The Question of the Measure of Electrolytes in Organic Reactions. Calculation of Activity Coefficients of Electrolytes in Solvolytic Media†

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The use of the stoicheiometric concentration as a measure of electrolytes in the study of their effects in organic and particularly solvolytic reactions is considered and questioned. As an aid to information on this subject and as a better approximation to the proper measure of the active electrolyte, a practical approach to activity coefficients of 1 : 1 electrolytes in solvolytic media is proposed by calculation using Harned's rule. Test values are compared with experimentally available activity coefficients and the applicability of this approach as well as some of its limitations are discussed. The rule is applied to various salts in ethanol and aqueous dioxan. The features of the coefficients reported are discussed including the large deviation from proportionality between activity and concentration which they indicate. Some of the possible implications for solvolytic studies and the need for caution in this respect are pointed out.

NUMEROUS studies and arguments in organic chemistry and more particularly solvolytic reactions have been based on electrolyte effects. Except for the use of constant ionic strength in certain cases [1] and scattered exceptions where either the activity [2-6] or the association [7-11] have been taken into account, it has been common practice to use the stoicheiometric concentration as a measure of the effective electrolyte. This situation is not altered by the fact that medium effects [12-14] and the effects of electrolytes on the activity coefficients of non-electrolytes [15-18] have been considered in certain systems. The above practice which in some cases can lead to serious errors,[3-8,10] contrasts with the respective practice in the physicochemical and inorganic fields where activities and ionic association are taken into account in considerable detail.[19-33]

Why then is the stoicheiometric concentration the measure of choice in organic systems? Except for the fact that it is the most easily available one, its use has been supported by the notion of complete dissociation of strong electrolytes and by repeatedly reported linear dependence of rate and product data against electrolyte concentration. Such linearities are usually taken as indication that concentrations are proportional to activities.[34] However, for reasons such as the following ones, we have objected to the generality of such linearities [3-6] while our careful re-examination of some of them has shown that they were incorrectly assigned.[3,5] Such reasons include on one hand the fact that there is by now ample evidence of association [7-10,22] even for strong electrolytes in aqueous solutions at low concentrations,[35] and on the other the possibility that limited accuracy of experimental data and/or operation over a narrow or near the plateau range could have rendered slight curvatures undetected. The resultant power of habit for accepting such linearities is another factor, and there are cases where linear plots are drawn [36] even though curved ones seem to be favoured by the experimental points.

Thus, it seemed to us that our reservations regarding the simple use of concentration could not be proven unjustified by the alleged literature evidence to the contrary, and that there was a need for taking up the subject of the measure of electrolytes in organic reactions and considering other measures as well, such as the activity of the electrolyte or the concentration of free ions. In the present paper, a practical approach to the former, and specifically to activity coefficients of single 1 : 1 electrolytes, is suggested which is within reach of organic chemists, *i.e.* does not necessitate elaborate physicochemical measurements. With such information at hand one could then compare this measure with stoicheiometry, *e.g.* by repeated checks of the fit of kinetic and product data, and even with the concentration of free ions if pertinent information becomes available. Our previous calculation of the latter in some systems is only rough and will not be dealt with at present. No *a priori* answer and choice as to which measure is a better approximation is possible [37] or attempted here, at least for the usually employed concentrations in solvolytic reactions and ' charged species–uncharged substrate ' interactions,[2,23,38] even though at very low concentrations ($m \longrightarrow 0$) classical theory [39] suggests that activity coefficients will tend to cancel out for such interactions, thus implying that the concentration of free ions would be the measure of choice.

METHOD

The abundance of information on activity coefficients of aqueous electrolytes [19,30] and our belief that the ratio of the coefficients of two electrolytes could be more or less maintained in media of similar structure led us to search for such a relationship. This brought us to the equation suggested as a rule by Harned in 1962 [40] stated as equation (1), where the subscripts aq and org stand

$$(\gamma_s/\gamma_{HCl})_{aq} = (\gamma_s/\gamma_{HCl})_{org} \qquad (1)$$

for aqueous and organic–water/organic systems respectively and γ_s is the activity coefficient of the electrolyte under study. The rule concerns single electrolytes in mixed aqueous–organic solvents and is expected to have a satisfactory validity in mixtures of dielectric constant 80—20. It was tested [40] by Harned for alkali metal chlorides in highly aqueous methanol and once later for

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† Taken in part from the doctoral thesis of Mrs. Helen Ioannou-Kakouri.

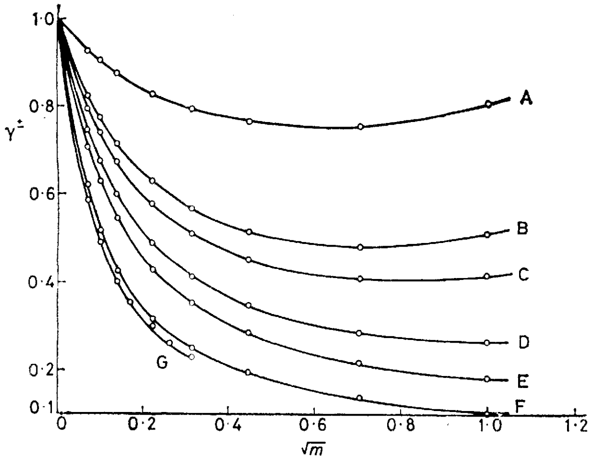

FIGURE 1 Plots of activity coefficients of hydrochloric acid in aqueous ethanol solutions at 25 °C *vs.* the square root of molality: [Curve, alcohol % w/w, (ref.)]: A, 0, (ref. 19*a*); B, 65; C, 79.95 (80% v/v); D, 90; E, 99.94 (ref. 42); F, 100, (ref. 44); G, 100, (ref. 45). Values for curves B, C, D, and E interpolated from data in ref. 42

sodium chloride in up to 60% aqueous dioxan and 90% aqueous methanol.[31] No other tests of the rule in aqueous organic media and no tests at all in pure organic solvents seem to have been reported, nor has the rule been applied for obtaining activity coefficients. We decided to test the rule in solvolytic media and, if satisfied, use it in our studies.

TABLE 1

Mean activity coefficients of HCl in H_2O, MeOH, and EtOH at 25 °C [a]

m	H_2O [b] γ_{HCl}	MeOH [c] γ_{HCl}	EtOH [d] γ_{HCl}
0.005	0.928		0.728
0.01	0.905		0.632
0.02	0.875		0.544
0.03	(0.858)		(0.500)
0.05	0.830		0.426
0.06	(0.820)		
0.07	(0.812)		
0.08	(0.806)		
0.1	0.796	(0.436)	0.352
0.2	0.767	(0.378)	0.286
0.3	(0.759)	(0.351)	(0.254)
0.5	0.757	(0.324)	(0.211)
0.7	(0.776)		(0.198)
1.0	0.809		0.177

[a] In all the Tables values in parentheses denote values interpolated from plots of γ *vs.* $\sqrt{m}$. [b] Ref. 19*a*. [c] Ref. 19*b*. [d] Refs. 42 and 43.

The experimental information required is given in the literature. Thus, the activity coefficients of hydrochloric acid are available in water [19a] and methanol,[19b,28a] aqueous methanol,[41] aqueous ethanol,[42,43] ethanol,[19b,44,45] aqueous dioxan,[19c] and aqueous acetone,[28a,46,47] as well as in acetic acid.[48] We have as yet no information on these coefficients in other solvents of solvolytic interest such as trifluoroethanol, trifluoroacetic acid, formic acid, and hexafluoroisopropyl alcohol. On the other hand, activity coefficients for hydrochloric acid are available in solvents such as formamide,[30b] dimethylformamide,[30c] dimethyl sulphoxide,[28a,30d] and tetrahydrofuran.[28a] Regarding the activity coefficients of salts, those for the common 1 : 1 electrolytes in water are readily available [19d] along with some information on 2 : 1 and 1 : 2 electrolytes.[19c] Unfortunately, no direct information is available for the strongly nucleophilic azide and cyanide salts whereas the activity coefficients for sodium and potassium thiocyanate are reported both in water [19d] and some aqueous solvents.[49]

For convenience, the activity coefficients of hydrochloric acid, are plotted in Figure 1 as a function of concentration for a series of aqueous ethanol mixtures. The curves are based on values obtained by interpolation from plots of activity coefficients, calculated from literature data,[42] *vs.* the dielectric constant of the various aqueous ethanol solutions at a given constant molality of hydrogen chloride for each plot.

TESTS AND RESULTS

Comparison with Known Values.—To test the rule in pure hydroxylic solvents, equation (1) was applied in methanol and ethanol to electrolytes for which the activity coefficients were already known from experiment. The necessary data for hydrochloric acid and the aqueous solutions of salts are given in Tables 1 and 2 respectively. The calculated values along with the available experimental ones are shown in Table 3 for methanol and Table 4 for ethanol. In the latter, where minute amounts of water can drastically change the activity coefficients,[45] Scatchard's values [42] for hydrochloric acid obtained in 99.9% ethanol were used.

The test of the rule was then extended to other solvents (aqueous dioxan, formamide, *N*-methylacetamide) for which activities of salts were also known from the literature (Tables 5 and 6).

As a further check of the rule, values calculated by equation (1) were compared with activity coefficients obtained by application of the Debye–Hückel equation in

TABLE 2

Mean activity coefficients of various salts in H_2O at 25 °C

m	γ_{LiCl} [a,b]	γ_{HBr} [c]	γ_{LiBr} [a]	γ_{NaBr} [a,d]	γ_{NaI} [d]	γ_{LiNO_3} [a]
0.005	0.929		[0.934] [e]	[0.937]		0.925 [f]
0.01	0.905		[0.912]	[0.916]		0.898 [f]
0.02	(0.878)		[0.886]	[0.891]		
0.05	(0.830)	0.838	[0.847]	[0.847]		(0.825)
0.1	0.792	0.805	0.794	0.782	0.787	0.788
0.2	0.761	0.782	0.764	0.741	0.751	0.751
0.3	0.748	(0.785)	0.757	0.719	0.735	0.737
0.5	0.742	(0.790)	0.755	0.697	0.723	0.728

[a] Ref. 19*f*. [b] Ref. 19*g*. [c] Ref. 19*h*. [d] R. A. Robinson and R. M. Stokes, *Trans. Faraday, Soc.* 1949, **45**, 612. [e] Values in brackets based on freezing point data (ref. 19*i*). [f] H. S. Harned, *Discuss. Faraday Soc.*, 1957, **24**, 7.

TABLE 3

Mean activity coefficients of LiCl and LiBr in MeOH at 25 °C

m	γ_{LiCl}		γ_{LiBr}	
	Calc.[a]	Lit.	Calc.[a]	Lit.
0.1	0.434		0.435	
0.2	0.375		0.377	
0.3	0.346	0.361 [b]	0.350	0.361 [b]
0.5	0.317	0.331,[b] 0.268 [c]	0.323	0.331 [b]

[a] Unless otherwise noted, all the calculated values (calc.) in Tables 3—10 have been obtained from equation (1) and data in the corresponding Table and Tables 1 and 2 also. [b] P. A. Skabischewskii, *Russ. J. Phys. Chem.*, 1969, **43**, 1432. [c] Ref. 30*i*.

the form of equation (2) where the molality m is used instead of the ionic strength I and where the parameters are defined in the usual way.[19,28,30] It should, however,

$$\log \gamma_{\pm} = \frac{-|Z_1Z_2|Am^{\frac{1}{2}}}{1 + aBm^{\frac{1}{2}}}. \qquad (2)$$

be noted that although the Debye–Hückel equation is used for comparison, it is not very practical for organic chemists. A severe limitation is the need for the adjustable parameter 'a' which is available in a few cases only. Also, expressed as above, the equation is only approximate since it is strictly valid only for completely dissociated 1 : 1 electrolytes.[28b,50] In a more rigid application, the degree of dissociation of the electrolyte α is required which, however, is often not available.

In the present case, equation (2) was used for electrolytes for which 'a' was known from conductometric studies. The values obtained were then compared with the coefficients calculated by Harned's rule (Table 7). The comparison, expected to be only approximate because of the assumptions involved in both equations, was carried out in ethanol only but could be similarly extended to other solvents provided that A, B, and a are known.

Application to Azide and Other Salts in Aqueous Dioxan and Ethanol.—Azide salts are important in solvolytic studies. For this reason, the activity of sodium azide has been calculated in 25 and 30% aqueous dioxan where it is of special interest,[4-6,51] and that of

TABLE 4

Mean activity coefficients of LiCl, HBr, NaBr, and NaI in EtOH at 25 °C

m	γ_{LiCl}		γ_{HBr}		γ_{NaBr}		γ_{NaI}	
	Calc.	Lit.[a]	Calc.	Lit.[b]	Calc.	Lit.[b]	Calc.	Lit.[b]
0.005	0.726	0.717		0.649	0.735			
0.01	0.631	0.645		0.590	0.639	0.609		0.552, 0.571
0.02	0.545	0.567		0.537	0.554	0.519		0.482, 0.493
0.05	0.426	0.465	0.430	0.474	0.434			
0.1	0.350	0.394	0.356	0.431	0.346	0.314	0.348	0.407, 0.379
0.2	0.284	0.334	0.291		0.276	0.268	0.280	0.430
0.3	0.250	0.304	0.263		0.241		0.246	
0.5	0.205	0.271	0.220				0.202	

[a] Calculated from data and equation given in ref. 42. [b] Ref. 30*j*.

TABLE 5

Activity coefficients of $NaClO_3$ and $LiClO_3$ in 44.5 and 64.5% aqueous dioxan

			44.5% dioxan					64.5% dioxan				
				γ_{NaClO_3}		γ_{LiClO_3}			γ_{NaClO_3}		γ_{LiClO_3}	
m	$\gamma^{H_2O}_{\text{NaClO}_3}$ [a]	$\gamma^{H_2O}_{\text{LiClO}_3}$ [b]	γ_{HCl} [c]	Calc.	Lit.[d]	Calc.	Lit.[d]	γ_{HCl} [c]	Calc.	Lit.[d]	Calc.	Lit.[d]
0.1	0.772	0.810	0.550	0.533	0.500	0.560	0.472	0.305	0.296	0.207	0.310	0.202
0.2	0.720	0.782	0.498	0.467	0.428	0.508	0.393	0.265	0.249	0.146	0.270	0.144
0.3	0.688	0.771	0.480	0.435	0.392	0.488	0.356	0.242	0.219	0.120	0.246	0.123
0.5	0.645	0.769	0.467	0.398	0.355	0.474	0.325	0.237	0.202	0.096	0.241	0.109
1.0	0.589	0.808	0.500	0.364	0.313	0.499	0.326	0.261	0.190	0.074	0.261	0.119

[a] Ref. 19*f*. [b] G. A. Scatchard, S. S. Prentiss, and P. T. Jones, *J. Amer. Chem. Soc.*, 1934, **56**, 805. Freezing-point values. [c] Interpolated from data in ref. 19*c*. [d] A. N. Cambell and B. G. Oliver, *Canad. J. Chem.*, 1969, **47**, 2671.

TABLE 6

Activity coefficients of NaCl in formamide and *N*-methylacetamide (NMA) at 25 °C

m	$\gamma^{HCONH_2}_{HCl}$ [a]	γ^{NMA}_{HCl} [b]	$\gamma^{H_2O}_{NaCl}$ [d]	$\gamma^{HCONH_2}_{NaCl}$		γ^{NMA}_{NaCl}	
				Calc.	Lit.[e]	Calc.	Lit.[f]
0.01		0.966	0.903			0.965	0.967
0.05	0.904	0.925	0.821	0.894	0.883	0.915	0.966
0.06	0.899	0.919	(0.807)	0.885	0.869		
0.07	0.895	0.912	(0.797)	0.878	0.863		
0.08	0.895	0.907	(0.789)	0.876	0.857		
0.10	0.893	0.896	0.778	0.873	0.845	0.876	0.971
0.20		(0.870) [c]	0.734			0.830	0.996
0.30			0.710				1.031

[a] R. K. Agarwal and B. Nayak, *J. Phys. Chem.*, 1967, **71**, 2062. [b] L. R. Dawson, W. H. Zuber, and M. C. Echstrom, *J. Phys. Chem.*, 1965, **69**, 1335. Data at 35 °C but γ does not show any considerable change in the region 25—35 °C. [c] Estimated as ($\gamma^{H_2O}_{HCl}$ + 0.100), based on the differences between values in water and NMA (Table 1 *vs.* 6). [d] Ref. 50*b*. [e] Ref. 30*k*. [f] Ref. 29*c*.

TABLE 7

Comparison of activity coefficients calculated by Harned's rule (H) and the Debye–Hückel (D–H) equation in EtOH at 25 °C

	γ_{LiCl}		γ_{LiNO_3}		$\gamma_{\text{Me}_4\text{NCl}}$		γ_{MeNBr}	
m	D–H [b,c]	H	D–H [b,d]	H	D–H [b,e]	H [a]	D–H [b,f]	H [a]
0.01	0.612	0.631	0.603	0.627				
0.05	0.410	0.426	0.390	0.423				
0.1	0.331	0.350	0.306	0.348	0.324	0.330	0.321	0.330
0.2	0.264	0.284	0.235	0.280	0.256	0.255	0.252	0.251
0.3	0.232	0.250	0.201	0.247	0.223	0.215	0.219	0.209

[a] $\gamma^{\text{H}_2\text{O}}$ of Me_4NCl and Me_4NBr are: 0.746, 0.746; 0.683, 0.672; 0.644, 0.624 for 0.1; 0.2; 0.3 *m* respectively (ref. 27). [b] Calculated on the basis of equation (2). In ethanol $A = 2.621\ \text{mol}^{-\frac{1}{2}}\ \text{kg}^{\frac{1}{2}}$ and $B = 0.5235 \times 10^8\ \text{cm}^{-1}\ \text{mol}^{-\frac{1}{2}}\ \text{kg}^{\frac{1}{2}}$ (ref. 28*b*). The values of '*a*' used are given next. [c] $a = 4.4$ Å (ref. 39*h* and R. L. Kay, *J. Amer. Chem. Soc.*, 1960, **82**, 2099). [d] $a = 3.7$ Å (G. D. Parfitt and A. L. Smith, *Trans. Faraday Soc.*, 1963, **59**, 257.) [e] $a = 4.2$ Å (D. F. Evans and P. Gardam, *J. Phys. Chem.*, 1968, **72**, 3281). [f] $a = 4.1$ Å (D. F. Evans and P. Gardam, *J. Phys. Chem.*, 1968, **72**, 3281).

TABLE 8

Mean activity coefficients of NaN_3 in 25 and 30% aqueous dioxan at 25 °C, as calculated by Harned's rule

	H_2O [a]					25% dioxan		30% dioxan	
m	$\gamma^2_{\text{HN}_3}$ [b,c]	$\gamma^2_{\text{H}^+}$ [d]	γ_{Na^+} [d]	$\gamma_{\text{N}_3^-}$ [e]	γ_{NaN_3} [i]	γ_{HCl} [f]	γ_{NaN_3} [f]	γ_{HCl} [f]	γ_{NaN_3}
0.03	0.727	0.869 [g]	0.855 [h]	0.837	0.846	0.772	0.761	0.744	0.733
0.1	0.618	0.807	0.783	0.766	0.774	0.689	0.670	0.653	0.635
0.2	0.565	0.788	0.744	0.717	0.730	0.644	0.613	0.605	0.576
0.5	0.519	0.812	0.701	0.639	0.669	0.622	0.550	0.582	0.514
1.0	0.581	0.940	0.697	0.618	0.656	0.665	0.539	0.622	0.504

[a] All the values correspond to 25 °C except those for hydrazoic acid (22 °C). [b] Ref. 52. [c] These are actually *y* values, *i.e.* for the concentration expressed as M instead of *m*. However, the difference between γ and y is negligible for our results (ref. 19*j*). [d] Ref. 53. [e] $\gamma_{\text{N}_3^-} = \gamma^2_{\text{HN}_3}/\gamma_{\text{H}^+}$. [f] Interpolated from data in ref. 19*c*. [g] Calculated as $\gamma_{\text{H}^+} = \gamma^2_{\text{HCl}}/\gamma_{\text{HCl}^-} \simeq \gamma^2_{\text{HCl}}/\gamma_{\text{Cl}^-} = 0.736/0.847$ (ref. 19*a*, 50*b*) where the MacInnes assumption (D. A. MacInnes, *J. Amer. Chem. Soc.*, 1919, **41**, 1086), is used, *i.e.*, $\gamma_{\text{Cl}^-} = \gamma_{\text{KCl}}$ at low concentrations. [h] Calculated from $\gamma_{\text{Na}^+} = \gamma^2_{\text{NaCl}}/\gamma_{\text{KCl}}$. Data interpolated from 50*b*. [i] $\gamma_{\text{NaN}_3} = (\gamma_{\text{Na}^+} \cdot \gamma_{\text{N}_3^-})^{\frac{1}{2}}$.

lithium azide in ethanol (where the solubility of the sodium salt is very low and lithium or tetrabutylammonium azides can serve as sources of azide ions). Since the required activity coefficients of these salts in water are not available they were calculated from the corresponding activity coefficients of hydrazoic acid,[52] H^+, and Na^+ or Li^+ [53] (see related footnotes in Tables 9 and 10). The necessary coefficients of hydrochloric acid in 25 and 30% aqueous dioxan were obtained by interpolation from plots of $\gamma_{\pm\text{HCl}}$ *vs.* percent dioxan at the various given molalities.[19c] Application of Harned's rule gave the coefficients shown in Tables 8 and 9.

TABLE 9

Activity coefficients of LiN_3 in EtOH at 25 °C, calculated by Harned's rule

m	H_2O [a] γ_{Li^+}	H_2O [b] γ_{LiN_3}	EtOH [c] γ_{LiN_3}
0.03	0.867 [c]	0.852	0.497
0.1	0.799	0.782	0.346
0.2	0.775	0.745	0.278
0.5	0.786	0.709	0.199

[a] Ref. 53. [b] $\gamma_{\text{LiN}_3} = (\gamma_{\text{Li}^+} \cdot \gamma_{\text{N}_3^-})^{\frac{1}{2}}$ (N_3^- data given in Table 8). [c] Calculated from the value of LiCl (Table 2) and the MacInnes assumption (D. A. McInnes, *J. Amer. Chem. Soc.*, 1919, **41**, 1086).

The coefficients of certain other salts in ethanol and more specifically those of alkali metal bromides, perchlorates, and of the strongly nucleophilic thiocyanates were also calculated (Table 10).

DISCUSSION

Comparison of the values calculated by Harned's rule with the respective experimentally available activity coefficients in the systems examined (Tables 3—6) as well as with the values calculated by the Debye–Hückel equation in ethanol (Table 7) shows a surprisingly good fit except in 64.5% aqueous dioxan. The agreement is particularly good in dilute solutions, deviations increasing with concentration. These are generally smaller than 5 or 10% for solutions up to 0.1*m* and less than 5 or 20% up to 0.3*m*. Significantly, they are not greater than the variations between some experimental values (Tables 3, 4). The poor results in 64.5% aqueous dioxan ($D = 23.5$) particularly as compared to those in the 44.5% medium ($D = 39$) could possibly be associated

TABLE 10

Activity coefficients of some representative electrolytes in EtOH at 25 °C, calculated by Harned's rule [a]

	$\gamma^{\text{H}_2\text{O}}$ [b]				γ^{EtOH}				
m	NaClO_4	LiClO_4	NaSCN	KSCN	NaClO_4	LiClO_4	LiBr	NaSCN	KSCN
0.005	[0.929]	[0.935]			0.728	0.733	0.732		
0.01	[0.904]	[0.915]			0.631	0.639	0.636		
0.02	[0.873]	[0.890]			0.543	0.553	0.551		
0.05	[0.821]	[0.853]			0.421	0.437	0.434		
0.1	0.775	0.812	0.787	0.769	0.342	0.359	0.351	0.348	0.340
0.2	0.729	0.794	0.750	0.716	0.272	0.296	0.285	0.280	0.267
0.5	0.668	0.808	0.715	0.646	0.186	0.225	0.211	0.199	0.180

[a] Values in brackets obtained from freezing-point data (ref. 19*i*). [b] Ref. 19*f*.

with Harned's suggestion [40] that the rule should be more valid for dielectric constants between 20 and 80. However, the dielectric constant does not seem to be the only or decisive factor as illustrated by the respective success of the rule in ethanol ($D = 24.5$), a fact which parallels the expected importance of solvation in this region ($D > 15$).[12] It is evident that since the rule follows closely the ratio of the activity coefficients in water it should, and the present results agree with this, be most applicable in protic and highly aqueous or water-like solvents in which the solvation trend is not very different from that in water. This and the success of the rule in the pure alcohols examined suggest that it should be satisfactorily applicable to the aqueous mixtures of the latter and specifically in aqueous ethanol where a large body of solvolytic studies are conducted and where activity coefficients of hydrochloric acid are available (Figure 1).

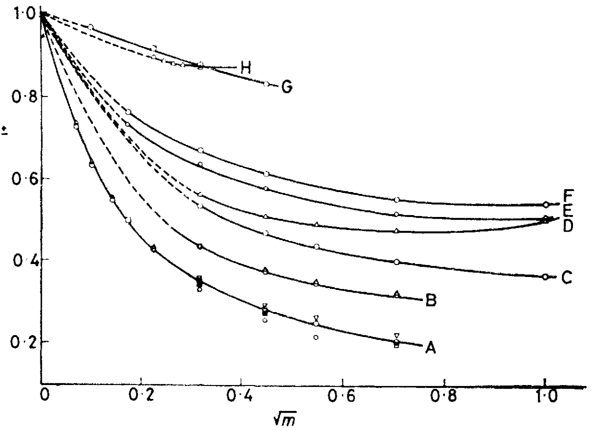

FIGURE 2 Plots of activity coefficients of some representative systems, as calculated by Harned's rule, against the square root of molality: A; ○ LiCl, □ LiN_3, △ NaBr, ▽ HBr, ○ Me_4NCl in EtOH; the curve drawn is that for lithium chloride coefficients; B, ○ LiCl, △ LiBr in MeOH; C, D ○ $NaClO_3$, △ $LiClO_3$ in 44.5% aqueous dioxan; E, ○ NaN_3 in 30% aqueous dioxan; F, ○ NaN_3 in 25% aqueous dioxan; G; ○ NaCl in *N*-methylacetamide; H; △ NaCl in formamide

The present activity coefficients which are given at 25 °C can be used at other temperatures as well with little error because although no general and clear answer has been given to the temperature dependence of activity coefficients,[28b,54,55] little change is observed in most cases for molalities below $1m$.[19,30]

Examining the features of the presently reported activity coefficients, most of which are plotted in Figure 2,* one observes a steep decrease with increasing concentration before the plateau or near plateau (another general feature) is reached. The steepness is greater the lower the concentration and the polarity of the solvent, the span of the curve increasing as the dielectric constant decreases. In fact, in media of still lower dielectric constant, even steeper curves are observed. Thus, in acetic acid ($D = 6.2$), a solvent of high solvolytic interest where activity coefficients of hydrochloric acid only are available, literature data show that $\gamma_{\pm\mathrm{HCl}}$ plunges down to 0.200 at just 0.001 $6m$ and the plateau is reached at $0.04m$.[48] In 80% aqueous acetone, also of solvolytic interest, the same activity coefficient drops to 0.590 at $0.02m$.[46]

This observed drop of γ with increasing m, which implicitly illustrates and measures the deviation from proportionality between the activity and the stoicheiometric concentration of the electrolyte ($\alpha = m\gamma$), indicates that this deviation is a general phenomenon in the usual solvolytic media, particularly at low concentrations where most such studies are conducted. This phenomenon is shown not only to be extremely pronounced at low polarities but to extend to highly aqueous media as well. Expressing the percent deviation between two concentrations m_1 and m_2 as 100 $(\gamma_1 - \gamma_2)/\gamma_2$, the maximum value in going from zero concentration ($\gamma = 1$) to m_2 is: 400% for hydrochloric acid in acetic acid [48] for 0.001 $6m$ ($\gamma = 0.200$); 194% for lithium azide in ethanol at $0.113m$ ($\gamma = 0.340$), in large contrast to the previously assumed [34] proportionality; 57% for sodium azide in the highly aqueous 30% dioxan at $0.1m$ ($\gamma = 0.635$). Incidentally, it is to the above deviations that the aforementioned differences between the calculated and experimental activity coefficient values should be compared in order to appreciate how satisfactory the present approximations are for practical purposes.

Another feature of the plots is the narrowness of the spread of the activity coefficients of various salts in a given medium, especially at low concentrations. This is helpful in that it offers a means for obtaining a rough value for an electrolyte for which data are not available and also a rough check for the validity of calculated coefficients. In this respect, the fact that the lithium azide values in ethanol fall nicely in place (Figure 2) confirms indirectly the calculations of this salt in water.

In conclusion, the present findings have shown that Harned's rule is satisfactorily applicable to the calculation of activity coefficients of 1 : 1 electrolytes in organic and aqueous organic media, particularly protic ones, provided the limitations and considerations discussed are taken into account.† They also prove the large non-proportionality between activity and concentration which can have significant implications concerning the use of electrolytes in solvolytic studies.[3-6] This supports our objections regarding the general use of stoicheiometric concentration and reported linearities against this measure, if one were to accept that activities are closer to the proper measure of the active electrolyte. In this respect, hitherto published [3-6] and unpublished kinetic and product results of ours have given excellent linear fits against electrolyte activity, as compared to curved dependence *vs.* their concentration, suggesting that the former may constitute a satisfactory approxim-

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* Due to the proximity of values for the several salts in ethanol, only few are represented. The results in 64.5% aqueous dioxan have also been omitted.

† The theory from which the rule is derived does not exclude application to 1 : 2 and 2 : 1 electrolytes, which has not been attempted here and which might involve larger errors.

ation. However, as already mentioned in the introduction, any conclusions are premature and further tests involving activities, as well as the concentration of free ions if possible, will be needed. The present information should assist in this respect and in warning against, and modifying the prevailing practice regarding the title subject as well as help in understanding the effects of electrolytes in organic reactions in solution. Forthcoming publications from this laboratory will illustrate these points.

[8/1458 *Received, 7th August*, 1978]

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