Solubility and Activity Coefficient of Thallium (I) Chloride in the System TICl + HCl + NaCl + H2O at 25°C

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The solubility of thallium (I) chloride has been studied in aqueous mixtures of HCl and NaCl at 25°C at ionic strengths ranging from 0.10 to 3.20 mol-kg⁻¹. Activity coefficients were derived and fitted to Pitzer's equations. This required values of the single-electrolyte parameters, β₀, β¹ and C₀ for TICl. Since these are not available in the literature, owing to the low solubility of TICl in water, a method has been devised for evaluating these parameters. These were then used to determine the mixing parameters, θ and ψ, for the system. Consideration of the higher-order limiting law for symmetrical mixing did not improve the accuracy of the fit. The success with which the ion-interaction theory in its simplest form has been able to model the present system to such a high ionic strength shows that it is not necessary to treat ion association in the system explicitly in terms of an ion association equilibrium constant.

KEY WORDS: Solubility; activity coefficient; thallium (I) chloride; mixtures; constant total ionic strength; Pitzer's parameters; higher-order limiting law; ion association.

1. Introduction

Pitzer's ion-interaction theory has had considerable success in modeling the properties of electrolyte solutions. To some extent, this has led to renewed interest in the study of activity coefficients in electrolyte solutions. Systems which have been successfully described by the Pitzer approach range from simple ternary systems to more complex mixtures over a wide ionic strength range from as low as 0.06 to as high as 20m (mol-kg⁻¹). While the single-electrolyte parameters, β₀, β¹ and C₀ for several electrolytes are available, those for

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salts of low solubility are not. This becomes a problem when the activities of such salts are required in mixtures with other electrolytes at high ionic strengths, as in the present system. A similar problem was encountered and addressed by Chan and Khoo(3) for mixtures involving the perchlorates of potassium, rubidium and cesium.

No equilibrium method has been exploited as extensively as the electromotive-force method for studies of activity coefficients in mixed electrolytes at constant total ionic strength. It is shown in this paper that the solubility method can also be used to determine activity coefficients in constant ionic strength media, provided that the solubility of the salt is low enough so as not to make an appreciable contribution to the total ionic strength of the mixture, and that there must be at least two added salts present to mix in different proportions in order to produce a series of solutions of constant total ionic strength. The solubility of TlCl in HCl or in NaCl is less than \(4 \times 10^{-5} \text{m}\) when the added chloride concentration is 0.1m. It passes through a minimum before rising as the added chloride concentration increases to high values. This imposes a lower and an upper limit to the range of constant total ionic strength.

Here, we report the solubility and activity coefficient of TlCl in the system TlCl + HCl + NaCl + H2O at 25°C at constant total ionic strength \(I = 0.10 - 3.20 \text{m}\). It is well known that TlCl is associated in aqueous solutions and one of the objectives of the study was to determine if the system can be described by an ion-interaction treatment using virial coefficients only without the need to incorporate an ion association equilibrium constant.

2. Experimental

2.1. Materials and Solutions

Thallium (I) chloride was prepared by dropwise addition of dilute solutions of A.R. Tl2SO4 and A.R. HCl to about 1L of water under constant stirring. The precipitate was washed free from sulphate, dried at 120°C and stored in the dark. The purity of the salt was determined by iodate titration for thallium (see later) and found to be (99.9±0.2)%. A.R. NaCl was used without further purification. A.R. HCl was diluted to the azeotrope composition and distilled with considerable rejection of top and bottom fractions. It was analyzed gravimetrically for chloride. KIO3 of A.R. grade was twice recrystallized. The salts were dried to constant weight before use. Solutions were prepared by volume using glassware calibrated at the temperature of application. Air buoyancy corrections were applied to all weighings.