phosphorus. An array of easily prepared $SiCl_3(NCO)$, $SiCl_2(NCO)_2$, $SiCl(NCO)_3$, and $SiCl_3(SCN)$ compare with $PCl_2(NCO)$ alone. Silicon fluorobromides are all stable,[5] while PF_2Br and $PFBr_2$ were somewhat unstable.[6]

3. Phosphoryl and thiophosphoryl mixed halides are more stable than those of tervalent phosphorus. Booth and Seabright concluded this also[7] on the basis of fluorohalides. $POCl_2(SCN)$ or $POCl_2Br$ *versus* apparently unstable $PCl_2(SCN)$ or PCl_2Br.[8]

The author is indebted to Professor G. S. Forbes of this Laboratory for helpful suggestions. Other investigations are under way.

Summary

1. Two new chlorothiocyanates, $SiCl_3(SCN)$, b. p. 129.5°, and $POCl_2(SCN)$, b. p. 173°, have been prepared; one new chloro(iso)cyanate, $PCl_2(NCO)$, b. p. 104.4°, also has been synthesized. Their chief physical properties have been determined. $PCl(NCO)_2$ was also indicated, but rearranged too rapidly for feasible isolation.

2. $PCl_2(NCO)$ is fairly stable at 25°, whereas $PCl(NCO)_2$ is considerably less stable.

3. A comparison of the stability of various mixed halides of silicon and phosphorus is presented.

CAMBRIDGE, MASS. RECEIVED MAY 4, 1944

(5) Schumb and Anderson, THIS JOURNAL, **58**, 994 (1936).

(6) Booth and Frary, *ibid.*, **61**, 2934 (1939).

(7) Booth and Seabright, *ibid.*, **65**, 1834 (1943), and references therein.

(8) See, however, T. Mitobedski, *Chem. Abstracts*, **27**, 474 (1933).

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

The Electrical Conductivity of Thallous Chloride Solutions of Ethylene Glycol–Water

BY A. B. GARRETT AND SIMON J. VELLENGA

The purpose of this investigation was to study the equilibria of thallous chloride in ethylene glycol–water solutions from electrical conductivity data. This supplements a study of these equilibria by e. m. f. and solubility data in this solvent mixture[1] and in alcohol–water mixtures[2] by solubility measurements. A method for determining dissociation constants of thallous chloride was developed in that study.[2]

The dissociation constants in ethylene glycol–water have a minimum value at 60% glycol.[1] This unpredicted effect required further investigation; it was deemed desirable to determine the dissociation constants of thallous chloride by the conductance method.

Experimental

1. **Ethylene Glycol.**—The ethylene glycol was purified by the method of Smyth and Walls[3] in which the ethylene glycol was distilled three times under reduced pressure using the middle fraction of the distillate each time. The boiling point under the reduced pressure was about 90°. The first distillate was shaken with anhydrous sodium sulfate and the second and third distillates were kept under nitrogen in glass-stoppered bottles. In the distillation under reduced pressure a stream of purified nitrogen was passed through the ethylene glycol in the still by means of a capillary to prevent bumping.

2. **Thallous Chloride.**—Thallous chloride was prepared by means of the method of Hogge and Garrett.[2]

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

The conductances of the samples were determined by means of the Jones electrolytic conductance bridge. The oscillator used was an 8-A oscillator, manufactured by the Western Electric Company. It was adjusted to give a frequency of 2400 cycles. The conductivity cells incorporated the Jones and Bollinger[4] feature which has the filling tubes as far apart as possible. The cells were suspended in an oil thermostat bath at 25 ± 0.005° by a Thyratron controlled circuit. The ethylene glycol–water samples and the thallous chloride solvent mixtures were all made up by weight. All work was done under nitrogen; the samples were transferred to the cells under nitrogen pressure.

Cells were rinsed at least seven times with the solution to be used before they were filled. The resistances of the samples were determined after temperature equilibrium had been reached. This required approximately an hour. The weight molality was transformed into volume molarity by use of the density of the solvent.[5]

TABLE I

ELECTRICAL CONDUCTANCE OF THALLOUS CHLORIDE IN WATER

	Molarity, m	Λ_0
A	Data from Bray and Winninghoff, THIS JOURNAL, **33**, 1663 (1911); Δ = legend	
	0.00507	143.10
	.00604	142.25
	.01000	139.00
	.01108	138.35
	.01607	135.4
B.	Data from "International Critical Tables," **6**, 232, 257; ○ = legend	
	0.002	146 (extrapolated)
	.005	142.9
	.010	138.8
	.0167	135.3
C.	Data from this Research; x = legend	
	0.00150	148.40
	.00750	141.13
	.01501	136.03

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(1) Black and Garrett, THIS JOURNAL, **65**, 862 (1943).

(2) Hogge and Garrett, *ibid.*, **63**, 1089 (1941).

(3) Smyth and Walls, *ibid.*, **53**, 2115 (1931).

(4) Jones and Bollinger, *ibid.*, **53**, 411 (1931).

(5) Black, Ph. D. Thesis, The Ohio State University, 1942.

TABLE II

ELECTRICAL CONDUCTIVITY OF THALLOUS CHLORIDE IN ETHYLENE GLYCOL–WATER SOLUTIONS

80% Water–20% ethylene glycol		60% Water–40% ethylene glycol		40% Water–60% ethylene glycol		20% Water–80% ethylene glycol		100% Ethylene glycol	
m^a	$\Lambda_c{}^b$	m	Λ_0	m	Λ_0	m	Λ_0	m	Λ_0
0.00123	96.66 ohms⁻¹	0.00043	63.26	0.00046	37.51	0.00082	20.55	0.00084	9.82
.00139	96.42	.00056	61.70	.00151	36.44	.00118	20.30	.00103	10.00
.00168	96.13	.00102	61.99	.00173	36.26	.00127	20.39	.00121	9.82
.00181	96.08	.00125	61.76	.00254	35.76	.00160	20.26	.00171	9.73
.00343	94.50	.00133	61.27	.00408	35.22	.00252	19.83	.00412	9.26
.00374	94.26	.00157	61.34	.00567	34.72	.00444	19.31	.00431	9.27
.00494	93.31	.00162	61.34						
.00526	93.29	.00286	60.42						
.00757	92.00	.00306	60.20						
.01321	89.86	.00312	60.33						
		.00335	59.88						
		.00498	59.09						
		.00529	59.16						
		.00921	58.06						

[a] m = molality. [b] Λ_0 in ohms⁻¹.

Data.—The experimental data for the equivalent conductivity, Λ_c, at various molarities of thallous chloride are given in Tables I and II and shown in Fig. 1. Λ_c values are ±0.01 ohm.

Values of Λ_c were obtained for pure water and compared with literature data in Table I. The agreement is good.

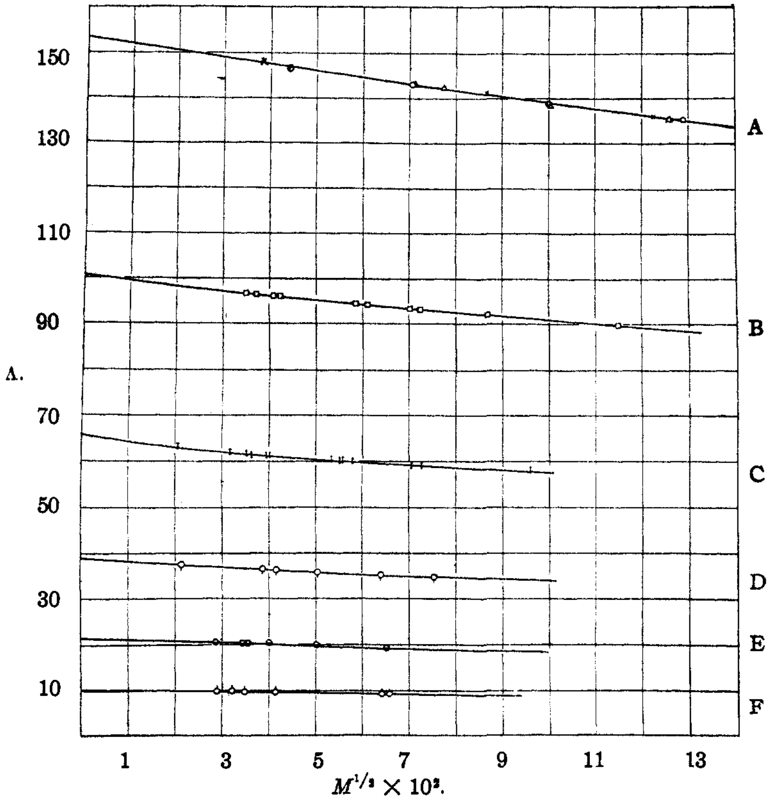

Fig. 1.—The conductivity, Λ, of solutions of TlCl in A, water; B, 80% water–20% ethylene glycol; C, 60% water–40% ethylene glycol; D, 40% water–60% ethylene glycol, E, 20% water–80% ethylene glycol; and F, 100% ethylene glycol.

The values of the ionization constants, K, were calculated by the Davies[6] modification of the Onsager[7] equation

$$K = k\gamma_{\pm}^2 = \frac{\Lambda_0^2 m \gamma_{\pm}^2}{\Lambda^1(\Lambda^1 - \Lambda_c)} \quad (1)$$

where

$$\Lambda^1 = \Lambda_\infty - (A + B\Lambda_\infty)\sqrt{\frac{\Lambda_0}{\Lambda^1}m} \quad (2)$$

$$k = \frac{m_{\mathrm{Tl^+}} \cdot m_{\mathrm{Cl^-}}}{m_{\mathrm{TlCl}}} \quad (3)$$

m is the molarity, γ is the mean activity coefficient, Λ_∞ is the equivalent conductivity at infinite dilution, $A = 82.4/(DT)^{1/2}\eta$, $B = 8.2 \times 10^5/(DT)^{3/2}$, D is the dielectric constant, T is the absolute temperature, and η is the viscosity.

The data used for determining dissociation constants are at rounded concentrations. Activity coefficients were taken from data of Black and Garrett[1]; dielectric constants from the data of Akerlof[8]; viscosities were taken from the "International Critical Tables."[9]

The ionization constants of thallous chloride are calculated by Equation (1) and are tabulated in Table III, Col. 2. It is to be noted that these values of K vary with concentration and that they are not in complete agreement with the values of K calculated from cell data[1] (see Column 5).

Table III gives a summary of the dissociation constants as determined by various methods.

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(6) Davies, *Trans. Faraday Soc.*, **23**, 351 (1927); **26**, 592 (1930); **27**, 621 (1931); **28**, 609 (1932).

(7) Onsager, *Physik. Z.*, **27**, 388 (1926); *ibid.*, **28**, 277 (1927).

(8) Akerlof, THIS JOURNAL, **54**, 4125 (1932).

(9) "International Critical Tables," Vol. V, p. 22.

TABLE III

SUMMARY OF DATA ON DISSOCIATION CONSTANTS OF THALLOUS CHLORIDE

% Ethylene glycol in water	Molar concn. TlCl	K (Eq. 1)	K^a Shedlovsky method	K^b Black and Garrett[1]
0%	0.0000	...	0.23	0.22
	.0009	0.25		
	.0016	.21		
	.0020	.24		
	.0030	.25		
	.0050	.27		
20%	0.0000	...	0.14	0.09
	.0009	0.06		
	.0016	.07		
	.0020	.09		
	.0030	.10		
	.0050	.14		
40%	0.0000	...	0.06	0.05
	.0009	0.023		
	.0016	.032		
	.0020	.037		
	.0030	.047		
	.0050	.063		
60%	0.0000	...	0.04	0.04
	.0009	0.023		
	.0016	.031		
	.0020	.033		
	.0030	.041		
	.0050	.053		
80%	0.0000	...	0.05	0.21
	.0009	0.030		
	.0016	.034		
	.0020	.036		
	.0030	.044		
	.0050	.048		
100%	0.0000	...[c]	0.10[c]	4.6[c]
	.0009	0.03		
	.0016	.06		
	.0020	.06		
	.0030	.07		
	.0050	.05		

[a] Shedlovsky, *J. Franklin Inst.*, **225**, 739–743 (1938) (a graphical method similar in treatment to Eq. 1.) [b] These are corrected for the α term in the equation $-\log \gamma = C\sqrt{\alpha m}$. These values calculated in the earlier publication will differ slightly due to the fact that they were calculated by the equation $-\log \gamma = c\sqrt{m}$. [c] K (Eq. 1) for 100% ethylene glycol are not consistent due to the small value of $(\Lambda^1 - \Lambda_0)$ in the denominator $K = \Lambda_0^2 m\gamma_{\pm}^2/\Lambda^1(\Lambda^1 - \Lambda_0)$. A small error in either Λ^1 or Λ_0 will cause a large variation in K.

The lack of complete agreement of values of K determined with known reliable equations requires further interpretation of the data.

Λ_c and γ are from experimental data which are presumably reliable. The value m is also an experimental value, but there is a possibility of association or triple ion formation such as Tl_2Cl^+ and $TlCl_2^-$ which would reduce the molar concentration, m, from that based on the formula thallous chloride. This has precedence.[10] If the equilibria

$$Tl^+ + Cl^- \longrightarrow TlCl$$

and

$$TlCl + Tl^+ \longrightarrow Tl_2Cl^+$$

and

$$TlCl + Cl^- \longrightarrow TlCl_2^-$$

occur it is easily understood why, in 100% ethylene glycol, the equivalent conductance seems to remain at nearly the same value even though it is a quite low value. At higher concentrations of thallous chloride an abundance of Tl_2Cl^+ and $TlCl_2^-$ ions might exist which would carry the current, however, meagerly. On dilution the equilibrium is shifted forming

$$Tl_2Cl^+ \longrightarrow TlCl + Tl^+$$
$$TlCl_2^- \longrightarrow TlCl + Cl^-$$

with the resulting Tl^+ and Cl^- association to form thallous chloride units. Therefore, the increase of conductivity to be expected does not materialize appreciably with increasing dilution. It is surprising that this occurs at such high values of dielectric constant (see later discussion of the possibility of sorting solvent molecules).

It must be noted that the same error in m would appear in the calculations of K from both the cell data the conductance data where the value of $\sqrt{m}$ or $\sqrt{\mu}$ is involved. Also an error in m would make a difference in the calculation of the "stoichiometrical" constant, k, defined as $k = \Lambda_c^2 m/\Lambda^1(\Lambda - \Lambda_c)$ and as $m_{Tl^+} \cdot m_{Cl^-}/m_{TlCl}$. The values of k were calculated for the conductivity data from the expression $\Lambda_c^2 m/\Lambda^1(\Lambda^1 - \Lambda_c)$; for the cell data $m_{Tl^+} \cdot m_{Cl^-}/m_{TlCl}$ was used but the value of m was adjusted by an approximation method to fit the experimental data to the slope as given by the limiting law (see refs. 1 and 2). The values of k calculated from the cell data will contain the error due to the incorrect value of m as well as any error made in assuming that the dielectric constant of the ion atmosphere is the same as the "dielectric constant of the solution." The error in m is distributed in both terms of the ratio $m_{Tl^+} \cdot m_{Cl^-}/m_{TlCl}$ whereas it appears only in the numerator of the ratio $\Lambda_c^2 m/\Lambda^1(\Lambda^1 - \Lambda_c)$ and in the $\sqrt{m}$ in the correction term used to obtain Λ^1. These seem to be the major sources of error and a probable reason for differences in ionization constant values calculated by the two methods.

Another explanation of these changing K values with changing concentration is that there may be a sorting of the solvent molecules by the solute (thallous chloride). It is to be noted that the minimum in the K values coincides with the position in compound formation of $C_2H_4(OH)_2 \cdot 2H_2O$. On one side of this point there would be more water molecules and on the other more ethylene glycol molecules for solvation. This might ac-

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[10] See Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, p. 268, for the Tl_2^{++} ion in solution; also see Kraus and Fuoss, THIS JOURNAL, **55**, 476 (1933), for effect of solvent on double and triple ion formation.

count for the minimum in the K values at approximately 60% glycol.

This solvent sorting effect may serve to reduce the value of the "microscopic" dielectric constant (in the immediate neighborhood of the ion) below the value of the macroscopic dielectric constant of the mixture so that triple ion formation may occur more readily. It is very probable that absorption spectra studies must be made to give further information on this issue.

It appears that the values of the dissociation constants of thallous chloride in various mixtures of ethylene glycol and water as determined by Black and Garrett[1] are reasonable. This research corroborates their values and suggests possible reasons for the seemingly anomalous behavior which the previous work showed to exist in this thallous chloride–ethylene glycol–water system.

Summary

1. The equivalent conductances of various concentrations of thallous chloride in water, 20, 40, 60 and 80% ethylene glycol in water, and in ethylene glycol were determined.

2. Dissociation constants of the thallous chloride in the various solvents were calculated by various methods.

3. An increase in the thermodynamic dissociation constant with concentration was attributed to association, to triple ion formation, or sorting of solvent molecules.

COLUMBUS, OHIO RECEIVED AUGUST 1, 1944

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

The Molecular Condition of Phenols in Benzene Solution

BY JOHN A. DAVISON[1,2,3]

The early freezing point measurements made by Auwers and Beckmann[4] in aprotic solvents demonstrated that many organic solutes exhibited molecular weights which were much greater than their formula weights. In addition, the molecular weight was observed to vary with the concentration. These investigators divided the compounds that they had studied into three principal classes according to the manner in which the molecular weight varied with concentration.[5]

By far the largest class consisted of polar organic compounds such as ketones, amines, nitro compounds and mercaptans, which gave a small, steady rise in molecular weight as the concentration was increased. Weak hydrogen bonds and dipole–dipole orientation prevail here.

A second distinct group comprised the carboxylic acids. The molecular weight appeared to increase very rapidly at low concentrations, levelling off at approximately double the formula weight. An equilibrium exists between the single and double molecules.[6] The picture of the dimer has been established as an eight-membered ring, in which each acidic hydrogen atom resonates between two oxygen atoms.

The third group included phenols, alcohols, anilides and oximes, whose molecular weights increased almost linearly and apparently without limit as the concentration increased. The infrared absorption spectra of their solutions have shown the existence of hydrogen bonds. Since there is very little possibility of ring formation in these compounds, aggregates of all orders probably are present in equilibrium with one another. Lassettre[7] has shown that once the exact equation connecting the molecular weight with the concentration is known, it is possible to calculate the set of equilibrium constants corresponding to the formation of these aggregates. In using this approach it is assumed that the deviations from the laws of perfect solutions are due to the presence of polymers. It is, therefore, necessary to work in sufficiently dilute solutions so that other deviations from these laws will not interfere. The present work was undertaken in order to cover the range of high dilutions, supplementing the work which has been done over a period of years by users of the Beckmann technique.

Apparatus and Experimental Method

The apparatus used in this work was especially designed to measure freezing points of solutions at 0.002 to 0.10 molal. The freezing point measurement was made with a sensitive thermel and a potentiometer. The principle of the method was to place one arm of the thermel in an equilibrium mixture of pure liquid benzene and solid benzene and the other arm in a mixture of the benzene solution and solid benzene. The apparatus was designed so that both freezing mixtures had the same thermal environment. The twin cell freezing point apparatus was entirely similar to that described by Kraus.[8]

Procedure.—The apparatus was carefully examined while in an unassembled condition and dried in an oven at about 50°. It was then assembled outside the thermo-

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[1] This paper is based on a dissertation presented by John A. Davison to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1942.

[2] George L. Harrison Fellow in Chemistry, 1939–41; du Pont Fellow in Chemistry, 1941–42. Present address: General Laboratories, United States Rubber Company, Passaic, New Jersey.

[3] The author gratefully acknowledges the assistance and guidance of Professor Martin Kilpatrick throughout this investigation.

(4) See Lassettre, *Chem. Rev.*, **20**, 259 (1937).

(5) Beckmann, *Z. physik. Chem.*, **2**, 715 (1888).

(6) MacDougall, THIS JOURNAL, **58**, 2585 (1936).

(7) Lassettre, *ibid.*, **59**, 1383 (1937).

(8) (a) Kraus and Vingee, *ibid.*, **56**, 511 (1934); (b) Batson and Kraus, *ibid.*, **56**, 2017 (1934).