

[CONTRIBUTION FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

## ACTIVITY COEFFICIENTS OF SODIUM, POTASSIUM AND LITHIUM CHLORIDES AND HYDROCHLORIC ACID AT INFINITE DILUTION IN WATER-METHYL ALCOHOL MIXTURES

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RECEIVED FEBRUARY 26, 1930

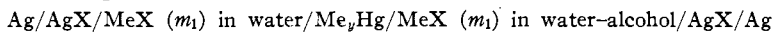
PUBLISHED JUNE 6, 1930

### I. Introduction

The activity coefficients of a number of the alkali halides in pure aqueous solutions have recently been redetermined with great precision by Harned.<sup>1</sup> He used cells of the type



where X designates the halide and Me the alkali metal present. In the present investigation cells of the same general type have been used, but the concentration of the electrolyte was the same on both sides of the cells and the composition of the solvent used as a variable



Through suitable recombining of these cells with those for pure aqueous solutions it was possible with the use of the Debye-Hückel activity function to calculate the activity coefficients of the electrolytes employed in the water-alcohol solutions. This also gave the means of determining the activity coefficients at infinite dilution in relation to the corresponding water value which was assumed to be unity in accordance with custom. As has been predicted by the simplest theory possible, it was found that within the errors due to uncertainties of the calculation and experimental difficulties, the logarithm of the activity coefficient at infinite dilution is approximately inversely proportional to the dielectric constant of the pure water-methyl alcohol mixtures. It is the first time this has actually been shown to be the case and therefore, although expected, it is of considerable importance.

### II. Experimental Methods

The methyl alcohol used was free from acetone and aldehydes; the density corresponded very closely to the accepted value for pure, absolute alcohol. As the alcohol always was used in mixture with water a correction for the very small water content of the original product was considered unnecessary. All salts used were of the analyzed variety and further purification was not carried out. Hydrochloric acid was carefully redistilled as constant-boiling mixture and middle portions were used. All solutions

<sup>1</sup> Harned, *THIS JOURNAL*, 51, 416 (1929); compare further MacInnes and Parker, *ibid.*, 37, 1445 (1915); Allmand and Polack, *J. Chem. Soc.*, 115, 1020 (1919); Pearce and Hart, *THIS JOURNAL*, 43, 2483 (1921); Harned and Douglas, *ibid.*, 48, 3095 (1926). Measurements with hydrochloric acid: Ellis, *ibid.*, 38, 737 (1916); Noyes and Ellis, *ibid.*, 39, 2532 (1917); Linhart, *ibid.*, 39, 2601 (1917); Scatchard, *ibid.*, 47, 641 (1925).

were generally made up through diluting standard solutions with calculated amounts of water and alcohol. All concentrations of the electrolytes are given in molality per 1000 g. of the solvent. The methyl alcohol concentration is expressed in weight per cent.

Silver-silver chloride electrodes<sup>2</sup> were prepared from silver deposited on a small platinum-spiral through decomposition of silver oxide paste at 500°.

The electrolysis in one molal hydrochloric acid was carried out with 10 milliamperes during two hours. Hydrogen electrodes<sup>2</sup> were obtained through electrolysis with a small platinum-foil in an approximately 1%, strongly acid, PtCl<sub>4</sub> solution. The amount of current used was about 0.1 amp. per sq. cm. of surface of the foil during six minutes. The alkali metal amalgams were made by the method described by Harned.<sup>2b</sup> The lithium amalgam was found to work fairly well without any special precautions. The design of the amalgam cells employed is given in Fig. 1. The procedure for measurements of these cells has been described sufficiently elsewhere.<sup>2,3</sup> The temperature for all measurements was 25.00°.

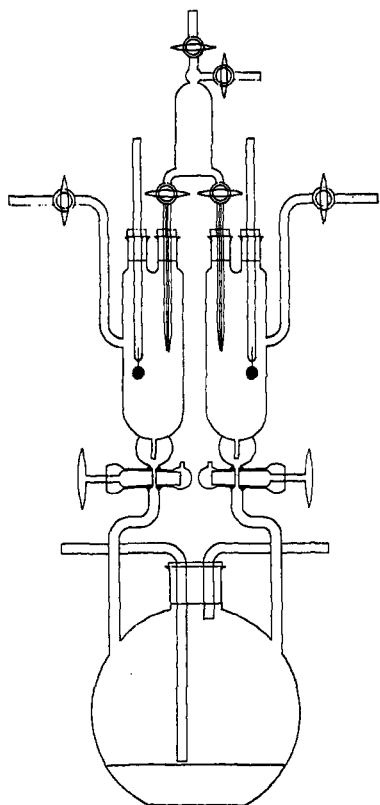


Fig. 1.—Apparatus for the amalgam cells.

If the amount of solvent evaporated had been the same on both sides of

### III. Accuracy of the Results

The electromotive force of the amalgam cells was wholly due to the differences in the composition of the solvent used in the two half cells. The amount of solvent employed in making up the solutions varied between 600 to 800 g. Before the cells were filled the two solutions that were to be used were boiled in

<sup>2</sup> A review of the methods and the literature for Ag/AgCl electrodes is given (a) by Harned, Ref. 1; regarding hydrogen electrodes compare also Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926); (b) Harned, *THIS JOURNAL*, **47**, 676 (1925); preparation of lithium amalgam, Harned and Swindells, *ibid.*, **48**, 126 (1926).

<sup>3</sup> Åkerlöf, *ibid.*, **48**, 1160 (1926).

the cell the effect of the electromotive force could scarcely have been noticed even with a very high measuring accuracy. To compensate for the larger loss on the alcohol side a slight excess of pure alcohol was added. The excess increased somewhat with the alcohol concentration and corresponded sufficiently closely with the actual loss. For dilute or fairly concentrated water-alcohol mixtures (up to 60%) this precaution worked very well. At still higher alcohol concentrations the difficulties in obtaining good results increased very rapidly. Usually the same measurement had to be repeated with new solutions three or four times and then their mean used. The measurements were carried out with a series of water-alcohol mixtures differing by 10% in alcohol content. Dividing the electromotive force by the alcohol content and plotting the values obtained against it usually gave a very smooth curve at lower alcohol concentrations. At higher ones the deviations were sometimes quite large, indicating possible errors of 2-3 millivolts. Up to 50% alcohol the errors seemed hardly to exceed 0.2-0.3 of a millivolt but systematic errors might easily have been present. For the measurements with solutions of hydrochloric acid errors due to evaporation of alcohol were unlikely to occur. Immediately before the hydrogen entered the cell it had passed through a long bubbling tower almost completely immersed in the water of the thermostat and containing about 200 cc. of the solution used. The measurements with these solutions may therefore have only the ordinary, apparent errors of 0.1-0.2 of a millivolt through the entire series.

#### IV. The Calculation of the Results

The limiting function of Debye-Hückel for the logarithm of the activity coefficient of a strong electrolyte is given by the well-known equation

$$\ln \gamma = - \frac{\epsilon^2 \cdot z_i^2}{k \cdot T \cdot D \cdot 2} \sqrt{\frac{8\pi \cdot N \cdot \epsilon^2 \cdot z_i^2 \cdot m}{K \cdot T \cdot D}} \text{ or } \ln \gamma = -u \sqrt{2m} \quad (1)$$

where  $\epsilon$  is the electron charge,  $k$  the Boltzmann constant,  $T$  the absolute temperature,  $D$  the dielectric constant of the medium,  $N$  the number of Avogadro,  $k$  the "mean distance of ionic approach,"  $z_i$  the valence number of ions of the  $i$ th kind and  $m$  the concentration of the electrolyte. Recently Gronwall, LaMer and Sandved<sup>4</sup> have extended this simplified equation to the so-called terms of higher order. They showed that in cases with symmetrical ions, where very small or negative distances of ionic approach were obtained with the original Debye-Hückel theory, their extended form gave positive and constant values, which seemed to be reasonable. However, their improved equations could only be used for very dilute solutions where the dielectric constant of the medium might be assumed to remain practically unchanged with varying concentration of the electrolyte. In this concentration range the electromotive force methods of determining

<sup>4</sup> Gronwall, LaMer and Sandved, *Physik. Z.*, **29**, 338 (1928).

activities are more or less unreliable and as we therefore were forced to use far higher concentrations, the equations mentioned could not be used in their present form. To obtain an equation which may be used for a large concentration range, Hückel<sup>5</sup> deduced an equation for the influence of the electric charges of the ions of the electrolytes. The fundamental assumption made was that the total change of the dielectric constant of the medium decreased linearly with increasing concentration. In a number of cases where the ions present had small dipole moments, this assumption was found to lead to negative dielectric constants in only fairly concentrated solutions, which is an impossibility. Nevertheless, a simplified form of Hückel's equation was shown by Hückel, Scatchard, Harned, Åkerlöf and others to be able to express the results of the activity measurements with great precision over a very large concentration range. The general form of the equation employed is

$$\log \gamma = -u \left( \frac{\sum \nu_i z_i^2}{\sum \nu_i} \right)^{3/2} \cdot \frac{\sqrt{\sum \nu_i c_i}}{1 + A \sqrt{\sum c_i z_i^2}} + B \sum c_i z_i^2 - \log \left( 1 + \frac{M}{1000} \sum m_i \right) \dots \quad (2)$$

where  $u$  is a universal constant,  $A$  and  $B$  are empirical constants,  $M$  is the molecular weight of the solvent,  $m$  and  $c$  are the concentration of the electrolyte in molality and molarity,  $\nu_i$  and  $z_i$  the number and valence of ions of the  $i$ th kind. So far in all cases where this equation has been used the theoretical value of the constant  $u$  has been employed, both for aqueous and non-aqueous solutions. As an example may be mentioned the calculation of Lucasse<sup>6a</sup> of the activity coefficient of hydrochloric acid in methyl alcohol from the measurements of Nonhebel and Hartley,<sup>6b</sup> in ethyl alcohol from those of Harned and Fleysher.<sup>6c</sup> Lucasse concluded that a very good agreement had been obtained between observed and calculated values. The quite appreciable deviations, especially at very low acid concentrations, were attributed to experimental difficulties such as hydrogen electrode errors, etc.

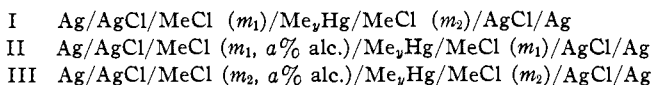
When Equation 2 was applied to some of the measurements presented here, it was soon found that it could not be used with the theoretical  $u$ -values. Since most of the results were obtained for fairly dilute solutions, the term  $B2m$  from Equation 2 was neglected in the case of potassium and sodium chloride solutions on account of its assumed smallness. As variables  $u$  and  $A$  were used. The measurements with lithium chloride solutions were extended over quite a large concentration range. In this case the influence of the term  $B2m$  is quite considerable at higher concentrations and could not be neglected. Therefore the  $u$ -values were first determined from measurements at lower concentrations and then the  $A$  and  $B$  values from a series of results at higher ones. As the difference between calculated

<sup>5</sup> Hückel, *Physik. Z.*, **26**, 93 (1925).

<sup>6</sup> (a) Lucasse, *Z. physik. Chem.*, **121**, 254 (1926); (b) Nonhebel and Hartley, *Phil. Mag.*, [6] **50**, 298, 729 (1925); (c) Harned and Fleysher, *THIS JOURNAL*, **47**, 82 (1925).

and theoretical  $u$ -values increases rapidly with increasing alcohol concentration, the  $u$ -values for lithium chloride solutions were calculated only for the two highest alcohol concentrations employed and then interpolated to give a curve of the same form as the curve for the theoretical values. For hydrochloric acid this method of calculation was found to be unnecessary and in this case the theoretical  $u$ -values were used.

The determination of the variables  $u$ ,  $A$  and  $B$  each required a separate electromotive force value that was to be obtained from the measurements in the following manner. Consider the three cells



The electromotive forces of these three cells may be expressed by the equations

$$E_1 = \frac{RT}{NF} \ln \frac{\gamma_1 \cdot m_1 \text{ (water)}}{\gamma_2 \cdot m_2 \text{ (water)}} \quad (3a)$$

$$E_2 = \frac{RT}{NF} \ln \frac{\gamma_1^* \cdot m_1^* \text{ (alc.)}}{\gamma_1 \cdot m_1 \text{ (water)}} \quad (3b)$$

$$E_3 = \frac{RT}{NF} \ln \frac{\gamma_2^* \cdot m_2^* \text{ (alc.)}}{\gamma_2 \cdot m_2 \text{ (water)}} \quad (3c)$$

An asterisk marks activity coefficients and concentrations in alcohol-water solutions. Subtraction of the second equation from the first one and addition of the third gives

$$E_4 = \frac{RT}{NF} \ln \frac{\gamma_2^* \cdot m_2^* \text{ (alc.)}}{\gamma_1^* \cdot m_1^* \text{ (alc.)}} \quad (3d)$$

Finally there is also a measurement necessary for the elimination of  $E_0$  according to the equation

$$E_4 - E_0 = \frac{RT}{NF} \ln \gamma \cdot m \quad (3e)$$

For potassium, sodium and lithium chlorides the values of  $E_1$  were calculated from the measurements of Harned. The measurements for hydrochloric acid gave directly the values of  $E_4$ . As previously indicated it has been customary to express the concentrations for these calculations in two units, molar and molal. In order to avoid a rather unnecessary labor, all concentrations in the following will always be expressed and used as molality. This makes the logarithmic end term in Equation 2 unnecessary for the calculations. The measurements were generally used interpolated from curves.

## V. Experimental Results

In Tables I, II, III and IV are given the results of the measurements and calculations with potassium, sodium and lithium chlorides and hydrochloric acid, respectively. All measurements with cells containing hydrogen electrodes are corrected to a partial hydrogen pressure of 760 mm. of

mercury. The vapor pressures of the water-methyl alcohol mixtures without electrolytes present were obtained from the measurements of Konowalow<sup>7</sup> in the following manner. The values for constant alcohol concen-

TABLE I

## ELECTROMOTIVE FORCE MEASUREMENTS AND ACTIVITY COEFFICIENTS FOR POTASSIUM CHLORIDE IN WATER-METHYL ALCOHOL SOLUTIONS

1. E. m. f. measurements and empirical constants derived from them. The e. m. f. values refer to the cells: Ag/AgCl/KCl (*m*) in pure water/K<sub>2</sub>Hg/KCl (*m*) in water-alcohol/AgCl/Ag.

Alc., wt. %	<i>E</i> 0.02 <i>m</i>	<i>E</i> 0.05 <i>m</i>	<i>E</i> 0.10 <i>m</i>	<i>E</i> 0.50 <i>m</i>	<i>u</i>	<i>A</i>	<i>B</i>
0	0.00000	0.00000	0.00000	0.00000	0.357	0.737	0.0112
10	.01807	.01747	.01705	.01612	.499	1.20	....
20	.03640	.03510	.03436	.03240	.645	1.50	....
30	.05508	.05310	.05202	.04894	.880	2.00	....
40	.07470	.07152	.07012	.06600	1.270	2.75	....
50	.09420	.09075	.08925	.08350	1.72	3.75	....
60	.1158	.1116	.1097	.1028	2.87	5.00	....
70	.1402	.1348	.1326	....	4.37	6.50	....
80	.1681	.1603	.1577	....	6.72	8.25	....
90	.1968	.1883	.1854	....	10.93	10.50	....

## 2. Activity coefficients at infinite dilution and at concentrations used

Alc., wt. %	$\gamma_{0.02 m}$ calcd.	$\gamma_{0.02 m}$ obs.	$\gamma_{0.05 m}$ calcd.	$\gamma_{0.05 m}$ obs.	$\gamma_{0.10 m}$ standard	$\gamma_{0.50 m}$ calcd.	$\gamma_{0.50 m}$ obs.
0	0.867	0.867	0.812	0.812	0.762	0.639	0.639
10	.831	.831	.767	.769	.716	(.593)	.611
20	.796	.796	.727	.726	.672	(.552)	.585
30	.749	.749	.675	.674	.620	(.509)	.552
40	.686	.691	.610	.609	.556	(.458)	.506
50	.636	.646	.564	.566	.516	(.434)	.484
60	.517	.515	.445	.443	.402	(.333)	.385
70	.416	.417	.352	.351	.316	..	..
80	.312	.312	.258	.257	.229	..	..
90	.197	.197	.159	.156	.139	..	..

## 3. E. m. f. measurements by Harned for pure aqueous solutions

KCl <i>m</i>	<i>E</i> obs.	<i>E</i> calcd.	$\gamma_{obs.}$	$\gamma_{calcd.}$
0.02	....	-0.07605	0.867	0.867
.05	....	-.03237	.812	.812
.10	0.00000	.00000 <sup>a</sup>	.762	.762
.20	.03198	.03187	.710	.709
.50	.07390	.07365	.642	.639
1.00	.10565	.10565 <sup>a</sup>	.596	.596
1.50	.12459	.12493	.574	.578
2.00	.13877	.13903	.568	.571
2.50	.15018	.15045	.567	.570
3.00	.15976	.15976 <sup>a</sup>	.570	.570

<sup>a</sup> These measurements used for the calculation of the empirical constants.

<sup>7</sup> Konowalow, *Wied. Ann.*, **14**, 34 (1881); Landolt-Börnstein, "Tabellen," 5th ed., 1923, Vol. II, p. 1398; Foote and Dixon, *Am. J. Sci.*, [5] **17**, 146 (1929).

TABLE II

## ELECTROMOTIVE FORCE MEASUREMENTS AND ACTIVITY COEFFICIENTS FOR SODIUM CHLORIDE IN WATER-METHYL ALCOHOL SOLUTIONS

1. E. m. f. measurements and empirical constants derived from them. The e. m. f. values refer to the cell: Ag/AgCl/NaCl (*m*) in pure water/Na<sub>2</sub>Hg/NaCl (*m*) in water-alcohol/AgCl/Ag.

Alc. wt. %	<i>E</i> 0.02 <i>m</i>	<i>E</i> 0.05 <i>m</i>	<i>E</i> 0.20 <i>m</i>	<i>E</i> 0.50 <i>m</i>	<i>u</i>	<i>A</i>	<i>B</i>
0	0.00000	0.00000	0.00000	0.00000	0.357	0.832	0.0232
10	.01777	.01732	.01681	.01641	.420	1.05	....
20	.03568	.03475	.03370	.03290	.503	1.12	....
30	.05402	.05241	.05079	.04965	.603	1.30	....
40	.07268	.07045	.06816	.06670	.733	1.50	....
50	.09215	.08935	.08610	.08425	.904	1.75	....
60	.1129	.10974	.10518	.10272	1.15	2.00	....
70	.1357	.1309	.1257	.1228	1.46	2.50	....
80	.1621	.1570	.1487	.1459	1.97	3.00	....
90	.1910	.1836	.1744	....	2.80	3.90	....

## 2. Activity coefficients at infinite dilution and at concentrations used

Alc. wt. %	$\gamma_{0.02 m}$ calcd.	$\gamma_{0.02 m}$ obs.	$\gamma_{0.05 m}$ standard	$\gamma_{0.20 m}$ calcd.	$\gamma_{0.20 m}$ obs.	$\gamma_{0.50 m}$ calcd.	$\gamma_{0.50 m}$ obs.
0	0.871	0.871	0.818	0.727	0.727	0.673	0.673
10	.852	.852	.795	.693	.699	.624	.643
20	.828	.827	.763	.651	.664	.579	.606
30	.802	.804	.732	.618	.630	.547	.571
40	.771	.773	.696	.578	.591	.509	.532
50	.735	.735	.655	.535	.545	.469	.488
60	.685	.678	.599	.477	.486	.414	.430
70	.639	.645	.552	.439	.443	.383	.388
80	.567	.563	.479	.372	.362	.322	.318
90	.485	.493	.401	.317	.298	..	..

## 3. E. m. f. measurements by Harned for pure aqueous solutions

NaCl <i>m</i>	<i>E</i> obs.	<i>E</i> calcd.	$\gamma_{obs.}$	$\gamma_{calcd.}$
0.02	....	-0.07660	0.871	0.871
.05	....	-.03270	.818	.818
.10	0.00000	.00000 <sup>a</sup>	.773	.773
.20	.03247	.03242	.727	.727
.50	.07566	.07560	.673	.673
1.00	.10957	.10957 <sup>a</sup>	.652	.652
1.50	.13033	.13063	.651	.655
2.00	.14621	.14640	.666	.668
2.50	.15923	.15930	.686	.687
3.00	.17037	.17044 <sup>a</sup>	.711	.711

<sup>a</sup> These measurements used for the calculation of the empirical constants.

tration at varying temperature were interpolated for 25°. Then the curve obtained was used for interpolation to the alcohol concentration desired. The vapor pressure for pure methyl alcohol at 25° was taken from the measurements of Foote and Dixon.<sup>7</sup> The decrease in vapor pressure on addition of the electrolytes used was calculated from Raoult's law assum

TABLE III

## ELECTROMOTIVE FORCE MEASUREMENTS AND ACTIVITY COEFFICIENTS FOR LITHIUM CHLORIDE IN WATER-METHYL ALCOHOL SOLUTIONS

1. E. m. f. measurements and empirical constants derived from them. The e. m. f. values refer to the cell: Ag/AgCl/LiCl (*m*) in pure water/Li<sub>2</sub>Hg/LiCl (*m*) in water-alcohol/AgCl/Ag.

Alc. wt., %	<i>E</i> 0.02 <i>m</i>	<i>E</i> 0.05 <i>m</i>	<i>E</i> 0.10 <i>m</i>	<i>E</i> 0.50 <i>m</i>	<i>E</i> 1.00 <i>m</i>	<i>u</i>	<i>A</i>	<i>B</i>
0	0.00000	0.00000	0.00000	0.00000	0.00000	0.357	0.808	0.0611
10	.01280	.01188	.01158	.01085	.01091	.411	.700	.077
20	.02578	.02386	.02322	.02148	.02190	.476	.700	.086
30	.03876	.03603	.03507	.03240	.03300	.551	.730	.100
40	.05208	.04848	.04708	.04326	.04424	.640	.800	.100
50	.06575	.06180	.05965	.05530	.05595	.748	.890	.104
60	.08082	.07584	.07301	.06640	.06828	.887	.950	.115
70	.09730	.09107	.08715	.08005	.08134	1.07	1.05	.111
80	.1150	.1095	.1029	.09404	.09552	1.33	1.20	.090
90	.1371	.1276	.1204	.1087	.1109	1.80	1.60	.080

## 2. Activity coefficients at infinite dilution and at concentrations used

Alc. wt., %	$\gamma_{0.02 m}$		$\gamma_{0.05 m}$		$\gamma_{0.10 m}$	$\gamma_{0.50 m}$		$\gamma_{1.00 m}$	
	calcd.	obs.	calcd.	obs.	stand.	calcd.	obs.	calcd.	obs.
0	0.873	0.873	0.824	0.824	0.785	0.731	0.731	0.770	0.762
10	.853	.854	.798	.792	.750	.684	.689	.728	.727
20	.832	.836	.768	.760	.716	.640	.645	.682	.684
30	.809	.815	.738	.730	.683	.605	.603	.656	.643
40	.783	.790	.705	.695	.645	.555	.557	.596	.599
50	.753	.757	.670	.661	.605	.511	.516	.550	.552
60	.717	.709	.625	.616	.555	.457	.454	.495	.496
70	.672	.674	.572	.563	.497	.388	.403	.410	.435
80	.615	.602	.506	.510	.427	.306	.334	.304	.363
90	.538	.542	.427	.426	.352	.244	.261	.240	.287

## 3. E. m. f. measurements by Harned for pure aqueous solutions

LiCl <i>m</i>	<i>E</i> obs.	<i>E</i> calcd.	$\gamma_{obs.}$	$\gamma_{calcd.}$
0.02	...	-0.07725	0.873	0.873
.05	...	-.03313	.824	.824
.10	0.00000	.00000 <sup>a</sup>	.785	.785
.50	.07900	.07900 <sup>a</sup>	.731	.731
1.00	.1168	.11733	.762	.770
2.00	.1624	.16292	.926	.936
3.00	.1958	.19580 <sup>a</sup>	1.183	1.183

<sup>a</sup> These measurements used for the calculation of the empirical constants.

complete dissociation. The correction of this decrease with the activity function is entirely negligible. The interpolated vapor pressures of water-methyl alcohol mixtures at 25° and their values at various concentrations of the electrolyte added are given in Table V.

A graphical representation of the results obtained for lithium chloride solutions is shown in Fig. 2. This figure gives also a good conception of the corresponding curves for potassium and sodium chloride and hydrochloric acid, because the distribution of these curves with varying alcohol



TABLE IV

## ELECTROMOTIVE FORCE MEASUREMENTS AND ACTIVITY COEFFICIENTS FOR HYDROCHLORIC ACID IN WATER-METHYL ALCOHOL SOLUTIONS

1. E. m. f. measurements and empirical constants derived from them. The measurements were carried out for the cell:  $H_2/HCl(m)$ , alc.-wat./AgCl/Ag.

Alc. wt. %	$E$ 0.02 $m$	$E$ 0.05 $m$	$E$ 0.50 $m$	$u^b$	$A$	$B$
0	0.4292 <sup>a</sup>	0.3849 <sup>a</sup>	0.2712 <sup>a</sup>	0.357	0.984	0.0604
10	...	...	...	.382	..	..
20	.4191	.3753	.2621	.420	.99	.076
30	.4135	.3700	.2578	.465	.99	.085
40	.4075	.3644	.2534	.517	1.00	.094
50	.4005	.3579	.2483	.582	1.00	.103
60	.3915	.3496	.2417	.662	1.00	.112
70	.3806	.3395	.2337	.760	0.98	.120
80	.3637	.3237	.2206	.887	0.95	.128
90	.3292	.2902	.1910	1.050	1.10	.097

<sup>a</sup> These e. m. f. values calculated from the measurements of Scatchard. <sup>b</sup> The theoretical  $u$ -values used. All e. m. f. values corrected to 760 mm. partial hydrogen pressure.

## 2. Activity coefficients at infinite dilution and at concentrations used

Alc. wt. %	$\gamma$ 0.02 $m$ calcd.	$\gamma$ 0.02 $m$ obs.	$\gamma$ 0.05 $m$ standard	$\gamma$ 0.50 $m$ calcd.	$\gamma$ 0.50 $m$ obs.
0	0.877	0.877	0.831	0.759	0.759
10	..	..	..	..	..
20	.857	.860	.806	.733	.730
30	.843	.846	.786	.710	.698
40	.828	.831	.768	.685	.666
50	.808	.811	.742	.649	.627
60	.784	.788	.711	.604	.581
70	.755	.758	.674	.545	.529
80	.718	.719	.627	.471	.466
90	.679	.679	.580	.395	.400

## 3. E. m. f. measurements by Scatchard for pure aqueous solutions

HCl $m$	$E$ obs.	$\gamma$ calcd.	$\gamma$ obs.
0.01002	0.46376 <sup>a</sup>	0.905	0.905
.05005	.38568	.831	.828
.09834	.35316	.797	.794
.2030	.31774 <sup>a</sup>	.767	.767
.3063	.29332	.757	.754
.3981	.28407	.756	.753
.5009	.27197	.759	.757
.6367	.25902	.769	.767
1.0008	.23290	.812	.810
1.5346	.20534 <sup>a</sup>	.903	.903

<sup>a</sup> These measurements used for the calculation of the empirical constants.

concentration is very similar for the four electrolytes mentioned. Figure 3 gives an idea of the variation in distribution of the activity coefficient curves for potassium and sodium chlorides and hydrochloric acid at various alco-

TABLE V

TOTAL NUMBER  $N$  OF MOLES OF WATER AND METHYL ALCOHOL IN 1000 G. OF THE WATER-ALCOHOL MIXTURES, VAPOR PRESSURES IN MM. OF MERCURY AT 25° OF THE PURE MIXTURES AND WITH SUCCESSIVELY 1, 2, 3 AND 4 MOLES OF A UNI-UNIVALENT ELECTROLYTE ADDED. PRESSURE,  $p$ , MM.

Alc. wt. %	$N$	Concentration of electrolyte added				
		0 $m$ , $p$	1 $m$ , $p$	2 $m$ , $p$	3 $m$ , $p$	4 $m$ , $p$
0	55.55	23.7	22.9	22.1	21.2	20.3
10	53.06	32.7	31.5	30.2	29.0	27.8
20	50.64	41.6	39.9	38.3	36.7	35.0
30	48.21	50.6	48.5	46.4	44.3	42.2
40	45.78	59.5	56.9	54.3	51.7	49.1
50	43.42	68.6	65.4	62.3	59.1	56.0
60	40.92	76.8	73.0	69.3	65.5	61.8
70	38.49	86.5	82.0	77.5	73.0	68.5
80	35.95	97.6	92.2	86.7	81.3	75.9
90	33.62	111.5	104.9	98.2	91.6	85.0
100	31.19	126.1	118.0	109.9	101.8	93.7

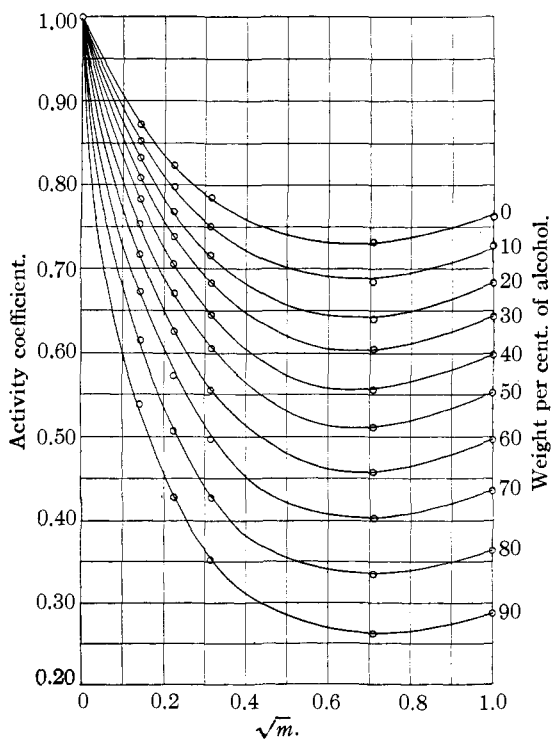


Fig. 2.—Curves for the activity coefficient of lithium chloride in water-methyl alcohol mixtures. The top curve is the one for pure water; then follow in order those for 10, 20... etc., weight per cent. of alcohol.

hol concentrations in relation to each other. The figure shows that the order of distribution of the curves for the different electrolytes remains unchanged although their dispersion with increasing alcohol concentration changes by a very large amount. In this connection might be mentioned

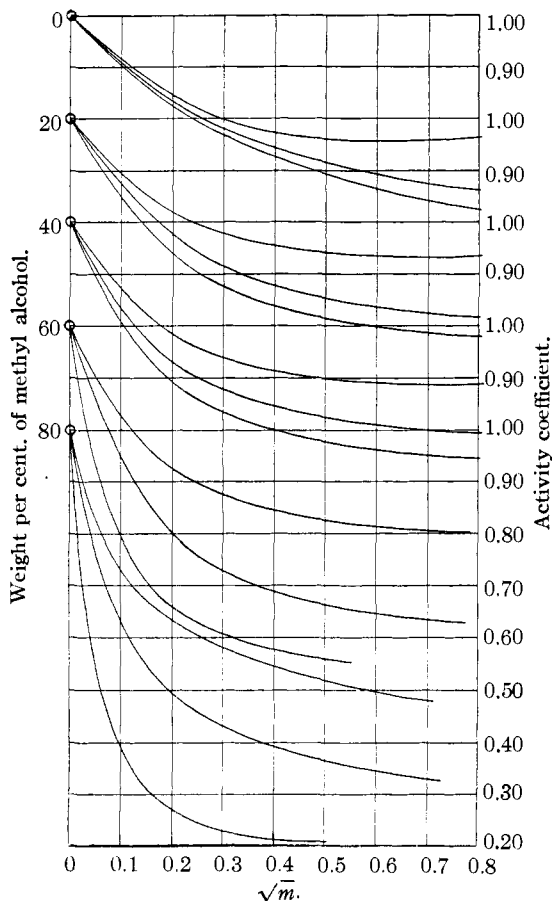


Fig. 3.—Distribution of the activity coefficient curves for potassium, sodium and hydrogen chloride in water-methyl alcohol mixtures. For each set of three curves the top one is always for hydrochloric acid, the middle one for sodium chloride. The scale is successively moved down in such a way that for a given water-alcohol mixture the circle corresponds to unity.

the result of a number of measurements of the activity coefficient of hydrochloric acid in acid-sodium chloride solutions at varying constant total molality and at varying alcohol concentration. The curves for the logarithm of the activity coefficient as plotted against the acid concentration

are straight lines and their slope is a constant independent of the total molality and alcohol concentration. In other words, strong electrolytes in alcohol solutions seem to show also in this respect the same general behavior, that has been demonstrated to be valid for water by Harned and Åkerlöf,<sup>2a</sup> Harned and Harris<sup>8</sup> and others.

Figure 4 gives the curves for the logarithm of the activity coefficients at infinite dilution in relation to unity for pure water as plotted against the inverse values of the dielectric constants of the pure water-methyl alcohol

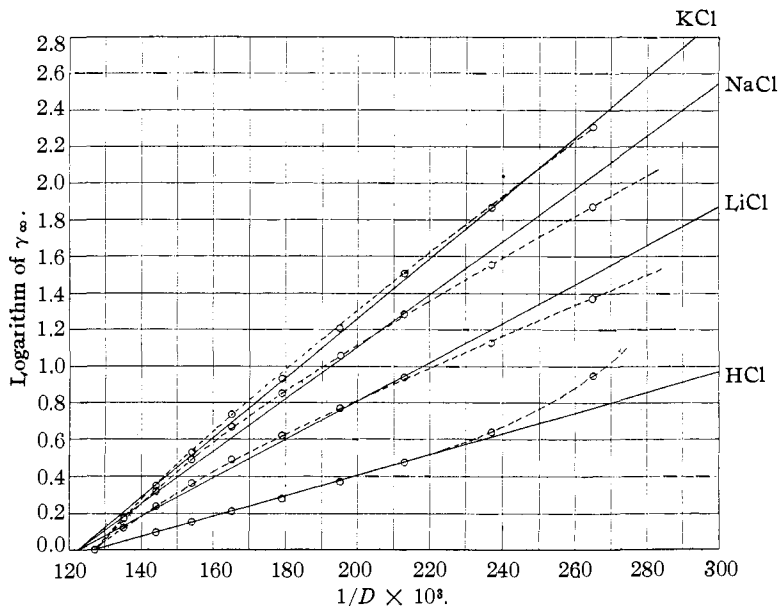


Fig. 4.—Curves for the logarithm of the activity coefficients of potassium, sodium, lithium and hydrogen chlorides at infinite dilution in water-methyl alcohol mixtures as plotted against the inverse values of the dielectric constants of these same mixtures. The dotted lines correspond to even curves through as many experimental points as possible.

mixtures. The values for the dielectric constants were obtained from the measurements of Drude.<sup>9</sup> Since he found a linear variation of these constants with the alcohol concentration in weight per cent. and the temperature coefficient is not particularly well known, the pure water value was interpolated to 25°, the one for the pure alcohol taken as given by Drude for 19° and then interpolation was carried out linearly. A summary of all values used for Fig. 4 is given in Table VI. The values for log  $\gamma_\infty$  given in this table were calculated from the measurements for 0.02 molal solutions

<sup>8</sup> Harned and Harris, *THIS JOURNAL*, 50, 2633 (1928).

<sup>9</sup> Drude, *Z. physik. Chem.*, 23, 267 (1897); compare also "International Critical Tables," 1929, Vol. VI, p. 100.

in the following manner. The electromotive force values for the concentration mentioned gave first the ratios between the activity coefficients in pure water and the water-methyl alcohol mixtures, the last two values both related to unity at infinite dilution. Multiplication of the ratio obtained with the activity coefficient for 0.02 molal solutions in pure water and division with the corresponding value in water-alcohol gave for the alcohol mixture the desired value at infinite dilution.

TABLE VI

MOLE FRACTION OF METHYL ALCOHOL  $n$ , DIELECTRIC CONSTANTS  $D$ , THEIR INVERSE VALUES  $1/D$  FOR THE PURE WATER-ALCOHOL MIXTURES, ACTIVITY COEFFICIENTS OF POTASSIUM, SODIUM AND LITHIUM CHLORIDES AND HYDROCHLORIC ACID AT INFINITE DILUTION IN THE SAME WATER-ALCOHOL MIXTURES IN RELATION TO THE CORRESPONDING WATER VALUE ASSUMED TO BE UNITY

Alc. wt., %	$n$	$D$	$1/D$	KCl $\log \gamma_{\infty}$	NaCl $\log \gamma_{\infty}$	LiCl $\log \gamma_{\infty}$	HCl $\log \gamma_{\infty}$
0	0.0000	78.8	0.0127	0.000	0.000	0.000	0.000
10	.0588	74.2	.0135	.171	.160	.118	..
20	.1232	69.7	.0144	.345	.324	.239	.095
30	.1941	65.1	.0154	.528	.492	.361	.150
40	.2725	60.6	.0165	.733	.667	.487	.208
50	.3608	56.0	.0179	.931	.853	.620	.278
60	.4574	51.4	.0195	1.204	1.059	.769	.367
70	.5673	46.9	.0213	1.504	1.282	.936	.476
80	.6941	42.3	.0237	1.866	1.557	1.124	.640
90	.8350	37.8	.0265	2.307	1.870	1.369	.956
100	1.0000	33.2	.0301	...	...	..	..

### Discussion

The purpose of the present investigation was primarily to obtain the curves for the activity coefficient of the electrolytes used at infinite dilution as a function of the composition and dielectric properties of the solvent. To gain this result it was considered as fully justified to employ the simplest methods possible, although those selected appear to have a large theoretical disadvantage. The Debye-Hückel theory gives as a limiting function for the logarithm of the activity coefficient of a strong electrolyte in very dilute solutions:  $\log \gamma = -u \sqrt{2m}$ . In the case of aqueous solutions it has generally been possible to use the theoretical value for the constant  $u$ . The instances in which a very small or even negative distance of ionic approach was obtained may be due to neglect of the higher terms. Actually Gronwall, LaMer and Sandved showed for the measurements of Bray<sup>10</sup> with zinc sulfate solutions that a positive, constant and reasonable limiting distance could be calculated from their extended theory.

In the case of the measurements presented in this paper for potassium and sodium chloride solutions, it proved to be impossible to use the theoretical  $u$ -values of the limiting function. The equation of Gronwall, La-

<sup>10</sup> Bray, THIS JOURNAL, 49, 2372 (1927).

Mer and Sandved, which should be applied only to electrolytes having anions and cations of equal valence has the following form:

$$\ln \gamma = -\frac{\epsilon^2 \cdot z^2 \cdot X}{2 \cdot k \cdot T \cdot Da(1 + X)} + \sum_{m=1}^{\infty} \left( \frac{\epsilon^2 \cdot z^2}{k \cdot T \cdot D \cdot a} \right)^{2m+1} \cdot \left[ \frac{1}{2} X_{2m-1}(x) - 2m Y_{2m-1}(x) \right]$$

where  $a$  is the ionic diameter, assumed to be the same for both positive and negative ions,  $X$  and  $Y$  are very complicated functions of  $x = Ha$ , where

$$H = \sqrt{\frac{8\pi \cdot N \cdot \epsilon^2 \cdot z^2 \cdot C}{1000 \cdot k \cdot T \cdot D}}$$

This equation might have given positive and constant ionic distances, but aside from the large difficulties for practical use, widely varying values

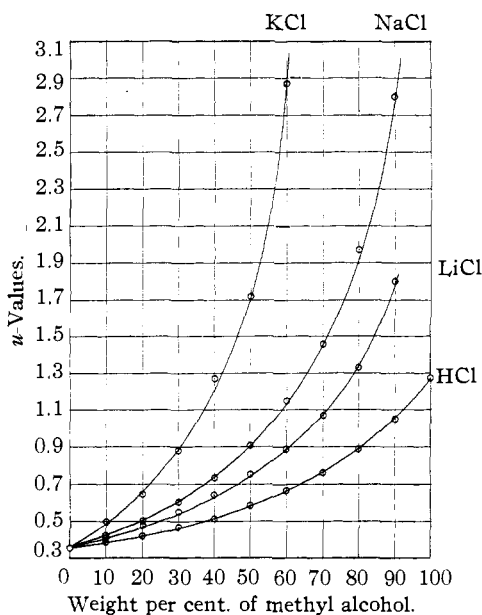


Fig. 5.—Curves for the  $u$ -values used for potassium, sodium, lithium and hydrogen chlorides in water-methyl alcohol solutions. The theoretical curve is identical with the one for hydrochloric acid.

for the different electrolytes used and, further, as  $\log \gamma$  as a first approximation is inversely proportional to the dielectric constant of the medium, the concentration range over which this formula may be regarded as valid decreases rapidly with increasing alcohol concentration. Therefore, it seemed to be far simpler to use  $u$  as a variable even though this procedure brings in an apparent theoretical disadvantage. On account of the very large differences between theoretical and calculated  $u$ -values for potassium chloride solutions, the results for sodium and lithium chloride were treated in a manner similar to that for the first mentioned electrolyte. A graphical picture of the change of the  $u$ -values for the different electrolytes is shown in Fig. 5. The curve for the potassium chloride solutions deviates with increasing alcohol concentration very much from the theoretical one. Those for sodium and lithium chloride come considerably nearer the one for hydrochloric acid, which is the same as the curve given by the theory. The activity coefficients calculated in the manner described above from the empirical constants obtained agree in most cases very well with the observed values. The  $A$ - and  $B$ -values do not always give smooth curves but this should not be taken too seriously

would have been obtained for the different electrolytes used and, further, as  $\log \gamma$  as a first approximation is inversely proportional to the dielectric constant of the medium, the concentration range over which this formula may be regarded as valid decreases rapidly with increasing alcohol concentration. Therefore, it seemed to be far simpler to use  $u$  as a variable even though this procedure brings in an apparent theoretical disadvantage. On account of the very large differences between theoretical and calculated  $u$ -values for potassium chloride solutions, the results for sodium and lithium chloride were treated in a manner similar to that for the first mentioned electrolyte. A graphical picture of the change of the  $u$ -values for the

on account of the disturbing influence of small experimental errors in the electromotive force measurements.

According to Debye and Hückel, in very dilute solutions the potential of one ion with respect to another of opposite sign is approximately inversely proportional to the dielectric constant of the medium and the distance between the ions. If we in our case assume that in very dilute solutions the distance two ions may approach reaches a limiting value independent of the properties of the solvent, then the logarithm of the activity coefficient of the electrolytes employed would at infinite dilution give a constant ratio with the dielectric constant of the medium. The dotted

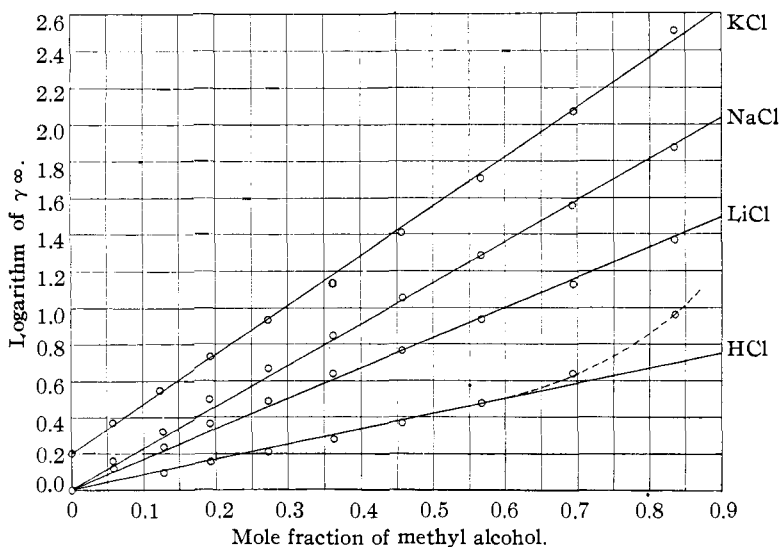


Fig. 6.—Curves for the logarithm of the activity coefficients of potassium, sodium, lithium and hydrogen chlorides at infinite dilution in water-methyl alcohol mixtures as plotted against the mole fraction of alcohol.

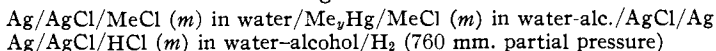
lines in Fig. 4 give the experimental curves for  $\log \gamma_{\infty}$  when plotted against  $1/D$ . Considering the uncertainty of both the electromotive force and dielectric constant measurements as they were obtained from a single series of experiments, the deviations of the dotted lines from linearity may be regarded as fairly small at alcohol concentrations up to 80%. Above this concentration, especially, hydrochloric acid begins to show large deviations and for pure alcohol the measurements of Nonhebel and Hartley give a point that is very far above the one indicated by the extended straight line for lower alcohol concentrations. In Fig. 6  $\log \gamma_{\infty}$  is plotted against the mole fraction of the alcohol. In this case it seems to be possible that the deviations from straight lines may be attributed to experimental errors except for hydrochloric acid at high alcohol concentrations. From the

known activities of potassium and sodium chloride as extrapolated from the measurements of Harned for the saturated solutions of these salts in pure water, their solubilities in pure methyl alcohol give the corresponding activity coefficients in this solvent, because the activity of the solid salt is constant. The values thus obtained give, when extrapolated to zero salt concentration, coefficients which agree quite well with those predicted through extension of the straight lines in Fig. 6 to pure alcohol solutions. The solubility of lithium chloride in pure water is far too high to give a reasonably safe value for the activity at the saturation point and consequently also for the activity coefficient at infinite dilution in pure methyl alcohol, but at least the order of distribution of this point in relation to the lithium chloride curve for the water-alcohol mixtures is the expected one. The reason for the deviation of the curve for hydrochloric acid from linearity is difficult to trace. At present it seems to be somewhat improbable that the hydrogen- or silver-silver chloride electrodes could be in error. Scatchard,<sup>11</sup> who previously noted this behavior of hydrochloric acid, did not succeed in giving a plausible explanation.

Aside from the deviations for hydrochloric acid at high alcohol concentrations, which may be due to purely chemical causes, we thus find the theory of the inverse proportionality of the dielectric constant to the logarithm of the activity coefficient at infinite dilution to be fairly well supported by the experimental evidence. There are two questions that should be considered in relation to this result. Is the value for  $\log \gamma_{\infty}$  at constant dielectric constant independent of the solvent mixture used and further will the slope of the activity coefficient curves under the same conditions be the same in all cases? Measurements to be found in the literature that might be used for a study of these two points seem to be rather unreliable or in a given case too few and it has not been possible to deduce any definite safe information from them.

### Summary

The thermodynamic properties of potassium, sodium and lithium chlorides and hydrochloric acid in water-methyl alcohol mixtures have been measured at 25° with the following cells



From these measurements were calculated the activity coefficients at the concentrations used, which in turn gave the values at infinite dilution in relation to the corresponding pure water value assumed to be unity.

The connection between the infinity values for the activity coefficients and the composition and dielectric properties of the water-methyl alcohol mixtures has been briefly discussed.

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<sup>11</sup> Scatchard, *THIS JOURNAL*, **47**, 2098 (1925); **49**, 217 (1927).