J. CHEM. SOC. FARADAY TRANS., 1994, 90(13), 1895–1898

Pitzer Model Parameters for Sparingly Soluble Salts from Solubility Measurements: Thallium(I) Chloride in Aqueous Solutions of Ammonium Chloride, Rubidium Chloride and Caesium Chloride at 298.15 K

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Measurements are reported of the solubility of thallium(I) chloride in aqueous solutions of ammonium chloride, rubidium chloride and caesium chloride at 298.15 K at concentrations of added salt up to 4.0 mol kg^{-1}. Pitzer model parameters for TlCl, $\beta^{(0)}$ and $\beta^{(1)}$, were evaluated assuming $C^{\phi} = 0$. These parameters can account satisfactorily for the ionic interactions between Tl^+ and Cl^- without the need to assume ion association explicitly, thus simplifying the interpretation of the experimental data. Although the parameter $\alpha = 2$, which is customarily used for a broad class of electrolytes, is found to be satisfactory for TlCl, larger values of α generally gave better fits to the experimental data. Mixture parameters, θ and ψ, relevant to the various mixed electrolytes are also reported.

There is a general lack of information in the literature regarding Pitzer model parameters for sparingly soluble salts.[1–3] This situation is ascribed to the low solubility of these salts, which precludes evaluation of these parameters in the usual manner using pure solution activity or osmotic coefficient data. Problems arise when it is necessary to estimate the activities of such salts in concentrated brines. Pitzer model parameters for such salts can be obtained indirectly by using activity or osmotic coefficient data for simple mixtures of these salts, the simplest being a three-ion mixture. A convenient method for obtaining the required activity data is to study the solubility of the salt in question in the presence of another salt with a common ion, as is the case in the present study where we report the solubility of thallium(I) chloride in aqueous solutions of ammonium chloride, rubidium chloride and caesium chloride at concentrations of added salt up to 4.0 mol kg^{-1} at 298.15 K.

Thallium (I) chloride has a number of interesting applications for which some knowledge of its solubility and activity in aqueous solutions would be desirable. For example, in view of its similarity in ionic radii, Tl^+ may substitute for K^+ in biological cells and this makes it poisonous to man; but because it is a $d^{10}s^2$ ion, it can be conveniently monitored by spectroscopic, NMR or polarographic techniques so that it can serve as a useful probe for the role of K^+ in biological systems.[4–8] Thallium(I) chloride also finds applications in IR spectrometry.

Experimental

Thallium(I) chloride was prepared by the slow and simultaneous addition of stoichiometric amounts of 0.05 mol dm^{-3} thallium(I) sulfate (BDH, AnalaR) and 0.1 mol dm^{-3} hydrochloric acid (Ajax, UnivaR) in *ca.* 2 dm^3 of rapidly stirred water at *ca.* 333 K. These solutions were filtered prior to mixing to remove insoluble material. The coarse crystalline product was collected on a glass frit, washed several times with doubly distilled water and dried at 383 K. It was stored in the dark. Analysis for thallium gave the purity of the product as (99.9 ± 0.2)%. As before,[1–3,9,10] analysis for thallium was by iodate titration in the presence of concentrated hydrochloric acid, making use of the overall reaction:

$$IO_3^- + 2Tl^+ + 6H^+ = I^+ + 2Tl^{3+} + 3H_2O$$

$$I^+ + Cl^- = ICl$$

The indicator was carbon tetrachloride, and the end-point was visually detected by the disappearance of the purple colouration (due to iodine liberated in an intermediate reaction) in the organic phase. In this work, a 10 cm^3 burette, calibrated and readable to 0.01 cm^3, was used and the standard iodate solutions were prepared so as to deliver titres close to 10 cm^3. Potassium iodate (Ajax, UnivaR, >99.9%) was twice recrystallized from water. Ammonium chloride (BDH, AnalaR), rubidium chloride (Aldrich, 99.9%) and caesium chloride (Ajax, UnivaR, 99.9–100.1%) were used without further purification. Ammonium chloride solutions were prepared directly from the dried salt while the other salt solutions were prepared by weight from stock solutions which were analysed gravimetrically for chloride. Calibrated glassware was used and corrections were made for air buoyancy. The apparatus and further experimental details are given elsewhere.[1–3] Experiments were performed in subdued light as thallium(I) chloride is light-sensitive. However, exposure to light in the course of the experiments, which turned the outer layers of the salt purple, did not have a deleterious effect on the solubility measurements.

Results and Discussion

Table 1 lists the solublity of thallium(I) chloride in aqueous solutions of the added chlorides in the concentration range 0.005–4.0 mol kg^{-1} at 298.15 K. The solid phase in equilibrium with the saturated solutions in all cases is anhydrous TlCl and there is no evidence of mixed solid phases. As expected from the common-ion effect, the solubility decreases with increasing added chloride concentration (Fig. 1). The solubility passes through a minimum and then increases as the concentration of the added chloride increases further. This is consistent with association of ions into pairs, and possibly triplets, at higher added chloride concentrations:

$$Tl^+(aq) + Cl^-(aq) \rightleftharpoons TlCl(aq) \quad (1)$$

$$TlCl(aq) + Cl^-(aq) \rightleftharpoons TlCl_2^-(aq) \quad (2)$$

Consideration of eqn. (1) and (2) complicates the analysis of the solubility data. For example, in determining the ionic strength of the solutions, the fraction of the ions forming the neutral molecule would have to be calculated. Assumptions would also have to be made about its activity coefficient.[12]

Table 1 Solubility and activity coefficient of thallium(I) chloride in the system TlCl (m_A)–MCl (m_B)–H_2O at 298.15 K (solid phase TlCl)

	$m_A/10^{-3}$ mol kg^{-1}			γ_{TlCl}			γ_{Cl^-}			γ_{Tl^+}		
m_B/mol kg^{-1}	NH_4Cl	RbCl	CsCl	NH_4Cl	RbCl	CsCl	NH_4Cl	RbCl	CsCl	NH_4Cl	RbCl	CsCl
0	16.25	16.25	16.25	0.844	0.844	0.844	—	—	—	—	—	—
0.005	14.10	14.11	14.12	0.836	0.837	0.836	0.870	0.869	0.866	0.802	0.806	0.807
0.01	12.34	12.33	12.34	0.826	0.828	0.828	0.862	0.861	0.857	0.791	0.797	0.799
0.02	9.700	9.755	9.766	0.808	0.807	0.805	0.846	0.844	0.840	0.771	0.771	0.772
0.03	8.013	8.027	8.041	0.786	0.786	0.786	0.832	0.829	0.824	0.742	0.746	0.749
0.04	6.807	6.823	6.857	0.768	0.769	0.767	0.818	0.815	0.809	0.721	0.725	0.726
0.05	5.955	5.987	6.025	0.751	0.751	0.748	0.807	0.803	0.796	0.699	0.701	0.702
0.06	5.362	5.355	5.386	0.732	0.734	0.732	0.796	0.792	0.785	0.674	0.681	0.683
0.07	4.858	4.858	4.904	0.719	0.721	0.717	0.787	0.783	0.774	0.657	0.663	0.664
0.08	4.457	4.477	4.532	0.707	0.707	0.702	0.778	0.774	0.764	0.642	0.645	0.645
0.09	4.134	4.158	4.238	0.695	0.694	0.688	0.771	0.766	0.755	0.627	0.630	0.626
0.10	3.896	3.906	3.963	0.682	0.682	0.677	0.763	0.758	0.747	0.608	0.614	0.613
0.20	2.646	2.658	2.721	0.592	0.592	0.585	0.713	0.705	0.689	0.491	0.497	0.497
0.30	2.177	2.200	2.263	0.535	0.533	0.525	0.683	0.673	0.652	0.418	0.422	0.423
0.40	1.942	1.980	2.041	0.491	0.487	0.480	0.662	0.650	0.625	0.364	0.365	0.368
0.50	1.806	1.847	1.916	0.455	0.451	0.443	0.646	0.632	0.605	0.321	0.322	0.326
0.60	1.719	1.769	1.838	0.426	0.421	0.413	0.633	0.618	0.588	0.287	0.287	0.290
0.70	1.659	1.724	1.793	0.402	0.395	0.387	0.623	0.607	0.575	0.259	0.257	0.261
0.80	1.628	1.693	1.764	0.380	0.373	0.365	0.614	0.597	0.563	0.234	0.233	0.237
0.90	1.602	1.677	1.754	0.361	0.353	0.345	0.607	0.589	0.553	0.215	0.212	0.216
1.00	1.585	1.665	1.747	0.344	0.336	0.328	0.600	0.582	0.544	0.197	0.195	0.198
1.50	1.619	1.732	1.836	0.278	0.269	0.262	0.580	0.558	0.514	0.133	0.131	0.133
2.0	1.727	1.861	2.008	0.266	0.225	0.217	0.568	0.545	0.495	0.096	0.093	0.095
2.5	1.874	2.099	2.240	0.200	0.190	0.184	0.562	0.538	0.484	0.071	0.067	0.070
3.0	2.058	2.337	2.528	0.174	0.164	0.158	0.559	0.535	0.477	0.054	0.050	0.052
3.5	2.194	2.648	2.870	0.156	0.143	0.137	0.558	0.535	0.474	0.044	0.038	0.040
4.0	2.548	2.985	3.278	0.136	0.126	0.120	0.559	0.537	0.472	0.033	0.029	0.030

Previous workers have assumed the activity coefficient of neutral molecules in an ionic solution to be unity, but this is strictly valid only at low ionic strength. This problem can be circumvented by using the ionic interaction approach of Pitzer since thallium(I) chloride represents an intermediate type of weak electrolyte so that its interactions may be simply accounted for in terms of virial coefficients without having to refer to an ion association reaction. Thus, ignoring ion association, we have for the system TlCl(m_A)–MCl(m_B)–H_2O, (M = NH_4, Rb, Cs),

$$TlCl(s) \rightleftharpoons Tl^+(aq) + Cl^-(aq) \tag{3}$$

and

$$\ln K_S = \ln P' + 2 \ln \gamma_{TlCl} \tag{4}$$

where K_S is the thermodynamic solubility product of TlCl, γ_{TlCl} is its mean ionic activity coefficient and $P' = m_A(m_A + m_B)$.

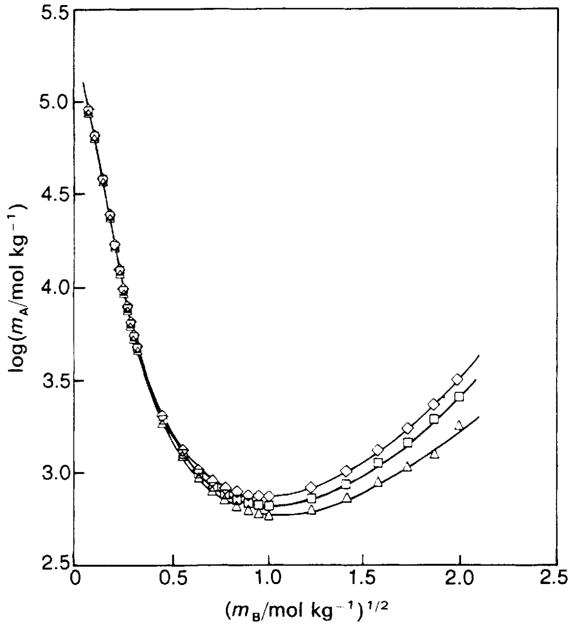

Fig. 1 Effect of added chloride on the solubility of thallium(I) chloride in aqueous solutions at 298.15 K. △, NH_4Cl; □, RbCl; ◇, CsCl.

Pitzer's Equations

We recapitulate the salient features of the Pitzer equations relevant to the present study. The reader is referred to Pitzer's original papers[13–17] for the meaning of the various terms and symbols. The mean ionic activity coefficient of thallium(I) chloride in the system TlCl(m_A)–MCl(m_B)–H_2O is given by the following set of equations:

$$\begin{aligned}\ln \gamma_{TlCl} = {} & f^{\gamma} + mB^{\gamma}_{TlCl} + m_B(B^{\phi}_{MCl} - B^{\phi}_{TlCl} + \theta_{TlM}) \\ & + m_A m_B \theta'_{TlM} + m^2 C^{\gamma}_{TlCl} \\ & + m m_B(C^{\phi}_{MCl} - C^{\phi}_{TlCl} + \tfrac{1}{2}\psi_{TlMCl}) \\ & + \tfrac{1}{2} m_A m_B \psi_{TlMCl}\end{aligned} \tag{5}$$

$$m = m_A + m_B \tag{6}$$

$$f^{\gamma} = -A^{\phi}[\sqrt{m}/(1 + b\sqrt{m}) + (2/b)\ln(1 + b\sqrt{m})] \tag{7}$$

$$\begin{aligned}B^{\gamma}_{TlCl} = {} & 2\beta^{(0)}_{TlCl} + 2\beta^{(1)}_{TlCl}[1 - (1 + \alpha\sqrt{m} - \tfrac{1}{2}\alpha^2 m] \\ & \times \exp(-\alpha\sqrt{m})\end{aligned} \tag{8}$$

$$B^{\phi}_{ca} = \beta^{(0)}_{ca} + \beta^{(1)}_{ca} \exp(-\alpha\sqrt{m}) \tag{9}$$

$$C^{\gamma}_{ca} = (3/2)C^{\phi}_{ca} \tag{10}$$

The subscripts c and a denote cation and anion, respectively. $\beta^{(0)}_{ca}$, $\beta^{(1)}_{ca}$ and C^{ϕ}_{ca} are single electrolyte parameters which have been extensively tabulated by Pitzer and Mayorga[14] for several electrolytes, but not sparingly soluble electrolytes. It is one of the objectives of our ongoing investigation to evaluate these parameters for a sparingly soluble salt such as thallium(I) chloride. For 1 : 1 electrolytes, C^{ϕ} is usually very small and it is found here and previously that C^{ϕ}_{TlCl} can be set equal to zero without affecting the fit of the experimental data. The parameters θ_{TlM}, θ'_{TlM} and ψ_{TlMCl} pertain to the mixtures. It is customary to set θ'_{TlM} equal to zero. Then θ_{TlM} and ψ_{TlMCl} can be evaluated alongside $\beta^{(0)}_{TlCl}$ and $\beta^{(1)}_{TlCl}$ by linear regression using the procedure described previously.[2,3] The $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} values for the added chlorides required in the calculations are taken from the compilation of Pitzer and Mayorga[14] (Table 2). It is also customary in the Pitzer formalism to fix $b = 1.2$ for all solutes in aqueous solution and A^{ϕ}, the Debye–Hückel coefficient, is numerically equal to 0.3915 in water at 298.15 K. The results of the calculations are shown in Table 3. These were obtained assuming $\alpha = 2$ in eqn. (8) and (9), which is the value used by Pitzer and other workers for 1 : 1 electrolytes.

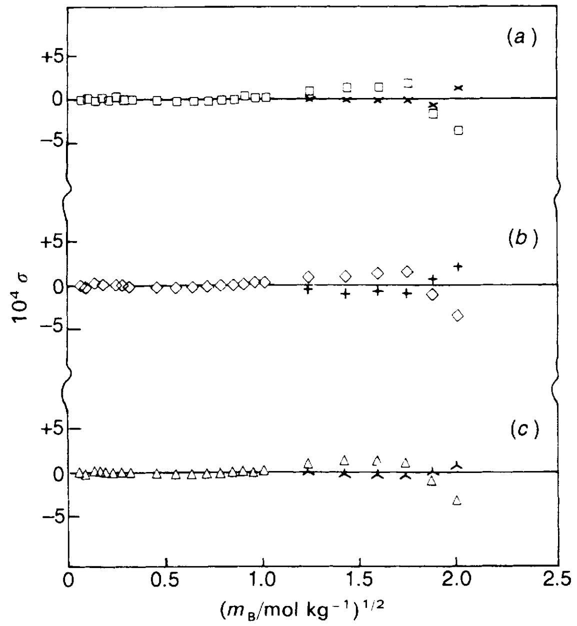

Fig. 2 Fit of the Pitzer equations shown as plots of differences, σ, between experimental solubilities and solubilities calculated using $\alpha = 2$ and the best-fit value of α for each mixture. (a) NH_4Cl: □, $\alpha = 2$; ×, $\alpha = 5$. (b) RbCl: ◇, $\alpha = 2$; +$\alpha = 6$. (c) CsCl: △, $\alpha = 2$; ⅄, $\alpha = 4$.

Since $\beta^{(0)}$, $\beta^{(1)}$ and K_S are properties of the pure electrolyte, they should have the same values for thallium(I) chloride, irrespective of the mixture in which it is present. Table 3 shows that the values of these parameters are reasonably consistent for all the mixtures. To determine whether this will apply over a broad range of mixtures, measurements are being extended to other mixtures, such as asymmetrical mixtures of the type $TlCl–MCl_2–H_2O$, in which higher-order electrostatic effects can be quite pronounced. The Pitzer approach is thus successful in describing the ionic interactions in the systems. A further indication of the quality of fit of the Pitzer model can be found in Fig. 2, in which differences between experimental results and those calculated using $\alpha = 2$ and the best-fit α values for each mixture are plotted as a function of $m_B^{1/2}$. Best-fit values of α pertaining to each of the mixtures are reported in Table 4, together with values of the associated parameters. Fig. 2 shows that whereas the fit of the experimental data is good up to *ca.* 1 mol kg^{-1} with α equal to two, the fit in each case can be extended to a higher concentration if a higher α value is used. In principle, a different value of α for each solute is permissible, but b must be the same for all solutes. However, α should preferably be kept the same for a broad class of electrolytes so that a systematic and meaningful relationship between the $\beta^{(0)}$ and $\beta^{(1)}$ values can be obtained. The poorer fit of the experimental data at higher concentrations could also suggest that as the proportion of $TlCl_2^-$ ion in solution increases, $\beta^{(1)}$ may become less able to absorb the effects of triplet ion interaction, in which case a $\beta^{(2)}$ term could be added, as in the case of bivalent metal sulfates.[15] Also a larger value of α may be more appropriate for an intermediate type of weak electrolyte such as thallium(I) chloride.

Table 2 Pitzer model single electrolyte parameters for aqueous solutions of added chlorides at 298.15 K[a]

MCl	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	validity range/mol kg^{-1}
NH_4Cl	0.0522	0.1918	−0.00301	6
RbCl	0.0441	0.1483	−0.00101	5
CsCl	0.0300	0.0558	0.00038	5

[a] Ref. 14.

Table 3 Pitzer model single electrolyte and mixture parameters for thallium(I) chloride in $TlCl–MCl–H_2O$ systems at 298.15 K assuming $C^{\phi} = 0$

MCl	$\beta^{(0)}$	$-\beta^{(1)}$	θ_{TlM}	$-\psi_{TlMCl}$	10^4K_S	ref.
HCl	−0.10	1.29	0.0462	0.0919	1.867	2
LiCl	0.01	1.29	−0.0777	0.0879	1.880	3
NaCl	−0.07	1.26	0.0130	0.0657	1.873	2
KCl	−0.06	1.35	0.0464	0.0774	1.865	3
NH_4Cl	0.03	1.31	−0.0505	0.0659	1.880	this work
RbCl	0.02	1.19	−0.0874	0.0590	1.888	this work
CsCl	0.01	1.21	−0.0731	0.0597	1.888	this work

One may also consider the ionic strength dependence of θ_{TlM} which arises from the higher-order limiting law, but this has been shown to be insignificant for activity coefficients under the present level of experimental precision.[15] Indeed, calculations show that the fit of the experimental data is often worse if the higher-order limiting law is included in the analysis of the data.[1,2]

The mean ionic activity coefficient of TlCl in each of the mixtures studied in this work has been calculated using eqn. (4) and the K_S values in Table 3. The results are given in Table 1. A referee has commented that the apparent variation between the data for the different mixtures could be removed by considering single ionic activity coefficients. The concentration of TlCl in the solutions is so low that the activity coefficient of the Cl^- ion is almost entirely controlled by the NH_4^+, Rb^+ and Cs^+ ions. Hence, it should be possible to calculate single ionic activity coefficients for the Cl^- ion using the Pitzer model by assuming pure MCl and combine

Table 4 Best-fit values of α for thallium(I) chloride in the various added chloride systems

added chloride	α	$-\beta^{(0)}$	$\beta^{(1)}$	$-\theta$	ψ	$10^4\ K_S$
NH_4Cl	5	0.31	1.45	0.0302	0.0460	1.881
RbCl	6	0.32	1.50	0.0777	0.0634	1.869
CsCl	4	0.25	1.25	0.0791	0.0331	1.876

these with the measured solubilities to obtain activity coefficients for the Tl^+ ion in each of the mixtures. The ionic activity coefficients for Cl^- and Tl^+ are given in Table 1 and, as expected, the results for Tl^+ are very close.

The conclusion is that the Pitzer treatment in its simplest form is capable of describing the interactions between Tl^+ and Cl^- ions without the need to consider ion association explicitly. The large negative value of $\beta^{(1)}$ reflects the weak electrolyte behaviour adequately and a value of α larger than two is necessary if the fit of the experimental data at higher concentrations is desired. A consideration of the higher-order limiting law is not necessary. Thermodynamically, it is a matter of choice how one wishes to describe the systems at the molecular level. As an associated electrolyte, part of the interactions between Tl^+ and Cl^- will have to be absorbed in an association constant for the reaction given by eqn. (1) and a less negative $\beta^{(1)}$ would then describe the interaction between the remaining free ions. But then the distinction between free and paired ions still has to be made together with a host of assumptions about the behaviour of the ion pair. This renders the ionic interaction approach using the simple Pitzer treatment far more attractive than the ion association approach.

We gratefully acknowledge support of this research by Universiti Brunei Darussalam under Grant UBD/T/RG.63.

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Paper 3/04983C; *Received* 17*th August*, 1993