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Construction of solid–liquid phase diagrams in ternary systems by titration calorimetry

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Abstract

Titration calorimetry was used to construct the solid–liquid equilibrium line in ternary systems containing the solute and an aqueous mixed solvent by measuring the heat of dissolution of the solid solute during successive additions of the liquid solvent. The plot of cumulated heats versus the mole ratio, $n_{\text{solvent}}/n_{\text{solute}}$, yields two (almost) linear increases of different slopes. These two lines represent successively the enthalpy of dissolution then the enthalpy of dilution of the medium; their intersection gives the solubility and the enthalpy of dissolution of the solute. Phase diagrams have been established over the whole concentration range for *o*-anisaldehyde, 1,3,5-trimethoxybenzene and vanillin, in water + methanol, +ethanol, or +*n*-propanol at 303, 313 and 318 K.

Keywords: Titration calorimetry; Heat of dissolution; Solid–liquid equilibrium; Ternary systems; Benzene substituted derivatives; Vanillin; Alcohol–water mixed solvents

1. Introduction

The present study develops a method useful for the acquisition of thermodynamic data on phase equilibria in crystallization engineering. Crystallization is of particular interest since it very often constitutes the final step in the purification of solids. Several methods have been used to obtain phase diagrams of a solid solute in a liquid medium acting as crystallization solvent. Such methods were often optical ones in which appearance of a crystal phase (or disappearance), due to temperature or concentration changes was observed. Besides the advantage of observing the type of crystallinity, such methods are rather qualitative. More recently, more precise quantitative techniques have been used to detect the solubility limit through the disappearance of the last crystal. In such dissolution techniques the solution concentration is observed continuously by following the change with temperature of a physical property of the solution, spectroscopic signal, density, vapor pressure, conductivity, etc. (see for example the automatic method based on conductivity measurements by Berthet and Counioux [1]). However, since rigorous control of temperature is essential in solubility phenomena, isothermal experimental techniques should be favoured. The construction of a phase diagram containing a solid solute and a liquid solvent is simply based on the determination of the solubility of the solid solute in the solvent. The solvent can be a pure liquid component or a liquid mixture for efficient solvent–antisolvent selective capability. In such ternary systems the crystallization of the solute can be obtained by adding the antisolvent to a concentrated solution of the solute in the other (“good”) solvent. Thus, the choice of solvents in crystallization processes rests on the knowledge of the solid phase contour of the precipitate in the presence of the solvent–antisolvent mixture. When the solute is organic, the solvent is generally a binary mixture of water + a hydrophilic organic component. The aqueous mixed solvent behaves as a homogeneous phase over its entire mole fraction range. Determination of the maximum solubility of the solid solute at points along the solid–liquid line of the ternary system provides data from which the locus of the maximum solubility is readily obtained.

The solubility limit was determined by slowly adding (to remain at thermodynamic equilibrium) successive small incre-

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ments of the binary solvent to a known amount of the solid solute until solubilisation of the solid crystals was complete. Titration calorimetry was used to detect the dissolution of the solid in the binary solvent through the heat effect during each addition. Titration calorimetry has been traditionally used for titration or acid–base reactions [3]. Isothermal titration calorimetry, ITC, is also currently used to study complex formation and numerous examples of such investigations can be found in recent publications where different calorimeters have been used [4–6]. However, titration calorimetry has been very rarely used to measure solubilisation or dissolutrion of solid compounds.

In this work the "target" molecule was vanillin; it represents a class of important molecules where the three functional groups, hydroxyl, aldehyde, methoxy, are present on an aromatic ring. Vanillin is a product of technological importance produced industrially in large amounts. The ultimate step in the production line is crystallisation in an appropriate solvent in order to obtain an end-product of pure small crystals. Water–alcohol binary mixtures are the most suitable solvents in terms of cost and recycling. Phase diagrams have been established over the whole concentration range for *o*-anisaldehyde, 1,3,5-trimethoxybenzene and vanillin in water + methanol, +ethanol, or +*n*-propanol. The effect of temperature was examined through measurements in the temperature range of 303–318 K.

2. Experimental

2.1. Chemicals

4-Hydroxy-3-methoxybenzaldehyde (vanillin) with 99 mol% purity, *o*-anisaldehyde with 98 mol% purity and 1,3,5-trimethoxybenzene with 99 mol% purity were provided by (Fine Chemicals) Acros Organics, France; methyl alcohol with purity >99.8 mol% was provided by Fluka Chemika, France; ethyl alcohol absolute RE was provided by Carlo Erba, France; *n*-propanol p.a. with purity >99.5 mol% was provided by (Fine Chemicals) Acros Organics, France. All chemicals were used without further purification. Solutions were prepared by weight with freshly bidistilled water.

2.2. Instrumentation

The titration calorimeter, Titrys by Setaram, was used to perform the measurements. The calorimetric block temperature is regulated to ±20 mK; it houses two thermopiles in which are placed the measuring and reference cells. The detection limit is 0.1 μW. The instrument can be operated in the temperature range from 303.15 to 318.15 K. Each cell has an active volume from 1 to 12 cm^3 and the contents of each cell can be stirred by a small magnetic bar activated by a single motor which ensures the same (adjustable) stirring speed in both cells. The injection system is a Dual Syringe Pump Model 33 from Harvard Instruments, that delivers identical volumes through stainless capillaries at the same rate in both cells. To ensure control of the volumes delivered by the pumps, the whole assembly was placed in a small air bath thermostatted to ±50 mK. Before injection into the calorimetric cells, liquids coming from the pumps are further thermostatted as the capillary tubes are coiled in two small thermostats placed inside the calorimetric block on top of each cell.

2.3. Experimental procedure

An initial mass, 0.05–2.50 g depending on the type of solid, of finely hand-ground (in a mortar) crystallized powder, is placed in the measuring cell. The two syringe pumps are filled with the same water–alcohol solution of known composition. A dissolution run consists in adding the same volume of the solution simultaneously in both cells. The heat repeatedly evolved during each addition is due to the heat of dissolution of part of the solid in the added solution. Typically, each injection consists in adding 0.20 cm^3 of solution at the rate of 0.10 cm^3 min^{-1} and a complete run is achieved after an average of 10 successive additions. The volume for an injection may vary from 0.04 to 2.00 cm^3 at a rate between 0.02 and 0.70 cm^3 min^{-1}. Each run yields a series of peaks of heat rate versus time. The cumulative sums ΔH of peak areas divided by n_1 ($n_1 = n_{\text{solute}}$, initial number of moles of solute), are plotted versus $\alpha = n_{\text{solvent}}/n_{\text{solute}}$ which represents the ratio of the number of moles of solvent to the number of moles of solute. Each run yields the type of plot shown in Fig. 1. Typically each plot is composed of two parts. First an approximately linear increase of $\Delta H/n_{\text{solute}}$ represented by

$$\Delta H/n_1 = A_1\alpha \qquad (1)$$

When all the solid has dissolved, the second part, which is simply related to the heat of dilution of the medium, is generally well

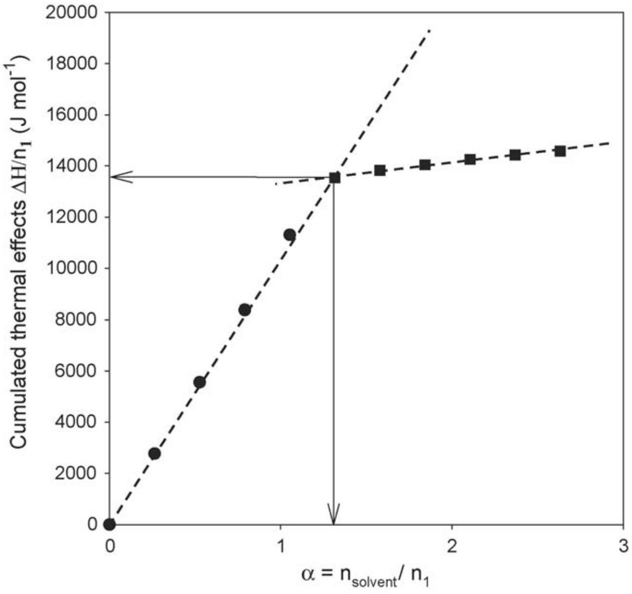

Fig. 1. Plot of cumulated thermal effects, $\Delta H/n_1$ (in J mol^{-1}), vs. $\alpha = n_{\text{solvent}}/n_1$, obtained during a run, showing the initial dissolution (●) of the solid solute followed by the dilution (■) of the solution. The intersection gives the enthalpy of dissolution and the ratio α_S at saturation; n_1 is the initial number of moles of solute n_{solute} placed in the measuring cell.