Ebulliometric Study of Solubility and Ion-association Equilibria

Walace A. de Oliveira and Terezinha S. M. Omoto
Instituto de Química, Universidade Estadual de Campinas, C.P. 6154, Campinas, SP, Brazil

Precipitation equilibrium plays an important role in various fields of chemistry and the determination of solubility products is required for a quantitative description of species present in solution. The study of precipitation equilibria at elevated temperatures is more difficult because the experimental conditions are not favourable for the use of common methods. At the boiling temperature the determination of solubility products can be accomplished by means of recently described ebulliometric methods.[1] These procedures are based on the changes in the boiling temperature that accompany the precipitation equilibrium and permit the acquisition of data over a range of temperatures and for different types of compounds.

Equilibria involving ion association in solution are also important and the study of these systems has been an active area of chemical research. Frequently, both precipitation and dissociation equilibria are present and the complete assessment of all species in solution requires a knowledge of both the solubility product and the ion-pair formation constant.

This paper describes a method for the determination of both solubility products and ion-pair formation constants. The method is based on the changes in boiling temperatures that occur during an ebulliometric titration.[2] In order to test the procedure the constants for calcium sulphate were determined.

Theoretical

At the beginning of an ebulliometric titration, the amount of titrant added is not sufficient to cause precipitation and only the association equilibrium takes place. The data from this region of the titration curve were first used to calculate the ion-pair formation constant. The remainder of the data, up to the equivalence point, were then used for the calculation of the solubility product.

Equation for the Ion-pair Formation Constant

Considering the species present in the titration of a solution of calcium chloride with sodium sulphate and following procedures previously described,[3] it is possible to write

$$d\theta/K_b = dm_{Ca^{2+}} + dm_{Cl^-} + dm_{SO_4^{2-}} + dm_{Na^+} + dm_{CaSO_4} \quad (1)$$

where $d\theta$ is the change in the boiling temperature during the titration, K_b is the ideal ebullioscopic constant and m represents molality. It was assumed in the derivation of equation (1) that the activity coefficients do not vary during the titration. This assumption is based on the fact that titration is performed in a solution of high ionic strength and only small portions of titrant are added. Moreover, ion association decreases the ionic strength whereas addition of titrant favours an increase. Introducing in equation (1) the analytical molality of the titrant, $m_{Na_2SO_4}$, and remembering that m_{Cl^-} does not vary during titration, gives

$$d\theta/K_b = dm_{Ca^{2+}} + dm_{SO_4^{2-}} + 2dm_{Na_2SO_4} + dm_{CaSO_4} \quad (2)$$

Integration of equation (2) within the limits of the titration yields

$$\Delta\theta/K_b = m_{Ca^{2+}} - m_{iCaCl_2} + m_{SO_4^{2-}} + 2m_{Na_2SO_4} + m_{CaSO_4} \quad (3)$$

where m_{iCaCl_2} is the initial molality of the titrand. Conservation of mass gives

$$m_{iCaCl_2} = m_{Ca^{2+}} + m_{CaSO_4} \quad (4a)$$

and

$$m_{Na_2SO_4} = m_{SO_4^{2-}} + m_{CaSO_4} \quad (4b)$$

Solving equations (3) and (4) simultaneously and substituting the result in the expression for the molal ion-pair formation constant, $K_f' = m_{CaSO_4}/(m_{Ca^{2+}} m_{SO_4^{2-}})$, gives

$$K_f' = (3m_{Na_2SO_4} - \Delta\theta/K_b)/[(\Delta\theta/K_b - 2m_{Na_2SO_4})(\Delta\theta/K_b + m_{iCaCl_2} - 3m_{Na_2SO_4})] \quad (5)$$

Calculation of Solubility Product

Following the arguments given above and considering the part of the titration where both equilibria exist, we obtain

$$\Delta\theta/K_b = 2m_{SO_4^{2-}} + m_{Na_2SO_4} + K_f' m_{SO_4^{2-}} (m_{iCaCl_2} - m_{Na_2SO_4}) + K_f'(m_{SO_4^{2-}})^2 \quad (6)$$

Solving equation (6) and retaining only the root with physical meaning gives expressions for $m_{Ca^{2+}}$ and $m_{SO_4^{2-}}$, which are substituted in the equation for the molal solubility product $K_{so}' = m_{Ca}^{2+} m_{SO_4^{2-}}$, giving

$$K_{so}' = (a + b - 1/K_f') (a - b - 1/K_f') \quad (7)$$

where

$$a = [(K_f' m_{iCaCl_2} - K_f' m_{Na_2SO_4} + 2)^2 + 4K_f'(\Delta\theta/K_b - m_{Na_2SO_4})]^{1/2}/(2K_f') \quad (8)$$

and

$$b = (m_{iCaCl_2} - m_{Na_2SO_4})/2 \quad (9)$$

Experimental

An apparatus similar to that previously described[4] was used, consisting of a pair of identical ebulliometers assembled in such a way that one is used as a reference for the other. Boiling-temperature changes were measured with a pair of calibrated thermistors connected to a Wheatstone bridge. The imbalance voltage of the bridge was presented to a strip-chart recorder. The temperature uncertainty was about 6×10^{-5} °C.

The procedure used began by charging the ebulliometers with a solution of calcium chloride of various concentrations and ionic strength adjusted with sodium chloride. After the establishment of boiling-temperature equilibrium, pellets of sodium sulphate decahydrate were added through the condensers, alternately to each ebulliometer, while recording the changes in the boiling temperatures. Analytical-reagent grade chemicals were used throughout.

Results and Discussion

A typical ebulliometric titration curve is shown in Fig. 1. As can be seen, the slope of the curve decreases after the beginning of the titration and increases thereafter. This profile probably reflects the effects of the two equilibria in the boiling temperature of the solution, because the ion-pair formation

$$Ca^{2+}_{(aq.)} + SO_4^{2-}_{(aq.)} \rightleftharpoons CaSO_{4(aq.)} \qquad (10)$$
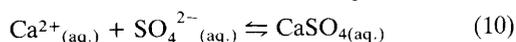
represents a net increase of 2 mol of particles per mole of titrant (if the reaction is complete), whereas the precipitation

$$CaSO_{4(s)} \rightleftharpoons Ca^{2+}_{(aq.)} + SO_4^{2-}_{(aq.)} \qquad (11)$$
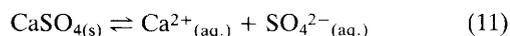
causes an increase in solution of only 1 mol of particles per mole of titrant.

Extrapolation to Infinite Dilution

The data for each titration were used to calculate molal constants using equations (5) and (7). The average values of these constants are listed in Table 1. At each ionic strength four to six values were obtained and the standard deviation of the average was between 5 and 20%, with more uncertainty for the measurements of very small $\Delta\theta$, required to calculate K'_f.

The thermodynamic solubility product, K^0_{so}, defined in terms of the activity of the ions is related to the molal solubility product by the expression $K^0_{so} = K'_{so}\gamma_{\pm}^2$, where $\gamma_{\pm}$ is the mean activity coefficient. Similarly, the thermodynamic ion-pair formation constant K^0_f is given by $K^0_f = K'_f/\gamma_{\pm}^2$, if the activity coefficient of the ion pair is regarded as unity. Using these expressions and the Debye - Hückel equation to represent $\gamma_{\pm}$, we obtain

$$\text{Log } K'_{so} = \log K^0_{so} + 4.723\ \sqrt{I}/(1 + 0.3406a^0\ \sqrt{I}) \qquad (12)$$

and

$$\text{Log } K'_f = \log K^0_f - 4.723\ \sqrt{I}/(1 + 0.3406a^0\ \sqrt{I}) \qquad (13)$$

where a^0 is the distance of closest approach, I is the ionic strength and the numerical constants[5] are for a temperature of 98.3 °C and the molal scale. The data in Table 1 were fitted to equations (12) and (13) with the help of a general multiparametric curve-fitting program[6] and the following results were obtained:

$$K^0_{so} = 4.5 \pm 0.3 \times 10^{-6}\ mol^2\ kg^{-2};\ a^0 = 5.0\ \text{Å}$$

and

$$K^0_f = 5.0 \pm 0.5 \times 10^2\ mol^{-1}\ kg;\ a^0 = 7.6\ \text{Å}.$$

The precision of our results for K^0_f and K^0_{so} is around 10%. This seems to be satisfactory considering that the determination of these constants required the measurement of very small boiling-temperature changes. Evaluation of the accuracy of our results is impaired by the discrepancies found in the literature for the values of these constants. For instance, at 25 °C over 20 values for the ion-pair formation constant were found, which varied by as much as three orders of magnitude.[7,8] At about the temperature of our measurements the following values are given in the literature: Yeatts and Marshall[9] report $K^0_f = 320\ mol^{-1}$ kg and $K^0_{so} = 4.35 \times 10^{-6}$ mol² kg⁻² and Gardner and Glueckauf[10] give $K^0_f = 621$ mol⁻¹ kg and $K^0_{so} = 3.48 \times 10^{-6}$ mol² kg⁻². These values compare favourably with the results obtained in this work.

The value of a^0 for calcium sulphate has been considered[11] to be equal to 5 Å at 25 °C. Taking into account that the value of this parameter is little affected by changes in temperature,[1] it is expected that at the boiling temperature the value of a^0 should be around 5–6 Å. In the calculation of the solubility product the result for a^0 is in agreement with this prediction. However, for the calculation of K^0_f the value of a^0 found (7.6 Å) is slightly higher. Although higher values of a^0 have been used by other workers,[12] this result could perhaps be caused
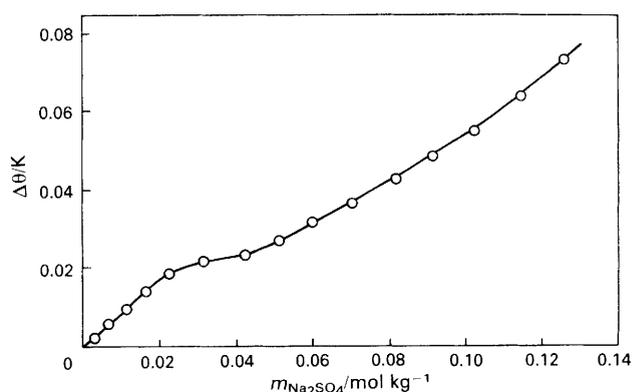

Fig. 1. Ebulliometric titration of a 0.1000 mol kg⁻¹ solution of Ca²⁺, of ionic strength 0.300 mol kg⁻¹ with sodium sulphate solution

Table 1. Molal solubility product, K'_{so}, and ion-pair formation constant, K'_f, as functions of the ionic strength, I

I/mol kg⁻¹	K'_f/mol⁻¹ kg	$10^5\ K'_{so}$/mol² kg⁻¹
0.090	79.4	3.50
0.130	50.1	4.57
0.174	72.4	5.75
0.210	52.5	8.70
0.260	50.1	10.0
0.300	43.7	11.0
0.390	38.0	11.0
0.520	29.5	13.0

by the assumption that the activity coefficient of the ion pair is equal to unity.

The ebulliometric method described here requires simple and inexpensive instrumentation and permits the acquisition of data over a range of temperatures, by varying the barometric pressure in the ebulliometer. The major requirement is that all solutes must be non-volatile at the boiling temperature of the solvent. An over-all evaluation of the proposed method led to the conclusion that ebulliometric measurements can be useful in the study of multiple equilibria in solution.

References

1. De Oliveira, W. A., *Anal. Chim. Acta*, 1982, **141**, 337.
2. De Oliveira, W. A., *Anal. Lett.*, 1981, **14**, 1391.
3. De Oliveira, W. A., *J. Coord. Chem.*, 1979, **9**, 7.
4. De Oliveira, W. A., and Meites, L., *Anal. Chim. Acta*, 1977, **93**, 3.
5. Robinson, R. A., and Stokes, R. H., "Electrolyte Solutions," Butterworths, London, 1955, p. 491.
6. Meites, L., "The General Multiparametric Curve-Fitting Program CFT4," Computing Laboratory, Department of Chemistry, Clarkson College of Technology, Potsdam, NY, 1976.
7. Yokoyama, H., and Yamatera, H., *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2719.
8. Pitzer, K. S., *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 101.
9. Yeatts, L. B., and Marshall, W. L., *J. Phys. Chem.*, 1969, **73**, 81.
10. Gardner, A. W., and Glueckauf, E., *Trans. Faraday Soc.*, 1970, **66**, 1081.
11. Meites, L., Pode, J. S. F., and Thomas, H. C., *J. Chem. Educ.*, 1966, **43**, 667.
12. Yokoyama, H., and Yamatera, H., *Bull. Chem. Soc. Jpn.*, 1975, **48**, 2708.