[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF YALE UNIVERSITY]

The Variation of the Activity Coefficient of Hydrochloric Acid in Hydrochloric Acid–Sodium Chloride Solutions of Constant Total Ionic Strength from 0 to 50° and the Solubility of Sodium Chloride in Hydrochloric Acid Solutions at 25° with Methyl Alcohol–Water Mixtures as Solvent

BY GÖSTA ÅKERLÖF, JOHN W. TEARE AND HARLOW TURCK

Introduction

To study the applicability of the general solubility equation previously suggested by one of us for heterogeneous equilibria of strong electrolytes, in the case of systems containing solvents other than water it is necessary to have not only the solubility data themselves but also a knowledge of the variation of the logarithm of the activity coefficient of the electrolyte present as a solid phase in solution with the co-solute at constant total ionic strength and the curve for the activity coefficient of a reference electrolyte in the particular solvent used. The literature does not give a single case where any one of these three requirements is filled either with respect to the accuracy needed or for a sufficiently long concentration range.

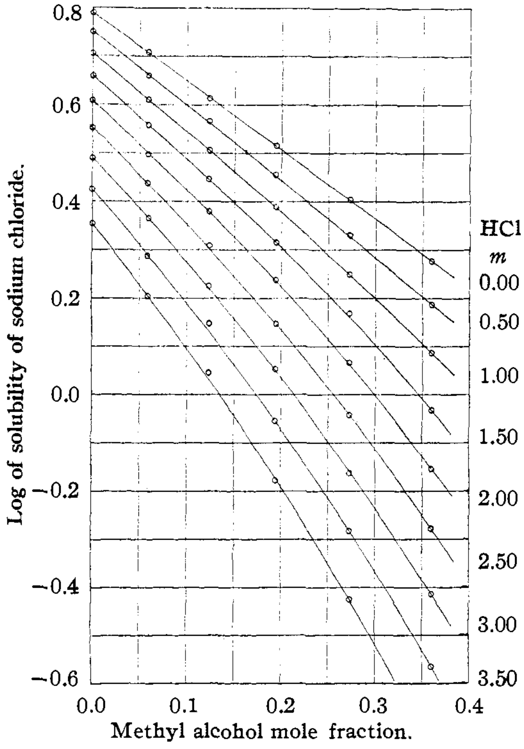

Fig. 1.—Curves for the solubility of sodium chloride at 25° in hydrochloric acid solutions with methyl alcohol–water mixtures as solvent.

The solubility determinations do not, in most cases, represent any particular difficulties. The second point, however, is as a rule very arduous or impossible to approach directly. Therefore, in the present case, the inverse problem has been studied, that of the variation of the activity coefficient of hydrochloric acid in sodium chloride solutions at constant total ionic strength. The data obtained have a relatively very high accuracy and they seem to give the very remarkable result that, at least in the case treated, at constant total ionic strength the slope of the straight lines obtained as curves for the variation of the logarithm of the activity coefficient of a strong electrolyte as plotted against its concentration, is independent of the composition of the solvent. The identical result had previously been obtained by Åkerlöf[1] although at that time the number of measurements carried out was considered insufficient to stress a definite conclusion.

The experimental procedure followed to obtain our results agreed in all essential details with the methods previously described[2] both in the case of the electromotive force and the solubility measurements and a description may therefore be omitted. Our electromotive force data and those of Harned and Thomas for 1 molal pure acid solutions with 10 and 20 weight per cent. methyl alcohol–water mixtures as solvent agree to a few hundredths of a millivolt.

Experimental Data

The electromotive force data obtained for the cell: Pt/H$_2$/HCl m, NaCl $1 - m$, CH$_3$OH X w.%/AgCl/Ag corrected to one atmosphere hydrogen pressure are summarized in Table I. Values given are the averages of duplicate or triplicate measurements all having an agreement better than two-tenths of a millivolt. The vapor pressures of the solutions employed are presented in Table II. These data were interpolated from

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(1) Åkerlöf, THIS JOURNAL, **52**, 2353 (1930).

(2) Åkerlöf and Teare, *ibid.*, **59**, 1855 (1937); Harned and Thomas, *ibid.*, **57**, 1666 (1935); Åkerlöf and Thomas, *ibid.*, **56**, 593 (1934); Åkerlöf and Turck, *ibid.*, **56**, 1875 (1934).

TABLE I

CORRECTED ELECTROMOTIVE FORCE IN VOLTS OF THE CELL

$Pt/H_2/HCl\ m,\ NaCl\ 1 - m,\ CH_3OH\ X$ w. %/AgCl/Ag

X	HCl, *m*	0°	10°	20°	30°	40°	50°
0	1.00	0.24456	0.24052	0.23599	0.23105	0.22550	0.21939
	0.80	.25076	.24680	.24244	.23758	.23216	.22615
	.60	.25847	.25477	.25050	.24593	.24066	.23476
	.40	.26902	.26549	.26162	.25724	.25222	.24668
	.20	.28618	.28330	.27994	.27599	.27147	.26653
	.10	.30298	.30060	.29785	.29448	.29065	.28605
10	1.00	.23763	.23440	.23031	.22570	.22066	.21502
	0.80	.24379	.24076	.23685	.23220	.22722	.22174
	.60	.25149	.24858	.24475	.24044	.23563	.23027
	.40	.26209	.25940	.25589	.25188	.24738	.24229
	.20	.27941	.27723	.27421	.27074	.26678	.26216
	.10	.29618	.29459	.29218	.28924	.28582	.28176
20	1.00	.23242	.22962	.22602	.22164	.21674	.21107
	0.80	.23866	.23597	.23247	.22814	.22335	.21765
	.60	.24639	.24387	.24055	.23647	.23184	.22639
	.40	.25677	.25457	.25155	.24771	.24335	.23820
	.20	.27412	.27245	.27000	.26673	.26290	.25831
	.10	.29099	.28991	.28796	.28524	.28196	.27779
30	1.00	.22916	.22617	.22244	.21807	.21295	.20716
	0.80	.23539	.23253	.22894	.22470	.21973	.21404
	.60	.24301	.24035	.23686	.23279	.22800	.22251
	.40	.25345	.25105	.24790	.24409	.23959	.23435
	.20	.27102	.26913	.26649	.26321	.25904	.25440
	.10	.28787	.28648	.28440	.28167	.27825	.27396
40	1.00	.22743	.22375	.21939	.21439	.20873	.20251
	0.80	.23359	.23001	.22586	.22090	.21544	.20929
	.60	.24135	.23791	.23396	.22919	.22389	.21797
	.40	.25193	.24884	.24513	.24062	.23557	.22963
	.20	.26903	.26651	.26330	.25933	.25483	.24961
	.10	.28596	.28401	.28132	.27792	.27390	.26922
50	1.00	.22535	.22085	.21572	.20992	.20368	.19666
	0.80	.23167	.22725	.22225	.21656	.21048	.20358
	.60	.23934	.23509	.23019	.22468	.21876	.21207
	.40	.24992	.24593	.24127	.23605	.23033	.22381
	.20	.26719	.26376	.25966	.25495	.24973	.24372
	.10	.28402	.28134	.27775	.27356	.26884	.26334
60	1.00	.22146	.21594	.20987	.20320	.19614	.18840
	0.80	.22765	.22226	.21628	.20975	.20286	.19523
	.60	.23544	.23021	.22433	.21789	.21112	.20356
	.40	.24590	.24089	.23527	.22912	.22279	.21553
	.20	.26330	.25882	.25358	.24809	.24191	.23523
	.10	.28014	.27615	.27163	.26657	.26108	.25496

TABLE II

VAPOR PRESSURES OF METHYL ALCOHOL–WATER MIXTURES WITH AN IONIC STRENGTH OF UNITY AS CORRECTED USING RAOULT'S LAW

CH_3OH, w. %	0°	10°	20°	30°	40°	50°
0	4.5	9.1	17.2	31.3	54.4	91.0
10	7.9	15.0	26.8	46.8	78.6	130
20	10.7	19.2	34.0	58.7	98.0	158
30	13.2	23.4	41.0	70.2	117	188
40	15.2	27.2	47.5	81.2	134	216
50	17.1	30.7	53.1	90.9	151	242
60	19.2	34.2	59.5	101	167	268
70	21.9	38.4	66.4	112	184	290

a compilation of all measurements found cited in "International Critical Tables," "Landolt–Börnstein" and "Tables Annuelles." The lowering of the vapor pressure due to the presence of the two electrolytes was computed using Raoult's law and an activity coefficient of 0.7 for the solutes. The solubility data are given in Table III and shown graphically in Fig. 1. All concentrations of the solutes are expressed as ionic strength per 1000 g. of the total solvent mixture.

TABLE III

SOLUBILITY OF SODIUM CHLORIDE AT 25° IN HYDROCHLORIC ACID SOLUTIONS WITH METHYL ALCOHOL-WATER MIXTURES AS SOLVENT

Alcohol, w. %	0	10	20	30	40	50
Mole fraction	0.0000	0.0588	0.1233	0.1941	0.2727	0.3600
HCl, *m*	Molality of sodium chloride					
0.00	6.162	5.104	4.133	3.282	2.543	1.892
.10	6.058	4.983	4.039	3.221	2.474	1.811
.20	5.951	4.866	3.959	3.112	2.383	1.727
.30	5.846	4.767	3.856	3.032	2.295	1.666
.50	5.631	4.574	3.702	2.858	2.144	1.535
.75	5.361	4.325	3.435	2.645	1.957	1.376
1.00	5.096	4.082	3.213	2.454	1.780	1.222
1.50	4.567	3.616	2.800	2.070	1.477	0.9267
2.00	4.054	3.146	2.397	1.730	1.165	.7005
2.50	3.569	2.741	2.041	1.404	0.9079	.5266
3.00	3.100	2.318	1.683	1.129	.6878	.3850
3.50	2.660	1.936	1.406	0.8801	.5208	.2716
4.00	2.261	1.605	1.112	0.6639	.3757	.1902

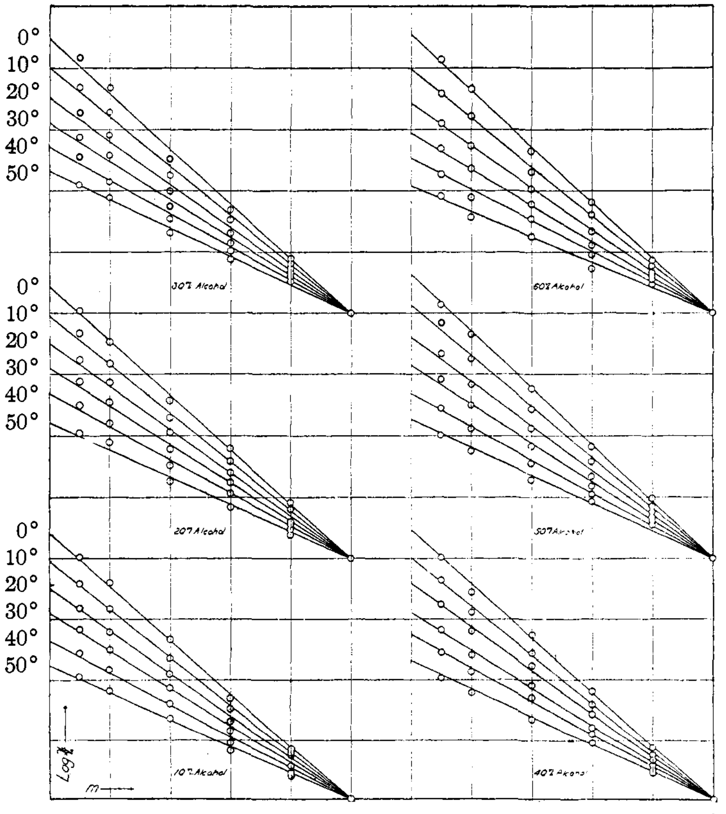

Fig. 2.—The variation of the logarithm of the activity coefficient of hydrochloric acid in HCl-NaCl solutions of constant total ionic strength of unity from 0 to 50° and with methyl alcohol-water mixtures as solvent.

Results Obtained from the Electromotive Force Data

In the case of the cell employed the ratio of the activity coefficients of hydrochloric acid at two different concentrations may be calculated according to the equation

$$\log (\gamma_2/\gamma_1) = (E_1 - E_2)/2k - \log (m_2/m_1)^{1/2} \quad (1)$$

where E_1 and E_2 denote the measured electromotive force values, m_1 and m_2 the corresponding acid concentrations and γ_1 and γ_2 the activity coefficients of the acid. For values of k see Part I of Table V in the preceding paper by Åkerlöf and Teare. Using as reference points the data for the pure acid solutions the values computed for $\log (\gamma_1 / \gamma_2)$ fall, when plotted against the acid concentration, on what appears to be straight lines as shown in Fig. 2 for every one of the different alcohol-water mixtures employed. The diameter of the points in Fig. 2 is equivalent to an error of 0.1 millivolt in the electromotive force readings.

The most remarkable property of the family of lines given in Fig. 2 seems, as indicated above, to be that at corresponding temperatures their slopes are constant and independent of the alcohol concentration. Since this result in the future may be found to be of considerable importance, a careful study of the precision of the experimental data is in place. The largest error appears probably in the definition of the electromotive force of the electrodes employed. The magnitude of the resulting error in the value of the slopes of the curves in Fig. 2 depends naturally on where it occurs but as an average an increment of one-tenth of a millivolt has been found to change these slopes by about 0.0014. The errors caused by incorrect weighing of the components of the solutions, standard acid, absolute methyl alcohol, water and solid sodium chloride are relatively small and may amount to a total of about 0.0002. The temperature errors should be very small although it is quite difficult to reset a mercury thermo-regulator a large number of times exactly each time to the desired temperature. Also the errors caused by using incorrect values for the vapor pressures of the solutions in correcting the electromotive force data are probably practically negligible. As total resultant error we should therefore expect to find deviations of about ±0.0020 between observed

TABLE IV

SLOPES OF THE CURVES FOR LOG (γ_1/γ_2) AS OBTAINED BY LEAST SQUARING LINEARLY THE DATA IN TABLE I

X	0°	10°	20°	30°	40°	50°
0	−0.0434	−0.0389	−0.0358	−0.0304	−0.0265	−0.0225
10	.0452	.0396	.0350	.0317	.0278	.0233
20	.0442	.0401	.0357	.0320	.0278	.0233
30	.0460	.0408	.0362	.0318	.0274	.0248
40	.0442	.0403	.0358	.0312	.0272	.0222
50	.0455	.0417	.0361	.0316	.0264	.0215
60	.0460	.0400	.0339	.0298	.0244	.0204
Mean	− .0450	− .0402	− .0355	− .0312	− .0268	− .0226

and true values of the slopes for the lines in Fig. 2.

To find the most probable values of these slopes the values calculated for log (γ_1/γ_2) were least squared assuming a linear variation. A summary of the results is given in Table IV. The individual values obtained at a given temperature deviate in only two cases very slightly more from their mean than the error allowed of ±0.0020. However, in these two cases, the 60% alcohol values at 40 and 50°, the deviations may be caused by errors in the rather large vapor pressure corrections of the electromotive force. Therefore it may seem that we are fully justified in drawing the conclusion that within ordinary experimental errors the slopes obtained are independent of the alcohol concentration throughout the concentration and temperature range employed. Unfortunately the solubility of sodium chloride in methyl alcohol–water mixtures decreases very rapidly in the presence of hydrochloric acid and measurements at higher alcohol concentrations than slightly above 60 weight per cent. cannot be obtained at an ionic strength of unity. Lowering the ionic strength increases the probable experimental error very rapidly and combined with errors caused by very large vapor pressure corrections of the electromotive force readings the low precision obtained would make the results practically worthless. Sodium chloride might have been substituted with lithium chloride but in this case the magnitude of the slopes is comparable to that of the experimental errors due to the small differences between the activity coefficients of the acid and the salt.

Results of the Solubility Measurements

Using as reference point the solubility of sodium chloride in pure water at 25° the relative activity coefficients of this salt at the acid–salt concentrations given in Table III have been calculated. The values obtained are summarized in Table V and shown graphically in Fig. 3 as plotted against the methyl alcohol mole fraction. Figure 3 presents a very interesting result. The curves are probably all within the experimental error straight lines. Their slopes increase slowly with the acid concentration but on the whole the behavior of the salt with respect to the composition of the solvent remains practically unchanged. This being the case we should expect to be able to apply the previously mentioned general solubility equation to the data in Table III.

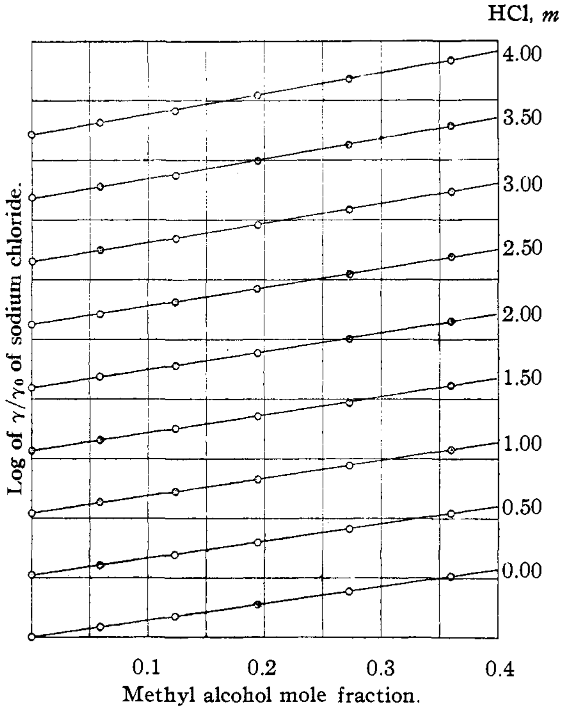

Fig. 3.—Curves for the logarithm of the relative activity coefficient of sodium chloride in hydrochloric acid solutions at 25° with methyl alcohol–water mixtures as solvent.

Summary

The variation of the logarithm of the activity coefficient of hydrochloric acid in hydrochloric

TABLE V

LOGARITHM OF THE RELATIVE ACTIVITY COEFFICIENT OF SODIUM CHLORIDE AS CALCULATED FROM THE SOLUBILITY DATA IN TABLE III

Alcohol, w. %	0	10	20	30	40	50
mole fraction	0.0000	0.0588	0.1233	0.1941	0.2727	0.3600
HCl, *m*	Log of relative activity coefficient					
0.00	0.000	0.082	0.174	0.274	0.385	0.513
.10	.004	.088	.178	.275	.388	.500
.20	.008	.094	.182	.283	.395	.529
.30	.006	.098	.188	.288	.402	.532
.50	.021	.107	.194	.299	.413	.543
.75	.032	.119	.211	.312	.428	.557
1.00	.044	.132	.224	.326	.443	.573
1.50	.069	.156	.250	.356	.468	.614
2.00	.095	.185	.279	.385	.506	.652
2.50	.122	.211	.316	.421	.545	.689
3.00	.152	.245	.342	.456	.588	.732
3.50	.183	.279	.371	.497	.629	.785
4.00	.215	.313	.413	.545	.682	.838

acid–sodium chloride solutions of constant total ionic strength equal to unity has been studied from 0 to 50° using methyl alcohol–water mixtures as solvent. In accordance with earlier measurements of Åkerlöf it was found that log γ_{HCl} varies linearly with the acid concentration and the slopes of the curves are independent of the alcohol concentration at least within the range studied. The solubility of sodium chloride at 25° in methyl alcohol–water mixtures with hydrochloric acid at various concentrations has also been measured. As in the case of the pure solvent mixtures the logarithm of the activity coefficient of sodium chloride varies in the range studied linearly with the alcohol mole fraction independent of the acid concentration.

NEW HAVEN, CONN. RECEIVED JULY 14, 1937

[CONTRIBUTION FROM THE RESEARCH BUREAU OF BROOKLYN EDISON COMPANY, INC.]

Potentiometric Titration of Acids in Mixtures of *n*-Butanol and Water

BY R. N. EVANS AND J. E. DAVENPORT

The study of the strength of acids in *n*-butanol has been carried out both potentiometrically and colorimetrically in an attempt to correlate the thermodynamic behavior of acids in aqueous and non-aqueous solvents.[1-3] It has been demonstrated clearly that the relative strengths of acids vary in a manner which bears some relation to the dielectric constant of the solvent. Further confirmation of the fact that acids become stronger or weaker when compared to a single standard acid as the nature of the solvent is varied was observed by us in connection with our determination of acids in insulating oil. Potentiometric titration of a mixture of picric and benzoic acids each in 0.00005 *M* concentration gave one point of inflection in water and in equal molarity in *n*-butanol gave two points of inflection. It has been stated frequently that two acids must differ approximately by 10^3 in acid constants in order that two points of inflection may occur in the potentiometric titration curve. Although the effect of concentration has been implied, it is not generally emphasized that the appearance of two points of inflection is a function of concentration since many acids of the weak type are almost completely dissociated in 0.00005 *M* aqueous solutions. In Table XI (reference 3) the ratio of picric acid constant to that of benzoic acid in *n*-butanol is 1.08×10^6 whereas in water the ratio is 2.5×10^3. It is apparent that the four-hundred fold increase in the ratio in *n*-butanol over that in water offsets the effect of lowered concentration.

In Fig. 1, the results of the titration of equivalent amounts of picric and benzoic acids in several water–*n*-butanol mixtures are shown graphically. The procedure and apparatus have been described elsewhere.[4] The cell used in all curves except the upper two was 0.1 *N* calomel (aqueous)/x solution/glass/x solution/0.1 *N* calomel (aqueous). One hundred ten milliliters of solution was prepared containing the indicated amount of acids and water and, after removal of carbon dioxide by bubbling purified nitrogen, 10 ml. was placed inside the glass bulb and 100 ml. in the titration beaker. Since 1 ml. of aqueous 0.005 *M* acid was used in making up the 110 ml., each acid in the titration beaker was approximately 0.000045 *M*. The two upper curves were produced employing the electrode system of reference 4—a change necessitated because of

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(1) Wynne-Jones, *Proc. Roy. Soc.* (London), **A140**, 440 (1933).

(2) Wooten and Hammett, THIS JOURNAL, **57**, 2289 (1935).

(3) Mason and Kilpatrick, *ibid.*, **59**, 572 (1937).

(4) R. N. Evans and J. E. Davenport, *Ind. Eng. Chem., Anal. Ed.*, **8**, 287 (1936).