THE ACTIVITY COEFFICIENT OF THE UNDISSOCIATED PART OF WEAK ELECTROLYTES

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In the preceding two papers it was shown that the quotient of the logarithm of the activity coefficient of gases and non-electrolytes by the ionic strength of an added salt was approximately constant. This paper will show that this law is also true for the undissociated part of a weak electrolyte, when very simple assumptions are made regarding the activity coefficient of the ions.

The effect of salts upon the activity of weak electrolytes has long been a subject of controversy. Various authors, notably Arrhenius (1) have advanced the view that the dissociation of weak acids is increased by salts. McBain and Coleman (2) have objected to this view. They concluded that there was no experimental evidence for the supposed increase in the dissociation constant of weak acids and bases in the presence of neutral salts.

McBain and Kam (3) determined the vapor pressure of acetic acid over solutions containing added salt and concluded "the undissociated acid must be regarded as exhibiting enhanced chemical potential in the presence of such salts." We have recalculated their results in table 5, which shows that the effect of salts on the undissociated part of acetic acid is approximately the same as that upon non-electrolytes.

Brönsted (4) points out that the form of the solubility curves of weak acids in salt solutions are to be explained as due to the rapid decrease in the activity coefficient of the ions at low salt concentrations and the increase in γ_u (undissociated) at high salt concentration. Rördam (5) measured the solubility of benzoic, *o*-toluylic, and *o*-nitrobenzoic acids in salt solutions. He calculated the activity coefficient of the undissociated molecules and found it to increase with the salt concentration.

The activities of the ions of sodium, and potassium acetates in pure aqueous solutions have been shown by Randall, McBain and White (6) to closely approximate the activity coefficient of the corresponding chlorides. We shall in the following make the approximate assumption that the activity coefficient of the dissociated part of any monobasic acid at small molalities, in salt solutions of varying ionic strengths is equal to the activity coefficient of hydrochloric acid in the same or similar salt solution. Further we shall assume in all solutions of sodium salts the values of Harned (7) for the activity coefficient of 0.01 *M* hydrochloric acid in solutions of sodium chloride referred to $\gamma_{\pm} = 0.795$ in 0.1 *M* pure hydrochloric acid. We shall take the activity coefficient in solutions of potassium salts as equal to that found by Harned for the activity coefficient of 0.01 *M* hydrochloric acid in a solution of potassium chloride having the same ionic strength as the solution in which our weak acid is dissolved. The activity coefficient in solutions of barium salts is taken from the work of Randall and Breckenridge (8). These assumptions are not fully justified, but their use in the absence of experiments on very dilute hydrochloric acid in the presence of these salts, does not greatly affect our calculated values for the activity coefficient of the undissociated molecules.

We shall take the dissociation constant, K, of the acid as that determined from conductivity data, corrected in case K is large, for changes in activity coefficients and ionic mobilities by the method of Sherrill and Noyes (9).

ACTIVITY COEFFICIENT OF THE UNDISSOCIATED MOLECULES FROM SOLUBILITY MEASUREMENTS

When a solution is saturated with a weak acid the activity of the acid is fixed; $a_2 = \text{constant} = m_+ m_- \gamma_{\pm}^2$, where m_+ and m_- are the molalities of the hydrogen and acid ions, and since $m_+ = m_-$, we have $m_{\pm}\gamma_{\pm}$ also constant. By dividing this constant quantity (calculated from K, $\gamma_{\pm}$, and the solubility in pure water by successive approximations) by the value of the activity coefficient of hydrochloric acid in a salt solution of ionic strength equal to that in which the solubility determination was made, we obtain the molality of hydrogen ion m_+, assuming always that $\gamma_\pm$ may be obtained by the principle of ionic strength. Subtracting m_+ from the solubility m, gives us the molality of undissociated acid m_u. To obtain the activity coefficient of the undissociated molecules of the acid, we divide the molality of the undissociated molecules in pure water, $m_u{}^\circ$, by their molality in the salt solution: $\gamma_u = m_u{}^\circ/m_u$. We then find that for a given acid in a solution of a given salt at various ionic strengths: $(\log \gamma_u)/\mu(\text{salt}) =$ approximately constant.

Calculations of $m_u{}^\circ$ *and* $m_+\gamma_\pm$ *for pure saturated solutions of weak acids in water.* Given m, the solubility in water, K, the dissociation constant, and a plot of the activity coefficient of hydrochloric acid against ionic strength in pure solution (10), we can obtain $m_u{}^\circ$ and $m_+\gamma_\pm$ by successive approximations. The molality of undissociated molecules, $m_u{}^\circ$ is equal to the solubility in water less m_+, the molality of the hydrogen ion. Setting the activity coefficient of undissociated molecules equal to unity, $m_u{}^\circ = m - m_+$, also $m_+ = m_-$. Therefore $(m_+\gamma_\pm)^2 = K\ (m - m_+)$. Solving for m_+ we introduce a new value of $\gamma_\pm$ corresponding to the ionic strength found, and repeat the calculation. Thus we obtain m_+, $m_+\gamma_\pm$, and $m_u{}^\circ$.

The data of Hoffmann and Langebeck (11) and of Rördam (5) on the solubility of benzoic, *o*-toluylic, salicylic, and *o*-nitrobenzoic acids are given in tables 1 to 4. In each table the first column gives the added salt, the second the ionic strength of the added salt, the third the molality of the dissolved weak acid, the fourth the activity coefficient of hydrochloric acid at the ionic strength of the solution, which is the sum of the third and fifth columns. The fifth column is the quotient of $m_+\gamma_\pm$, which in the saturated solution of a given acid is a constant, by $\gamma_\pm$. The sixth column is the molality of the undissociated acid or the difference between Cols. 3 and 5. The seventh column gives the activity coefficient of the undissociated part of the acids, and the last the quotient of the logarithm of the undissociated part by the ionic strength of the added salt. The ionic strength of the added salt, rather than the ionic strength of the solution, is used in obtaining this last quotient, because the salting-out effect of acids

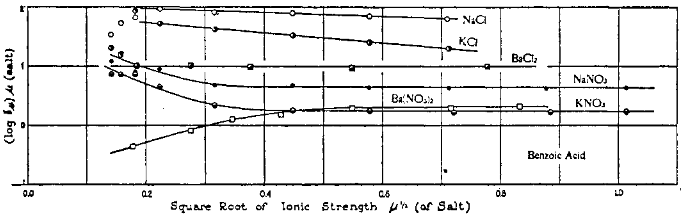

FIG. 1. ACTIVITY COEFFICIENT OF UNDISSOCIATED BENZOIC ACID

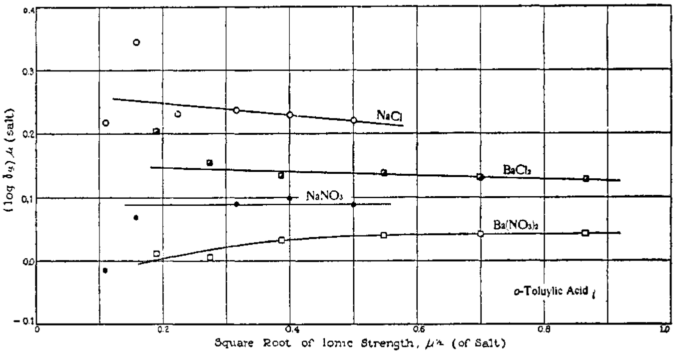

FIG. 2. ACTIVITY COEFFICIENT OF UNDISSOCIATED o-TOLUYLIC ACID

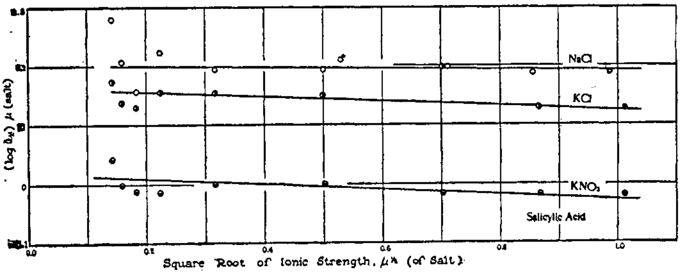

FIG. 3. ACTIVITY COEFFICIENT OF UNDISSOCIATED SALICYLIC ACID

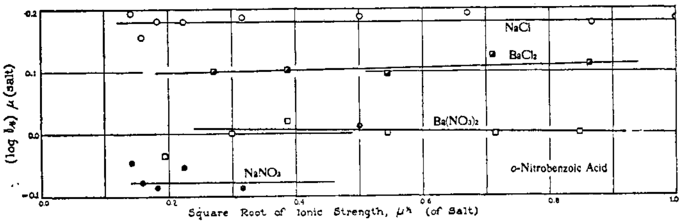

FIG. 4. ACTIVITY COEFFICIENT OF UNDISSOCIATED o-NITROBENZOIC ACID

TABLE 1

*Activity coefficient of the undissociated molecules of benzoic acid in salt solutions at 25°**

$K_{298.1} = 6.61 \times 10^{-5}$, Solubility in water = 0.02793, $m_+ \gamma_\pm = 0.001326$, $m_u{}^\circ = 0.02655$

SALT	μ	m	$\gamma_\pm$	m_+	m_u	γ_u	$\frac{\log \gamma_u}{\mu(\text{salt})}$
NaCl[11]	0.01982	0.02790	0.864	0.00153	0.02637	1.007	0.153
	0.02502	0.02783	0.862	0.00154	0.02629	1.010	0.173
	0.03320	0.02775	0.849	0.00156	0.02619	1.014	0.182
	0.05010	0.02755	0.829	0.00160	0.02595	1.023	0.197
	0.1002	0.02708	0.789	0.00168	0.02540	1.045	0.191
	0.2009	0.02607	0.755	0.00176	0.02431	1.092	0.190
	0.3356	0.02481	0.737	0.00180	0.02301	1.154	0.185
	0.5022	0.02338	0.733	0.00181	0.02157	1.231	0.180
$NaNO_3$[11]	0.02001	0.02794	0.872	0.00152	0.02642	1.005	0.108
	0.02501	0.02791	0.861	0.00154	0.02637	1.007	0.121
	0.03333	0.02794	0.849	0.00156	0.02638	1.007	0.091
	0.05012	0.02790	0.816	0.00163	0.02627	1.011	0.095
	0.1003	0.02780	0.789	0.00168	0.02612	1.016	0.069
	0.2009	0.02749	0.754	0.00176	0.02573	1.032	0.068
	0.3360	0.02707	0.737	0.00180	0.02527	1.051	0.065
	0.5072	0.02646	0.734	0.00181	0.02465	1.077	0.064
	0.7656	0.02556	0.749	0.00177	0.02379	1.116	0.062
	1.030	0.02458	0.773	0.00172	0.02286	1.161	0.063
KCl[11]	0.02004	0.02791	0.872	0.00152	0.02639	1.006	0.130
	0.02540	0.02791	0.861	0.00154	0.02637	1.007	0.119
	0.03349	0.02773	0.849	0.00156	0.02617	1.015	0.193
	0.05008	0.02767	0.816	0.00163	0.02604	1.020	0.172
	0.1001	0.02727	0.784	0.00169	0.02558	1.038	0.162
	0.2008	0.02654	0.741	0.00179	0.02475	1.073	0.152
	0.3339	0.02566	0.723	0.00183	0.02383	1.114	0.140
	0.5074	0.02466	0.716	0.00185	0.02281	1.164	0.130
KNO_3[11]	0.02002	0.02795	0.872	0.00152	0.02643	1.004	0.087
	0.02501	0.02796	0.861	0.00154	0.02642	1.005	0.087
	0.03336	0.02798	0.849	0.00156	0.02642	1.005	0.087
	0.05011	0.02800	0.816	0.00163	0.02637	1.007	0.061
	0.1003	0.02803	0.784	0.00169	0.02634	1.008	0.035
	0.2011	0.02802	0.741	0.00179	0.02623	1.012	0.026
	0.3340	0.02787	0.723	0.00183	0.02604	1.020	0.026
	0.5182	0.02768	0.716	0.00185	0.02583	1.028	0.023
	0.7812	0.02731	0.716	0.00185	0.02546	1.043	0.023
	1.030	0.02694	0.723	0.00183	0.02511	1.057	0.023

TABLE 1—*Continued*

SALT	μ	m	$\gamma_\pm$	m_+	m_u	γ_u	$\frac{\log \gamma_u}{\mu(\text{salt})}$
$BaCl_2$[5]	0.03441	0.02789	0.850	0.00156	0.02633	1.008	0.101
	0.07629	0.02775	0.795	0.00167	0.02608	1.018	0.102
	0.1425	0.02744	0.763	0.00174	0.02570	1.033	0.099
	0.2998	0.02668	0.720	0.00184	0.02484	1.069	0.097
	0.6048	0.02503	0.686	0.00193	0.02310	1.149	0.100
$Ba(NO_3)_2$[5]	0.03162	0.02817	0.853	0.00155	0.02662	0.997	−0.036
	0.07635	0.02823	0.795	0.00167	0.02659	0.998	−0.009
	0.1202	0.02821	0.761	0.00174	0.02647	1.003	0.011
	0.1827	0.02803	0.742	0.00179	0.02624	1.012	0.019
	0.3015	0.02785	0.718	0.00185	0.02600	1.021	0.030
	0.5130	0.02753	0.694	0.00191	0.02562	1.036	0.030
	0.6933	0.02712	0.682	0.00194	0.02518	1.054	0.033

[*] The citations in the tables are to the corresponding papers.

on gases and non-electrolytes was found to be small. Moreover, the contribution to the ionic strength of the weak acid is not large, and the ionic strength of the added salt is directly obtained.

The quotients in the last columns of the tables are plotted in figures 1 to 4 against the square root of the ionic strength of the added salt, again, for convenience, using this quantity rather than the square root of the ionic strength of the solution. These plots will be discussed later.

THE ACTIVITY COEFFICIENT OF THE UNDISSOCIATED MOLECULES OF ACETIC ACID IN THE PRESENCE OF SALTS FROM MEASUREMENTS OF DISTRIBUTION AND OF THE COMPOSITION OF A DISTILLATE

It seemed desirable in view of the importance of the subject to obtain evidence as to the effect of salts on the undissociated molecules of weak acids by an independent method.

Sugden (12) has measured the distribution of acetic acid between amyl alcohol and water.

If R° is the quotient of the concentration in amyl alcohol by the molality in water, and R is the corresponding ratio when the acid is dissolved, not in pure water, but in a salt solution, we shall set

$$\gamma_u = R/R^\circ \tag{1}$$

In so doing we neglect the small amount of ionization but as Sugden does not give his acid concentrations but only the distribution ratios, it is impossible to correct for dissociation.

TABLE 2

Activity coefficient of the undissociated molecules of ortho-toluylic acid in salt solutions at 25°

$K_{298.1} = 1.30 \times 10^{-4}$, Solubility in water $= 0.008783$, $m_+ \gamma_\pm = 0.001003$, $m_u^\circ = 0.007745$

SALT	μ	m	$\gamma_\pm$	m_+	m_u	γ_u	$\frac{\log \gamma_u}{\mu(\text{salt})}$
$NaCl$[5]	0.01200	0.008825	0.892	0.001124	0.007701	1.006	0.217
	0.02500	0.008756	0.863	0.001162	0.007594	1.020	0.344
	0.05000	0.008755	0.829	0.001210	0.007545	1.027	0.231
	0.1000	0.008607	0.789	0.001271	0.007336	1.056	0.237
	0.1600	0.008433	0.765	0.001311	0.007122	1.088	0.229
	0.2500	0.008172	0.746	0.001345	0.006827	1.135	0.220
$NaNO_3$[5]	0.01200	0.008872	0.892	0.001124	0.007748	0.999	−0.015
	0.02500	0.008874	0.863	0.001162	0.007712	1.004	0.069
	0.05000	0.008902	0.829	0.001210	0.007692	1.007	0.061
	0.1000	0.008860	0.789	0.001271	0.007589	1.021	0.090
	0.1600	0.008779	0.765	0.001311	0.007468	1.037	0.099
	0.2500	0.008710	0.746	0.001345	0.007365	1.052	0.088
$BaCl_2$[5]	0.03600	0.008806	0.842	0.001191	0.007615	1.017	0.203
	0.07500	0.008806	0.794	0.001263	0.007543	1.027	0.154
	0.1494	0.008730	0.752	0.001334	0.007396	1.047	0.134
	0.3000	0.008451	0.718	0.001397	0.007054	1.098	0.138
	0.4800	0.008140	0.697	0.001439	0.006701	1.156	0.131
	0.7500	0.007681	0.680	0.001475	0.006206	1.248	0.128
$Ba(NO_3)_2$[5]	0.03600	0.008926	0.842	0.001186	0.007740	1.001	0.012
	0.07500	0.008976	0.794	0.001241	0.007735	1.001	0.006
	0.1500	0.008987	0.752	0.001325	0.007662	1.011	0.032
	0.3000	0.008919	0.718	0.001382	0.007537	1.028	0.040
	0.4800	0.008791	0.697	0.001401	0.007390	1.048	0.042
	0.7500	0.008597	0.630	0.001403	0.007194	1.077	0.043

From distillation experiments, McBain and Kam (3) give a quantity which is proportional to the partial pressure of the acetic acid over its solution divided by the concentration of undissociated molecules in the solution. From these the values of the activity coefficient of the undissociated molecules are obtained directly. The values of γ_u and of (log γ_u)/μ(salt) for acetic acid in various salt solutions are given in table 5. The first column

TABLE 3

Activity coefficient of undissociated molecules of salicylic acid in salt solutions at 25°

$K_{298.1} = 1.06 \times 10^{-3}$, Solubility in water = 0.01602, $m_+ \gamma_\pm = 0.003591$, $m_u^\circ = 0.01218$

SALT	μ	m	$\gamma_\pm$	m_+	m_u	γ_u	$\frac{\log \gamma_u}{\mu(\text{salt})}$
NaCl[11]	0.02003	0.01616	0.867	0.00414	0.01202	1.013	0.280
	0.02502	0.01621	0.858	0.00418	0.01203	1.012	0.207
	0.03331	0.01629	0.845	0.00425	0.01204	1.012	0.156
	0.05000	0.01621	0.827	0.00434	0.01187	1.026	0.223
	0.0999	0.01614	0.789	0.00455	0.01159	1.051	0.216
	0.2499	0.01570	0.746	0.00481	0.01089	1.118	0.194
	0.4927	0.01463	0.733	0.00490	0.00973	1.252	0.198
	0.7325	0.01363	0.745	0.00482	0.00881	1.383	0.192
	0.9714	0.01270	0.767	0.00468	0.00802	1.519	0.187
KCl[11]	0.02002	0.01622	0.867	0.00414	0.01208	1.008	0.173
	0.02503	0.01626	0.858	0.00418	0.01208	1.008	0.138
	0.03331	0.01631	0.845	0.00425	0.01206	1.010	0.130
	0.05000	0.01631	0.827	0.00434	0.01197	1.018	0.155
	0.1000	0.01634	0.784	0.00458	0.01176	1.036	0.154
	0.2492	0.01608	0.732	0.00491	0.01117	1.090	0.150
	0.4915	0.01474	0.717	0.00500	0.00974	1.251	0.198
	0.7495	0.01470	0.716	0.00501	0.00969	1.257	0.133
	1.004	0.01399	0.724	0.00496	0.00903	1.348	0.129
KNO_3[11]	0.02003	0.01630	0.867	0.00414	0.01216	1.002	0.043
	0.02504	0.01635	0.858	0.00418	0.01217	1.000	0.000
	0.03324	0.01643	0.845	0.00424	0.01219	0.999	−0.011
	0.05000	0.01654	0.827	0.00434	0.01220	0.998	−0.014
	0.1004	0.01674	0.784	0.00458	0.01216	1.002	0.009
	0.2529	0.01710	0.728	0.00493	0.01217	1.000	0.000
	0.5052	0.01740	0.717	0.00501	0.01239	0.983	−0.015
	0.7528	0.01755	0.716	0.00501	0.01254	0.971	−0.017
	1.004	0.01766	0.724	0.00495	0.01271	0.958	−0.018

gives the added salt, the second the ionic strength of the added salt, the third the activity coefficient of the undissociated acid and the last the quotient of this quantity by the ionic strength μ.

The results are plotted in the usual manner in figure 5. The solid curves are for Sugden's measurements at 25° and the dotted curves for McBain and Kam's measurements at 100°. The curves are in general in agreement with those of the non-electrolytes and weak acids previously studied. The salting-out effect

TABLE 4

Activity coefficient of undissociated molecules of ortho-nitrobenzoic acid in salt solutions at 25°

$K_{298.1} = 6.12 \times 10^{-3}$, solubility in water = 0.04415, $m_+ \gamma_\pm = 0.01334$, $m_u^\circ = 0.02908$

SALT	μ	m	$\gamma_\pm$	m_+	m_u	γ_u	$\frac{\log \gamma_u}{\mu(\text{salt})}$
NaCl[11]	0.02005	0.04453	0.849	0.01571	0.02882	1.009	0.194
	0.02502	0.04466	0.842	0.01584	0.02882	1.009	0.156
	0.03336	0.04470	0.832	0.01603	0.02867	1.014	0.181
	0.05003	0.04482	0.816	0.01635	0.02847	1.021	0.180
	0.1002	0.04493	0.781	0.01708	0.02785	1.044	0.187
	0.2513	0.04396	0.746	0.01788	0.02608	1.115	0.188
	0.4967	0.04155	0.733	0.01820	0.02335	1.245	0.192
	0.7518	0.03926	0.747	0.01786	0.02140	1.359	0.177
	0.9989	0.03637	0.770	0.01732	0.01905	1.527	0.184
$NaNO_3$[6]	0.02001	0.04485	0.849	0.01571	0.02914	0.998	−0.046
	0.02510	0.04505	0.842	0.01584	0.02921	0.996	−0.078
	0.03338	0.04529	0.832	0.01603	0.02926	0.994	−0.085
	0.05015	0.04560	0.812	0.01635	0.02925	0.994	−0.054
	0.09986	0.04610	0.781	0.01708	0.02902	1.002	0.009
	0.2509	0.04676	0.746	0.01788	0.02888	1.007	0.012
$BaCl_2$[5]	0.03726	0.04544	0.820	0.01627	0.02917	0.997	−0.036
	0.07317	0.04564	0.783	0.01704	0.02860	1.017	0.100
	0.1499	0.04586	0.750	0.01779	0.02807	1.036	0.103
	0.2963	0.04577	0.719	0.01855	0.02722	1.068	0.096
	0.5040	0.04433	0.694	0.01922	0.02511	1.158	0.126
	0.7383	0.04344	0.680	0.01962	0.02382	1.221	0.118
$Ba(NO_3)_2$[5]	0.03432	0.04555	0.825	0.01617	0.02938	0.990	−0.140
	0.08943	0.04637	0.770	0.01732	0.02905	1.001	0.005
	0.1494	0.04668	0.750	0.01779	0.02889	1.007	0.020
	0.2973	0.04747	0.719	0.01855	0.02892	1.006	0.009
	0.5109	0.04838	0.696	0.01917	0.02921	0.996	−0.004
	0.7188	0.04849	0.681	0.01959	0.02890	1.006	0.004

TABLE 5

Activity coefficient of acetic acid in aqueous salt solutions

SALT	μ	γ_u	$\frac{\log \gamma_u}{\mu(\text{salt})}$
$MgSO_4$,[12] 25°	0.4	1.013	0.014
	1.0	1.041	0.018
	2.0	1.094	0.020
	4.0	1.229	0.022
	8.0	1.580	0.025
$LiCl$,[12] 25°	0.100	1.017	0.073
	0.251	1.046	0.078
	0.505	1.046	0.039
	1.019	1.207	0.080
	1.560	1.326	0.079
$NaCl$,[12] 25°	0.1001	1.013	0.056
	0.251	1.038	0.065
	0.5045	1.075	0.062
	1.018	1.162	0.064
	2.072	1.348	0.063
$NaCl$,[3] 100°	0.1202	1.022	0.079
	0.2108	1.050	0.101
	0.2915	1.058	0.084
	0.4129	1.063	0.064
	0.6689	1.053	0.033
	1.060	1.199	0.074
	1.415	1.286	0.077
	2.394	1.479	0.071
Na_2SO_4,[3] 100°	0.1050	0.992	−0.033
	0.1953	0.997	−0.007
	0.3312	0.992	−0.011
	0.5286	0.999	−0.001
	0.9270	1.023	0.011
	1.688	1.076	0.019
	2.161	1.133	0.025
	2.384	1.168	0.028
$NaC_2H_3O_2$,[3] 100°	0.1406	1.005	0.016
	0.5105	0.989	−0.009
	1.043	0.968	−0.014
	1.951	0.938	−0.014
KCl,[12] 25°	0.1003	1.006	0.026
	0.2520	1.015	0.026
	0.5075	1.032	0.027
	1.031	1.064	0.026
	2.124	1.145	0.028
KCl,[3] 100°	0.2520	1.047	0.079
	0.4740	1.066	0.059
	0.7154	1.101	0.058
	0.9498	1.144	0.061
	1.212	1.165	0.055
	2.072	1.240	0.045
KBr,[12] 25°	0.1004	1.003	0.013
	0.2525	1.008	0.014
	0.510	1.016	0.014
	1.041	1.035	0.014
	2.164	1.071	0.014
K_2SO_4,[12] 25°	0.3768	1.004	0.005
	0.7575	1.017	0.010
	1.532	1.059	0.016
KNO_3,[12] 25°	0.1256	0.994	−0.021
	0.2525	0.988	−0.021
	0.5105	0.975	−0.021
	1.043	0.957	−0.018
$KSCN$,[3] 100°	0.3048	1.003	0.004
	0.5758	1.033	0.024
	1.809	1.002	0.001
	2.770	1.063	0.010
Sugar,[3] 100°	0.1027	1.005	0.021
	0.1027	1.007	0.030
	0.1480	1.008	0.024
	0.1480	1.009	0.026
	0.2110	1.009	0.018
	0.2110	1.010	0.020
	0.2670	1.035	0.056
	0.2670	1.014	0.021
	0.3637	1.017	0.020
	0.3637	1.018	0.021
	0.5685	1.038	0.029
	0.5685	1.035	0.026
	1.274	1.104	0.034
	1.274	1.108	0.035
	3.096	1.349	0.042
	3.096	1.363	0.043

appears to be lower at the lower temperatures, while in the previous cases studied the effect was lower at higher temperatures. The result is inconclusive, however, as the measurements at the two temperatures were by different authors by different methods. The result by McBain and Kam (3) using sodium sulfate, is not in agreement with previous results. Sugden's (12) results show no abnormal effect with sulfates, such as is found with stronger acids, which will be discussed later.

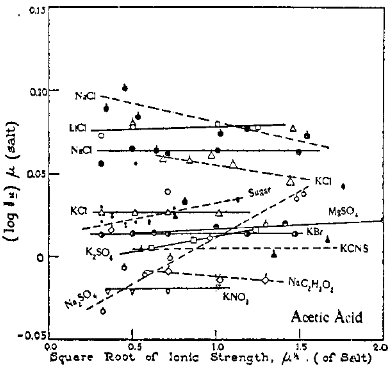

FIG. 5. ACTIVITY COEFFICIENT OF UNDISSOCIATED ACETIC ACID

DISTRIBUTION OF MONOCHLORO- AND DICHLOROACETIC ACIDS BETWEEN NORMAL DI-BUTYL ETHER AND AQUEOUS SALT SOLUTIONS

We will now consider experimentally the activity coefficient of two moderately strong acids. The distribution ratio was used to study the activity coefficient of the undissociated part of monochloro- and dichloroacetic acids. The former is weaker than *o*-nitrobenzoic acid, the strongest acid used in the previous studies, but the latter is much stronger. Thus, measurements with these acids, by an accurate method, make possible a more severe test of our assumptions of the mechanism of the dissociation of weak acids than has heretofore been possible.

Normal di-butyl ether was found to be the reference solvent best suited to our purpose.

PREPARATION OF MATERIALS

Normal di-butyl ether obtained from the Eastman Kodak Company was treated successively with dilute sulfuric acid, sodium carbonate, and metallic sodium and then subjected to a series of fractional distillations. The fraction which distilled between 141.5 and 142.8° was used.

The monochloroacetic acid was a student preparation. Its melting point was 63°, and the equivalent weight corresponded to the formula.

The dichloroacetic acid was obtained from the Eastman Kodak Company. Considerable difficulty was experienced in the final purification. After some ten fractional crystallizations its melting point was 12.5°, and the equivalent weight was 0.7 per cent too low. A Carius halogen determination indicated that the impurity was probably monochloroacetic acid, no inorganic acid being present. Fractional distillation failed to improve the acid but an extended series of fractional crystallizations gave 200 cc. of acid of M.P. 13.00° and an equivalent weight 0.2 per cent low, which was used in the experiments.

CALCULATION OF THE ACTIVITY COEFFICIENT OF THE UNDISSOCIATED PART OF A WEAK ACID FROM DISTRIBUTION EXPERIMENTS

From distribution data the calculation of the activity coefficient of the undissociated molecules is slightly more involved than in the case of solubility determinations in which the activity of the solid phase is constant. We assume that at a given mol fraction,[1] N, in the non-aqueous layer, the activity is fixed. Then $m_{\pm}\gamma_{\pm}^2$ is fixed and as $m_+ = m_-$ we have $m_+\gamma_{\pm}$ also fixed. Calculating $m_+\gamma_{\pm}$ and m_u° for various total molalities of the weak acid in pure aqueous solutions, we plot them against the values

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[1] The stoichiometric mol fraction of the acid will be designated as N in the non-aqueous layer, the molality of the hydrogen ion as m_+, of the acid ion as m_-, and of the undissociated acid as m_u in the presence of salt and m_u° in pure acid solutions of total stiochiometric molality, m. The activity coefficient of the undissociated part will be called γ_u, and other symbols have the same meaning as those used by Lewis and Randall (Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill Book Co., New York, 1923).

of N found to be in equilibrium with solutions of these strengths. In the presence of salts we then determine total acid molality, m, in the aqueous layer, and the mol fraction of acid in the non-aqueous layer.

We may assume that the mean activity coefficient of the dissociated part of the acid is the same as that of hydrochloric acid at the same ionic strength. This assumption is not fully justified, for undoubtedly a part of the abnormality of the activity coefficient of hydrochloric acid arises from the "hydration" of the ions. But in moderately concentrated solutions all strong acids behave more or less like hydrochloric acid. The activity coefficients of sodium and potassium acetates were shown by Randall, McBain and White (6) to approximate closely or even exceed those of the corresponding chlorides. The effect of an error in this assumption is greater in the case of dichloroacetic acid, since the proportion of the ions is greater.

Reading $m_+\gamma_\pm$ from the plot of $m_+\gamma_\pm$ vs. N, and dividing by $\gamma_\pm$ of hydrochloric acid we obtain m_+. The molality of the undissociated molecules is $m_u = m - m_+$. From the plot of m_u° against N we then obtain m_u°, the molality of undissociated molecules in equilibrium with the given value of N in pure aqueous solutions, whence

$$\gamma_u = m_u^\circ/m_u \tag{2}$$

The method of calculation here used makes no assumption of a constant proportionality of the activity of the acid to its mol fraction in the butyl ether phase. The only assumption made is that a given mol fraction in the ether phase represents the same activity of the acid in either pure water or a salt solution, which is in equilibrium.

THE DISTRIBUTION OF MONOCHLORO- AND DICHLORO-ACETIC ACIDS BETWEEN NORMAL DI-BUTYL ETHER AND WATER AT 25°

Our assumption that the activity is determined by the mol fraction N in the non-aqueous layer involves the assumption that neither water nor salts enter the butyl ether phase, so as to change the activity of the acid. The absence of salts was in all cases proved by flame tests and tests for the anions. The solubility of dibutyl ether in pure water or in water containing the acids in the concentrations used in the experiments was in all cases less than 0.1 per cent.

The solubility of water in an ether solution in equilibrium with *M* monochloro-acetic acid is 0.25 per cent. The solubility of water in dibutyl ether containing dichloroacetic acid of about the concentration with which we worked is less than 0.3 per cent. The mol fraction of anhydrous monochloroacetic acid in dry normal di-butyl ether at 0° was 0.270, and with 0.25 per cent water present in the ether the mol fraction (neglecting the water in the ether phase) was 0.275. These values are identical within the limits of error of these crude experiments.

TABLE 6

Distribution of monochloroacetic acid between water and normal di-butyl ether at 25°

$D\frac{25^\circ}{4^\circ}$	m	N
0.994	0.07867	0.003688
0.995	0.08840	0.004167
0.995	0.08924	0.004146
0.995	0.08979	0.004211
0.995	0.09970	0.004724
0.995	0.1025	0.004896
0.995	0.1030	0.004899
0.995	0.1062	0.005056
0.996	0.1356	0.006542
0.997	0.1373	0.006626
0.996	0.1410	0.006808
0.999	0.2152	0.01057
0.999	0.2206	0.01083
1.009	0.5202	0.02580
1.010	0.5483	0.02689
1.010	0.5502	0.02729
1.010	0.5590	0.02771
1.023	1.047	0.05080
1.025	1.067	0.05155
1.025	1.096	0.05292

TABLE 7

Distribution of dichloroacetic acid between water and normal di-butyl ether at 25°

$D\frac{25^\circ}{4^\circ}$	m	N
0.994	0.04222	0.007855
0.994	0.04263	0.007946
0.997	0.07682	0.01862
0.997	0.08928	0.02283
0.998	0.1068	0.02885
0.999	0.1225	0.03471
1.000	0.1400	0.04129
1.001	0.1601	0.04861
1.001	0.1654	0.05033
1.003	0.2055	0.06574
1.004	0.2213	0.07182

Some of the equilibria were obtained by agitating the layers gently by hand, the greater part were mechanically rotated, and gave the same result. Samples were driven by air pressure through glass tubes, containing a plug of cotton wool into the weighing bottles. The first 30 cc. were rejected in all cases. The distribution experiments with pure acid were repeated at the end of the series. From the fact that the distribution ratios were unchanged we may conclude that the butyl ether had not been altered.

TABLE 8

Dissociation constant of monochloroacetic acid[13] *at 25°*

$K_{298 \cdot 1} = 0.00139$

c	Λ	Λ/Λ°	$\Lambda_{m^+}+\Lambda_{m^-}$	α	$c\alpha^2/(1-\alpha)$	$\gamma_\pm^2$	$\alpha^2 c\gamma_\pm^2/(1-\alpha)$
0.000976	265.6	0.688	384.6	0.6906	0.001505	0.943	0.00142
0.001953	219.1	0.569	383.7	0.5710	0.001484	0.928	0.00138
0.003906	174.8	0.453	382.5	0.4566	0.001499	0.910	0.00136
0.007813	136.1	0.353	381.2	0.3570	0.001549	0.891	0.00138
0.01563	103.2	0.267	379.6	0.2719	0.001587	0.871	0.00138
0.03125	77.2	0.200	377.6	0.2044	0.001641	0.847	0.00139
0.0625	56.6	0.147	375.2	0.1509	0.001676	0.821	0.00138

TABLE 9

Dissociation constant of dichloroacetic acid[14] *at 25°*

c	Λ_0	Λ/Λ°	$\Lambda_{m^+}+\Lambda_{m^-}$	α	$c\alpha^2/(1-\alpha)$	$\gamma_\pm^2$	$\alpha^2 c\gamma_\pm^2/(1-\alpha)$
0	385.6						
0.003906	359.2	0.932	376.7	0.9535	0.07638	0.876	0.06691
0.007813	338.7	0.887	374.2	0.9051	0.06744	0.838	0.05651
0.01563	309.7	0.803	371.1	0.8346	0.06581	0.795	0.05232
0.03125	273.1	0.708	367.3	0.7435	0.06735	0.749	0.05045
0.06250	231.6	0.601	362.9	0.6382	0.07359	0.706	0.05195
0.1250	190.2	0.493	358.3	0.5309	0.07511	0.662	0.04972

The results of the distribution measurements with the pure acids are given in tables 6 and 7. The first column gives the density of the aqueous phase, the second the molality (mols per 1000 grams in vac.) and the third the mol fraction of the acid in the normal di-butyl ether phase.

DISSOCIATION CONSTANT AND CONCENTRATION OF THE UNDISSOCIATED PART OF THE ACIDS

Before presenting the results of the distribution measurements in aqueous salt solutions we will explain the calculation of the dissociation constants of the acids from conductivity data, and the method of obtaining the molality of the undissociated part of the acids. The calculations of the dissociation constants by the method proposed by Sherrill and Noyes (9) are given in table 8 (Ostwald (13)) table 9, (Kendall (14)), and table 10 (Schreiner (15)). The first columns give the concentration (mols per liter), and the second the equivalent conductance, Λ, in reciprocal international ohms. The third columns give Λ/Λ° the approximate degree of dissociation. From the first and third columns we obtain the ionic strength of the solution. The fourth column headed $\Lambda_m^+ + \Lambda_m^-$ gives the sum of the conductances of the positive and negative ions in a solution of the ionic strength equal to the one being measured. The quotient of the corresponding figure of the second column by this quantity gives the true degree of dissociation α (column five). The stoichiometric dissociation constant (column six) is equal to $\alpha^2 c/(1-\alpha)$, and to obtain the thermodynamic or true dissociation constant (column eight) we multiply by the square of the activity coefficient of hydrochloric acid (16) (column seven) in a solution of the same ionic strength.

TABLE 10

Dissociation constant of dichloroacetic acid[15] *at 18°*

$K_{291.1} = 0.0583$; $K_{298.1} = 0.0553$

c	Λ	Λ/Λ°	$\Lambda_m^+ + \Lambda_m^-$	α	$c\alpha^2/(1-\alpha)$	$\gamma_\pm^2$	$c\alpha^2\gamma_\pm^2/(1-\alpha)$
0.0	344.8						
0.001	336.7	0.977	342.0	0.9845	0.06253	0.931	0.0582
0.002	332.5	0.965	341.0	0.9751	0.07637	0.906	0.0692
0.005	316.0	0.917	338.9	0.9324	0.06430	0.864	0.0556
0.01	298.3	0.866	336.7	0.8860	0.06886	0.823	0.0567
0.02	274.8	0.797	333.8	0.8162	0.07249	0.778	0.0564
0.05	231.6	0.672	329.0	0.7040	0.08400	0.715	0.0601
0.1	195.2	0.566	324.6	0.6014	0.09074	0.671	0.0609
0.2	157.6	0.457	320.3	0.4920	0.09530	0.632	0.0602

Schreiner (15) obtained $K_{291} = 0.0583$ for dichloroacetic acid, which with the heat of dissociation given by Steinwehr (17) gives $K_{298} = 0.0553$ which is in good agreement with the less concordant measurements of Kendall (14). We shall use the value calculated from Steinwehr's measurements.

To obtain the total molality of each acid in equilibrium with various concentrations of its ions we have calculated tables **11** and 12. The first column gives the molality of hydrogen ion, which is equal to the molality of acid ion, in the solution which we are considering. The second column gives the activity coefficient in a solution of this ionic strength. The third column gives $m_+m_-\gamma_+\gamma_- = Km_u\gamma_u$. Dividing by the dissociation constant we obtain the activity of the undissociated molecules.

TABLE 11

Calculation of undissociated part of monochloroacetic acid in equilibrium with various concentrations of ions

$K_{298.1} = 0.00139$

m_+	$\gamma_\pm$	$(m_+\gamma_\pm)^2$	m_u°	m	N	$m_+\gamma_\pm$
0.0100	0.903	0.00008154	0.05866	0.06866	0.00320	0.00903
0.0125	0.893	0.0001245	0.08957	0.1021	0.00486	0.01116
0.0150	0.886	0.0001766	0.1271	0.1421	0.00684	0.01329
0.0175	0.879	0.0002365	0.1701	0.1876	0.00912	0.01538
0.0200	0.873	0.0003049	0.2194	0.2394	0.01174	0.01746

TABLE 12

Calculation of undissociated part of dichloroacetic acid in equilibrium with various concentrations of its ions

$K_{298.1} = 0.0553$

m_+	$\gamma_\pm$	$m_+m_-\gamma_\pm^2$	m_u°	m	N	$m_+\gamma_\pm$
0.04	0.840	0.001129	0.02042	0.06042	0.0134	0.03360
0.05	0.828	0.001714	0.03099	0.08099	0.0200	0.04140
0.06	0.819	0.002415	0.04367	0.1037	0.0278	0.04914
0.07	0.811	0.003223	0.05828	0.1283	0.0368	0.05677
0.08	0.804	0.004137	0.07481	0.1548	0.0466	0.06432
0.09	0.799	0.005170	0.09350	0.1835	0.0574	0.07190
0.10	0.795	0.006320	0.1143	0.2143	0.0691	0.0795

We have found the salting out effect of acids upon non-electrolytes to be very small. As the effect of salts on non-electrolytes and weak acids was about the same, we, therefore, neglected the salting out effect of the ions of the acid itself upon the activity coefficient of the undissociated part. Any error in this assumption will be partially cancelled out because the mean molality of the acid and hydrogen ions is approximately constant. Therefore, if we take the activity coefficient of the undissociated molecules in pure solutions of the acids as equal to unity, we set $m_+m_-\gamma_\pm^2/K = m_u^\circ$, (fourth column). The total molality which is the sum of undissociated and dissociated molecules is given in the column headed m. The column N shows the mol fraction of acid in butyl ether found to be in equilibrium with a pure aqueous solution of acid of the given molality, m. The column of $m_+\gamma_\pm$ is also given. Plots are then made of $m_+\gamma_\pm$ against N, and of m_u° against N.

THE DISTRIBUTION OF MONOCHLORO- AND DICHLOROACETIC ACIDS BETWEEN AQUEOUS SALT SOLUTIONS AND NORMAL DIBUTYL ETHER AT 25°

The results of the distribution measurements with the acids in aqueous solutions without a common chloroacetate ion are given in tables 13 and 15. The first columns give the densities, the second the ionic strengths of the salts, the third the molalities of the acids and the fourth their mol fractions in the butyl ether. The fifth columns, $\gamma_\pm$, are the activity coefficients of hydrochloric acid in a mixture of hydrochloric acid and barium chloride of the ionic strength in the second columns and the same fraction of acid as determined by Randall and Breckenridge (8), or the activity coefficient of hydrochloric acid in a mixture with sodium or potassium chloride as determined by Harned and Åkerlöf (18) recalculated to give 0.795 at 0.1 M. The activity coefficient in mixtures with potassium bromide, potassium nitrate, sodium monochloroacetate and sodium dichloroacetate was arbitarily assumed to be the same as that with the chlorides. The mol fraction in the ether phase fixes the activity $m_+m_-\gamma_\pm^2$ and therefore since $m_+ = m_-$ we know $m_+\gamma_\pm$ (columns six). Reading $m_+\gamma_-$ from the plot of $m_+\gamma_\pm$ against N and dividing by the value

TABLE 13

Monochloroacetic acid in aqueous salt solutions at 25°

$D\frac{25°}{4°}$	μ SALT	m	N	$\gamma_\pm$	$m_+\gamma_\pm$	m_+	m_u	m_u°	γ_u	$\frac{\log \gamma_u}{\mu \text{ (salt)}}$
In sodium chloride solutions										
0.999	0.100	0.1017	0.004846	0.789	0.01114	0.0141	0.0876	0.0895	1.022	0.094
1.003	0.200	0.1017	0.004915	0.755	0.01120	0.0148	0.0869	0.0907	1.044	0.094
1.015	0.500	0.0980	0.004977	0.733	0.01129	0.0154	0.0826	0.0920	1.114	0.094
1.033	1.000	0.0954	0.005338	0.770	0.01170	0.0152	0.0802	0.0985	1.228	0.089
1.070	2.000	0.1018	0.006956	0.896	0.01339	0.0149	0.0869	0.1288	1.482	0.085
1.102	3.000	0.0898	0.007271	1.094	0.01372	0.0125	0.0773	0.1350	1.746	0.081
In barium chloride solutions										
1.008	0.200	0.1084	0.005177	0.740	0.01154	0.0156	0.0928	0.0955	1.029	0.062
1.025	0.497	0.0991	0.004829	0.705	0.01115	0.0158	0.0833	0.0893	1.072	0.061
1.054	0.988	0.1013	0.005230	0.690	0.01154	0.0167	0.0846	0.0965	1.141	0.059
1.108	1.950	0.0995	0.005693	0.720	0.01210	0.0168	0.0827	0.1053	1.275	0.054
In potassium chloride solutions										
1.018	0.500	0.1058	0.005038	0.717	0.01139	0.0159	0.0899	0.0931	1.035	0.030
1.018	0.500	0.0991	0.004704	0.717	0.01098	0.0153	0.0838	0.0865	1.032	0.027
1.039	1.000	0.0993	0.004780	0.722	0.01106	0.0153	0.0840	0.0877	1.044	0.019
1.039	1.000	0.1022	0.004984	0.722	0.01131	0.0157	0.0865	0.0922	1.066	0.028
In potassium bromide solutions										
1.036	0.500	0.1008	0.004680	0.717	0.01094	0.0153	0.0855	0.0865	1.012	0.009
1.075	1.000	0.1036	0.004829	0.722	0.01115	0.0154	0.0882	0.0893	1.012	0.005
In potassium nitrate solutions										
1.024	0.500	0.1042	0.004580	0.717	0.01079	0.0150	0.0892	0.0845	0.947	−0.047
1.052	1.000	0.1074	0.004576	0.722	0.01079	0.0149	0.0925	0.0843	0.911	−0.041

TABLE 14

Monochloroacetic acid in sodium monochloroacetate solutions at 25°

$D\frac{25°}{4°}$	μ_{NaAcCl}	m	N	$\gamma_\pm^2$	$m_+m_-\gamma_\pm^2 \times 10^4$	$m_+m_- \times 10^4$	m_+	m_u	m_u°	γ_u	$\frac{\log \gamma_u}{\mu \text{ (salt)}}$
1.009	0.2010	0.1265	0.006699	0.552	1.725	3.125	0.0015	0.1250	0.1246	0.997	−0.006
1.028	0.527	0.0897	0.004729	0.512	1.210	2.363	0.0005	0.0892	0.0875	0.980	−0.017
1.057	1.032	0.0994	0.005054	0.523	1.290	2.467	0.0002	0.0992	0.0934	0.942	−0.025

of $\gamma_{\pm}$ given in the table we obtain m_+ (columns seven), the molality of hydrogen ion. We subtract m_+ from the total molality m and obtain m_u, the molality of undissociated acid. (Columns eight). But from our m_u° vs. N plot we find that a pure aqueous solution

TABLE 15

Dichloroacetic acid in aqueous salt solutions at 25°

$D\frac{25°}{4°}$	μ_{SALT}	m	N	$\gamma_{\pm}$	$m_+\gamma_{\pm}$	m_+	m_u	m_u°	γ_u	$\frac{\log \gamma_u}{\mu\ (\text{salt})}$
					In sodium chloride solutions					
1.005	0.100	0.1651	0.05013	0.758	0.0669	0.0883	0.0768	0.0807	1.051	0.216
1.009	0.200	0.1703	0.05287	0.741	0.0689	0.0930	0.0773	0.0856	1.107	0.221
1.020	0.500	0.1644	0.05424	0.736	0.0698	0.0948	0.0696	0.0879	1.263	0.203
1.038	1.000	0.1487	0.05526	0.779	0.0705	0.0905	0.0582	0.0898	1.543	0.188
					In barium chloride solutions					
1.013	0.200	0.1843	0.05624	0.735	0.0711	0.0968	0.0875	0.0915	1.046	0.097
1.027	0.497	0.1751	0.05327	0.715	0.0692	0.0968	0.0783	0.0863	1.103	0.086
1.031	0.497	0.1699	0.05146	0.715	0.0679	0.0950	0.0749	0.0830	1.108	0.090
1.058	0.988	0.1638	0.05254	0.710	0.0687	0.0968	0.0670	0.0850	1.268	0.104
1.112	1.950	0.1557	0.05764	0.745	0.0721	0.0968	0.0589	0.0939	1.594	0.104
					In potassium nitrate solutions					
1.031	0.500	0.1751	0.05101	0.715	0.0675	0.0944	0.0807	0.0824	1.021	0.018
1.059	1.000	0.1782	0.05193	0.726	0.0682	0.0939	0.0841	0.0838	0.996	−0.002

TABLE 16

Dichloroacetic acid in potassium dichloroacetate solutions at 25°

$D\frac{25°}{4°}$	μ KAcCl$_2$	m	N	$\gamma_{\pm}^2$	$m_+m_-\gamma_{\pm}$	m_+m_-	m_+	m_u	m_u°	γ_u	$\frac{\log \gamma_u}{\mu\ (\text{salt})}$
1.007	0.1083	0.1201	0.04550	0.599	0.004032	0.006729	0.0440	0.0761	0.0728	0.09566	−0.178
1.018	0.2667	0.0880	0.03815	0.532	0.003352	0.006301	0.0218	0.0662	0.0610	0.09215	−0.133
1.047	0.6273	0.0753	0.03391	0.510	0.002970	0.005824	0.0915	0.0661	0.0535	0.08094	−0.146

of the acid of a molality m_u° (columns nine) in undissociated molecules is also in equilibrium with the mol fraction N in butyl ether and therefore has the same activity. Then, $m_u\ \gamma_u = m_u^\circ\ \gamma_u^\circ$. As γ_u° the activity coefficient of undissociated molecules in a pure solution of the acid is equal to unity we have $\gamma_u = m_u^{\circ}/m_u$. Columns 10 give the activity coefficient of undissociated acid molecules, γ_u. Columns 11 give the logarithm of the activity coefficient of undissociated acid molecules divided by the ionic strength of the salt solution.

Tables 14 and 16 present measurements made in the presence of a common anion. The calculation is very similar. We observe m and N. From the plot against N we obtain $m_+\gamma_\pm$ in pure acid solution in equilibrium with a butyl ether phase of the same mol fraction. Squaring this, one obtains $(m_+\gamma_\pm)^2$ in pure solution and this equals $m_+m_-\gamma_\pm^2$ in any solution of the same activity with or without a common ion. We have given the

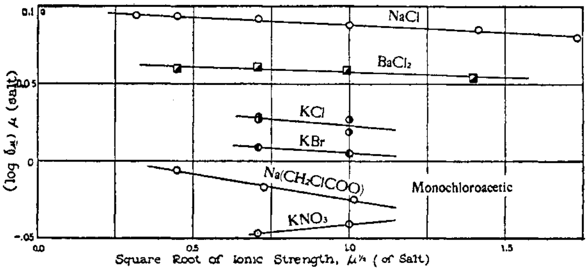

FIG. 6. ACTIVITY COEFFICIENT OF UNDISSOCIATED MONOCHLOROACETIC ACID

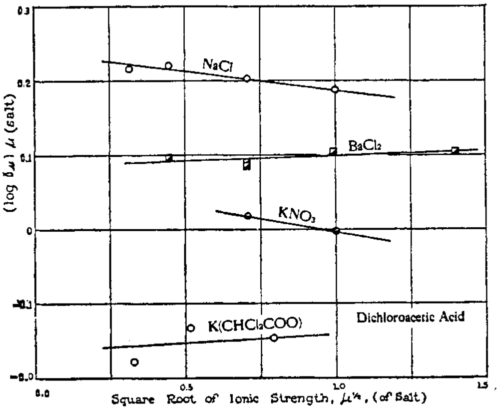

FIG. 7. ACTIVITY COEFFICIENT OF UNDISSOCIATED DICHLOROACETIC ACID

molality of acid anion added as the salt. By successive approximations we find m_+ and m_- such that m_- (total) $-m_-$ (added anion) $= m_+$ and m_- (total) $\cdot m_+\gamma_\pm^2 = m_+m_-\gamma_\pm^2$ obtained above. Then $m_u = m - m_+$ and again $\gamma_u = m_u^\circ/m_u$.

The results are plotted in figures 6 and 7 in which the ordinate is the quotient of the logarithm of the activity coefficient of the undissociated molecules by the ionic strength of the salt. For convenience the square root of the ionic strength of the added salt rather than of the solution was used as the abscissae of the plots.

DISCUSSION OF THE ACTIVITY COEFFICIENT OF THE UNDISSOCIATED PART OF MONOCHLORO- AND DICHLOROACETIC ACIDS

The plots of figures 6 and 7 show a striking similarity to similar plots of the gases, non-electrolytes and weak acids studied in the previous papers. The magnitude of the salting out effect is small with acetic acid, is slightly larger with monochloro- and largest with dichloroacetic acid.

The curves are nearly horizontal, and therefore give additional evidence as the validity of the prediction made in the earlier paper that the quotient of the logarithm of the activity coefficient of a non-electrolyte or of the undissociated part of a weak acid by the ionic strength of the added salt is approximately a constant. However, we must remember that certain assumptions regarding the ions were made, namely, that the activity coefficient of the dissociated ions was the same as that of hydrochloric acid at the same ionic strength, and second, that the salting out effect of the dissociated part of the acid itself was negligible. The dissociated part of the acid contributes from 0.4 to 12 per cent in the case of monochloro- and from 5 to 40 per cent in the case of the dichloroacetic acid. The salting out effect of the common chloroacetate ion is negative, for the effect of sodium and potassium ions is predominately positive. We have not, however, attempted to make a correction for this effect.

We have also neglected the activity coefficient of the undissociated part of the acid in the pure aqueous solutions. In the case of acetic acid it is small, but its magnitude in the substituted acids is unknown.

THE ACTIVITY OF WEAK ACIDS IN AQUEOUS SULFATE SOLUTIONS

When sulfates are added to solutions of weak acids, there is a distribution of the hydrogen ion constituent between the weak acid ion and the hydrosulfate ion. We have as yet insufficient data to fully consider such cases. We show in figure 8 the ratio of the molality of several acids in pure water, to the molality in a sulfate solution in which its activity has the same value (19).

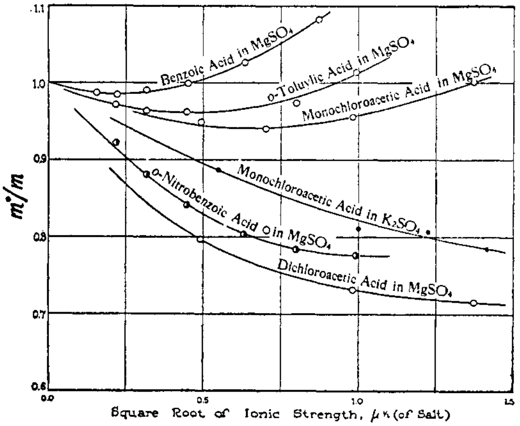

FIG. 8. "ACTIVITY COEFFICIENT" AT CONSTANT ACTIVITY OF WEAK ACIDS IN AQUEOUS SULFATE SOLUTIONS AT 25°C.

GENERAL DISCUSSION

The results of this and the preceding papers are summarized in table 17. In this table we have assembled the data under the head of the added salt, which is given in the first column. The second column gives the non-electrolyte or weak acid, and the third the average value of the quotient of the logarithm of the activity coefficient by the ionic strength of the added salt.

In examining the table we find that the salting-out effect of the salts is about the same upon the undissociated part of the weak acids as upon gases and non-electrolytes. The effect is small for acetic, somewhat larger for monochloroacetic, and largest for dichloroacetic acid. As was pointed out in the article dealing with gases, if the relation of Debye and McAulay is true

TABLE 17

Summary of all calculations on activity coefficients of undissociated weak acids and non-electrolytes

ADDED SALT	SUBSTANCE	$\frac{\log \gamma}{\mu(\text{salt})}$
HCl	O_2	0.036
	H_2	0.020
	N_2O	0.016
	CO_2	0.009
	H_2S	0.014
	a	−0.036
H_2SO_4	O_2	0.030
	H_2	0.018
	CO_2	0.017
	H_2S	0.052
HNO_3	O_2	0.023
	H_2	0.007
	N_2O	−0.014
	CO_2	−0.022
	a	−0.025
$ZnSO_4$	N_2O	0.061
	C_2H_2	0.061
$Zn(NO_3)_2$	N_2O	0.042
	C_2H_2	0.031
$Cu(NO_3)_2$	N_2O	0.065
$MnSO_4$	N_2O	0.059
	C_2H_2	0.056
$FeSO_4$	N_2O	0.033
	C_2H_2	0.061
$FeCl_3$	C_2H_2	0.030
$Fe_2(SO_4)_3$	N_2O	0.027
	C_2H_2	0.027
$CoSO_4$	N_2O	0.081
	C_2H_2	0.061
$NiSO_4$	N_2O	0.080
	C_2H_2	0.066
$Cr_2(SO_4)_3$	N_2O	0.022
	C_2H_2	0.021
$AlCl_3$	H_2	0.028
	C_2H_2	0.044
	b	0.070
$Al_2(SO_4)_3$	N_2O	0.046
	C_2H_2	0.043
$Al(NO_3)_3$	N_2O	0.045
	C_2H_2	0.023
$MgCl_2$	C_2H_2	0.055
$MgSO_4$	H_2	0.057
	N_2O	0.070
	C_2H_2	0.064
	b	0.075
$Mg(NO_3)_2$	N_2O	0.035
	C_2H_2	0.026
$CaCl_2$	H_2	0.065
	N_2O	0.064
	C_2H_2	0.058
$Ca(NO_3)_2$	N_2O	0.040
	C_2H_2	0.027
$BaCl_2$	N_2	0.120
	N_2O	0.073
	CO_2	0.060
	C_2H_2	0.065
	b	0.075
	c	0.100
	d	0.134
	e	0.105
	ClAc	0.056
	Cl_2Ac	0.098
$Ba(NO_3)_2$	*c*	0.030
	d	0.040
	e	0.004
LiOH	NH_3	0.080

TABLE 17—*Continued*

ADDED SALT	SUBSTANCE	$\frac{\log \gamma}{\mu(\text{salt})}$
LiCl	H_2	0.066
	N_2O	0.084
	NH_3	−0.020
	Ac	0.075
LiBr	NH_3	−0.035
LiI	NH_3	−0.062
$LiNO_3$	*b*	−0.012
NaOH	O_2	0.188
	H_2	0.140
	NH_3	0.090
NaCl	O_2	0.133
	H_2	0.094
	N_2	0.200
	N_2O	0.100
	H_2S	0.060
	NH_3	0.027
	C_2H_2	0.093
	a	0.089
	b	0.013
	c	0.191
	d	0.232
	e	0.180
	f	0.196
	Ac	0.066
	ClAc	0.088
	Cl_2Ac	0.204
$NaClO_3$	*b*	0.033
$NaClO_4$	*b*	−0.020
NaBr	N_2O	0.090
	H_2S	0.016
	NH_3	−0.014
	C_2H_2	0.080
NaI	NH_3	−0.025
	b	−0.030
Na_2SO_4	N_2O	0.110
	H_2S	0.180
	C_2H_2	0.100
	I_2	0.107
	b	0.130
$NaNO_3$	H_2	0.082
	N_2O	0.072
	H_2S	0.034
	C_2H_2	0.050
	I_2	0.045
	a	−0.130
	b	0.020
	c	0.064
	d	0.089
	f	−0.078
NaH_2PO_4	I_2	0.140
NaAc	Ac	−0.014
NaClAc	ClAc	−0.016
KOH	O_2	0.175
	H_2	0.120
	N_2O	0.130
	NH_3	0.120
KCl	H_2	0.080
	N_2O	0.081
	CO_2	0.063
	H_2S	0.054
	NH_3	0.035
	C_2H_2	0.064
	a	0.034
	b	0.120
	c	0.152
	f	0.140
	Ac	0.033
	ClAc	0.026
$KClO_3$	NH_3	0.064
	b	0.020

TABLE 17—*Concluded*

ADDED SALT	SUBSTANCE	$\frac{\log \gamma}{\mu(\text{salt})}$
KBr	N_2O	0.068
	CO_2	0.050
	H_2S	0.006
	NH_3	0.062
	C_2H_2	0.050
	b	0.055
	Ac	0.014
	ClAc	0.008
$KBrO_3$	NH_3	0.043
KI	N_2O	0.015
	CO_2	0.039
	H_2S	−0.012
	NH_3	−0.010
	b	−0.060
KIO_3	NH_3	0.023
KIO_4	N_2O	0.055
K_2SO_4	O_2	0.104
	H_2S	0.130
	NH_3	0.055
	C_2H_2	0.082
	b	0.120
KNO_3	H_2	0.062
	N_2O	0.047
	CO_2	0.031
	H_2S	0.018
	NH_3	0.033
	C_2H_2	0.030
	a	−0.160
	b	0.000
	c	0.025
	f	−0.006
	Ac	−0.020
	ClAc	−0.043
	Cl_2Ac	0.010
K_2CO_3	H_2	0.090
KCl_2Ac	Cl_2Ac	−0.150
KSCN	Ac	0.010
RbCl	N_2O	0.076
	CO_2	0.050
$RbNO_3$	*b*	−0.050
CsCl	N_2O	0.058
	CO_2	0.042
$CsNO_3$	*b*	−0.130
NH_4Cl	N_2O	0.030
	CO_2	0.020
	H_2S	0.001
	C_2H_2	0.023
NH_4Br	N_2O	0.024
	H_2S	−0.018
	C_2H_2	0.012
$(NH_4)_2SO_4$	C_2H_2	0.045
NH_4NO_3	H_2	0.010
	N_2O	0.008
	H_2S	0.021
	b	−0.070
g	H_2	0.000
	N_2O	−0.017
	CO_2	0.022
Sugar	H_2	0.050
	CO_2	−0.010
	Ac	0.025
Urea	N_2	0.000
	N_2O	−0.004
	H_2S	−0.027

(*a*) *o*-nitrobenzaldehyde; (*b*) phenylthiourea; (*c*) benzoic acid; (*d*) *o*-toluylic acid; (*e*) *o*-nitrobenzoic acid; (*f*) salicylic acid; (*g*) chloral hydrate; (Ac) acetic acid; (ClAc) monochloroacetic acid; (Cl_2Ac) dichloroacetic acid.

then the ratio of $(\log \gamma)/\mu$ for one non-electrolyte to $(\log \gamma)/\mu$ for another non-electrolyte within the group should be the same as the ratio for the same non-electrolytes in another group. We note that this is qualitatively the rule for the weak acids as well as for non-electrolytes.

It is difficult to interpret negative values of $(\log \gamma)/\mu$. In general nitrates and organic anions give very small or negative values of $(\log \gamma)/\mu$ and the bromides and iodides in several cases are negative. The iodides have large ionic radii in the Debye and Hückel sense, while the ionic radius of nitrates is thought to be quite small (20).

It must be remembered, however, that to some extent the values of the function which we are considering are dependent on the units chosen for expressing concentrations. For example if we were to use the ratio of the activity of the undissociated substance to its mol fraction, then the activity coefficient would have different values in moderately concentrated solutions. Further generalizations do not seem possible at the present time.

In the case of the added sulfates the quantity m°/m defines a quantity which is analogous to the activity coefficient for solutions of the same activity. The quantity m°/m is lowered by a larger amount the larger the dissociation constant of the acid. This is in agreement with an assumption of a larger amount of hydrosulfate ion formed with the stronger acid. The ordinary salting-out effect, which is pronounced in the case of sulfates on non-electrolytes, is more noticeable with the weaker acids.

GENERAL SUMMARY

The activity coefficient of gases, of solid non-electrolytes, and of the undissociated part of weak acids, has been considered as the measure of the deviation of the properties of these substances from the laws of the perfect solution.

The quotient of the logarithm of the activity coefficient of the gases and of the non-electrolytes by the quotient of the ionic strength in aqueous salt solutions is approximately constant.

This constant varies with the salt or the non-electrolyte being considered.

The value of this constant, which may be called the salting-out effect, may be used as the basis for arranging a salting-out series of the ions. In the series so arranged, the valence of the ion has little effect in determining the order.

The distribution of monochloro- and dichloroacetic acid between aqueous salt solutions and normal di-butyl ether has been determined.

If the simple assumption that the dissociated part of weak acids acts in the presence of added salts in the same way as the ions of hydrochloric acid, then the quotient of the logarithm of the activity coefficient of the undissociated part by the ionic strength of the added salt is also approximately constant. The salting-out order of the ions is also the same as that for non-electrolytes.

When sulfates are added to solutions of weak acids, some hydrosulfate ion is formed. The results of partition and solubility measurements in the presence of sulfates are qualitatively explained by this assumption and effects similar to the above.

A general summary of the effect of individual electrolytes on the several non-electrolytes is given.

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