THE SOLUBILITY AND ASSOCIATION OF THALLOUS CHLORIDE IN AQUEOUS SOLUTIONS AT 30°*

By K. H. Khoo†

Introduction

Macaskill and Panckhurst[1,2] have determined the solubility of thallous chloride in aqueous solutions of several added salts at 25°. From these solubility data, an association constant for thallous chloride is calculated, the value of which depends upon assumptions made about the mean ionic activity coefficient. The spectrophotometric measurements of Khoo and Panckhurst[3] leave little doubt as to the presence of associated species in saturated thallous chloride solutions. Khoo and Panckhurst have also extended the measurements of Macaskill and Panckhurst to mixed methanol/water solvents.

In the present communication, measurements are reported of the solubility of thallous chloride in aqueous solutions of sodium chloride, sodium perchlorate, barium chloride, and barium perchlorate at $30{\cdot}0\pm0{\cdot}02°$. Using the Brönsted–Guggenheim expression[4] for the mean ionic activity coefficient of thallous chloride, Macaskill and Panckhurst[2] arrived at the following parameters for the association process, using the notations of these authors:

$$\alpha = (7{\cdot}6\pm1{\cdot}6)\times10^{-4} \text{ mole l.}^{-1}\ddagger$$

$$\beta_{\mathrm{Tl,Cl}} = -0{\cdot}02\pm0{\cdot}20 \text{ l. mole}^{-1}$$

$$P = (1{\cdot}805\pm0{\cdot}010)\times10^{-4} \text{ mole}^2 \text{ l.}^{-2}$$

$$K = 4{\cdot}2\pm1{\cdot}0 \text{ mole}^{-1}$$

The limits on these parameters appear somewhat pessimistic. In this communication, we shall also investigate if these limits may be reduced by a similar comparison between calculated and experimentally determined solubilities.

Experimental

The apparatus and experimental methods are the same as those given by Macaskill and Panckhurst.[1] Hopkin and Williams G.P.R. sodium perchlorate was used without further

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† Department of Chemistry, University of Malaya, Kuala Lumpur, Malaysia.

‡ The figure $7{\cdot}6\pm1{\cdot}6$ mole l.$^{-1}$ which appears on p. 920 of ref. 2 should read $(7{\cdot}6\pm1{\cdot}6)\times10^{-4}$ mole l.$^{-1}$.

[1] Macaskill, J. B., and Panckhurst, M. H., *Aust. J. Chem.*, 1964, **17**, 522.

[2] Macaskill, J. B., and Panckhurst, M. H., *Aust. J. Chem.*, 1966, **19**, 915.

[3] Khoo, K. H., and Panckhurst, M. H., unpublished data.

[4] Guggenheim, E. A., and Turgeon, J. C., *Trans. Faraday Soc.*, 1955, **51**, 747.

purification. All other chemicals used were of AnalaR grade. Barium perchlorate was prepared by neutralizing barium carbonate with 60% perchloric acid and filtering off excess solid. The solution was evaporated to dryness and the solid was recrystallized from distilled water.

TABLE 1

THE SOLUBILITY OF THALLOUS CHLORIDE IN AQUEOUS SOLUTIONS AT 30°
(All concentrations are in moles $l.^{-1}$)

In NaCl		In $NaClO_4$		In $BaCl_2$		In $Ba(ClO_4)_2$	
Concn.	Solubility	Concn.	Solubility	Concn.	Solubility	Concn.	Solubility
0	0·01884	0·01001	0·01936	0·00500	0·01503	0·00287	0·01928
0·01000	0·01483	0·02002	0·01977	0·01000	0·01229	0·00574	0·01968
0·02000	0·01202	0·03003	0·02021	0·01500	0·01039	0·00860	0·02001
0·03000	0·00997	0·04004	0·02054	0·02000	0·00902	0·01147	0·02033
0·04342	0·00820	0·05005	0·02084	0·02500	0·00795	0·01434	0·02057
0·06000	0·00677	0·06006	0·02112	0·03000	0·00715	0·01721	0·02084
0·07000	0·00616						
0·08000	0·00569						
0·09000	0·00528						

TABLE 2

LEAST SQUARES PARAMETERS FROM THE SOLUBILITY OF THALLOUS CHLORIDE IN AQUEOUS SOLUTION AT 30°

$10^4\alpha$ (mole $l.^{-1}$)	$\beta_{Tl,Cl}$ (l. $mole^{-1}$)	$4+\log P$	$10^5\Sigma\Delta^2$
7	$-0·245\pm0·017$	$0·3840\pm0·0009$	5·897
9	$-0·055\pm0·016$	$0·3825\pm0·0008$	5·101
9·4	$-0·016\pm0·016$	$0·3822\pm0·0008$	5·067
9·5	$-0·006\pm0·016$	$0·3822\pm0·0008$	5·054
9·6	$0·004\pm0·016$	$0·3821\pm0·0008$	5·065
10	$0·044\pm0·016$	$0·3818\pm0·0008$	5·133
11	$0·147\pm0·016$	$0·3812\pm0·0009$	5·501

Results and Discussion

The solubilities are given in Table 1. The general equation[2] used to obtain the overall best-fit parameters by the method of least squares is

$$y = \log P - 2\beta_{Tl,Cl}x$$

where x and y are known for an assumed value of α. However, y contains terms in $\beta_{Na,Cl}$, β_{Tl,ClO_4}, or $\beta_{Ba,Cl}$ and values of these coefficients are not available at 30°. We therefore assume that the values of these coefficients at 25° also apply at 30°, and we may check this assumption by comparing the activity coefficients of these electrolytes at the two temperatures.

Table 2 shows the results of the calculations. $\Sigma\Delta^2$ represents the sum of the squares of the deviations, obtained in the least squares treatment and the limits on $\beta_{Tl,Cl}$ and $\log P$ are derived from $\Sigma\Delta^2$. A plot of $\Sigma\Delta^2$ against a leads to the following overall best-fit parameters:

$$a = (9{\cdot}5 \pm 0{\cdot}2) \times 10^{-4} \text{ mole l.}^{-1}$$

$$\beta_{Tl,Cl} = 0{\cdot}00 \pm 0{\cdot}02 \text{ l. mole}^{-1}$$

$$P = (2{\cdot}411 \pm 0{\cdot}004) \times 10^{-4} \text{ mole}^2 \text{ l.}^{-2}$$

$$K = 3{\cdot}94 \pm 0{\cdot}08$$

The limits on a are obtained by plotting the values of $\beta_{Tl,Cl}$ in Table 2 against a. The intersections of this plot with the error bars of $\beta_{Tl,Cl}$ at $a = 9{\cdot}5 \times 10^{-4}$ mole l.$^{-1}$ give the limits of a at this overall best-fit value of $9{\cdot}5 \times 10^{-4}$ mole l.$^{-1}$. The limits of error for K are calculated from the percentage uncertainty in a.

Using the parameters obtained at $a = 9{\cdot}5 \times 10^{-4}$ mole l.$^{-1}$, calculated and experimental solubilities agree to within the estimated error of 0·25% for the heteroionic salt systems, except for 0·02002M sodium perchlorate solution where the difference was 0·35%; for the chlorides, differences of more than 0·25%, but not exceeding 0·60%, were found at the three highest concentrations of barium chloride and at concentrations of 0·02000, 0·03000, and 0·07000M sodium chloride. However, within the range of values of the parameters given above, agreement between calculated and experimental solubilities can be found for all the solutions. We think that the limits given by Macaskill and Panckhurst[2] on their overall best-fit parameters may be reduced by a similar consideration.