

502. *Standard Potentials in Aqueous Organic Media: a General Discussion of the Cell $\text{H}_2(\text{Pt})|\text{HCl}|\text{AgCl}-\text{Ag}$.*

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Relations for the standard potential of the cell $\text{H}_2(\text{Pt})|\text{HCl}|\text{AgCl}-\text{Ag}$ in various aqueous organic media, based on the Born equation, are briefly reviewed, and the limitations of this method noted. A new stoichiometric relationship is developed, based on a simple treatment of ion solvation in liquid mixtures. The resulting equation shows that a plot of the standard potential E_o° on the molar scale should be linearly related to the logarithm of the volume fraction ϕ_w of water in the solvent medium. The correlation achieved experimentally is considerably better than anything obtained with plots based on the Born equation, and is free from marked solvent effects. Certain observed deviations are discussed.

FOLLOWING work on aqueous ketone and glycol solutions (cf. *J.*, 1957, 2284), we can discuss the standard potentials of the cell $\text{H}_2(\text{Pt})|\text{HCl}|\text{AgCl}-\text{Ag}$ in a large number of aqueous solutions of the commoner water-soluble organic substances, particularly where the water content is high.

In Table 1 are given all the available standard potentials of the cell for such systems on the molal (E_m°), molar ($E_o^\circ = E_m^\circ + 2k \log d_0$), and mole fractional [$E_N^\circ = E_m^\circ - 2k \log (1000/M_{xy})$] scales ($k = 2.3026 RT/F$, d_0 = density of pure solvent mixture $M_{xy} = 100/[X/M_x + (100 - X)/M_y]$ = mean molecular weight of solvent (X = weight % of organic substance of molecular weight M_x , and M_y = molecular weight of water). Values of the dielectric constant ϵ , and of the density d_0 of each mixture are recorded. Where not given by the original author, the values of ϵ are taken from Åkerlöf's data,¹ and the d_0 values from International Critical Tables or from Griffiths's data.^{2,3} The mole fraction of water, N_w , has been calculated for each mixture.

The difference between the standard potentials, ${}^wE^\circ$ in water and ${}^sE^\circ$ in another solvent, is related to a free-energy difference ΔG by the equations

$$-\Delta G = F({}^wE^\circ - {}^sE^\circ) = -2RT \ln a_1/a_2 = -2RT \ln f_1c_1/f_2c_2$$

ΔG is the difference in solvation energies of hydrogen chloride in the two solvents, referred to standard conditions in the gas phase and the standard state in the given solvent, f_1 and f_2 are mean ion-activity coefficients referred to a standard state of unity at infinite dilution in pure water, *i.e.*, $f_1 = 1$. By the definition of standard potential, interionic attractions are eliminated, and we are concerned solely with ion-solvent interactions.

It would be convenient to choose the standard state such that the work done in transferring the ions, considered uncharged, is zero; in other words, that terms of the type $2RT \ln c_1/c_2$ vanish. Classically this is assumed to be the case if the mole fraction of

¹ Åkerlöf, *J. Amer. Chem. Soc.*, 1937, **59**, 2098.

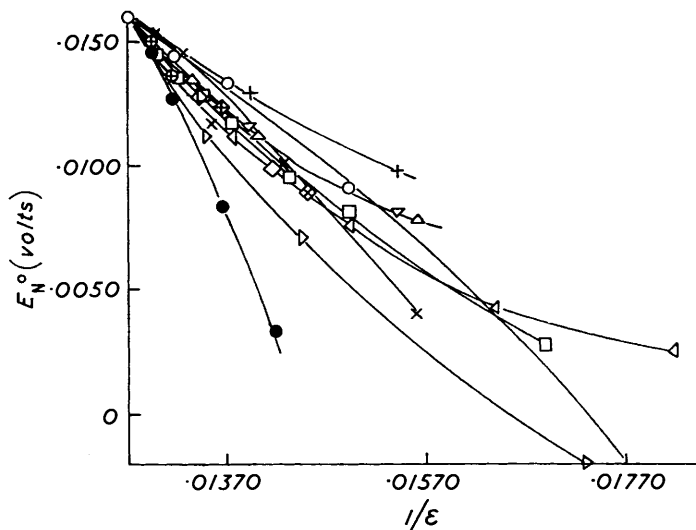
² Griffiths, *J.*, 1952, 1326.

³ *Idem, ibid.*, 1954, 860.

TABLE 1. Standard potentials of binary aqueous systems at 25°.

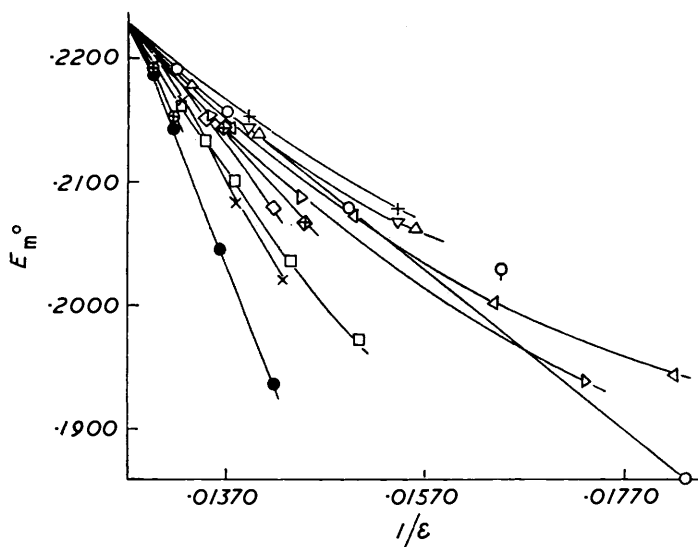
Organic component	X	N_w	d_0	ϵ	E_m°	E_N°	E_o°	Ref.	
							(See p. 2583)		
Acetone	5	0.9839	0.9904	75.9	0.2190	0.0144 _s	0.2185	<i>a</i>	
	10	0.9667	0.9838	73.0	0.2156	0.0129	0.2148	<i>a</i>	
	20	0.9280	0.9697	67.0	0.2079 _s	0.0091 _s	0.2063 _s	<i>a</i>	
	40	0.8286	0.9367	54.6	0.1859 _s	-0.0038 _s	0.1824	<i>a</i>	
	50	0.7632	0.9173	48.2	0.158	-0.027	0.154	<i>b</i>	
	90	0.2637	0.8160	24.0	-0.034	-0.190	-0.044	<i>b</i>	
	100	0	0.7850	19.1	-0.53	-0.78	-0.542	<i>c</i>	
	MeEtCO	10	0.9729	0.9845	71.8	0.2153 _s	0.0129 _s	0.2144	<i>d</i>
		20	0.9412	0.9703	64.9	0.2078	0.0098	0.2064 _s	<i>d</i>
		40	0.8286	0.9367	54.6	0.1859 _s	-0.0038 _s	0.1824	<i>a</i>
Methanol	10	0.9412	0.9799	74.0	0.2154 _s	0.0112	0.2144	<i>e</i>	
	20	0.8767	0.9644	69.2	0.2088	0.0071	0.2069 _s	<i>e</i>	
	43.3	0.6996	0.9248	58.0	0.1941	-0.0022	0.1901	<i>f</i>	
	64	0.5001	0.8814	48.0	0.1764	-0.0130	0.1699	<i>f</i>	
	84.2	0.2502	0.8333	38.2	0.1319	-0.0508	0.1255	<i>f</i>	
	94.2	0.0987	0.8042	33.9	0.0840	-0.0950	0.0728	<i>f</i>	
	100	0	0.7865	31.5	-0.0101	-0.1869	-0.0224	<i>f</i>	
	10	0.9412	0.9799	74.18	0.2155	0.0114	0.2145	<i>g</i>	
	20	0.8768	0.9645	69.99	0.2094	0.0077	0.2076	<i>g</i>	
	40	0.7275	0.9319	60.94	0.1968	0.0003	0.1932	<i>g</i>	
	60	0.5426	0.8914	51.67	0.1818	-0.0089	0.1759	<i>g</i>	
	80	0.3059	0.8425	42.60	0.1492	-0.0350	0.1404	<i>g</i>	
	90	0.1650	0.8156	37.91	0.1135	-0.0672	0.1030	<i>g</i>	
	94.2	0.0987	—	35.76	0.0841	-0.0950	—	<i>g</i>	
	100	0	0.7864	32.66	-0.0099	-0.1867	-0.0223	<i>g</i>	
Ethanol	10	0.9583	0.9804	72.8	0.2144	0.0112	0.2136 _s	<i>h</i>	
	20	0.9109	0.9664	67.0	0.2073 _s	0.0076	0.2056	<i>h</i>	
	30	0.8566	0.9507	61.1	0.2003 _s	0.0043	0.1981	<i>i</i>	
	40	0.7932	0.9315	55.0	0.1949 _s	0.0025	0.1909	<i>i</i>	
	50	0.7189	0.9098	49.0	0.1859	-0.0018 _s	0.1810	<i>i</i>	
	71.9	0.5000	0.8588	37.0	0.1554	-0.0214	0.1476	<i>j</i>	
	88.5	0.2500	0.8176	27.4	0.1053	-0.0358	0.0950	<i>j</i>	
	98	0.0500	0.7912	25.1	0.0215	-0.1382	0.0095	<i>j</i>	
	100	0	0.7851	24.3	-0.0760	-0.2341	-0.0884	<i>j</i>	
	Propan-1-ol	10	0.9668	0.9811	71.8	0.2141	0.0115	0.2132	<i>k</i>
20		0.9296	0.9670	64.9	0.2066 _s	0.0080	0.2049	<i>k</i>	
Propan-2-ol	5	0.9832	0.9891	74.9	0.2180 _s	0.0135	0.2174 _s	<i>l</i>	
	10	0.9668	0.9812	71.4	0.2138 _s	0.0112	0.2127	<i>l</i>	
	20	0.9296	0.9669	64.1	0.2063 _s	0.0077 _s	0.2046	<i>l</i>	
Ethylene glycol	5	0.9848	1.005	76.9	0.2190 _s	0.0145 _s	0.2192 _s	<i>m</i>	
	10	0.9689	1.010	75.6	0.2161	0.0136	0.2166	<i>n</i>	
	15	0.9514	1.016	74.2	0.2133	0.0127 _s	0.2141	<i>m</i>	
	20	0.9322	1.023	72.8	0.2101	0.0117	0.2112 _s	<i>n</i>	
	30	0.8890	1.035	69.8	0.2036	0.0095 _s	0.2053	<i>m</i>	
	40	0.8377	1.049	66.6	0.1972	0.0080	0.1996 _s	<i>o</i>	
	60	0.7009	1.075	59.4	0.1807	0.0028	0.1884	<i>o</i>	
Propylene glycol	10	0.9745	1.0046	74.2	0.2150 _s	0.0128	0.2153	<i>m</i>	
	20	0.9440	1.0128	70.7	0.2077 _s	0.0099 _s	0.2084	<i>m</i>	
2 : 3-Butylene glycol	10	0.9785	1.0024	73.2	0.2144	0.0123 _s	0.2145	<i>m</i>	
	20	0.9524	1.0089	69.0	0.2067	0.0088 _s	0.2067	<i>m</i>	
Glycerol	4.9	0.9900	1.009	77.1	0.2196	0.0153	0.2200 _s	<i>p</i>	
	10	0.9789	1.021	75.5	0.2165	0.0145	0.2175 _s	<i>q</i>	
	21.2	0.9500	1.048	72.5	0.2084	0.0117	0.2108	<i>p</i>	
	30	0.9226	1.070	70.1	0.2022	0.0100	0.2057	<i>q</i>	
	50	0.8364	1.120	64.0	0.1840	0.0040	0.1896	<i>r</i>	
D-Glucose	5	0.9943	1.003	77.3	0.2186 _s	0.0146	0.2187 _s	<i>s</i>	
	10	0.9894	1.007	76.1	0.2142	0.0127	0.2144 _s	<i>s</i>	
	20	0.9754	1.016	73.4	0.2045	0.0083	0.2053	<i>s</i>	
	30	0.9587	1.025	70.5	0.1935 _s	0.0033	0.1947 _s	<i>s</i>	
D-Fructose	5	0.9943	1.003	77.3	0.2190	0.0150	0.2191 _s	<i>t</i>	
	10	0.9894	1.007	76.1	0.2150 _s	0.0135 _s	0.2154	<i>t</i>	
1 : 4-Dioxan	20	0.9513	1.014	60.8	0.2030 _s	0.0055 _s	0.2037 _s	<i>u</i>	
	45	0.8567	1.032	38.5	0.1635	-0.0201	0.1652	<i>u</i>	
	70	0.6770	1.038	17.7	0.0639 _s	-0.1006	0.0657	<i>u</i>	
	82	0.5177	1.034	9.5	-0.0413	-0.1934	-0.0396	<i>u</i>	

FIG. 1.



For all Figures.—○ Water, ○ acetone, + ethyl methyl ketone, ▷ methanol, ◁ ethanol, ▽ propan-1-ol, △ propan-2-ol, □ ethylene glycol, ◇ propylene glycol, ◈ 2:3-butylene glycol, × glycerol, ◊ dioxan, ● glucose, ◌ glucose (dihydrate), ⊕ fructose.

FIG. 2.



(a) Feakins and French, *J.*, 1956, 3168; (b) Izmailov and Zabara, *Zhur. fiz. Khim.*, 1946, **20**, 165 (from measurements with a quinhydrone electrode); (c) Everett and Rasmussen, *J.*, 1954, 2812; (d) Feakins and French, preceding paper; (e) Harned and Thomas, *J. Amer. Chem. Soc.*, 1935, **57**, 1666; 1936, **58**, 761; (f) Austin, Hunt, Johnson, and Parton, unpublished, see Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955, p. 457; (g) Oiwa, *J. Phys. Chem.*, 1956, **60**, 754; (h) Harned and Calmon, *J. Amer. Chem. Soc.*, 1939, **61**, 1491; (i) Harned and Allen, *J. Phys. Chem.*, 1954, **58**, 191; (j) Butler and Robertson, *Proc. Roy. Soc.*, 1929, **125**, A, 694; (k) Claussen and French, *Trans. Faraday Soc.*, 1955, **51**, 708; (l) Moore and Felsing, *J. Amer. Chem. Soc.*, 1947, **69**, 1076; (m) Crockford, Knight, and Staton, *ibid.*, 1950, **72**, 2164; (n) Claussen and French, *Trans. Faraday Soc.*, 1955, **51**, 1124; (o) Knight, Masi, and Roessel, *J. Amer. Chem. Soc.*, 1946, **48**, 661; (p) Lucasse, *Z. phys. Chem.*, 1926, **121**, 254; (q) Knight, Crockford, and James, *J. Phys. Chem.*, 1953, **57**, 463; (r) Harned and Nestler, *J. Amer. Chem. Soc.*, 1946, **68**, 665; (s) Williams, Knight, and Crockford, *ibid.*, 1950, **72**, 1277; (t) Crockford and Sahnovsky, *ibid.*, 1951, **73**, 4177; (u) Harned *et al.*, *ibid.*, 1936, **58**, 1908; 1938, **60**, 334, 336, 339, 2128, 2130, 2133; 1939, **61**, 44, 48, 49.

the acid is the same in both solvents. This assumption will not always be justified, since most of the liquid mixtures are far from ideal, and the contribution to ΔG from this source might be large.

By considering the ions to be spheres of radii r_+ and r_- respectively, in a uniform dielectric medium, we obtain the well-known Born expression for the free energy of transfer:

$$-\Delta G = F[{}^wE_N^\circ - {}^sE_N^\circ] = \frac{Ne^2}{2} \left[\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right] \left[\frac{1}{r_+} + \frac{1}{r_-} \right]$$

For the variation of standard potential with dielectric constant, ϵ , we find on rearranging that

$${}^sE_N^\circ = \text{const.} - \frac{Ne^2}{2F} \sum \frac{1}{r} \left(\frac{1}{\epsilon_s} \right) \quad \dots \quad (1)$$

Hence the plot of standard potential against $1/\epsilon$ should be a straight line.

Figs. 1 and 2 show plots of E_N° and E_m° respectively against $1/\epsilon$. The salient features of such plots are as follows. (a) Distinct plots, usually smooth curves and rarely straight lines, are obtained for the solutions for each organic solvent. (b) In general the decrease in E° with increase in $1/\epsilon$, though of the right order, is much less than predicted by the Born equation when we use reasonable values [*e.g.*, the crystallographic radii, when $\Sigma 1/r = 1.2 \text{ \AA}^{-1}$, or the experimental mean distance of closest approach (4.3 \AA) when

TABLE 2. Activity of water in glucose solutions and solvation numbers.

N_w	p (mm. Hg)	$a_w = p/p^\circ$	γ	N_w	p (mm. Hg)	$a_w = p/p^\circ$	γ
1	23.756 = p°	1	—	0.9050	21.117	0.8888	1.53
0.9882	23.476	0.9882	—	0.8909	20.668	0.8700	1.47
0.9492	22.563	0.9498	—	0.8696	19.943	0.8384	1.48
0.9239	21.727	0.9146	(1.4)	0.8402	19.002	0.7995	1.27
0.9066	21.151	0.8903	1.59	0.8050	17.751	0.7477	1.19

$\Sigma 1/r = 0.9 \text{ \AA}^{-1}$] for the ionic radii. The only values that fit the Born plot at all well are those of glucose solutions which are exceptional in this respect. (c) The curves fall into fairly distinct families, a feature that is particularly evident on examination of the E_m° against $1/\epsilon$ curves, where the rate of decrease of E_m° with increase in $1/\epsilon$ depends on the number of functional groups in the organic molecule, being larger the greater the number of such groups. Here the monofunctional ketones show a fairly close relation to the monohydric alcohols, at least in solutions of high dielectric constant. This relation disappears on the E_N° versus $1/\epsilon$ curves where, for example, there is an unexpected relation between the glycerol and the acetone curves.

Scatchard⁴ first suggested that the Born equation for the free energy of transfer required modification if it were assumed that the hydrogen ion is present as the species H_3O^+ . It can be shown, for example by arguments similar to those developed below (see also ref. 5), that in the transfer of ions from water to a water-organic compound mixture there will be an increase of free energy given by $\Delta G = -RT \ln a_w$, where a_w is the activity of water in the solvent mixture. If the remaining free energy is determined by the Born expression, then

$$F[{}^wE_N^\circ - {}^sE_N^\circ] = \frac{Ne^2}{2} \left[\frac{1}{\epsilon_s} - \frac{1}{\epsilon_w} \right] \sum \frac{1}{r} - RT \ln a_w$$

This can be rearranged in the form

$${}^sE_N^\circ - (RT/F) \ln a_w = \text{const.} - \frac{Ne^2}{2F} \sum \frac{1}{r} \left(\frac{1}{\epsilon} \right) \quad \dots \quad (2)$$

⁴ Scatchard, *J. Amer. Chem. Soc.*, 1925, **47**, 2098.

⁵ Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York, 1956, 2nd edn., p. 337.

For most of the solutions considered, the partial-pressure data available indicate that, provided the concentration of water in the aqueous organic medium is high, the mole fraction of water N_w can be substituted for a_w . Equation (2) then suggests the plot of

FIG. 3.

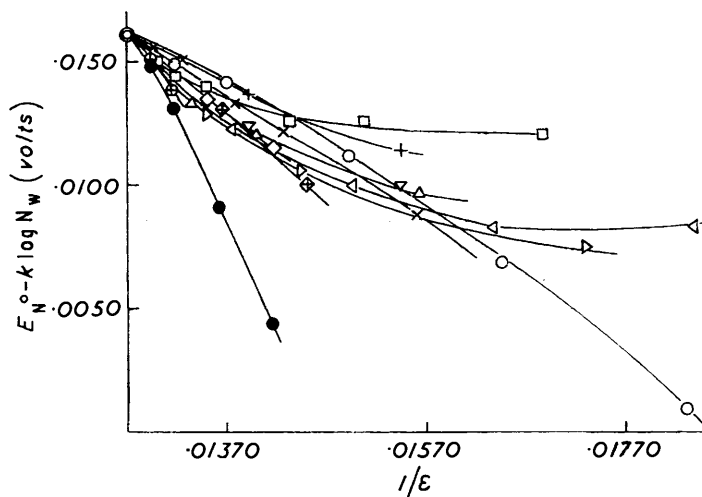


FIG. 4.

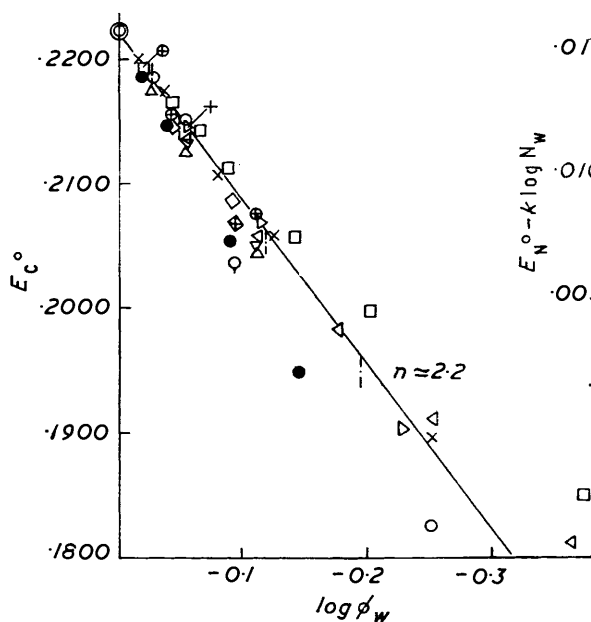
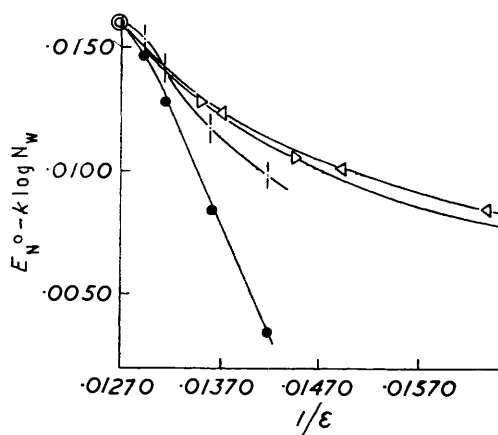


FIG. 5.



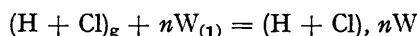
${}^sE_N^0 - k \log N_w$ against $1/\epsilon$, but with the exception that the monohydric alcohols form a very closely related series of curves, plots of this function do not in general achieve any better correlation between the different solvents (Fig. 3).

Any approach based on the Born equation thus appears to be unsuccessful. A particularly important stumbling block in this treatment is the apparent dependence of

the standard potential for a mixture of given dielectric constant on the nature of the organic component, which is unexpected. A simple approach to the problem of ionic solvation in liquid mixtures has been developed by Hudson and Saville.⁶ It is similar to the treatment of concentrated aqueous electrolyte solutions by Robinson and Stokes⁷ and by Glueckauf.⁸ The position can be put crudely as follows.

The equation for the potential of a charged sphere in a uniform dielectric, on which the Born equation depends, can be expected not to hold particularly well for an ion in solution, since the ion is comparable in dimensions with the solvent molecules. Conditions approaching dielectric saturation then obtain close to the ion. Thus the first layer of solvent molecules around the ion is completely orientated and can be regarded as a firmly bound solvation shell whose formation as the ion enters the solution from the gas phase will be accompanied by a loss of free energy by the co-ordinated water molecules. The remaining free-energy change, which could be computed by an equation of the Born type, is assumed to be comparatively small, especially in solutions of high dielectric constant. Further, in all the solutions considered, the ions are assumed to be preferentially solvated by the more polar molecules, in this case water. This will be particularly true when the water content is high.

Consider the free-energy changes involved in the solution of one mole of hydrogen chloride (as ions) from the gas phase to a standard state in aqueous solution. We can write for the co-ordination of n water molecules (H^+ and Cl^- ions are here written without their charges, and W stands for H_2O):



For this process

$$\Delta G^w = \mu_{(H+Cl), nW}^w - \mu_{(H+Cl)} - n\mu_w^w$$

For the same process in an organic solvent-water mixture:

$$\Delta G^s = \mu_{(H+Cl), nW}^s - \mu_{(H+Cl)} - n\mu_w^s$$

Consider the difference

$$\Delta G = \mu_{(H+Cl), nW}^s - \mu_{(H+Cl), nW}^w$$

If we assume that the interaction of the solvated ions with the solvent is negligible, then the difference in the partial molal free energies of the solvated ions in the two solvents depends only on the difference in the concentrations of the solvated ions in the two solvents. We will assume that this term is zero if the standard state is *either* the mole fractional *or* the molar one. It is unlikely of course that the adoption of either scale will make this assumption completely true.

Thus

$$\mu_{(H+Cl), nW}^s = \mu_{(H+Cl), nW}^w$$

$$\therefore \Delta G^s - \Delta G^w = n(\mu_w^w - \mu_w^s) = -nF(E^\circ - {}^wE^\circ)$$

The partial molal free energy of water in the aqueous mixture can be expressed either in terms of mole-fraction or of volume-fraction statistics. Although the mixtures considered are in practice far from ideal, for the sake of simplicity expressions will be developed for ideal mixtures, whence $\mu_w^w - \mu_w^s = -RT \ln N_w$ or $-RT \ln \phi_w$, where ϕ_w is the volume fraction of water.

⁶ Hudson and Saville, *J.*, 1955, 4114.

⁷ Robinson and Stokes, *J. Amer. Chem. Soc.*, 1948, **70**, 1870.

⁸ Glueckauf, *Trans. Faraday Soc.*, 1955, **51**, 1235.

Thus for the mole-fractional model, using E_N° we have

$${}^sE_N^\circ = {}^wE_N^\circ + (RT/F) \ln N_w \quad (3)$$

and for the volume-fractional model, using E_c° we have

$${}^sE_c^\circ = {}^wE_c^\circ + (RT/F) \ln \phi_w \quad (4)$$

Equation (3) and (4) reduce to

$${}^sE_m^\circ = {}^wE_m^\circ + nk \log w + k(n-2) \log (M_{xy}/M_y) \quad . . . (3a)$$

and

$${}^sE_m^\circ = {}^wE_m^\circ + nk \log w + k(n-2) \log \rho \quad (4a)$$

where w is the weight fraction of water, and ρ is the density. In solutions of high water content $\log \rho$ and $\log (M_{xy}/M_y)$ are small, and if n is also close to 2, both expressions approximate to

$${}^sE_m^\circ = {}^wE_m^\circ + nk \log w \quad (5)$$

Eqn. (5) is a better approximation to (4) than it is to (3) because $\log \rho$ is usually much smaller than $\log (M_{xy}/M_y)$.

Equations (3) and (4) suggest that the plots of E_c° against $\log \phi_w$ and of E_N° against $\log N_w$ should be straight lines from which the solvation number of hydrochloric acid, n , can be determined. The plot of E_N° against $\log N_w$ does not in practice achieve any striking correlation and will not therefore be considered further.

Fig. 4 shows the plot of E_c° against $\log \phi_w$ for all the available systems up to about 50% by volume of water. The correlation achieved is outstandingly better than any found with plots based on the Born equation. In high water concentrations a large number of points lie close to a line for which $n = 2.2$, particularly for first members of homologous series. A certain chain-length effect is apparent: at a concentration of about 20% of organic compound the alcohol points lie in order of their molecular weights, and this is also true of the glycols. At higher concentrations, however, the methyl and ethyl alcohol points are reversed in position. It would be of interest to extend the propanol measurements, for example, to higher propanol concentrations. The plot is, however fairly free from marked solvent effects, the only serious deviations being shown by the ethylene glycol, glucose, and dioxan solutions. 5-, 10- and 20-% Acetone solutions obey the stoichiometric relation closely, but the 40% solution deviates markedly. It is of interest to consider each of these deviations in turn.

Ethylene Glycol.—Ethylene glycol associates in acid solutions. Such association would effectively increase the volume fraction of water in the mixture, so causing E_c° to be higher than expected. The curve is shown to approach the straight line asymptotically at the origin: this is to be expected since the amount of association would decrease with increasing water content.

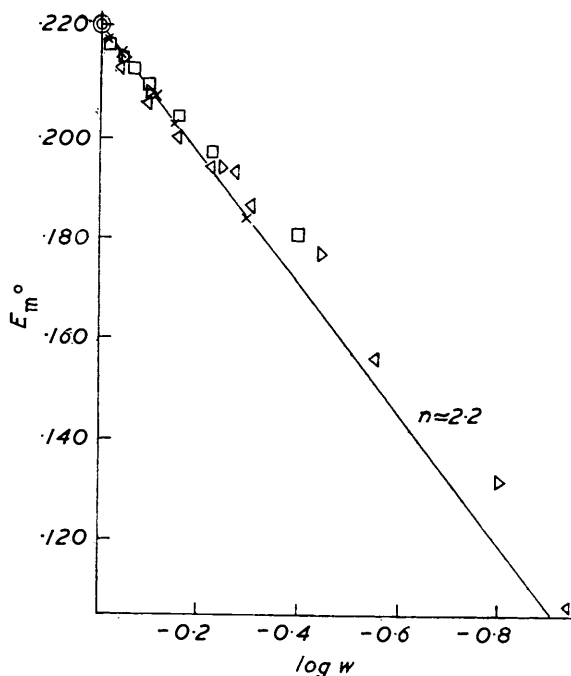
Glucose.—Taylor and Rowlinson⁹ have accurately measured vapour pressures of glucose solutions, which show negative deviations from Raoult's law. Scatchard assumed that the similar deviations shown by sucrose solutions are due to hydrate formation, and we have made the same assumption for glucose solutions. It is then possible to calculate a solvation number y by assuming that the activity of water in the solution is proportional to the mole fraction of uncombined water, whence it is easily shown that

$$y = \frac{N_w - a_w}{(1 - N_w)(1 - a_w)}$$

⁹ Taylor and Rowlinson, *Trans. Faraday Soc.*, 1955, **51**, 1183.

Table 2 shows the values of y at various glucose concentrations. If these are plotted against the concentration of glucose, the straight line so obtained, on extrapolation to zero concentration, yields $y = 2.0$. The four glucose solutions for which e.m.f. measurements are available are comparatively dilute, and y may be taken without great error as 2. On recalculating the volume fraction of water, based on a glucose dihydrate, we find that the results, shown in Fig. 4, are very close to the straight line. The assumption

FIG. 6.



of a glucose dihydrate affects also the calculation of E_N^0 values, and Fig. 5 shows the plot of $E_N^0 - k \log N_w$ against $1/\epsilon$ for methyl and ethyl alcohols and glucose. The curve based on the glucose dihydrate shows a marked relation to those of the alcohols. These conclusions are in general agreement with the inference by Taylor and Rowlinson from their thermodynamic measurements that the hydrogen bonding in glucose solutions is stronger than in water.

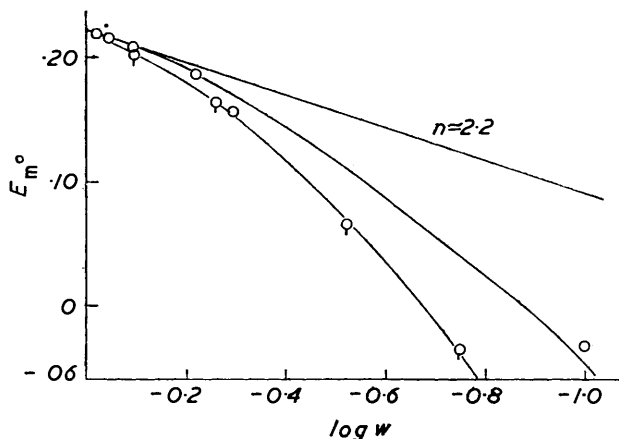
The discussion of the results for glucose solutions indicates that where some correction can be made for non-ideality, the simple stoichiometric model can be improved. Such corrections may, however, be difficult to make as the vapour-pressure measurements may not be sufficiently sensitive at such low concentrations of organic compound to indicate the extent of change in the effective mole or volume fraction of water.

Acetone and Dioxan.—Fig. 6 shows the plot of E_m^0 against $\log w$ for methyl and ethyl alcohols, glycerol, and ethylene glycol over the range 0–88% of water (v/v). Equation (5) is seen to hold over a wide range for the two alcohols, the only hydroxylic compounds to have been studied over the whole range. By contrast, Fig. 7 shows that acetone and dioxan solutions deviate markedly from the simple stoichiometric relationship over a wide range, although acetone solutions obey it up to a concentration of 20% acetone (w/w).

The derivation of eqns. (3) and (4) implies an ideal model for the solutions. Hudson and Saville assume in fact that the entropy of water in the solutions considered is ideal,

but stress that this assumption is less likely to be justified when the concentration of either component is small, which is the case for most of the solutions studied here. As mentioned earlier, the partial-vapour-pressure data indicate that the partial molal free energy of water is given by an ideal expression for most of the solutions considered at 25° c. This

FIG. 7.



may, however, be fortuitous, and does not necessarily imply that the entropy of water in the solution will be ideal, or heat-content changes zero or negligible. In ideal solutions the solvation entropy should be given by

$${}^w_s\Delta S = nR \log \phi_w = (F/T)({}^wE_m^0 - {}^sE_m^0)$$

or

$${}^w_s\Delta S = nR \log N_w = (F/T)({}^wE_N^0 - {}^sE_m^0)$$

In fact where entropy data are available from measurements at different temperatures, or from direct heat measurements, they do not follow a simple stoichiometric expression, and are often in the wrong direction.

The solvation number of hydrochloric acid, $n = 2.2$, found from the E_m^0 versus $\log \phi_w$ graph, is lower than that found by any other method, apart from diffusion measurements¹⁰ ($n = 2.1$). From consideration of activity coefficients in aqueous solution, Stokes and Robinson find $n = 8$, and Glueckauf $n = 4.7$. The E_N^0 versus $\log N_w$ graphs give a number of values, all somewhat higher than 2.2 (2.7–5.0).

The values given by Stokes and Robinson and by Glueckauf result from ascribing all the variation of activity coefficient with concentration apart from interionic attractions to specific solvation, and may well be too high on that account. Nevertheless, the present method must not be regarded yet as an entirely reliable method of determining n .

The authors thank Dr. R. F. Hudson for helpful discussions.

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[Received, December 31st, 1956.]

¹⁰ Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955, p. 319.