[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Thallous Chloride–Ethanol–Water System at 25°. The Activity Coefficients of Thallous Chloride in Ethanol–Water Mixtures

BY ERNEST HOGGE AND A. B. GARRETT

This investigation was undertaken with the purpose of studying the effect of the variation of dielectric constant upon certain equilibria occurring in solutions of thallous chloride. It has been found difficult to sort out all the effects of a change of solvent upon electrolytic solutions, since in addition to the effect upon the electrostatic forces operating between the ions, there are specific solvent effects for which there is, at present, no adequate theory. It was thought that the data presented here may be of value in testing such theories as have been proposed.

The salt, thallous chloride, was chosen for investigation for the following reasons: thallous chloride is moderately soluble in water (0.01617 mole/1000 g. of water at 25°), this making it possible to follow the solubility to fairly low values of the dielectric constant. It is intermediate between strong and weak electrolytes; Onsager[1] gives the value of 0.31 as the ionization constant of the thallous chloride in water at 25°. These properties would enable one to use the solubility in salt solutions to determine the activity coefficients in the various ethanol–water solvents at different values of the ionic strength.

It was decided to investigate rather thoroughly the effect of potassium chloride as added salt. The ions of potassium chloride are known to be of about the same size[2] since their transport numbers are nearly equal; this property makes its solutions most amenable to theoretical treatment. Also, it was thought that the excess chloride ion might disclose some complex ion formation, such as

$$\mathrm{TlCl} + x\mathrm{Cl}^- \rightleftarrows \mathrm{TlCl}_{x+1}^{-x}$$

however, such complex formation as might be present was too small to be detected by the present experimental method.

The proposed experimental procedure was the measurement of the solubility of thallous chloride in various concentrations of ethanol–water from 90% water to 60% ethanol and in ethanol–water solutions in the presence of added potassium chloride at 25°. Such data would then be used to evaluate the activity coefficients of thallous chloride in the presence of excess chloride ion. This would be done by the method of Lewis[3] from the relationship

$$\gamma_{\pm} = \frac{(1/m_{\pm})_{\mu=\mu}}{(1/m_{\pm})_{\mu=0}} \qquad (1)$$

where $\gamma_{\pm}$ is the mean activity coefficient, μ is the ionic strength and $m_{\pm} = \sqrt{m_+m_-}$.

Experimental

Solvent.—The ethanol–water mixtures were prepared from conductivity water and purified ethyl alcohol. The commercial 95% alcohol was refluxed over silver oxide for four hours and distilled; the middle fraction was taken for use.[4] The composition of the mixture was determined by means of the density. A 50-ml. pycnometer was used. The densities were reproducible to about 1 part in 10,000, corresponding to a difference in composition of about 0.5%.

Thallous Sulfate.—Commercial thallous sulfate was dissolved in water, acidified with sulfuric acid, and the solution saturated with hydrogen sulfide. Usually a small amount of brownish precipitate formed. The solid matter was then filtered off through a porous clay crucible, the thallium precipitated as chloride, washed free of sulfate, and the chloride was converted back into sulfate[5] by evaporation with sulfuric acid to the evolution of sulfur trioxide fumes. During this evaporation, a current of air, filtered through glass wool in order to remove dust and oil, was passed into the flask, which was in turn protected from dust by an inverted beaker. The mass of thallous sulfate crystals was dissolved in water, and fractionated by three crystallizations from conductivity water, after which the crystals were dried at 110°.

Thallous Chloride.—The thallous chloride was prepared by dropping solutions of 0.1 *m* thallous sulfate and 0.2 *m* hydrochloric acid into about a liter of hot water at nearly the same rate. During the precipitation a current of nitrogen was passed through the solution in the precipitation flask. The precipitated chloride was then washed by decantation in a flask similar to that used by Johnston, Cuta and Garrett[6] in washing silver oxide. Twelve washings with conductivity water were considered sufficient, since the eighth washing usually gave no test for sulfate with a drop of 0.1 *N* barium chloride.

Hydrochloric Acid.—Grasselli C. P. grade hydrochloric acid was distilled in an all-glass still; the middle fraction was taken for use.

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(1) L. Onsager, *Physik. Z.*, **28**, 277 (1927).

(2) H. S. Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1930, p. 683.

(3) Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," The McGraw-Hill Book Company, 1923, p. 369 ff.

(4) Gross, Kuzmany and Wald, THIS JOURNAL, **59**, 2692 (1937).

(5) Cowperthwaite, La Mer and Barksdale, *ibid.*, **56**, 544 (1934).

(6) Johnston, Cuta and Garrett, *ibid.*, **55**, 2311 (1933).

Potassium Chloride.—Baker analyzed potassium chloride was used.

Preparation of Samples.—Standard solutions of potassium chloride were prepared from the solvent to be used, and portions of this solution taken to rinse about 2-g. portions of solid thallous chloride. The thallous chloride was transferred to a 200-ml. sample flask together with the standard potassium chloride solution. The flask was then sealed, painted with black paint, and rotated in a water-bath at 25.00 ± 0.02° for several days to obtain solvation equilibrium. After equilibration they were sedimented and filtered through a Jena glass filter.

Analysis.—The 10% alcohol series was analyzed using the potassium bromate method of Kolthoff and of Zintl and Reinacker.[7] This method was found to give results which were a little high, and was discarded in favor of the potassium iodate method of Swift and Garner.[8] In the 30% series, the end-point was detected by shaking out the iodine with carbon tetrachloride, while in the 40, 50, and 60% series, the end-point was detected potentiometrically.[9]

The Data

The solubility data are summarized in Tables I, II, III, IV and V, and are shown graphically in Figs. 1, 2 and 3. All values have been expressed in moles per 1000 g. of solvent. It is apparent that the solubility drops rapidly due to the common ion effect, and reaches a minimum in each concentration of alcohol studied. There is no certain method of interpreting this minimum, but if we assume a small amount of association, we may hazard the guess that the minimum represents nearly the solubility of un-ionized thallous chloride. The small rise in solubility following the minimum might indicate a slight amount of complex formation, but this rise is so small that it may be due entirely to a variation in the activity coefficients of the ions.

TABLE I

10% ALCOHOL SOLUBILITY

KCl, mole/1000 g. solvent	d^{25}_4 solution	TlCl, mole/1000 g. solvent	$1/m_\pm$	$\sqrt{\mu}$
0.0	0.9827	0.01166	85.76	0.1080
.02043	.9825	.005845	80.68	.1621
.05108	.9834	.003376	73.75	.2334
.1023	.9854	.002300	64.49	.3234
.2051	.9905	.001627	54.53	.4546
.3084	.9946	.001371	48.52	.5566
.5111	1.0158	.001142	41.37	.7157
1.0515	1.0259	.001117	29.17	1.026
2.195	1.0617	.001416	18.79	1.482

TABLE II

30% ALCOHOL SOLUBILITY

KCl, mole/1000 g. solvent	d^{25}_4 solution	TlCl, mole/1000 g. solvent × 10^4	$1/m_\pm$	$\sqrt{\mu}$
0.0	0.9496	58.55	170.9	0.07646
.01061	.9496	29.47	158.1	.1165
.02647	.9500	17.06	143.6	.1685
.05293	.9512	11.39	127.4	.2325
.1057	.9532	8.097	107.6	.3264
.1589	.9552	6.959	94.9	.3995
.2658	.9591	6.009	79.1	.5161
.5361	.9694	5.49	57.8	.7325
1.093	.9909	6.62	36.2	1.046

TABLE III

40% ALCOHOL SOLUBILITY

KCl, mole/1000 g. solvent	d^{25}_4 solution	TlCl, mole/1000 g. solvent × 10^4	$1/m_\pm$	$\sqrt{\mu}$
0.0	0.9337	40.58	246.5	0.06375
.01071	.9342	16.62	220.5	.1113
.02145	.9342	10.01	200.7	.1502
.05369	.9351	6.653	166.3	.2331
.1075	.9377	5.064	135.2	.3286
.2157	.9423	4.238	104.5	.4648
.3246	.9467	4.006	87.0	.5704
.5440	.9558	4.18	66.2	.7381
1.108	.9774	5.20	41.5	1.053

TABLE IV

51.25% ALCOHOL SOLUBILITY

KCl, mole/1000 g. solvent	d^{25}_4 solution	TlCl, mole/1000 g. solvent × 10^4	$1/m_\pm$	$\sqrt{\mu}$
0.0	0.9076	25.71	388.3	0.05075
.01654	.9081	6.126	308.5	.1310
.03310	.9086	4.285	263.7	.1831
.08295	.9108	3.049	198.6	.2885
.1476	.9133	2.706	158.1	.3846
.1662	.9141	2.678	149.8	.4079
.1848	.9145	2.623	142.8	.4301
.3705	.9234	2.703	99.9	.6089
.7510	.9372	3.385	62.7	.8668

TABLE V

60% ALCOHOL SOLUBILITY

KCl, mole/1000 g. solvent	d^{25}_4 solution	TlCl, mole/1000 g. solvent × 10^4	$1/m_\pm$	$\sqrt{\mu}$
0.0	0.8882	17.93	558.0	0.04238
.01409	.8886	3.612	437.0	.1202
.02819	.8889	2.636	365.1	.1687
.05637	.8903	2.078	291.6	.2379
.09318	.8921	1.875	238.9	.3057
.1414	.8934	1.789	198.7	.3763
.1698	.8961	1.826	179.7	.4123
.2839	.8992	1.867	137.5	.5330
.3760	.9028	1.991	115.5	.6133
.4715	.9065	2.141	99.5	.6868

Discussion of Results

An interpretation of the data must involve first the consideration of the fact that a plot of log $1/m_\pm$ *vs.* $\sqrt{\mu}$ does not give the theoretical value of the limiting slope in any case. The

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[7] Kolthoff, *Rec. trav. Chim.*, **41**, 172 (1922); Zintl and Reinacker, *Z. anorg. allgem. Chem.*, **153**, 276 (1926).

[8] Swift and Garner, THIS JOURNAL, **58**, 113 (1936).

[9] Balwant Singh and Ijaz Ilahi, *J. Indian Chem. Soc.*, **13**, 717 (1936).

values of the limiting slopes were found by drawing what appeared to be the best line at a point near the end of the plot; these values are listed in the second column of Table VA, and in the last column the *theoretical values* as calculated from the limiting law,[10] namely

$$\log \gamma = -\frac{\pi^{1/2}\epsilon^3 Z_1 Z_2 N_0^2\sqrt{2\mu d_s}}{2.303 D^{3/2} T^{3/2} R^{3/2}} \qquad (2)$$

where d_s is the density of the solvent, and the other symbols have their customary meaning.

TABLE VA

% Alcohol	Experimental slope	Theoretical slope (Equation (2))
0.0	0.56	0.50
10.0	.62	.57
30.0	.85	.72
40.0	1.02	.84
51.25	1.22	.98
60.0	1.53	1.18

The dielectric constants of the alcohol–water mixtures were taken from the data of Åkerlöf.[11]

It should be noted that the introduction of the additional parameter, the ionic size, would involve the introduction of negative values of the ionic size, or the mean distance of ionic approach, in order to give a fit with the theory. Another explanation is needed, and it will be shown that the data can be brought into agreement with the theory by the correction for the small amount of association.[12]

Correction for Association of Thallous Chloride.—This correction must be made since it is known that thallous chloride is a moderately weak electrolyte; Onsager[1] found a value of the ionization constant 0.31 was necessary in order that he might interpret conductivity data of Kohlrausch. If this be true then the degree of association may be calculated from the solubility data. In making this calculation, the following assumptions have been made: (1) the molality of un-ionized thallous chloride present in a given solvent is constant in a saturated solution, and (2) the limiting slope of a plot involving the activity coefficients may be predicted from the Debye–Hückel theory. We define K_0 by equation (3)

$$K_0 = \frac{m_{Tl^+} m_{Cl^-} \gamma_{Tl^+} \gamma_{Cl^-}}{m_{TlCl}\gamma_{TlCl}} \qquad (3)$$

Assumption (1) states that $\gamma_{TlCl} = 1$ throughout. If we take logarithms of both sides and label the activity coefficients as γ' to distinguish them from the stoichiometrical activity coefficients, γ (Table VIII), we have

$$\log K_0 = \log \frac{m_{Tl^+} m_{Cl^-}}{m_{TlCl}} + 2 \log \gamma'_{\pm(TlCl)} \qquad (4)$$

Setting

$$\frac{m_{Tl^+} m_{Cl^-}}{m_{TlCl}} = K' \qquad (5)$$

an *apparent* or *stoichiometric* ionization constant, we have on rearranging

$$\log K' = \log K_0 - 2 \log \gamma'_{\pm TlCl} \qquad (6)$$

Substituting from the Debye–Hückel expression for $\log \gamma'_{\pm}$, we have

$$\log K' = \log K_0 + \frac{2\pi^{1/2}\epsilon^3 Z_1 Z_2 N_0^2\sqrt{2\mu d_s}}{2.303 D^{3/2} T^{3/2} R^{3/2}} \qquad (7)$$

Assuming a value of m_{TlCl}, we may calculate a set of values of log K'; by plotting log K' *vs.* $\sqrt{\mu}$ and drawing the limiting slope, we may observe the direction of the deviation from the Debye–Hückel limiting law. Too large a slope means that m_{TlCl} is too small, and the converse is true. A series of approximations then enables one to choose a value of m_{TlCl} which will give a curve consistent with the calculated Debye–

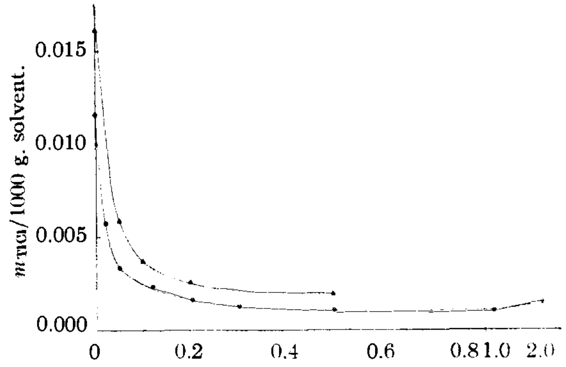

Fig. 1.—Thallous chloride: △, solubility in water ("Int. Crit. Tables"); ⊗, in 10% alcohol.

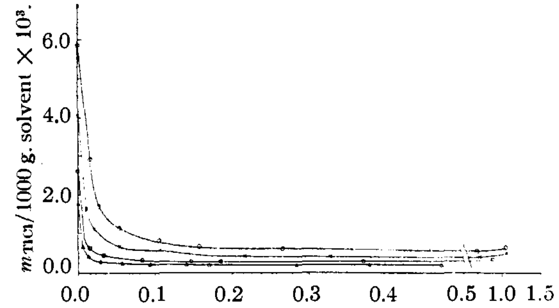

Fig. 2.—Alcohol solubility: ○, 30%; ×, 40%; □, 50%; △, 60%.

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(10) Debye and Hückel, *Physik. Z.*, **24**, 185, 305 (1923).

(11) G. Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

(12) Cases analogous to thallium chloride are the slightly dissociated cadmium halides; for interpretation of thermodynamic data of cadmium bromide see Bates, THIS JOURNAL, **61**, 308 (1939).

Hückel limiting law. It is then a simple matter to extrapolate the curve to a value of $\mu = 0$; the value of $\log K_0$ is then obtained at this point.

Table VI gives a summary of the results of this method of approximation.

TABLE VI

VALUES OF K_0 (BY THE METHOD OF APPROXIMATION)

Alcohol, %	m_{TlCl}	Slope exp. [Equation 6]	Slope theor. [Equation 7]	K_0
0.00	0.00086	1.00	1.00	0.22
10.00	.00070	1.14	1.14	.136
30.00	.000290	1.45	1.44	.083
40.00	.00020	1.60	1.68	.060
51.25	.000100	1.94	1.96	.050
60.00	.000060	2.50	2.36	.038

The value of $K_0 = 0.22$ in water may be compared with Onsager's[1] value of 0.31 obtained from conductance data. An estimate of the uncertainty in K_0 is ±10%. Although not as precise as might be desired, these constants are very difficult to obtain from other sources. While methods for the determination of the ionization of weak acids and bases in water and water-like solvents are available from cell measurements and solubility data, conductance measurements are the only other source of data which allows ionization constants of salts to be calculated in general. In view of the difficulty of extrapolating conductance measurements of salts which are only partially ionized, as most thallium salts are thought to be, it is doubtful if such data would give a value of K_0 of much greater precision than those obtained above. It would, of course, be very desirable to have an independent check on the above method of approximation.

The above treatment enables one to calculate a value of $(1/m_{\pm})_{\mu=0}$ corrected for association; these values are given in Table VII and described in the next section of this paper. In this calculation the value $K'_s = m_{\text{Tl}^+} m_{\text{Cl}^-}$ is used rather than $K' = m_{\text{Tl}^+} m_{\text{Cl}^-}/m_{\text{TlCl}}$ in order that the value $(1/m_{\pm})_{\mu=0}$ could be corrected for association.

TABLE VII

EXTRAPOLATED VALUES OF $(1/m_{\pm})_{\mu=0}$ IN THE ALCOHOL–WATER MIXTURES

Alcohol, %	m_{TlCl} (ions)	$\log K_0/K'_s$	$(1/m_{\pm})_{\mu=0}$[a]
0.00	0.01536	−0.0517	73.3
10.00	.01096	.046	101.4
30.00	.00556	.055	204.2
40.00	.003858	.048	290
51.25	.002465	.046	451
60.00	.001726	.046	644

[a] The values of the solubility products $K_{\text{s. p.}}$ may now be calculated from these data by means of the relationship $K_{\text{s. p.}} = (m_{\pm})^2_{\mu=0}$.

Calculation of Activity Coefficients.—The activity coefficients may be evaluated by means of the following relationship derived from Equations (3), (4), (5) and (6).

$$(1/m_{\pm})_{\mu=0} = \frac{1}{(m_{\text{Tl}^+})(m_{\text{Cl}^-})}\left(\frac{K'}{K^0}\right)^{1/2} \qquad (8)$$

where m_{Tl^+} and m_{Cl^-} are the stoichiometric molalities of these ions corrected for association. The details of the calculations are shown in Table VII; the values of m_{TlCl} (ions) are the values of the solubility in pure solvent less the concentration of un-ionized thallium chloride.

The "stoichiometrical activity coefficients"[12] may now be evaluated in the manner of Lewis[8]; $(m_{\pm})_{\mu=\mu}$ is calculated in the same manner as for a completely ionized salt. The so-called "stoichiometric activity coefficients" will then contain all deviations from ideality, and be referred to the infinitely dilute and completely ionized solution. The treatment of the previous section correcting for association then becomes an extrapolation device. The activity coefficients given in Table VIII have been calculated by this method. The values of $(1/m_{\pm})_{\mu=\mu}$ were taken from smooth curves of the data of Tables I to V.

TABLE VIII

STOICHIOMETRICAL ACTIVITY COEFFICIENTS OF THALLOUS CHLORIDE IN THE ALCOHOL–WATER MIXTURES

	0%	10%	30%	40%	50%	60%
0.001	0.961[a]	0.958	0.930	0.924	0.952	0.895
.001793						.867(s)
.002571					.861(s)	
.004058				.849(s)		
.00500	.912	.907	.846	.838	.828	
.005855			.838(s)			
.0064						.776
.01	.875	.854	.799	.781	.754	.728
.01166		.846(s)				
.01612	.848(s)[b]					
.02	.831	.819	.737	.707	.660	.629
.05	.757	.739	.634	.583	.523	.472
.07	.723	.695	.589	.533	.472	.417
.10	.682	.645	.536	.471	.414	.361
.15	.631	.584	.471	.415	.351	.299
.20	.595	.545	.423	.366	.309	.258
.25	.563	.511	.382	.340	.275	.230
.36		.455		.286	.225	.185
.49		.408		.243	.184	.151
.563		.390		.222		
.60	.519		.320			
.70	.459					
.81		.327				
.90						
1.00						
1.026		.288	.282			

[a] Data from "Int. Crit. Tables," The McGraw-Hill Book Company, New York, N. Y., 1930, Vol. VII, p. 319.

[b] The values at saturation are indicated by (s).

TABLE IX

Alcohol, %	Molality of Tl$^+$ and Cl$^-$ ions at saturation	$-\text{Log } K'_s$	$-\text{Log } K^0$	$-\text{Log } \gamma'_s$	Mole fraction (x) of ions $\times 10^{+4}$	$-\text{Log } X\gamma'_s$	$1/D$
0	0.01536	0.5612	0.675	0.0517	27.65	3.612	0.01274
10	.01096	.7755	.868	.046	21.01	3.723	.01375
30	.00556	.9722	1.082	.066	12.25	3.967	.01636
40	.003858	1.1282	1.225	.048	9.16	4.086	.01818
51.25	.002465	1.2592	1.305	.046	6.275	4.248	.0202
60	.001726	1.3525	1.445	.046	4.897	4.356	.02125

It is of interest to note that the values of the activity coefficients, γ, in saturated solutions (s) (Table VIII) are independent of the solvent, as has been observed by Ricci and Davis.[13] The limits of accuracy of the value of $(1/m_{\pm})_{\mu=0}$ have been set from a consideration of the extrapolated values of the log $1/m_{\pm}$ *vs.* $\sqrt{\mu}$ curves.

Solubility as a Function of the Dielectric Constant.—This relationship may be considered by means of the Scatchard[14] treatment of the Born[15] equation for the relation between the free energy of an ionic system and the dielectric constant of the solvent. The relation is

$$RT \ln x_D \gamma' - RT \ln x_w \gamma' = \frac{N\epsilon^2 Z_1 Z_2}{2b}\left(\frac{1}{D} - \frac{1}{D_w}\right) \quad (9)$$

x_D is the mole fraction of solute in the saturated solution of dielectric constant D, and x_w is the corresponding value in water, ϵ is the unit electrostatic charge of the valence, b the ionic radius, γ' is the activity coefficient; the term RT ln $x_D\gamma'$ represents the free energy of the ionic system in a solvent of dielectric constant D and the term RT ln $x_w\gamma'$ is the free energy for the system in water.

Since the Born equation applies only to the concentration of *ions* in equilibrium with the saturated solution, it will be necessary to correct the solubility data for association as well as for interionic attraction from the relationship

$$\log \gamma'_s = {}^1/_2(\log K_0 - \log K'_s)$$

The logarithm of the solubility, x, corrected for dissociation and for interionic attraction, γ'_s, is plotted against the reciprocal of the dielectric constant, Fig. 3, and see Table IX. These data (Fig. 3) indicate that the Born equation gives the order of magnitude of the solubility in water-like solvents down to dielectric constants of about 40 but deviations from the predicted behavior are found at these values of the dielectric constant.

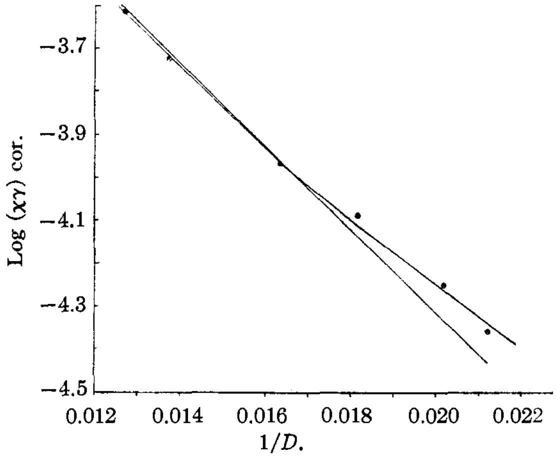

Fig. 3.

The problem of treatment of such data in solvents of low values of the dielectric constant has been discussed by others[16] who discussed the effect of ion clustering[17] as well as the changing values of nearest approach, a. Davis, Ricci and Sauter conclude that "a complete prediction of solubilities in light of modern theories would involve an estimation of the solubility by the corrected Born equation followed by a calculation of solvent segregation around the ions, a redetermination then of the ionic solubility and a determination of the Bjerrum ion association using the Kraus and Fuoss method of calculation." Such a procedure seems to be the necessary one unless one wishes to use a thermodynamic approach in which the solubility is expressed as a function of the free energy change due to ion (or molecule) sublimation and subsequent solvation of that ion (or molecule).[18] Such a procedure may prove to be a useful one for the treatment of solutions for which the use of the limiting law and the Born equation becomes complex.

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[13] Ricci and Davis, THIS JOURNAL, **62**, 407 (1940).

[14] Scatchard, *Chem. Rev.*, **3**, 383 (1927).

[15] Born, *Physik. Z.*, **1**, 45 (1920).

[16] See Davis, Ricci and Sauter, THIS JOURNAL, **61**, 3274 (1939), who give excellent references to other literature. These authors discuss the effect of the low dielectric on the a values as well as the K values.

[17] Bjerrum, *Kfl. Dankse Vidensk. Selskab*, **7**, No. 9 (1926).

[18] For treatment of energy changes on sublimation see Born, *Ber. deut. physik. Ges.*, **21**, 13 (1919), who discussed lattice energies. For a treatment of solvation of gas ions see Fajans, *ibid.*, **21**, 549, 714 (1919); Born, *Z. Physik*, **1**, 4 (1920); Webb, THIS JOURNAL, **48**, 2589 (1926).

Summary

1. The solubility of thallous chloride has been determined in alcohol–water mixtures of 10, 30, 40, 50 and 60% alcohol by weight, and with added potassium chloride. The densities of these solutions are given.

2. From these data, the activity coefficients of thallous chloride in each of the solvents have been calculated over a range of ionic strength. A correction for incomplete dissociation has been applied to the measurements.

3. The behavior of thallous chloride as a function of the dielectric constant has been compared with the predictions of the Born relation, and found to conform as to the order of magnitude, but shows deviations from the theory which increase as the dielectric constant decreases.

4. It is pointed out that these data permit the comparatively easy evaluation of the dissociation constant of a partially dissociated electrolyte.

COLUMBUS, OHIO RECEIVED OCTOBER 7, 1940

[CONTRIBUTION FROM THE MENDENHALL LABORATORY OF PHYSICS, THE OHIO STATE UNIVERSITY]

Spectroscopic Evidence for Intermolecular Hydrogen Bonds between Phenylacetylene and Various Organic Solvents

BY SPENCER C. STANFORD[1] AND WALTER GORDY[2]

In 1935 Kumler[3] suggested that the association of hydrogen cyanide is due to a —C—H ← N bond. The known examples of hydrogen bonds involving the —C—H linkage have been extended during the past few years by molecular polarization,[4] solubility and heat of mixing studies,[5] as well as by measurements of infrared absorption spectra. It has been found that in the haloforms and some other halogenated hydrocarbons[5,6] the hydrogen bonded to carbon is sufficiently active to form hydrogen bonds with organic oxygen and nitrogen compounds such as ethers, ketones, esters, amines and amides. Infrared spectroscopic measurements[7] have verified these results in the case of the haloforms, chloroform and bromoform.

Recent solubility and heat of mixing experiments[8] provide evidence that acetylene and phenylacetylene may act as proton donors in the presence of the organic solvents mentioned previously. We have undertaken the researches reported here to ascertain whether electron-donor solvents such as amines and ethers produce in the acetylenic CH of phenylacetylene perturbations which may be attributed to hydrogen bonding. If any CH group in phenylacetylene should donate its proton, it would probably be the CH joined through the triple bond to the remainder of the molecule, as this is the CH group which has the strongest acid properties.[9] Fortunately the ≡C—H vibrational band occurs in a region sufficiently removed from that of the ordinary aromatic and aliphatic CH bands that it can be easily separated from them.

Experimental.—The instrument, cells and general technique used have been described.[10] The cell thickness was 0.002 cm.; the effective slit width was 0.01 μ. The instrument was calibrated before and after the determination of each band, and as an added precaution each band was checked at least twice. The shifts are accurate to 0.01 μ; the intensities may be somewhat in error due to the difficulty of reproducing the thickness of the very thin cells. One to one volume mixtures were used for all determinations.

Results and Discussion

The experimental data are plotted in Figs. 1–3. The solid lines represent the experimentally determined transmission curves; the broken lines represent the theoretical transmission curves which the mixtures should give if there were no interaction between the components of the mixture. The method of calculation of the theoretical curves has been described elsewhere.[11]

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