

## A New Electrochemical Method for the Estimation of Thermodynamic Parameters for Proton Transfer between Strong Acids in Mixed Aqueous Solvents

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Equations are derived for the thermodynamic parameters of proton transfer between two acids in mixed aqueous solvents of identical composition. These are applied to electrochemical data on HClO<sub>4</sub> and HCl in tertiary butyl alcohol-water and DMF-water. HClO<sub>4</sub> is shown to be completely ionised in both systems whereas HCl ionisation drops sharply with DMF addition but is unaffected by tertiary butyl alcohol. The partial molal free energy, enthalpy and entropy of transfer are obtained.

### INTRODUCTION

The thermodynamic parameters associated with the transfer of electrolytes from water to mixed aqueous solvents are of considerable importance in the study of ion-solvent and solvent-solvent interaction. Single ion parameters, however, cannot be determined by a rigorous procedure, although a number of "extrathermodynamic" methods<sup>1-3</sup> are reported for estimating them. This work deals with the transfer of a proton between two acids dissolved in identical solvent media, thereby obviating the need to estimate the troublesome liquid junction potential at the interface between different solvents. No measurable changes should accompany such a transfer if both acids are in the same state of ionisation. If that is not the case, however, transfer parameters may be obtained. In this communication equations relating these parameters to observable quantities are derived and applied to electrochemical data on HCl and HClO<sub>4</sub> in aqueous solutions of tertiary butyl alcohol (TBA) and dimethyl formamide (DMF).

The activity of a proton in a nonaqueous solvent may be referred either to the standard state in this solvent

$$\bar{G}_H = {}_s\bar{G}_H^0 + RT \ln a_H(s) \quad (1)$$

or in water,

$$\bar{G}_H = {}_w\bar{G}_H^0 + RT \ln a_H(w) \quad (2)$$

where  $\bar{G}_H$  is the partial molal free energy and  ${}_s\bar{G}_H^0$  and  ${}_w\bar{G}_H^0$  are standard values in the solvent and in water, respectively. Since for equimolal solutions the activity ratio is identical to that of the activity coefficients, it is apparent that

$${}_s p a_H - {}_w p a_H = \log [\gamma_H(w)/\gamma_H(s)] = \log {}_m \gamma_H \quad (3)$$

where  ${}_m \gamma_H = {}_H \gamma(w)/{}_H \gamma(s)$  is the medium effect of the proton. In a given solvent,  $\gamma_H(s) \rightarrow 1$  as the ionic strength (I) approaches zero, but  $\gamma_H(w) = 1$  only in water at  $I = 0$ . From equations (1-3),

$$\Delta \bar{G}_{H,t}^0 = RT \ln [\gamma_H(w)/\gamma_H(s)] = RT \ln {}_m \gamma_H \quad (4)$$

in which  $\Delta \bar{G}_{H,t}^0$  given by  ${}_s \bar{G}_H^0 - {}_w \bar{G}_H^0$  is standard partial molal free energy of transfer of a proton from water to the solvent. For a pH-meter calibrated with an aqueous buffer, the operational pH is given by

$$pH = {}_w p a_H + \bar{E}_j \quad (5)$$

where  $\bar{E}_j$  is the residual liquid junction potential in pH units. Combination of equations (5) and (6) yields<sup>4</sup>

$$pH = {}_s p a_H - \log {}_m \gamma_H + \bar{E}_j = {}_s p a_H + \delta \quad (6)$$

where  $\delta$ , given by  $\bar{E}_j - \log {}_m \gamma_H$ , is a pH correction term for conversion from the standard state in water to one in the solvent. Here it may be noted that whereas  $\delta$  may be determined unambiguously, it is impossible to determine either  $\log {}_m \gamma_H$  or  $\bar{E}_j$  by thermodynamic means. Comparison of  $\delta$ 's for HCl and HClO<sub>4</sub> in media of identical composition gives

$$\begin{aligned} \Delta &= \delta(\text{HCl}) - \delta(\text{HClO}_4) \\ &= [\bar{E}_j(\text{HCl}) - \log {}_m \gamma_H(\text{HCl})] - [\bar{E}_j(\text{HClO}_4) - \log {}_m \gamma_H(\text{HClO}_4)] \quad (7) \end{aligned}$$

Since  $\bar{E}_j$  is entirely solvent dependent,  $\bar{E}_j(\text{HCl}) = \bar{E}_j(\text{HClO}_4)$  and equation (7) becomes

$$\Delta = \delta(\text{HCl}) - \delta(\text{HClO}_4) = \log [{}_m \gamma_H(\text{HClO}_4) / {}_m \gamma_H(\text{HCl})] \quad (8)$$

At infinite dilution  $\gamma_H(s) = 1$  and  ${}_m \gamma_H = {}_w \gamma_H$ . Hence,

$$\Delta^0 = \delta^0(\text{HCl}) - \delta^0(\text{HClO}_4) = \log [{}_w \gamma_H(\text{HClO}_4) / {}_w \gamma_H(\text{HCl})] \quad (9)$$

In the same solvent, the standard partial molal free energy of proton transfer from HClO<sub>4</sub> to HCl, as obtained from equations (4), (8) and (9), is given by

$$\Delta \bar{G}_t^0 = {}_s \bar{G}_H^0(\text{HCl}) - {}_s \bar{G}_H^0(\text{HClO}_4) = -2.303RT\Delta^0 \quad (10)$$

taking  ${}_w \bar{G}_H^0(\text{HCl}) = {}_w \bar{G}_H^0(\text{HClO}_4)$  since both acids are completely ionised in water at the low concentrations employed.

From the van't Hoff relation, the temperature variation of  $\gamma_H$  is given by

$$(\ln \gamma_H / dT)_{p,m} = -2.303(dPa_H / dT)_{p,m} = -\bar{L}_2 / RT^2 \quad (11)$$

where  $\bar{L}_2$  is the relative partial molal enthalpy of the proton. Equations (9) and (11) lead to

$$\begin{aligned} d\Delta^0/dT &= [\bar{L}_2^0(\text{HCl}) - \bar{L}_2^0(\text{HClO}_4)] / 2.303RT^2 \\ &= \bar{L}_{2,t}^0 / 2.303RT^2 \end{aligned} \quad (12)$$

Here,  $\bar{L}_{2,t}^0$  is the standard partial molal enthalpy of proton transfer from  $\text{HClO}_4$  to  $\text{HCl}$  solutions in identical solvent media. If  $\bar{L}_{2,t}^0$  remains constant within the temperature range investigated, equation (11) integrates to

$$\Delta^0 = -\bar{L}_{2,t}^0 / 2.303RT + \text{constant} \quad (13)$$

## EXPERIMENTAL

DMF and TBA were of spectro purity. All other chemicals were of reagent grade. Potentiometric measurements were carried out using a Beckman 4500 pH-meter and a combination Beckman glass and reference electrode No. 39142. This electrode is particularly suited to nonaqueous solvents and has been shown to be responsive in several mixed systems<sup>5,6</sup>. Sensitivity was improved by frequent immersions in dilute  $\text{HCl}$  and periodic changes of the internal electrolyte solution. Moreover, in order to avoid changes in the external swell film which could result in slow shift in the measured values, the electrode was allowed to equilibrate for at least 30 min in a given solvent prior to measurement. Calibration was made at each temperature using aqueous 0.05 M potassium hydrogen phthalate. Data were collected for  $10^{-3}$  M  $\text{HCl}$  and  $\text{HClO}_4$  solutions at 10, 15, 20, 25, 30 and  $35 \pm 0.02^\circ\text{C}$ . At these low concentrations the measured  $\delta^0$ 's are effectively  $\delta^{0s}$ . The solution composition was varied up to ca. 40% (w/w) organic cosolvent. At least three independent  $\delta^0$  values were obtained for each temperature and composition.

## RESULTS AND DISCUSSION

Tables 1 and 2 summarize the solvent and temperature dependence of  $\delta^0(\text{HCl})$  and  $\delta^0(\text{HClO}_4)$ , respectively. Precision in pH, and consequently  $\delta^0$ , ranged from 0.003 unit in water to ca. 0.008 unit in the water-poor solvent. In TBA-water,  $\delta^0$  values for both acids are seen to be quite small, with little dependence on temperature and solvent composition. This implies small  $\delta^{0s}$  and hence values near unity for the term  $w\gamma_{\text{H}}(\text{HCl})/w\gamma_{\text{H}}(\text{HClO}_4)$ . By contrast,  $\Delta^0$ 's in DMF-water typically exceed those in TBA-water by an order of magnitude, in addition to exhibiting marked dependence on solvent composition. Moreover, in DMF-water, when comparisons are made at the same temperature between solutions of identical DMF content,  $\delta^0(\text{HCl})$  values are seen to be considerably larger than those for  $\delta^0(\text{HClO}_4)$ . In such a case, equation (9) indicates that the activity coefficient of the  $\text{HCl}$  proton,  $w\gamma_{\text{H}}(\text{HCl})$ , is significantly less than that of  $\text{HClO}_4$ ,  $w\gamma_{\text{H}}(\text{HClO}_4)$ .

Tables 1 and 2 further reveal that enrichment of the solvent with DMF widens the activity coefficient gap. It thus appears that in TBA-water both acids are in the same state of ionisation. In DMF-water, by contrast,  $\text{HClO}_4$  ionisation is essentially unaffected by DMF addition while that of  $\text{HCl}$  is greatly diminished.

Tables 1 and 2 also reveal that, in DMF-water,  $\delta^0(\text{HCl})$  is much more temperature sensitive than  $\delta^0(\text{HClO}_4)$ . This implies that  $d\Delta^0/dT$  is chiefly determined by the temperature coefficient of  $\delta^0(\text{HCl})$  and that the main contribution to  $\bar{L}_{2,t}^0$  comes from  $\bar{L}_2^0(\text{HCl})$ .

$\Delta^0$  Values were calculated from Tables (1) and (2) at each temperature and composition then fitted to equation (12) by the method of least squares. The ensuing  $\bar{L}_{2,t}^0$ 's, listed in Table 3, are seen to increase with cosolvent addition, the effect being far more pronounced in DMF-water than in TBA-water. In the former system,  $\bar{L}_{2,t}^0$  rises steeply and uniformly, reaching  $45.2 \text{ kJ mol}^{-1}$  in 41.18% DMF. In the latter, the maximum  $\bar{L}_{2,t}^0$  value is only  $2.41 \text{ kJ mol}^{-1}$  for the same weight per cent TBA. The solvent dependence, at  $25^\circ\text{C}$ , of  $\Delta\bar{G}_t^0$  and  $\Delta\bar{S}_t^0$  is also given.

Table 3 indicates that the transfer parameters in TBA-water, when compared to those in DMF-water, are virtually insignificant and in many cases lie within the limits of experimental error. In the former system,  $\text{HCl}$  and  $\text{HClO}_4$  protons probably possess similar solvation shells which are unaffected by the type of anion. In the latter system, by contrast, the anion plays an important role. This may be due to the formation of H-bonded or conjugate ions such as  $\text{HCl}_2^-$ , a species already identified by Pocker<sup>7</sup> in mixed aqueous media. The large positive values of  $\bar{L}_{2,t}^0$  in DMF-water suggest the energy needed to strip the proton solvation shell, prior to its transport from  $\text{HCl}$  to  $\text{HClO}_4$ , is not sufficiently offset by the formation of  $\text{HCl}_2^-$ . The loss in the degree of solvation is also manifested by the behaviour of  $\Delta\bar{S}_t^0$  which rises regularly with DMF addition, reaching the fairly high value of  $160 \text{ JK}^{-1} \text{ mol}^{-1}$ . In this connection, it is noteworthy that no similar conjugate species for  $\text{HClO}_4$  has been reported. Thus it appears that TBA, a protic solvent, inhibits conjugation and ion-pair formation, presumably because it can itself compete for H-bonding with the proton. By comparison, the aprotic nature of DMF precludes its involvement in similar competition. Finally, the term  $w_{\text{YH}}(\text{HClO}_4)/w_{\text{YH}}(\text{HCl})$ , readily evaluated from  $\Delta^0$  by using equation (9), may be identified with the ratio of the degree of ionisation of the two acids,  $\alpha(\text{HClO}_4)/\alpha(\text{HCl})$ . Since the evidence suggests that  $\alpha(\text{HClO}_4)$  remains near unity, approximate values for  $\alpha(\text{HCl})$  may be calculated.

In conclusion, this method is seen to be capable of affording insight into the influence of organic solvent on the degree of proton ionisation. It suffers from the limitation of having to find suitable electrode responsive in the mixed solvent. Furthermore, the relatively high uncertainties typically associated with potentiometric measurements in nonaqueous systems limit the meaningful application of this method to systems for which  $\Delta^0$  values are fairly substantial.

TABLE 1  
DEPENDENCE OF  $\delta^0(\text{HCl})$  ON TEMPERATURE AND SOLVENT  
COMPOSITION IN (a) TBA-WATER (b) DMF-WATER

T, °C	% Organic Solvent (w/w)						
	9.09	16.67	23.07	28.57	33.33	37.50	41.18
(a) TBA-WATER							
10	-0.027	-0.006	-0.010	0.052	0.055	0.076	0.087
15	-0.034	-0.017	-0.004	0.035	0.050	0.082	0.087
20	-0.024	-0.004	-0.024	0.048	0.066	0.073	0.080
25	-0.019	0.003	0.023	0.053	0.061	0.072	0.071
30	-0.013	0.020	0.032	0.062	0.057	0.073	0.063
35	-0.008	0.033	0.054	0.047	0.044	0.052	0.051
(b) DMF-WATER							
10	0.092	0.160	0.231	0.305	0.373	0.524	0.566
15	0.090	0.171	0.266	0.355	0.430	0.575	0.621
20	0.118	0.230	0.341	0.428	0.530	0.704	0.765
25	0.142	0.270	0.404	0.486	0.598	0.794	0.860
30	0.230	0.401	0.569	0.693	0.818	1.047	1.124
35	0.268	0.449	0.612	0.745	0.881	1.107	1.170

TABLE 2  
DEPENDENCE OF  $\delta^0(\text{HClO}_4)$  ON TEMPERATURE AND SOLVENT  
COMPOSITION IN (a) TBA-WATER (b) DMF-WATER.

T, °C	% Organic solvent (w/w)						
	9.09	16.67	23.07	28.57	33.33	37.50	41.18
(a) TBA-WATER							
10	-0.035	-0.026	-0.002	0.034	0.047	0.061	0.096
15	-0.039	-0.030	-0.006	0.030	0.043	0.057	0.095
20	-0.029	-0.014	0.019	0.038	0.057	0.066	0.093
25	-0.015	0.003	0.036	0.055	0.069	0.068	0.072
30	-0.011	0.012	0.031	0.046	0.052	0.059	0.063
35	-0.007	0.020	0.053	0.050	0.054	0.057	0.051
(b) DMF-WATER							
10	0.069	0.127	0.208	0.279	0.332	0.404	0.459
15	0.058	0.112	0.171	0.223	0.280	0.342	0.393
20	0.068	0.134	0.207	0.277	0.322	0.382	0.441
25	0.066	0.128	0.193	0.250	0.314	0.352	0.394
30	0.089	0.166	0.227	0.286	0.339	0.386	0.423
35	0.085	0.160	0.224	0.288	0.340	0.392	0.427

TABLE 3  
 PROTON TRANSFER PARAMETERS, AT 25°C, IN (a) TBA-WATER, AND  
 (b) DMF-WATER.

	% Organic solvent (w/w)						
	9.09	16.67	23.07	28.57	33.33	37.50	41.18
	$\bar{L}_{2,r}^0$ , kJ mol <sup>-1</sup>						
a	0.73	0.59	0.92	0.34	0.90	1.74	2.41
b	10.9	17.6	25.2	29.2	33.9	41.7	45.2
	$\Delta\bar{G}_{2,r}^0$ , kJ mol <sup>-1</sup>						
a	0.021	0.002	0.037	-0.078	-0.047	-0.089	-0.057
b	-0.434	-0.810	-1.20	-1.35	-1.62	-2.52	-2.66
	$\Delta\bar{S}_r^0$ , kJ <sup>-1</sup> mol <sup>-1</sup>						
a	2	2	3	1	3	6	8
b	38	62	85	102	120	150	160

### ACKNOWLEDGEMENT

The author is grateful to the Deanship of Academic Research, University of Jordan, for supporting this work.

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(Received: 15 November 1992; Accepted: 1 December 1992)

AJC-521