Conductance of Thallous Chloride in Dioxane–Water Mixtures at 25°[1]

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Abstract: The conductance of thallous chloride at 25° has been measured in dioxane–water mixtures covering the range $78.54 \geqslant D \geqslant 21.98$ in dielectric constant. The association constant K_A increases as D decreases at about the same rate as that of the alkali halides, but is about an order of magnitude larger at a given value of dielectric constant. Assuming mutual polarization of the ions in a TlCl pair to produce dipoles which then are attracted by the inducing charges, an extra energy $u_p = (\epsilon^2/2n^4r_0^4)(\alpha_1 + \alpha_2)$ stabilizes the pair in addition to the charge-charge energy ϵ^2/aD. (ϵ = unit charge, n^2 = short-range dielectric constant $\approx$ square of index of refraction of salt, r_0 is internuclear distance in the pair, and α = polarizability.) The factor $\exp(u_p/kT)$ equals 13, which agrees with the observed increase in association constant of thallous chloride over that of the alkali halides. The limiting single ion conductance for Tl^+ is 73.74.

Thallous salts, especially the halides, are classical examples of "incompletely dissociated" 1:1 electrolytes. Various explanations of the difference between them and other 1:1 salts such as the alkali halides have been proposed, including partial covalent bonding and mutual polarization. In order to learn quantitatively how the thallous salts differ from the alkali halides, we measured the conductance of thallous chloride in a series of mixtures of water and dioxane, covering the range down to a dielectric constant of 20, where association of 1:1 salts due to cation–anion attraction is considerable ($K_A \approx 100$). It was found that a plot of the logarithm of association constant K_A of thallous chloride against reciprocal dielectric constant was nearly parallel to the curve for potassium chloride, showing that the usual electrostatic ion pairing was taking place, but the curve for thallous chloride lies about 1 decade higher on the log K_A–$(1/D)$ diagram, showing that some additional force stabilizes a TlCl ion pair after Coulomb forces have brought the ions into contact. If, instead of rigid charged spheres as the model for the ions, a positive nucleus in a spherical cloud of negative charge is used to represent the ions, dipoles are induced in the ions when they approach to short distances, and these dipoles are attracted by the charges which induce them. Calculation of the corresponding energy by classical electrostatic theory shows that the polarized ion pair is more stable than a rigid sphere pair by about 10×10^{-14} erg. The corresponding Boltzmann factor in the theoretical association constant is 13, which agrees with the experimental observations.

Experimental Section

Thallous chloride (Harshaw, random cuttings from melt-grown crystals) was recrystallized once from water (1.8 g/100 ml of boiling water). It was dried for 20 hr at 100° and kept over phosphorus pentoxide. The product was a fine crystalline powder, which dissolved only very slowly at room temperature in the solvents used. Consequently, portions were weighed into a weighed amount of solvent in the conductance cell (after determining solvent conductances); the cell was tightly capped and warmed to about 50° to dissolve the salt. The cell was then cooled from the bottom, to condense back the solvent which had condensed on the cap and walls, and then reweighed to check that no solvent had been lost.

Dioxane (Matheson Coleman and Bell) was refluxed for 3 days over potassium hydroxide and fractionally distilled. The vapor pressure chromatogram showed no impurities beyond a trace of water (which was harmless since measurements were to be made in dioxane–water mixtures). The water used was laboratory distilled water, boiled and allowed to cool under nitrogen; conductance 1–2 $\times 10^{-6}$. The physical properties of the solvents are given in Table I, where w is weight % dioxane, D is dielectric constant (measured at 1 Mc), ρ is density, η is viscosity, and σ_0 is solvent conductance.

Table I. Solvent Properties

No.	w	D	ρ	100η	$10^6\sigma_0$
1	0.0	78.54	0.9971	0.8903	1.58
2	19.8	61.60	1.0142	1.301	1.20
3	35.8	47.98	1.0260	1.661	0.92
4	43.6	41.25	1.0301	1.820	0.32
5	53.6	32.64	1.0344	1.968	0.39
6	58.2	28.63	1.0358	2.006	0.38
7	66.2	21.98	1.0366	1.988	0.22

Electrical equipment, cells, and technique have already been described.[3] The cells were calibrated[4] using aqueous potassium chloride solutions or by comparison; the constants were 1.07677, 0.51361, and 0.038757. Repeated calibrations checked within 0.01%.

The conductance data are summarized in Table II, where c is concentration (equiv/l. at 25 ± 0.003°) and Λ is equivalent conductance.

Discussion

The data were analyzed to determine the three parameters, Λ_0, K_A, and $\mathring{a}$, of the conductance equation[5]

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + E'c\gamma \ln \tau^2\gamma +$$
$$L(a)c\gamma - K_A c\gamma f^2 \Lambda \quad (1)$$

where Λ_0 is limiting conductance, K_A is association constant, a is center-to-center contact distance, S and E' are theoretical coefficients deriving from long-range ionic interaction, τ^2 is proportional to concentration ($\tau^2 = 6E_1'c$), and f is the limiting activity coefficient,

(3) J. E. Lind, Jr., and R. M. Fuoss, *J. Phys. Chem.*, 65, 999 (1961).
(4) J. E. Lind, Jr., J. J. Zwolenik, and R. M. Fuoss, *J. Am. Chem. Soc.*, 81, 1557 (1959).
(5) R. M. Fuoss, L. Onsager, and J. F. Skinner, *J. Phys. Chem.*, 69, 2581 (1965), eq 2.4.

Table II. Conductance of Thallous Chloride in Dioxane–Water Mixtures at 25°

$10^4 c$	Λ	$10^4 c$	Λ	$10^4 c$	Λ
$D = 78.54$		$D = 47.98$		$D = 28.63$	
68.567	140.88	31.546	73.86	13.497	46.10
48.859	142.62	22.247	75.32	10.108	47.84
37.247	143.80	16.987	76.29	8.150	49.04
26.741	145.04	12.678	77.19	6.318	50.32
18.960	146.08	9.048	78.07	4.712	51.60
12.958	147.06	6.187	78.86	3.367	52.85
8.064	148.01	3.968	79.59	2.185	54.12
67.188	140.97	$D = 41.25$			
41.204	143.34			$D = 21.98$	
30.733	144.50	29.310	62.73	5.2037	39.08
22.747	145.52	21.791	64.22	3.9485	40.82
15.896	146.51	17.093	65.31	2.9514	42.51
10.686	147.42	13.225	66.31	2.3114	43.82
6.627	148.30	10.400	67.16	1.8042	45.00
		7.318	68.16	1.3669	46.17
$D = 61.60$		4.767	69.12	0.9947	47.29
37.689	99.50	$D = 32.64$			
23.974	101.08				
17.391	101.97	20.930	51.09		
12.569	102.74	14.883	53.02		
9.332	103.31	11.875	54.18		
6.400	103.94	8.892	55.50		
3.986	104.56	6.403	56.78		
		4.339	58.02		
		2.766	59.19		

Table III. Derived Constants

D	Λ_0	K_A	$å$	σ
78.54	151.11	5.2 ± 0.5	5.5 ± 1.0	0.012
61.60	106.51	10.2 ± 1.4	6.8 ± 1.7	0.013
47.98	81.87	25.2 ± 0.6	6.3 ± 0.4	0.004
41.25	72.22	41 ± 2	4.3 ± 0.9	0.014
32.64	62.41	116 ± 2	6.1 ± 0.5	0.010
28.63	57.84	205 ± 4	3.8 ± 0.6	0.010
21.98	51.93	875 ± 20	9.2 ± 1.7	0.012

$\exp(-\tau\gamma^{1/2})$. The results are summarized in Table III, where σ, in the same units as Λ, is the standard deviation

$$\sigma^2 = \sum (\Lambda_{calcd} - \Lambda_{obsd})^2/(n - 3) \qquad (2)$$

As seen by the values of σ, the data are quite precisely reproduced by eq 1. The limiting conductance of thallous chloride in water, 151.11, agrees with the value of 151.16 calculated from the data of Bray and Winninghof,[6] which were analyzed, using eq 1; $K_A = 5.3 \pm 1.9$ and $å = 5.0 \pm 2.8$ for these data. By measuring the solubility of thallous iodate in potassium chloride, Bell and George[7] found 0.21 for the dissociation constant of thallous chloride, which corresponds to $K_A = 4.8$, in good agreement with our value of 5.2 ± 0.5.

The contact distances found range from 4 to 9, with a rather large uncertainty. This lack of sharpness in $å$ is a consequence of the low solubility of thallous chloride, which limited the available concentration range; the highest concentrations in Table II correspond to about 80% saturated. At low concentrations in solvents of high dielectric constant, the $Lc\gamma$ term contributes relatively little to the total conductance and is opposed by the association term which likewise varies as $c\gamma$. The

data were also analyzed using the conductance equation[8]

$$\Lambda = \gamma(\Lambda_0 - \Delta\Lambda)[1 + (\Delta X/X)]/[1 + (3\varphi/2)] \qquad (3)$$

which is explicit through terms of order $c^{3/2}$. It is a three-parameter equation, $\Lambda = \Lambda(c; \Lambda_0, a, K_A)$, and has been programmed for the IBM 7090-7094 computer. A sequence of a values was scanned using a program which finds the values of Λ_0 and K_A which minimize σ for a given value of a and a given set of data. When the data cover a wide enough range of concentration, a plot of σ against a shows a minimum[9] which locates the desired value of a; for the data of Table II, the σ–a curves were nearly horizontal for $4.0 \leq å \leq 7.0$, with $\sigma \approx 0.010$ for each system. This result is of course a confirmation of the large $\pm\Delta a$ obtained using (1). The limiting conductances are, however, quite precisely determined, independent of a. Since the L and K_A terms in (1) oppose each other, one would expect that a range of K_A values corresponding to the range of a values would be found such that σ would remain at a minimum of about 0.01. Calculation gives just this result. In Figure 1, the ratio $r = K_A(a)/K_A(4.0)$ is plotted against a; $K_A(4.0)$ is the association constant which minimizes σ for $a = 4.0$ and $K_A(a)$ the constant for any a in the range. In the solvents of higher dielectric constant, where the L and K_A terms are of the same order, K_A changes by about 25% as a increases from 4.0 to 7.0; as dielectric constant decreases, the relative contribution of the L term decreases rapidly, and the minimizing K_A becomes much less sensitive to a. In Figure 2, logarithms of association constants are plotted against reciprocal dielectric constant; the heights of the rectangles correspond to the minimizing values of K_A for $a = 4.0$ and $a = 7.0$. Seen on this scale, the uncertainty in association constants caused by the low range of concentrations covered by the data does not appear serious; it certainly is not enough to obscure the pattern of the large change (over 2 decades) of K_A with solvent composition.

The association constant of thallous chloride is considerably higher than that of most 1:1 salts; the circles in Figure 2 show the association constants for potassium chloride[3] for comparison. As dielectric constant decreases, the association increases, just as it does for other 1:1 salts, showing that K_A for thallous chloride contains a factor $\exp(\epsilon^2/aDkT) = e^b$ due to electrostatic charge–charge attraction in the ion pairs, but clearly an additional force stabilizes the TlCl pair, after Coulomb forces have brought the ions into contact. Mutual polarization has been suggested:[10,11] each ion induces in the other a dipole, and the extra stability for thallous chloride is a consequence of the ion–dipole attraction. (Dipole–dipole attraction is also present, but the corresponding contribution to energy is completely negligible.) George, Rolfe, and Woodward calculated ion–dipole energies for the ground state of a vibrating TlOH ion pair, using an approximating potential function in the wave equation;

(6) W. C. Bray and W. J. Winninghof, *J. Am. Chem. Soc.*, **33**, 1663 (1911).

(7) R. P. Bell and J. H. B. George, *Trans. Faraday Soc.*, **49**, 619 (1953).

(8) R. M. Fuoss and K. L. Hsia, *Proc. Natl. Acad. Sci. U. S.*, **57**, 1550 (1967); **58**, 1818 (1967).

(9) A. D. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **72**, 4710 (1968).

(10) J. H. B. George, J. A. Rolfe, and L. A. Woodward, *Trans. Faraday Soc.*, **49**, 375 (1953).

(11) M. H. Panckhurst, *Australian J. Chem.*, **15**, 194 (1962).
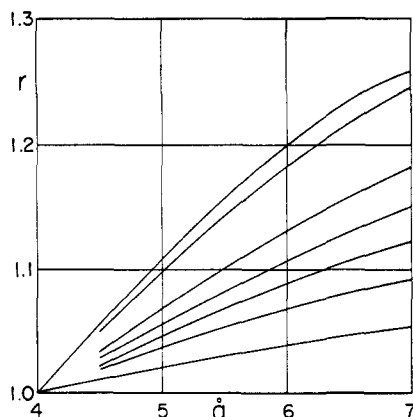
Figure 1. Correlation of K_A and $\mathring{a}$ parameters which minimize σ.

Figure 2. Dependence of association constants on dielectric constant: $\square$, TlCl; $\triangle$, TlNO$_3$; $\bigcirc$, KCl.

their values range from 1.1 to 14.6 $\times$ 10^{-14} erg, as the dielectric constant decreases from 80 to 1.0. These energies are small enough to justify calculation by the much simpler classical methods, where the problem of dielectric constant can be handled by a realistic approximation. Panckhurst has calculated the ion–dipole attraction by classical electrostatics, but concluded that "on a dielectric continuum model neither dielectric saturation of the solvent nor polarization of the ions can account for the association" of thallous salts in aqueous solutions; this conclusion, however, was the consequence of using the macroscopic dielectric constant of 80 for *all* center-to-center ionic distances. After contact, there is no solvent between the ions, except in the case of solvent-separated pairs, and here the dielectric constant must be far less than 80 due to dielectric saturation.[12] Since the polarization force varies as the inverse *fifth* power of distance, its contribution to the total binding energy of an ion pair must come from the very short range of distances immediately preceding the final equilibrium position, and the contributions from large distances are completely negligible. This r^{-5} dependence suggests a model which should be a close approximation to reality. Consider the case of two spherical ions of charges ϵ_1 and ϵ_2 and polarizabilities α_1 and α_2, at a distance r apart in a medium of dielectric constant D. Assume that ion–ion attraction brings them together to peripheral contact at a center-to-center distance a; during the approach, dipoles $\mu_1(r)$ and $\mu_2(r)$ are being induced in the ions. After initial contact at a, assume that the ions are distorted so that the internuclear distance is reduced to r_0, where $r_0 < a$. Approximate the dielectric constant by a step function such that D has the macroscopic value D_∞ for $r \geq a$ and is set equal to n^2 for $r_0 \leq r < a$, where n^2 is the electronic part of the dielectric constant of the ions. It is assumed that no solvent remains between the ions. Then the dipole moments

$$\mu_j = \epsilon_i \alpha_j / D r^2 \qquad (4)$$

in effect develop their full strength

$$\mu_j = \epsilon_i \alpha_j / D r_0^2 \qquad (5)$$

after contact of the bare ions.[13] The potential of a

(12) D. M. Ritson and J. B. Hasted, *J. Chem. Phys.*, **16**, 11 (1948).

(13) Since the contact distance $\mathring{a}$ found from conductance is considerably larger ($\mathring{a} \approx 5$–7) than the lattice distances, the nonconducting pair observed by a conductance measurement probably is the solvent-sepa-
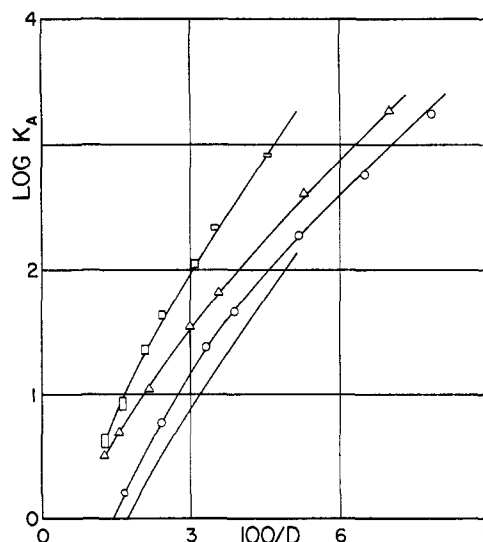
dipole is $V = (\mu/r^2 D) \cos \theta$; the force on the charge ϵ which induces it is $(-\text{grad } V)/D$, because θ is zero, of course. The energy of a pair is then given by

$$u_p = \int_{r_0}^{\infty} (\epsilon_1\epsilon_2/Dr^2 + 2\epsilon_1\mu_2/Dr^3 + 2\epsilon_2\mu_1/Dr^3) \, dr \qquad (6)$$

$$= \int_{r_0}^{\infty} (\epsilon_1\epsilon_2/Dr^2 + 2\epsilon_1^2\alpha_2/D^2r^5 + 2\epsilon_2^2\alpha_1/D^2r^5) \, dr \qquad (7)$$

$$= \int_{r_0}^{a} f(r) \, dr + \int_{a}^{\infty} f(r) \, dr \qquad (8)$$

In the integral over the range $r \geq a$, we set $D = D_\infty$ and drop the polarization terms in $1/D^2r^5$ as negligible compared to the charge–charge term. In the integral from r_0 to a, $D = n^2$ and the charge–charge term is omitted because the centers of the electron clouds of the ions no longer are located at the nuclei; the process occurring in the interval $r_0 \leq r < a$ is by hypothesis a rearrangement of charge to produce the induced dipoles μ_1 and μ_2 by displacement of the electrons with respect to the nuclei. Furthermore the contribution from the integral at the limit $r = a$ may be neglected compared to that from the limit at $r = r_0$; if $a = 2r_0$, the former is only about 6% of the latter because r^{-5} integrates to r^{-4}. The result is

$$u = \epsilon^2/aD + (\epsilon^2/2n^4r_0^4)(\alpha_1 + \alpha_2) \qquad (9)$$

The association constant for polarized ion pairs then is

$$K_A = K_0 e^b e^p \qquad (10)$$

where

$$p = (\epsilon^2/2n^4r_0^4kT)(\alpha_1 + \alpha_2) \qquad (11)$$

and K_0 is the factor which allows for the excluded volume. To evaluate p, values of n, r_0, α_1, and α_2 are

rated pair of solvated ions. Then solvent may be ejected to give a bare pair, after which the distortion to produce the final dipole moments is completed. Corresponding to this, the step function which would approximate the dielectric constant would be $D = D_\infty$ for $r \leq a$, $D = n_s^2$ for $a - d \leq r < a$, where d is the diameter of a solvent molecule and n_s^2 is the square of the index of refraction of the solvent, and $D = n^2$ for $r_0 \leq r < a - d$. The model with a single step in $D(r)$ will, however, be shown to suffice.

needed. The square of the index of refraction of solid thallous chloride will be used to approximate the short-range dielectric constant; extrapolation of Barth's data[14] to infinite wavelength gives $n = 2.13$. For r_0, we use 2.48×10^{-8} cm, the internuclear distance in thallous chloride vapor.[15] Heydweiller[16] gives molecular refractions 9.73 and 8.22 for the thallous and chloride ions, from which $\alpha_1 = 3.86 \times 10^{-24}$ and $\alpha_2 = 3.26 \times 10^{-24}$. Substituting these numerical values in (11), we find $p = u_\mu/kT = 2.57$ and $u_\mu = 10.6 \times 10^{-14}$ erg for the polarization energy. Now $e^{2.57} = 13.0$; that is, the association constant of thallous chloride should be 13 times larger than the association constant of a salt with the same size ions but whose net charges remain fixed at the centers. The solid curve of Figure 2 is a plot of $e^{-2.57}K_A(\text{TlCl})$; it lies fairly close to the curve for potassium chloride. The curve for thallous nitrate[9] (triangles in Figure 2) runs nearly parallel to the curve for potassium chloride, but higher by about 0.3 and lower than the curve for thallous chloride. Since the electrons of the nitrate ion are packed around four nuclei, it should be less polarizable than the chloride ion and, with its distributed charge, might polarize the thallous ion less than the chloride ion does; then the multiplier e^p would be smaller for the nitrate than for the chloride, which is the observed result.

The dependence of mobility on solvent composition for thallous chloride is similar to that of the alkali halides: the Walden product is high in water (1.34), goes through a maximum, and decreases as the polar content of the solvent decreases. If we assume that the transport numbers are independent of solvent composition, the single ion conductances can be computed, using Longsworth's value[17] of $n(\text{Cl}^-) = 0.5094$ for the limiting transport number of the chloride ion in potassium chloride, and Chiu's value[18] of $\Lambda_0(\text{KCl}) = 149.93$. These data give $\lambda_0(\text{Cl}^-) = 76.37$; from our value $\Lambda_0(\text{TlCl}) = 150.11$ from Table III, we then have $\lambda_0(\text{Tl}^+) = 73.74$, in practically perfect agreement with the value 73.75 which we obtained from thallous nitrate.[9] From the single ion conductances in the mixed solvents, Stokes radii R_s are calculated

$$R_s = 0.8194 \times 10^{-8}/\lambda_0 \eta \qquad (12)$$

The dependence of R_s on dielectric constant is shown in Figure 3; in the water-rich mixtures, the curve goes through a minimum, like lithium and sodium chlorides. In this region, the change of R_s reflects both the change in the solvent from a structured hydrogen-bonded medium to a normal fluid as the dioxane breaks up the water structure, and also the dielectric relaxation of the
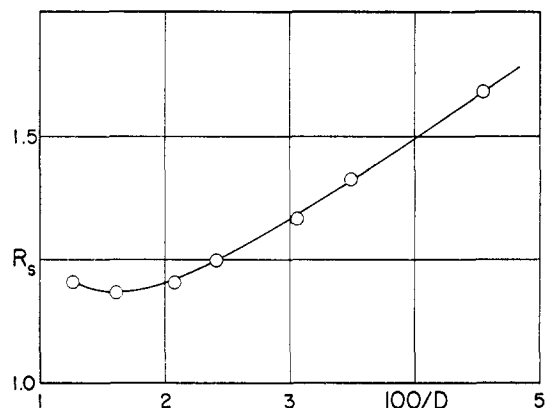

Figure 3. Dependence of Stokes radius on dielectric constant.

medium as the ions move through it.[19] Beyond about 40% dioxane, the Stokes radius becomes linear in $1/D$, showing that the relaxation effect alone is effective. The slope of the linear segment of the curve is 16.6×10^{-8}. Using Zwanzig's theoretical result[20]

$$\partial R_s/\partial D^{-1} = (\tau e^2/9\pi\eta R_\infty{}^3)(1 - \epsilon_\infty/\epsilon_0) \qquad (13)$$

where τ is dielectric relaxation time, R_∞ is the radius of the ion, ϵ_∞ is the infinite frequency dielectric constant, and ϵ_0 is the static dielectric constant, the slope can be evaluated. Neglecting $\epsilon_\infty/\epsilon_0$ compared to unity, and with the value[21] 8.3×10^{-12} sec for τ and an average of 10^{-2} for viscosity, we obtain

$$\partial \overset{\circ}{R}_s/\partial D^{-1} = 815/\overset{\circ}{R}_\infty{}^3 \qquad (14)$$

From the experimental slope, $R_\infty{}^+ = 3.4 \times 10^{-8}$ cm. The curve for the chloride ion parallels the one for the cation and lies close to it $[\lambda_0(\text{Cl}^-) \approx \lambda_0(\text{Tl}^+)]$. The sum of the hydrodynamic radii from the slopes is 6.8×10^{-8}, somewhat larger than the value 5.0×10^{-8} obtained as the contact distance a from the coefficient $L(a)$ in the conductance equation, and equal to twice the sum 3.21×10^{-8} of the lattice radii.[22] On the other hand, the radius R_∞ obtained by extrapolating the linear segment of the curve in Figure 3 to infinite dielectric constant is 1.0×10^{-8}, giving 2.0×10^{-8} for the sum of anionic and cationic radii, much smaller than the other two values. These discrepancies simply mean that the sphere-in-continuum which represents the ion hydrodynamically is different from the sphere which is its electrostatic equivalent. Both models are physical approximations, of course; it probably is the hydrodynamic model which most needs improvement.

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