Hoecker method of plot should in principle never lead to a constant slope except when A is zero. Within experimental error, however, in case A is not equal to zero, the plot can be considered constant in extremely dilute solutions.

It might thus be concluded that the Hoecker method is less sensitive to a systematic error in P_1 when measurements are made in very dilute solutions. In more concentrated solutions, however, it is applicable only to those solutions where little or no slope in the usual polarization curves is obtained.

The calculated moments using the P_∞ values obtained by both methods are in excellent agreement as reference to Table II will show. It suggests that the Hoecker method could be used to evaluate the moments of substances of limited solubility.

In the last column of Table II are given for comparison some of the dipole moments obtained by other workers. The agreement between our results and those of Mueller for nitrobenzene and chlorobenzene is excellent. Upon considering the measuring technique, reproducibility of results and agreement with previous workers, it might be concluded that the dipole moments reported here are within 1 per cent. of their actual value in the non-polar solvents used.

Summary

1. The dipole moments of nitrobenzene, *m*-nitroaniline, benzamide, ethyl benzoate, chlorobenzene, *d,l*-pinene, 3,6-dichloro-2,5-dimethoxybenzoquinone and 2,3-dichloro-5,6-dimethoxybenzoquinone were measured in either benzene or dioxane as the non-polar solvent.
2. The method of computing molecular polarizations suggested by Hoecker has been considered and found quite satisfactory under the proper conditions. It is suggested that this method be applied to measurements made on relatively insoluble compounds.
3. The abnormal behavior in polarization curves frequently obtained in very dilute solutions appears to be due to experimental error in measuring P_1 and thus has no physical significance.

COLLEGE PARK, MARYLAND RECEIVED FEBURARY 1, 1943

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

The Activity Coefficients of Thallous Chloride in Ethylene Glycol–Water Solutions Determined by E. m. f. and Solubility Data at 25°

BY OTIS D. BLACK AND A. B. GARRETT

Electromotive force and solubility data on thallous chloride in ethylene glycol–water solutions serve to supplement the data on a thermodynamic study of thallous chloride in alcohol–water solutions.[1]

Ethylene glycol lends itself well to the study of the relative solvation–dielectric constant effects because of its dihydric character. The cell data are used to determine (a) the value of $(1/m_\pm)_{\mu=0}$ and (b) the values of γ to saturation; the solubility data are used to determine the value of γ above saturation and also to give a qualitative idea of the degree of dissociation of thallous chloride.[2]

Experimental

The temperature was 25.00 ± 0.01°. The solubility data were obtained in the manner previously described.[1] The samples were analyzed by potentiometric titration with a silver electrode, using an excess of standard potassium iodide as the precipitant and back titrating with standard silver nitrate. A few drops of nitrobenzene were used in each sample to reduce the solubility of the thallous iodide (reduce the reverse reaction) as was recommended for silver chloride by Caldwell and Moyer.[3]

The Cell.—The Ag/AgCl/TlCl/Tl-Hg cell was used.[4] The silver chloride electrodes were prepared by chloridizing *999 fine* silver in 0.05 *m* hydrochloric acid at 5 volts with an initial amperage of 150 ma. This procedure gave a firm white coating of silver chloride. The electrodes reached equilibrium rapidly and gave a potential difference of less than 0.1 mv. among themselves. New electrodes were prepared for each cell. Cell data were first obtained for thallous chloride in pure water and compared with similar data obtained by Cowperthwaite, LaMer and Barksdale.[5] Agreement was obtained in the activity coefficients to within 0.2 of 1%.

The e. m. f. of the cells was measured with a Leeds and Northrup type K-2 potentiometer. The standard cell was calibrated by a cell certified by the National Bureau of Standards.

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(1) Hogge and Garrett, THIS JOURNAL, **63**, 1089 (1941).

(2) The symbols used throughout this paper are consistent with those used by Lewis and Randall "Thermodynamics," The McGraw-Hill Book Co., New York, N. Y., 1923.

(3) Caldwell and Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

(4) Carmody, THIS JOURNAL, **51**, 2905 (1929).

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

Solutions.—Conductivity water was used throughout. Oxygen was removed by boiling; the solutions were then cooled to room temperature under an atmosphere of purified nitrogen. All solutions were prepared on weight basis. The thallous chloride was prepared by the method described by Hogge and Garrett.[1] The ethylene glycol used in this work and in the study of the lead chloride-ethylene glycol-water systems,[6] was from three sources: (1) Eastman Kodak Co. specially purified, (2) redistilled and (3) oxygen-free ethylene glycol shaken with calcium oxide and redistilled. All other chemicals used were reagent quality.

The Data

The cell data are given in Table I and are shown in Fig. 1. The activity coefficients are calculated from the equation

$$E = E_0 - \frac{2RT}{nF} \ln m\gamma$$

which at 25° rearranges to

$$-\log \gamma = \left[\frac{E}{0.1183} + \log m\right] - \left(\frac{E_0}{0.1183}\right)$$

TABLE I

VALUES OF $\left[\frac{E}{0.1183} + \text{LOG } m\right]$ OF THALLOUS CHLORIDE AT ROUND VALUES OF THE IONIC STRENGTH[a]

$\mu^{1/2}$	Glycol, % 20	40	60	80	100
0.1160	3.8030(s)				
.1060		3.7615(s)			
.1000	3.7930	3.7525			
.0972			3.6710(s)		
.0890				3.5885(s)	
.0802					3.5100(s)
.0800	3.7795	3.7405	3.6530	3.5855	
.0600	3.7665	3.7240	3.6325	3.5470	3.4670
.0400	3.7530	3.7075	3.6115	3.5190	3.4245
.0200	3.7395	3.6905	3.5910	3.4910	3.3800
.0000	3.7260	3.6735	3.5690	3.4625	3.3360

[a] Values at saturation are indicated by (s).

The reproducibility of the cells was ±0.1 mv. All values are referred to the standard state of infinite dilution in the particular solvent used. The agreement among the cells can be shown by calculating the value of E(s) for the cell reaction

$$\text{AgCl(s)} + \text{Tl(s)} \longrightarrow \text{Ag(s)} + \text{TlCl(s)}$$

at saturation; here the value of E(s) is independent of the solvent. The values of E(s) so calculated for the different solvent concentrations have a maximum variation of ±0.3% (the average value of E(s) is 0.6735 v. for this Tl–Hg amalgam used).

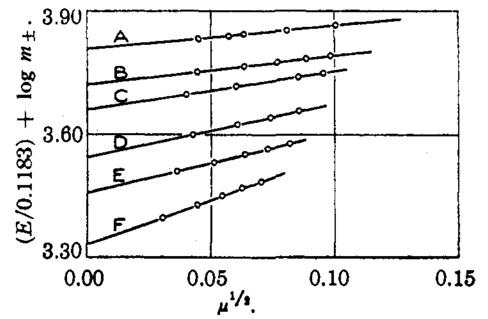

Fig. 1.—A, Water; B, 80% water; C, 60% water; D, 40% water; E, 20% water; F, ethylene glycol.

The solubility data are summarized in Table II and are shown in Figs. 2 and 3. The common ion effect is quite pronounced even in 100% glycol (dielectric constant 37.8). From these data the values of γ were calculated and are given in Table III. The accuracy of the values of γ is determined primarily by the accuracy of $(1/m_{\pm})_{\mu=0}$ and $(1/m_{\pm})_{\mu=\mu}$. These are accurate to ±0.5%, making the maximum probable error in γ not more than ±1%.

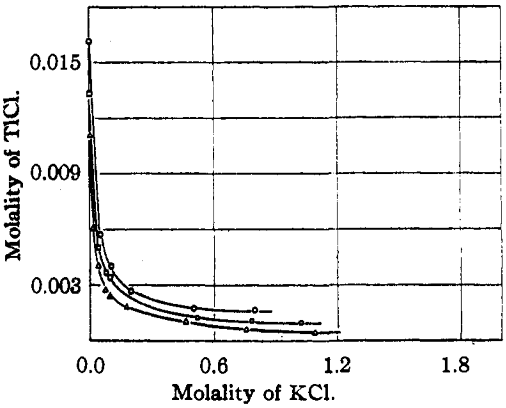

Fig. 2.—O, Water; □, 80% water; △, 60% water.

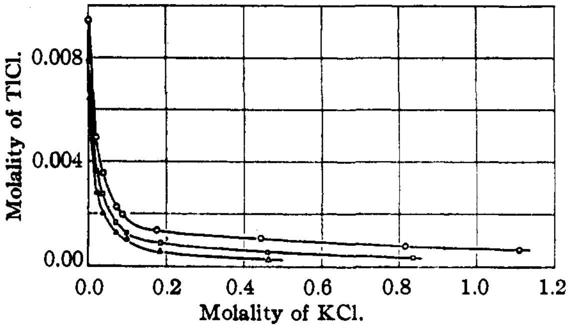

Fig. 3.—O, 40% water; □, 20% water; △, ethylene glycol.

The values of the solubility product of thallous chloride may be obtained from the values of $(1/m_{\pm})_{\mu=0}$ where $K_{\text{s.p.}} = (m_{\pm})^2_{\mu=0}$. These values are given in Table IV.

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[6] Kiefer, M.Sc. Thesis, and Bryant, M.Sc. Thesis, The Ohio State University, 1941. See Garrett, Noble, Kiefer and Bryant, THIS JOURNAL, 65, 293 (1943). To be followed by a paper by Garrett, Kiefer and Bryant in THIS JOURNAL.

Table II

Solubility of TlCl in Water–Glycol Solutions with Added KCl at 25.00 ± 0.01°

20% Glycol		40% Glycol		60% Glycol		80% Glycol		100% Glycol	
m_1[a]	m_2[b]	m_1	m_2	m_1	m_2	m_1	m_2	m_1	m_2
0.0000	0.01340	0.0000	0.01116	0.0000	0.00944	0.0000	0.00792	0.0000	0.00644
.0196	.00761	.0190	.00616	.0178	.00496	.0184	.00368	.0181	.00284
.0391	.00507	.0381	.00409	.0355	.00351	.0367	.00274	.0362	.00203
.0783	.00410	.0762	.00281	.0710	.00221	.0734	.00154	.0725	.00128
.0978	.00371	.0952	.00239	.0888	.00199	.0918	.00124	.0906	.00110
		.1904	.00180	.1775	.00135	.1834	.00084	.1812	.00054
.5253	.00135	.4759	.00123	.4437	.00108	.4589	.00051	.4530	.00015
.7879	.00124	.7615	.00054	.7099	.00065	.7341	.00026		
1.0501	.00110	1.1423	.00051	1.0649	.00050				

[a] m_1 is molality of KCl. [b] m_2 is molality of TlCl.

Table III

Values of the Activity Coefficients of Thallous Chloride at Round Values of the Ionic Strength[a]

Temperature 25.00 ± 0.01°. % glycol by weight.

μ	0[b]	20	40	60	80	100
0.000	1.000	1.000	1.000	1.000	1.000	1.000
.001	0.957	0.953	0.950	0.917	0.890	0.827
.004	.921	.911	.895	.848	.807	.721
.00644						.673(s)
.007	.897	.880	.861	.808	.763	.668
.00792					.749(s)	
.00944				.791(s)		
.010	.881	.862	.833	.780	.732	.635
.01120			.817(s)			
.01340		.835(s)				
.01617	.848(s)					
.040	.777	.739	.695	.642	.605	.503
.070	.718	.665	.622	.581	.551	.454
.100	.680	.615	.576	.544	.518	.427
.300	.529	.470	.441	.430		
.500	.450	.414	.387	.379		
.700	.395	.380	.357	.349		
1.000	.345	.349	.332	.326		

[a] Values at saturation are indicated by (s). [b] Calculated from solubility data from "Int. Crit. Tables," McGraw-Hill Book Co., New York, N. Y., 1930, Vol. VII, p. 321, with accurate value of $(1/m_\pm)_{\mu=0}$ obtained from e. m. f. data.

Table IV

Values of $K^*_{s.p.}$ and Slopes of Plot of Log γ *vs.* $\sqrt{\mu}$ for Thallous Chloride in Water–Glycol Solutions

Glycol concn., %	$K^a_{s.p.}$	E. m. f. slope	Theoretical slope
0	1.92×10^{-4}		0.51
20	1.25×10^{-4}	0.67	.58
40	0.831×10^{-4}	0.78	.67
60	$.558 \times 10^{-4}$	1.03	.81
80	$.352 \times 10^{-4}$	1.57	1.07
100	$.188 \times 10^{-4}$	2.18	1.62

[a] $K_{s.p.} = (m_\pm)^2_{\mu=0}$.

In Table IV are given the theoretical and experimental slopes for the plot of the log γ *vs.* $\sqrt{\mu}$. Following the interpretation of Hogge and Garrett[1] with respect to the thallous chloride–alcohol–water system, it seems probable that the deviations from the theoretical slope may be due to the moderately low degree of dissociation rather than to changing *a* values. Accordingly the values of the ionization constants, K_0, were calculated by the method used in the thallous chloride–water–alcohol system[1]; these values are given in Table V.

Table V

Value of K_0 Found by Method of Approximation[1]

% Glycol	m_{TlCl}	Experimental slope	Theoretical slope	K_0
0	0.0009	1.0	1.0	0.22[a]
20	.0011	1.17	1.16	.10
40	.0012	1.34	1.34	.06
60	.0010	1.60	1.61	.05
80	.00016	2.12	2.14	.24
100	.000005	3.2	3.23	4.6

This calculation of K_0 on the basis of the assumption of a small amount of association seems to fit the data well until a concentration of approximately 60% glycol is reached. Beyond this point the value of K_0 so calculated begins to increase and reaches a value of 4.6 at 100% glycol. This rapid increase in the calculated value of K_0 indicates that probably some factor other than association is the important one in this high glycol concentration range. If we assume that the ionic size increases better agreement will be obtained between theoretical and experimental limiting slopes, but no reasonable ionic size will give a value accounting for K_0 becoming larger than unity. Probably solvation, or glycolation, is the most important factor after 60% glycol is reached. It is of interest to note that the discontinuity in the curve of the plot of log K_0 *versus* mole fraction of water occurs at a mole fraction of water of approximately 0.67. This corresponds to the hydrate $C_2H_4(OH)_2 \cdot 2H_2O$ reported by de Forcrand.[7] The possibility of glycolation of the thallium ion is suggested indirectly by evidence obtained by Kiefer and Bryant,[6] in their study on the ethylene glycol–water–lead chloride system in

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[7] de Forcrand, *Compt. rend.*, **132**, 688 (1901).

TABLE VI

SOLUBILITY OF THALLOUS CHLORIDE IN MIXED SOLVENTS AT 25 ± 0.01°

(The solubility of thallous chloride is given in moles per 1000 g. solvent; the mole fraction of organic solvent is N_2; the mole fraction of H_2O is N_1; $N_1 + N_2 = 1$).

% H_2O by volume	Glycol–Water Density	Glycol–Water N_2	Glycol–Water TlCl	Dioxane–Water Density	Dioxane–Water N_2	Dioxane–Water TlCl	Morpholine–Water Density	Morpholine–Water N_2	Morpholine–Water TlCl
100	0.997	0.000	0.01617	0.997	0.000	0.01617	0.997	0.000	0.01617
80	1.025	.073	.01340	1.015	.052	.00924	1.011	.050	.01125
60	1.053	.177	.01116	1.028	.121	.00413	1.027	.121	.00680
40	1.077	.326	.00944	1.035	.257	.00139	1.034	.240	.00278
20	1.096	.564	.00792	1.035	.474	.00073	1.030	.457	.00101
0	1.110	1.000	.00644	1.027	1.000	.00031	0.996	1.000	.00020

which the formation of a glycolated lead ion was established. This feature of the work is now under investigation by means of electrical conductivity studies.

It was of interest to compare the effect of several solvents on the solubility of thallous chloride. Such data were obtained and are given in Table VI and are shown in Fig. 4. It is apparent from the comparison of the solubility data that ethylene glycol has the most pronounced solvation effect of the solvents studied.

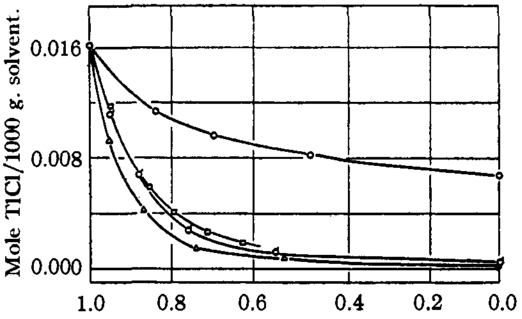

Fig. 4.—○, Ethylene glycol-water; □, ethyl alcohol-water; ȯ, 1 4-morpholine–water; △ 1,4-dioxane-water.

It also was of interest to compare the solubility of thallous chloride with the dielectric constant of the solvent for several different systems. That is shown in Fig. 5. A comparison of this graph with Fig. 4 indicates the pronounced effect of solvation as compared with the dielectric constant effect in these systems. This is consistent with the conclusions of Kraus,[8] who claims the effect of solvent character is the primary effect.

Acknowledgment.—The authors wish to acknowledge the splendid assistance of Miss Eleanor Young who analyzed many of the solutions used in this work; financial aid was given Miss Young by the National Youth Administration, Ohio State University Project Number 174.

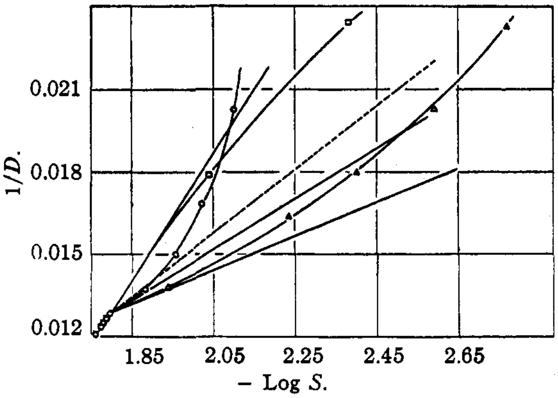

Fig. 5.—○, Ethylene glycol-water; □, 1,4-dioxane-water; △, ethyl alcohol-water (Hogge); ȯ, glycine-water (Failey).

Summary

1. The cell Tl-Hg/TlCl/AgCl/Ag was studied in water, 20, 40, 60 and 80% ethylene glycol-water solutions and in ethylene glycol.
2. The solubility of thallous chloride was studied in 20, 40, 60 and 80% ethylene glycol-water-potassium chloride solutions and in ethylene glycol-potassium chloride solutions.
3. Activity coefficients, solubility product constants and ionization constants of thallous chloride were calculated from the e. m. f. and the solubility data in 20, 40, 60 and 80% ethylene glycol-water solutions and in ethylene glycol.
4. Solubility data are tabulated for thallous chloride in solutions of ethylene glycol-water, morpholine-water, and dioxane water.

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(8) Kraus, *Science*, 90, 281 (1939).