Standard Potential of the Ag–AgCl Electrode and Related Thermodynamic Quantities in Butan-1-ol at Different Temperatures

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E.m.f. measurements of cells of the type Pt, H_2|HCl(m), BuOH|AgCl–Ag at nine temperatures ranging from 5 to 45 °C were used to derive the standard e.m.f. of the cell in butan-1-ol, the mean activity coefficient of HCl, the primary medium effect, the relative partial molal enthalpy of HCl, and the standard changes of Gibbs energy, enthalpy, entropy, and heat capacity for the transfer of HCl from water to butan-1-ol. These thermodynamic quantities were calculated from ΔE_N° and its temperature coefficient. The molality of the acid ranged from 0·005 to 0·15 mol kg^{-1}. The results have been discussed in the light of acid–base properties and the effect of structure of the solvent on the transfer process.

ION–SOLVENT interactions are important in accounting for acid–base equilibria and rates of reactions in partially aqueous and non-aqueous solvents.[1-3] Evaluation of the energetics is essential in order to clearly understand the acid–base equilibria as well as the electrochemical processes in general. In continuation of our previous studies on the standard potentials of the Ag–AgCl electrode in anhydrous propan-1-ol,[4] we have now determined the standard potentials of the Ag–AgCl electrode with associated thermodynamic quantities in butan-1-ol at nine temperatures in the range 5—45 °C. This temperature range should be sufficient to provide improved accuracy in the evaluation of those thermodynamic constants which depend on the temperature coefficient of the e.m.f.

As demonstrated by our present work, the variation of standard e.m.f. with temperature provides a useful insight into the phenomena of ion–solvent interactions. In this paper, we present the results on the standard electrode potential, the mean activity coefficient, the primary medium effects, the relative partial molal enthalpy, and the thermodynamic properties of HCl on the transfer process. A cell of type (I) has been used for this purpose.

$$\text{Pt, } H_2|\text{HCl}(m), \text{ BuOH}|\text{AgCl–Ag} \qquad \text{(I)}$$

EXPERIMENTAL

E.m.f. values were measured using a precision potentiometer (Leeds and Northrup type K-3) in conjunction with a sensitive galvanometer and an Eppley standard cell maintained at constant temperature. The e.m.f. readings were taken after appropriate times of equilibration when e.m.f. values remained constant within ±0·02 mV for ½ h. The temperatures of the constant temperature bath were known to ±0·01 °C.

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[1] R. G. Bates, *J. Electroanalyt. Chem.*, 1971, **29**, 1.

[2] R. N. Roy, W. Vernon, and A. L. M. Bothwell, *J. Electroanalyt. Chem.*, 1971, **30**, 335.

[3] D. Feakins in 'Physico-Chemical Processes in Mixed Aqueous Solvents,' ed. F. Franks, American Elsevier Publishing Co., New York, 1967, and references listed therein.

[4] R. N. Roy, W. Vernon, Alfred L. M. Bothwell, and James Gibbons, *J. Chem. Thermodynamics*, in the press.

The preparation of the Ag–AgCl electrodes has been described elsewhere.[5] The Ag–AgCl electrodes used were of the thermal electrolytic type and their bias potential was 0·01 mV after ageing. The hydrogen electrodes (lightly platinized) were prepared according to the method of Hills and Ives.[6] Freshly prepared hydrogen electrodes were used for each measurement. All cells were run in quadruplicate. The e.m.f. of each cell was measured in ascending order of temperature at 5° intervals from 5 to 45 °C. The purification of the hydrogen gas and the general experimental details have been previously described.[7,8]

Butan-1-ol (Fisher Certified ACS) was purified as described.[9] Reagent grade HCl was diluted approximately to the composition of the constant-boiling mixture (6M) and distilled twice, the middle third of the distillate being collected each time. Hydrogen chloride gas was generated by adding concentrated sulphuric acid, dropwise, to the distilled sample of HCl. The gas was dried by passing through a series of U-tubes filled with P_2O_5, fused calcium chloride, and Drierite, respectively. The gas was finally passed into pure butan-1-ol; the molality of the stock solution of HCl in butan-1-ol was *ca.* 0·3 mol kg^{-1}. In order to avoid any possible side reactions due to the evolution of heat resulting from dissolution of HCl in butan-1-ol, the flask containing the solvent was kept in an ice-bath. The cell solutions were were made by dilution of the stock solution with butan-1-ol and concentrations were known to within ±0·02% when titrated with a standard solution of sodium hydroxide (phenolphthalein indicator).

TABLE 1

E.m.f. (V) of cell (I) in butan-1-ol

m_{HCl} [a]	T/°C								
	5	10	15	20	25	30	35	40	45
0·1506	0·09416	0·09310	0·09174	0·09008	0·08749	0·08427	0·08074	0·07698	0·07340
0·1004	0·10830	0·10747	0·10595	0·10484	0·10240	0·09847	0·09418	0·09049	0·08720
0·08032	0·11681	0·11610	0·11497	0·11424	0·11150	0·10846	0·10568	0·10239	0·09918
0·06024	0·12681	0·12503	0·12144	0·11860	0·11506	0·11189	0·10848	0·10505	0·10118
0·04016	0·14290	0·13886	0·13539	0·13266	0·12865	0·12524	0·12247	0·11646	0·11350
0·02008	0·17239	0·17805	0·16383	0·15938	0·15583	0·15411	0·14951	0·14043	0·14028
0·010040	0·20279	0·19644	0·19357	0·19164	0·18298	0·17916	0·17380	0·16740	0·16282
0·005020	0·22813	0·22454	0·22222	0·21729	0·21199	0·20670	0·20088	0·19496	0·19002

[a] m = Molality.

RESULTS AND DISCUSSIONS

The measured e.m.f. values, corrected in the usual way to 760 mmHg pressure of hydrogen, are recorded in Table 1. Each entry is the mean value from four identical cells. The average difference between the e.m.f. values of the quadruplicate cells at all nine temperatures was 0·05 mV.

Standard E.m.f.—The standard potentials of the galvanic cells of type (I) have been determined by means of a theoretically justified non-linear extrapolation method.[10] Sen, Johnson, and Roy [10] have demonstrated that equation (1) (in which m is the molality, and A_0 is

$$E + (2RT/F)\ln m = A_0 + A_1m^{\frac{1}{2}} + A_2m + A_3m^{\frac{3}{2}} + \qquad (1)$$

identical with the standard potential $E_m°$) is theoretically sound.[11-13] Equation (1) can further be expressed by a polynomial of the form (2), in which $x = m^{\frac{1}{2}}$ and $y = E + (2RT/F)\ln m$.

$$y = A_0 + A_1x + A_2x^2 + A_3x^3 + \ldots \qquad (2)$$

The coefficients of the polynomial of equation (2) at 10, 25, and 40 °C, together with the standard error, are given in Table 2. The values of $E_m°$, $E_N°$ (the standard potentials on the molal and mole fraction scales respectively), and $-\Delta E_N°$ (the difference in standard e.m.f. between ordinary water [14] and non-aqueous solvent) are entered in Table 3. The value of the standard cell potential can be considered as correct to ±0·09 mV. The values of $E_N°$ have been computed with the help of equation (3), where $k = 2{\cdot}3026\ RT/F$ and $\bar{M}$ is the mean

$$E_N° = E_m° - 2\,k \log (1000/\bar{M}) \qquad (3)$$

molecular weight of the solvent.

TABLE 2

Coefficients of the polynomial [a]

$$y = A_0 = A_1m^{\frac{1}{2}} + A_2m + A_3m^{\frac{3}{2}} + \ldots$$

T/°C	A_0 (= $E_m°$)	A_1	A_2	A_3	Std. error
10	−0·04027	0·07113	0·33801	−0·64275	0·000001
25	−0·06863	0·09161	0·59898	−1·1398	0·000003
40	−0·10802	0·22411	0·40931	−1·1268	0·000005

[a] $y = E + 2RT(\ln m)/F$.

Activity Coefficients of HCl *in Butan*-1-*ol.*—The mean ionic activity coefficients of HCl in butan-1-ol at temperatures 5, 15, 25, 35, and 45 °C were calculated from

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[5] R. G. Bates, 'Determination of pH,' Wiley, New York, 1964, ch. 9.

[6] G. J. Hills and D. J. G. Ives in 'Reference Electrode,' eds. D. J. G. Ives and G. J. Janz, Academic Press, New York, 1961, p. 107.

[7] R. N. Roy and B. Sen, *J. Chem. and Eng. Data*, 1967, **12**, 584.

[8] R. N. Roy and A. Bothwell, *J. Chem. and Eng. Data*, 1970, **15**, 548.

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[10] B. Sen, D. A. Johnson, and R. N. Roy, *J. Phys. Chem.*, 1967, **71**, 1523.

[11] A. J. Dill, L. M. Itzkowitz, and O. Popovych, *J. Phys. Chem.*, 1968, **72**, 4580.

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[13] R. N. Roy, W. Vernon, and A. L. M. Bothwell, *J. Chem. Soc.* (*A*), 1971, 1242.

[14] R. G. Bates and V. E. Bower, *J. Res. Nat. Bur. Stand.*, 1954, **53**, 283.

TABLE 3

Standard potentials (V) of Ag–AgCl electrode in butan-1-ol (±0·09 mV)

T/°C	$E_m°$/V	$E_N°$/V	$^{\mathrm{w}}E_N°$/V [a]	$-\Delta E_N°$/mV
5	−0·02918	−0·15391	0·04159	195·50
10	−0·04027	−0·16724	0·03542	202·67
15	−0·04672	−0·17594	0·02911	205·05
20	−0·05602	−0·18748	0·02265	210·13
25	−0·06863	−0·20233	0·01596	218·29
30	−0·08709	−0·22303	0·00920	232·23
35	−0·10312	−0·24130	0·00235	243·65
40	−0·10802	−0·24844	−0·00467	243·77
45	−0·12659	−0·26926	−0·01187	257·38

[a] Ref. 14.

equation (4), where $E_m°$ is listed in Table 3. The inter-

$$\log \gamma_{\pm} = \{E_m° - [E + (2RT/F)\ln m]\}/(4\cdot6052RT/F) \quad (4)$$

polated values of $[E + (2RT/F)\ln m]$ at rounded molalities were obtained from the constants of equation (1). These values of $\gamma_{\pm}$ are listed in Table 4. An error of ±0·05 mV in the e.m.f. value corresponds to an error of ±0·002 in the values of $\gamma_{\pm}$.

TABLE 4

Stoicheiometric mean activity coefficient (γ_{F}) of HCl in butan-1-ol

	m_{HCl}						
T/°C	0·002	0·005	0·01	0·02	0·05	0·1	0·2
5	0·961	0·928	0·884	0·816	0·680	0·561	0·492
15	0·929	0·880	0·820	0·735	0·582	0·460	0·394
25	0·903	0·838	0·761	0·655	0·480	0·358	0·318
35	0·751	0·644	0·548	0·446	0·316	0·239	0·192
45	0·727	0·611	0·509	0·402	0·271	0·198	0·164

Relative Partial Molal Enthalpy.—Values of the relative partial molal enthalpy, $\bar{L}_2$, were evaluated from the temperature coefficient of log $\gamma_{\pm}$, using the relation (5),[15]

$$\bar{L}_2 = \bar{H} - \bar{H}^{\infty} = \bar{H} - \bar{H}^{0} = -2 \times 2\cdot303RT^2 (\delta \log \gamma_{\pm}/\delta T)_{p,m} \quad (5)$$

where T is the thermodynamic temperature in K. The values of $\bar{L}_2$ at 5, 15, 25, 35, and 45 °C are in Table 5. The abnormally large values of $\bar{L}_2$ reflect the enthalpy change on the dissociation of these ion pairs in butan-1-ol. Hydrochloric acid shows the characteristic behaviour of a weak electrolyte in butan-1-ol.

TABLE 5

Relative partial molal enthalpy ($\bar{L}_2$ in kcal mol^{-1}) of HCl

	T/°C				
n_{HCl}	5	15	25	35	45
0·002	0·12	1·19	2·42	3·81	5·36
0·005	0·45	1·93	3·62	5·53	7·66
0·01	0·93	2·74	4·81	7·13	9·73
0·02	1·94	3·94	6·20	8·74	11·6
0·05	4·28	6·09	8·12	10·4	12·9

Primary Medium Effect.—The primary medium effect[16] measures the difference in 'escaping' tendency of the hydrogen and chloride ions present in the reference states of two solvents (water and butan-1-ol). These differences are brought about largely by interactions between the ion and the solvent. It is customarily expressed as an activity coefficient and is given directly by the difference of the two standard potentials in (6),

$$^{\mathrm{w}}E_m° - E_m° = \lim_{m \to 0} (4\cdot6052RT/F) \log {}^{\mathrm{s}}_{\mathrm{w}}\gamma_{\pm} \quad (6)$$

where $\lim_{m \to 0} \log {}^{\mathrm{s}}_{\mathrm{w}}\gamma_{\pm}$ represents the primary medium effect, the values of which at 5, 15, 25, 35, and 45 °C are shown in Table 6. The superscript s in the term, ${}^{\mathrm{s}}_{\mathrm{w}}\gamma_{\pm}$, indicates that the measurements are carried out in a solvent s (butan-1-ol) relative to a value of unity for the infinitely dilute solution in the aqueous state (the subscript, w). The general trend of our results is very similar to those obtained in other solvents such as tetrahydrofuran–water[17] and methanol–water.[18]

TABLE 6

Primary medium effect, log ${}^{\mathrm{s}}_{\mathrm{w}}\gamma_{\pm}°$ (molal scale), of HCl in butan-1-ol

T/°C	5	15	25	35	45
log ${}^{\mathrm{s}}_{\mathrm{w}}\gamma_{\pm}°$(HCl)	2·385	2·407	2·459	2·606	2·653

Thermodynamic Quantities.—The standard Gibbs energy ($\Delta G°$), enthalpy ($\Delta H°$), entropy ($\Delta S°$), and heat capacity ($\Delta C_p°$) for the transfer process can be derived

$$\mathrm{HCl\ (in\ H_2O)} \longrightarrow \mathrm{HCl\ (in\ BuOH)}$$

from the standard e.m.f. of the cell in water[14] and in butan-1-ol together with the variation of $-\Delta E_N°$ with temperature. The values of $-\Delta E_N°$ (Table 3) were fitted, by the method of least squares, to equation (7),

$$-\Delta E_N°(\mathrm{mV}) = A + BT + CT^2 \quad (7)$$

where T is the thermodynamic temperature in K. The numerical values of A, B, and C were obtained by a least-squares fit and equation (7) then takes the form (8).

$$-\Delta E_N°(\mathrm{mV}) = 1766\cdot4 - 11\cdot94\,T + 22\cdot65 \times 10^{-3}T^2 \quad (8)$$

By the application of the usual thermodynamic relations to equation (8), one obtains $\Delta G°$, $\Delta S°$, $\Delta H°$, and $C_p°$ from equations (9)—(12). These equations are valid

$$\Delta G° = 40738\cdot0 - 275\cdot4T + 0\cdot5223T^2 \text{ cal mol}^{-1} \quad (9)$$

$$\Delta S° = 275\cdot4 - 1\cdot0447T \text{ cal K}^{-1}\text{ mol}^{-1} \quad (10)$$

$$\Delta H° = 40738\cdot0 - 0\cdot5223T^2 \text{ cal mol}^{-1} \quad (11)$$

$$\Delta C_p° = -1\cdot0447T \text{ cal K}^{-1}\text{ mol}^{-1} \quad (12)$$

in the range 5—45 °C. The values of these quantities obtained at 15, 25, and 45° are in Table 7.

The large positive value for the transfer Gibbs energy

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[15] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 2nd edn., 1965, p. 35.

[16] B. B. Owen, *J. Amer. Chem. Soc.*, 1932, **54**, 1758.

[17] R. N. Roy and B. Sen, *J. Chem. and Eng. Data*, 1968, **13**, 79.

[18] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions,' Reinhold, New York, 3rd edn., 1958, p. 672.

suggests that the transfer of HCl from water to butan-1-ol is not a spontaneous process. In other words, the affinity of butan-1-ol for HCl is less than that of water. This view is also consistent with the fact (Table 6) that the ' escaping ' tendency of HCl is greater in butan-1-ol than in the pure aqueous solutions. The values of ΔG° are estimated to be correct within $\pm 0{\cdot}012$ kcal.

TABLE 7

Thermodynamic quantities [a] (mole fraction scale) accompanying the transfer of HCl from water to butan-1-ol (1 cal = 4·184 J)

T/°C	ΔG°/kcal mol^{-1}	ΔH°/kcal mol^{-1}	ΔS°/cal K^{-1} mol^{-1}	$\Delta C_p{}^\circ$/cal K^{-1} mol^{-1}
15	4·75	−2·64	−25·6	−301
25	5·06	−5·70	−36·1	−311
45	5·99	−12·14	−57·0	−332

It is well known [19-21] that ΔH° and ΔS° contain important contributions from the effects of the ions on the solvent structure whereas the Gibbs energy function is less discriminating and can be explained on an acid–base theory of ionic solvation. It is interesting to note that the values of ΔH°, ΔS°, and $\Delta C_p{}^\circ$ (Table 7) decrease as might be expected, with increasing temperature. The negative value of ΔS° indicates that there is a breakdown of the structure of water during the transfer process.

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[19] F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1.

[20] R. G. Bates in ' Hydrogen-Bonded Solvent Systems,' eds. A. K. Covington and P. Jones, Taylor and Francis, London, 1968, p. 49.

[21] See ref. 3, p. 148.