvents,' ed. J. J. Lagowski, Academic Press, New York, 1967.

[6] K. K. Kundu, D. Jana, and M. N. Das, *J. Phys. Chem.*, 1970, **74**, 2625.

[7] B. B. Owen, *J. Amer. Chem. Soc.*, 1935, **57**, 1526.

using buffer solutions containing acetic acid (HOAc), sodium acetate (NaOAc), and sodium bromide (NaBr) has been adopted, the cell B with X = Br being used for the purpose.

$$\text{Pt, H}_2\text{(g, 1 atm)}|\text{HOAc}(m_1)\text{, NaOAc}(m_2)\text{,}$$
$$\text{NaX}(m_3)\text{, solvent}|\text{AgX–Ag} \quad \text{B}$$

The required dissociation constants $({}_{\text{s}}K_{\text{a}})_{\text{HOAc}}$ of HOAc in these solvents were also determined from the e.m.f. measurements of the cell B with X = Cl, using the ${}_{\text{s}}E^{\circ}$ values of the AgCl–Ag electrode in these solvents determined with the cell A.

EXPERIMENTAL

Propylene glycol (L.R., B.D.H.) was purified by the method described earlier.[8] The distilled glycol was preserved in a desiccator and redistilled before use. Methanol (G.R., Merck) was distilled twice, using a Vigreux column of nearly 1-m length. The characteristic properties of the solvents are given below.

	B.p. (1 atm)	d_{s}^{25}	n_{D}^{25}
PG	185—186	1·0326	1·4310
Methanol	64·1	0·7866	1·3266

Solvents of various compositions were made up by weight. The densities of the solvents were measured with a pyknometer of 5-ml capacity having a 10-cm long neck of 1-mm bore tubing and graduated in 1-mm divisions. All density measurements were made in a thermostat kept at a temperature of 25 ± 0·1°. The densities of the solvents are presented in Table 1.

TABLE 1

Parameters for the evaluation of $E^{\circ\prime}$ of equation (2) in methanol–propylene glycol solvents at 25°

Wt. % PG	M_{s}	Density d_{s}/g ml^{-1}	Vap. press. P/mmHg	ϕ_{PG}	D_{s} *	Excess volume V$^{\text{e}}$/ml mol^{-1}	S_{f}	B
0	32·03	0·7866	122·8	0·000	32·63	0·00	1·901	0·5099
10	33·97	0·8083	117·3	0·078	(32·51)	−0·13	1·912	0·5109
30	38·72	0·8542	104·0	0·246	(32·24)	−0·40	1·936	0·5130
50	45·02	0·9032	86·4	0·432	(31·43)	−0·59	1·963	0·5154
70	53·85	0·9534	62·0	0·640	(31·59)	−0·59	1·996	0·5183
90	66·85	1·0056	31·0	0·873	(31·21)	−0·28	2·032	0·5214
100	76·06	1·0326	0	1·000	31·0	0·00	2·052	0·5231

* The values in parentheses have been obtained by equation (1).

The dielectric constants D_{s} of the solvent mixtures were estimated by using the volume-fraction additivity rule for dielectric constants, suitable for ideal mixtures,[9] equation (1), where $(D_{\text{s}})_1$, $(D_{\text{s}})_2$, and D_{s} are the dielectric constants of

$$D_{\text{s}} = (D_{\text{s}})_1\phi_1 + (D_{\text{s}})_2(1 - \phi_1) \qquad (1)$$

the components 1, 2, and the mixtures respectively and ϕ_1 is the volume fraction of the component 1. The values so obtained are given in Table 1. It is probably reasonable to assume an ideal relationship as in equation (1), because (*a*) the two pure solvents mix without significant heat changes and (*b*) the excess volume of mixing (Table 1) is always small.

The vapour pressure of PG at 25°, being extremely small,[3] was neglected in comparison with that of methanol, and the vapour pressures of the solvent mixtures (Table 1) were taken to be equal to $P_{\text{m}}X_{\text{m}}$, where P_{m} is the vapour pressure of methanol at 25° and X_{m} its mole fraction in the mixture.

The experimental procedures for preparing the electrodes and the required solutions were similar to those described.[6,8,10] The general experimental set up was also similar,[8] with suitable modifications in view of the higher volatility of methanol. To avoid any change in the composition of the cell solution, pure dry H_2 was presaturated by passing the gas through the solvent in a bubbler and then through a series of six bubblers containing the same solution as in the cell, all of which were kept in a thermostat maintained at 25 ± 0·1°. E.m.f. measurements were made with the help of a Rubicon potentiometer and a moving-coil galvanometer. The readings were taken at intervals of 15 min until three successive readings were within 0·1 to 0·2 mV. About 4—5 h were necessary to reach equilibrium. In the case of buffer solutions containing NaCl in pure methanol, occasional poisoning of the platinized Pt-foil electrode was observed, but such difficulties did not occur in the case of HCl solutions.

RESULTS

Standard Potentials of the Ag–AgCl *Electrode*.—Assuming that HCl is completely dissociated in these solvents, ${}_{\text{s}}E_m{}^{\circ}$, the molal standard potential of the cell A, was obtained by using the function $E^{\circ\prime}$ defined[11] by equation (2), where E

$$E^{\circ\prime} \equiv E + 2k\log m - \frac{2kS_{\text{f}}c^{\frac{1}{2}}}{1 + a_0Bc^{\frac{1}{2}}} - 2k\log(1 + 0{\cdot}002\, mM_{\text{s}}) = {}_{\text{s}}E_m{}^{\circ} + f(m) \qquad (2)$$

is the observed potential of the cell at 1 atm pressure of hydrogen at a molal concentration m of HCl, S_{f} and B the Debye–Hückel constants for a particular solvent and temperature, c the molarity of HCl solution, a_0 the ion size parameter, $k = 2{\cdot}303\, RT/F$, and M_{s} the molecular weight or the average molecular weight of the solvent.

Table 2 gives the observed e.m.f. values (corrected for 1 atm pressure of H_2) of the cell A at different molalities of HCl. The $E^{\circ\prime}$ values were computed by using these e.m.f. values and the S and B values given in Table 1. In all the solvents the $E^{\circ\prime}$ values computed by taking $a_0 = 0$, resulted in fairly good straight lines when plotted against the molality of HCl, which on extrapolation to $m = 0$ gave the $({}_{\text{s}}E_m{}^{\circ})$ values. Reasonable alterations in the value of a_0 have no detectable influence on the values of ${}_{\text{s}}E_m{}^{\circ}$ in any solvent. Figure 1 shows the extrapolation of $E^{\circ\prime}$ against

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[8] K. K. Kundu and M. N. Das, *J. Chem. and Eng. Data*, 1964, **9**, 87.

[9] T. B. Hoover, *J. Phys. Chem.*, 1969, **73**, 57.

[10] K. K. Kundu and M. N. Das, *J. Chem. and Eng. Data*, 1964, **9**, 82.

[11] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolyte Solutions,' 3rd edn., Reinhold, New York, 1958.

the molality of HCl in each solvent. The values of the standard potentials on the molar (${}_sE_c^\circ$) and mole fraction (${}_sE_N^\circ$) scales have been computed from (${}_sE_m^\circ$) values with the help of the usual relations.[11] These values at 25° are in Table 3. The average standard deviation in ${}_sE^\circ$ values in these solvents is of the order of $\pm 0\cdot0005$ V. In each solvent the standard deviation was computed from the deviations of $E^{\circ\prime}$ values at different concentrations from those on the best plot drawn through them.

TABLE 2

E.m.f. (E) of the cell A in methanol–propylene glycol

Methanol		10% PG		30% PG		50% PG		70% PG		90% PG		100% PG	
m_{HCl} [a]	E/V	m_{HCl}	E/V	m_{HCl}	E/V	m_{HCl}	E/V	m_{HCl}	E/V	m_{HCl}	E/V	m_{HCl}	E/V
0·00558	0·2718	0·00394	0·2905	0·00493	0·2799	0·00528	0·2741	0·00438	0·2753	0·00568	0·2549	0·00454	0·2597
0·0133	0·2322	0·00621	0·2715	0·00956	0·2512	0·00628	0·2663	0·00544	0·2664	0·01067	0·2269	0·00586	0·2500
0·0183	0·2202	0·00796	0·2601	0·0138	0·2340	0·00989	0·2455	0·00598	0·2621	0·0152	0·2132	0·00889	0·2320
0·0276	0·2039	0·0119	0·2415	0·0192	0·2207	0·0128	0·2359	0·00655	0·2579	0·0217	0·1994	0·0120	0·2180
0·0323	0·1981	0·0138	0·2371	0·0233	0·2111	0·0171	0·2224	0·01002	0·2402	0·0261	0·1914	0·0159	0·2065
0·0449	0·1844	0·0232	0·2147	0·0294	0·2032	0·0213	0·2148	0·0200	0·2121	0·0393	0·1734	0·0206	0·1974
0·0591	0·1727	0·0271	0·2083	0·0325	0·2001	0·0235	0·2099	0·0300	0·1948	0·0527	0·1653	0·0264	0·1885
0·0633	0·1708	0·0307	0·2011	0·0398	0·1905	0·0309	0·1980	0·0394	0·1855	0·0533	0·1641	0·0305	0·1815
0·0762	0·1632	0·0438	0·1894	0·0636	0·1709	0·0451	0·1833	0·0480	0·1756	0·0643	0·1554	0·0319	0·1810
		0·0524	0·1813	0·0777	0·1627	0·0467	0·1830	0·0808	0·1535			0·0358	0·1770
		0·0549	0·1782	0·0832	0·1606	0·0602	0·1715					0·0566	0·1601
						0·0785	0·1626						

[a] m Represents molal concentrations throughout Parts I—IV.

The ${}_sE_m^\circ$ value in PG ($-0\cdot0320$ V) is in fair agreement with that obtained earlier ($-0\cdot0323$ V).[12] The value obtained for ${}_sE_m^\circ$ in methanol also agrees fairly well with the literature values,[13-16] and the slightly less negative value in the present case may be due to the fact that for evaluating S_f and B of equation (2) the value of D_s has been taken as 32·63, instead of 31·5, used in other cases.

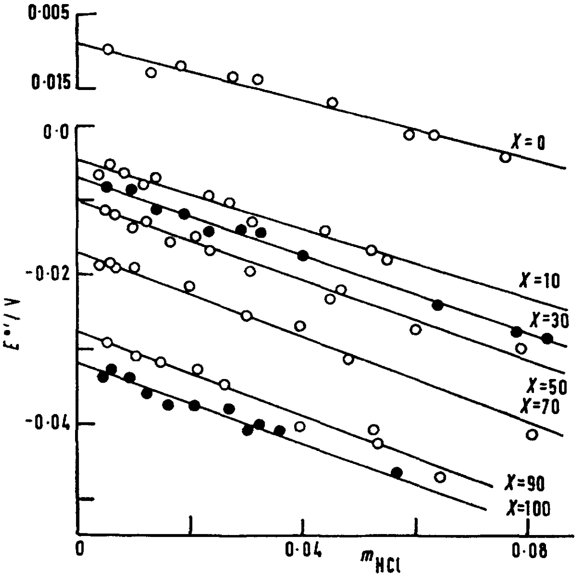

FIGURE 1 Extrapolation of e.m.f. data to give E_m° values for the Ag–AgCl electrode in methanol–propylene glycol mixtures at 25°. X = Wt. % PG

Activity Coefficients (${}^{s}_{s}\gamma$) *of* HCl.—The activity coefficients of HCl $({}^{s}_{s}\gamma)_{HCl}$ at different concentrations (0·005—0·07m), referred to the standard state in each solvent mixture, have been computed by equation (3). In each solvent $({}^{s}_{s}\gamma)_{HCl}$

$$\log ({}^{s}_{s}\gamma)_{HCl} = \frac{({}_sE_m^\circ - E)}{4\cdot606RT/F} - \log m_{HCl} \qquad (3)$$

values at round concentrations were obtained from a large scale plot of $({}^{s}_{s}\gamma)_{HCl}$ against m_{HCl}, and are collected in Table 4. At any concentration within this limited range, there is only a slightly decreasing trend in the $({}^{s}_{s}\gamma)_{HCl}$ values in different solvents, which is the result expected amongst these approximately ' isodielectric ' media wherein the interionic contribution to $({}^{s}_{s}\gamma)_{HCl}$ is expected to be substantially constant.

TABLE 3

Standard potentials of the Ag–AgCl Electrode in methanol–propylene glycol at 25°

Wt. % PG	${}_sE_m^\circ$/V	${}_sE_c^\circ$/V	${}_sE_N^\circ$/V
0	−0·0090	−0·0213	−0·1858
10	−0·0045	−0·0154	−0·1783
30	−0·0070	−0·0151	−0·1739
50	−0·0100	−0·0152	−0·1692
70	−0·0170	−0·0194	−0·1672
90	−0·0275	−0·0272	−0·1665
100	−0·0320	−0·0304	−0·1643

TABLE 4

Variation of $({}^{s}_{s}\gamma)_{HCl}$ with concentration of HCl in methanol–propylene glycol at 25°

m_{HCl} Wt. % PG	0·005	0·01	0·02	0·03	0·04	0·05	0·06	0·07
0	0·78	0·70	0·62	0·56	0·53	0·51	0·49	0·48
30	0·78	0·69	0·62	0·56	0·53	0·51	0·49	0·48
50	0·78	0·68	0·60	0·55	0·53	0·50	0·49	
70	0·75	0·67	0·58	0·53	0·51	0·48	0·47	0·46
90	0·74	0·66	0·57	0·52	0·49	0·47	0·45	
100	0·73	0·65	0·56	0·51	0·47	0·45		

Dissociation Constants (${}_sK_a$) *of Acetic Acid*.—The dissociation constants $({}_sK_a)_{HOAc}$ of acetic acid at 25° were determined in these solvents by extrapolating the plots of the

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[12] K. K. Kundu, P. K. Chatterjee, Debabrata Jana, and M. N. Das, *J. Chem. and Eng. Data*, 1970, **15**, 209.

[13] G. Nonhebel and H. Hartley, *Phil. Mag.*, 1925, **1**, 729.

[14] J. M. Austin, A. H. Hunt, F. A. Johnson, and H. N. Parton, in ' Electrochemical Data,' ed. B. E. Conway, Elsevier, Amsterdam, 1952.

[15] J. Koskikallio, *Soumen Kem.*, 1957, **30** *B*, 38, 43, 111.

[16] I. T. Oiwa, *J. Phys. Chem.*, 1956, **60**, 754.

function $p({}_{s}K_a)_{HOAc}'$, defined by equation (4), against the ionic strength (μ) to $\mu = 0$.

$$p({}_{s}K_a)_{HOAc}' \equiv \frac{E - {}_{s}E_m^{\circ}}{0{\cdot}05916} + \log \frac{m_{HOAc}\, m_{Cl^-}}{m_{OAc^-}}$$

$$= p({}_{s}K_a)_{HOAc} - \log \frac{\gamma_{HOAc}\gamma_{Cl^-}}{\gamma_{OAc^-}} = p({}_{s}K_a)_{HOAc} + f(\mu) \quad (4)$$

The $p({}_{s}K_a)_{HOAc}'$ values were computed by using (${}_{s}E_m^{\circ}$) values of the Ag–AgCl electrode in the solvents given in Table 3 and the measured e.m.f. values (corrected to 1 atm H_2) of the cell B with X = Cl, for the various compositions of buffer mixtures (Table 5). Assuming that NaCl and NaOAc are completely dissociated and in view of the fact that the dissociation of HOAc in each of the solvents is so small that it does not significantly alter the effective concentration of HOAc and OAc^-, we have $m_{Cl^-} = m_3$, $m_{HOAc} = m_1$, $m_{OAc^-} = m_2$, and $\mu = (m_{NaCl} + m_{OAc^-})d_s$.

TABLE 5

E.m.f. of the cell B in methanol–propylene glycol at 25° (X = Cl)

m_{HOAc}	m_{NaOAc}	m_{NaCl}	E/V
	Methanol		
0·0105	0·00533	0·00496	0·6687
0·0109	0·00877	0·00822	0·6662
0·0207	0·0113	0·00999	0·6527
0·00936	0·0124	0·0120	0·6704
0·0176	0·0145	0·0119	0·6581
0·0182	0·0160	0·0151	0·6547
0·0209	0·0217	0·0200	0·6512
0·0322	0·0321	0·0310	0·6381
0·0355	0·0429	0·0405	0·6357
	10 Wt. % PG		
0·00458	0·00678	0·00624	0·6881
0·0131	0·0129	0·0122	0·6598
0·0177	0·0191	0·0184	0·6519
0·0242	0·0248	0·0242	0·0431
	30 Wt. % PG		
0·00507	0·00629	0·00582	0·6804
0·01048	0·0125	0·0115	0·6612
0·0154	0·0186	0·0171	0·6507
0·0134	0·0202	0·0181	0·6547
0·0181	0·0228	0·0212	0·6468
0·0187	0·0270	0·0238	0·6464
0·0278	0·0398	0·0353	0·6363
0·0347	0·0450	0·0420	0·6294
	50 Wt. % PG		
0·00587	0·00536	0·00573	0·6676
0·00770	0·00796	0·00781	0·6625
0·0156	0·0177	0·0167	0·6459
0·0170	0·0190	0·0183	0·6427
0·0159	0·0199	0·0181	0·6463
0·0340	0·0363	0·0364	0·6235
	70 Wt. % PG		
0·00561	0·00495	0·00522	0·6638
0·00637	0·00605	0·00621	0·6615
0·00777	0·00797	0·00778	0·6566
0·00837	0·00793	0·00821	0·6546
0·01096	0·01090	0·01071	0·6493
0·00950	0·0111	0·0125	0·6491
0·0200	0·0199	0·0200	0·6319
0·0267	0·0299	0·0277	0·6264
	90 Wt. % PG		
0·00812	0·00935	0·00822	0·6503
0·01059	0·0151	0·0132	0·6434
0·0173	0·0191	0·0178	0·6293
0·0200	0·0249	0·0224	0·6259
0·0226	0·0230	0·0249	0·6183
0·0270	0·0316	0·0299	0·6167

The values of μ generally varied from 0·01 to 0·07. The $p({}_{s}K_a)_{HOAc}$ values obtained from the extrapolation are collected in Table 6. The average standard deviation of these values in different solvents is of the order ±0·01 unit.

TABLE 6

$p({}_{s}K_a)_{HOAc}$ values of acetic acid in methanol–propylene glycol at 25°

Wt. % PG	0	10	30	50	70	90	100
$p({}_{s}K_a)_{HOAc}$	9·45	9·33	9·29	9·26	9·29	9·32	9·32 [a]

[a] Ref. 6.

TABLE 7

E.m.f. (E) of the cell B in methanol–propylene glycol at 25° (X = Br)

m_{HOAc}	m_{NaOAc}	m_{NaBr}	E/V
	Methanol		
0·00646	0·00630	0·00593	0·5552
0·00114	0·0134	0·0118	0·5432
0·0175	0·0134	0·0164	0·5232
0·0258	0·0258	0·0263	0·5180
0·0352	0·0271	0·0329	0·5054
0·0392	0·0390	0·0403	0·5053
0·0440	0·0500	0·0471	0·5042
0·0528	0·0511	0·0537	0·4967
	10 Wt. % PG		
0·0149	0·01076	0·0129	0·5251
0·0264	0·0235	0·0248	0·5116
0·0416	0·0334	0·0401	0·4951
0·0503	0·0472	0·0499	0·4932
	30 Wt. % PG		
0·00729	0·00856	0·00840	0·5447
0·00994	0·0127	0·0120	0·5386
0·0135	0·0159	0·0157	0·5282
0·0178	0·0160	0·0181	0·5171
0·0191	0·0192	0·0203	0·5163
0·0254	0·0204	0·0250	0·5053
0·0380	0·0315	0·0370	0·4948
	50 Wt. % PG		
0·00578	0·00511	0·0551	0·5425
0·0120	0·01002	0·0111	0·5224
0·0292	0·0220	0·0257	0·4969
0·0272	0·0315	0·0294	0·5035
0·0286	0·0323	0·0387	0·4963
0·0424	0·0356	0·0391	0·4875
	70 Wt. % PG		
0·00584	0·00569	0·00582	0·5361
0·0146	0·0160	0·0159	0·5129
0·0246	0·0270	0·0266	0·4991
0·0342	0·0379	0·0369	0·4904
	90 Wt. % PG		
0·00426	0·00551	0·00503	0·5385
0·00958	0·00991	0·01042	0·5139
0·0127	0·0166	0·0149	0·5094
0·0171	0·0208	0·0206	0·4992
0·0211	0·0280	0·0246	0·4959
0·0261	0·0313	0·0309	0·4877
0·0312	0·0388	0·0346	0·4854

Standard Potentials (${}_{s}E^{\circ}$) *of the* AgBr–Ag *Electrode*.—The standard potential (${}_{s}E_m^{\circ}$) of the AgBr–Ag electrode at 25° in each of the solvents was obtained from the plot of the function $E^{\circ\prime}$, defined by equation (5), against μ, by extrapolation to $\mu = 0$ (Figure 2). The values of the function

$$E^{\circ\prime} \equiv E - 0{\cdot}05916\,p({}_{s}K_a)_{HOAc} + 0{\cdot}05916 \log \frac{m_{HOAc} m_{Br^-}}{m_{OAc^-}}$$

$$= ({}_{s}E_m^{\circ}) - 0{\cdot}05916 \log \frac{\gamma_{HOAc}\gamma_{Br^-}}{\gamma_{OAc^-}} = {}_{s}E_m^{\circ} + f(\mu) \quad (5)$$

$E^{\circ\prime}$ in each solvent were computed by using the values of $\mathrm{p}({}_{\mathrm{s}}K_{\mathrm{a}})_{\mathrm{HOAc}}$ (Table 6) and the measured e.m.f. values (corrected to 1 atm H_2) of the cell B with X = Br, for the various buffer compositions given in Table 7. Assuming NaBr to be completely dissociated in each of the solvents, we have $m_{\mathrm{HOAC}} = m_1$, $m_{\mathrm{OAc^-}} = m_2$, $m_{\mathrm{Br^-}} = m_3$, and $\mu = (m_2 + m_3)d_{\mathrm{s}}$. The ${}_{\mathrm{s}}E^\circ$ values on different scales are presented in Table 8, the average deviation being of the order of ±0·0005 V. The ${}_{\mathrm{s}}E_m^\circ$ value of the AgBr–Ag electrode in methanol agrees fairly well with −0·1328 and −0·1367 V reported earlier.[17,18]

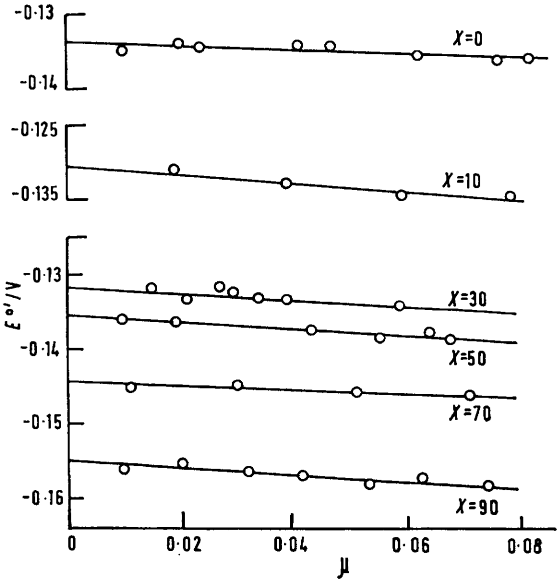

FIGURE 2 Extrapolation of e.m.f. data to give E_m° values for the Ag–AgBr electrode in methanol–propylene glycol mixtures at 25°. X = Wt. % PG

TABLE 8

Standard potentials of the Ag–AgBr electrode in methanol–propylene glycol in different scales at 25°

Wt. % PG	${}_{\mathrm{s}}E_m^\circ$/V	${}_{\mathrm{s}}E_c^\circ$/V	${}_{\mathrm{s}}E_N^\circ$/V
0	−0·1340	−0·1463	−0·3108
10	−0·1310	−0·1419	−0·3048
30	−0·1320	−0·1401	−0·2989
50	−0·1355	−0·1407	−0·2947
70	−0·1445	−0·1469	−0·2947
90	−0·1550	−0·1547	−0·2940
100[a]	−0·1633	−0·1617	−0·2956

[a] Ref. 6.

TABLE 9

Standard free energy of transfer, ΔG_t°(HCl) and ΔG_t°(HBr) from methanol to methanol–propylene glycol at 25°

Wt. % PG	0	10	30	50	70	90	100
ΔG_t°(HCl)/ cal mol^{-1}	0	−173	−274	−382	−428	−444	−495
ΔG_t°(HBr)/ cal mol^{-1}	0	−138	−274	−371	−371	−386	−350

DISCUSSION

The standard potentials of the Ag–AgX electrodes in different solvents may be used to compute the standard free-energy changes, ΔG_t°(HX) accompanying the transfer of 1 mole of HX from the standard state in one arbitrary reference solvent to the standard state in another. Taking methanol as the reference solvent, ΔG_t°(HX) values for both HCl and HBr have been computed by equation (6) where $({}_{\mathrm{m}}E_N^\circ)_{\mathrm{AgX-Ag}}$ and

$$\Delta G_t^\circ(\mathrm{HX}) = F[({}_{\mathrm{m}}E_N^\circ)_{\mathrm{AgX-Ag}} - ({}_{\mathrm{s}}E_N^\circ)_{\mathrm{AgX-Ag}}] \quad (6)$$

$({}_{\mathrm{s}}E_N^\circ)_{\mathrm{AgX-Ag}}$ are the standard reduction potentials of the Ag–AgX electrode on the mole fraction scale in methanol and the other solvent respectively. A proper allowance of the scale effect is generally believed to be attainable by taking the electrode potentials on the mole fraction scale.[19] The ΔG_t°(HX) values, which are expected to be accurate within ±23 cal, are shown in Table 5 and Figure 3.

The ΔG_t°(HX) values are found to decrease somewhat sharply at first with a distinct tendency to assume limiting values, as the proportion of PG increases (Figure 3). For any solvent, the values for HCl are more negative than for HBr; these indicate that the transfer of HCl is relatively easier than that of HBr. Thus for the chloride and bromide ions, the escaping tendency increases as the ionic size decreases. Most possibly this would occur,[4] if the interaction energy between X^- and the dipoles in PG or any of the mixed solvent exceeds that in pure methanol, resulting in negative values for $\Delta G_t^\circ(X^-)$. The halide ions show increasing escaping tendency from methanol to the solvents with increasing proportion of PG. Again, the nature of the variation of ΔG_t°(HX) with the solvent composition (Figure 3) suggests that an opposing factor must also operate so as to result in the observed flat nature of the curves in the glycol-rich portion. Assuming that the variation of $\Delta G_t^\circ(X^-)$ is monotonic with solvent composition, it is clearly the contribution of $\Delta G_t^\circ(H^+)$ to ΔG_t°(HX) that acts in the opposite direction, *i.e.* $\Delta G_t^\circ(H^+)$ values should have increasing positive values as the proportion of PG increases.

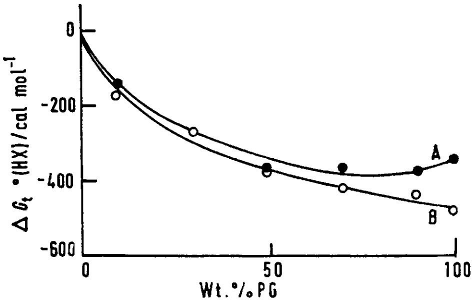

FIGURE 3 Variation of standard free energy of transfer, ΔG_t°(HX), of A, HBr and B, HCl from methanol to methanol–propylene glycol mixtures as a function of wt. % PG, at 25°

Now a simple analysis of the reactions of the cell A with

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[17] E. W. Canning and G. W. Campbell, *J. Amer. Chem. Soc.*, 1942, **64**, 517.

[18] C. L. de Ligny and A. A. Wieneke, *Rec. Trav. chim.*, 1960, **72**, 268.

[19] R. A. Robinson and R. H. Stokes, ' Electrolyte Solutions,' 2nd rev. edn., Butterworths, London, 1965, pp. 353—354.

$Cl^- = X^-$, in solvent (SH) and methanol (MH) indicates that $\Delta G_t^\circ(HX)$ represents the free energy change accompanying the process (7), where each of the species

$$MH_2^+(m) + SH(s) + X^-(m) \longrightarrow SH_2^+(s) + MH(m) + X^-(s) \quad (7)$$

involved is in the standard state in methanol or solvent, as indicated by (m) or (s). From this it follows that $\Delta G_t^\circ(H^+)$ is the free energy change of the process (8),

$$MH_2^+(m) + SH(s) \longrightarrow SH_2^+(s) + MH(m) \quad (8)$$

which is in effect the difference in free-energy changes accompanying the processes (9) and (10) depicting the

$$H^+(g) + SH(s) \longrightarrow SH_2^+(s) \quad (9)$$

$$H^+(g) + MH(m) \longrightarrow MH_2^+(m) \quad (10)$$

basicity of the solvent and methanol respectively, where (g) indicates the standard state of H^+ in the gaseous state. So, $\Delta G_t^\circ(H^+)$ effectively gives a measure of the relative basicity of the solvent with respect to that of methanol. As the ' electrostatic effect ' is negligibly small in these ' isodielectric ' media, $\Delta G_t^\circ(H^+)$ should rather stand for the difference of ' intrinsic ' basicity of the solvents. The expected increasingly positive magnitudes of $\Delta G_t^\circ(H^+)$ with increasing proportion of PG imply that the relative proton affinities of the mixed solvents gradually decrease as the proportion of PG increases. This indicates that methanol is more ' basic ' than PG.

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