Crystal growth of Li salts from aqueous solutions and gels studied by Raman spectroscopy

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ABSTRACT :

A Raman spectroscopic study of aqueous solutions of Li_2SO_4 , LiNaSO_4 and LiKSO_4 as function of concentration and temperature has been performed. From a band profile analysis of the internal modes of the sulphate ion, the spectroscopic association constant has been calculated at different temperatures.

It has been also possible to measure the diffusivity coefficients for Li_2SO_4 in bulk solutions and in gels, using Raman spectroscopy.

These data are used in the interpretation of the crystallization behaviour of Li salts from aqueous solutions and gels.

1. INTRODUCTION

The precise knowledge of the chemical processes occurring in the aqueous media and the mass transfer of fluids are very important stages in the understanding of the crystal growth from aqueous solutions. Although many of the available data on the properties of aqueous solutions of electrolytes come from macroscopic sources, data obtained from microscopic sources (mainly diffraction and vibrational spectroscopy) allow in some cases to introduce new insights on the understanding of these phenomena.

Of particular importance are the IR and Raman spectroscopy from which valuable information at molecular level can be obtained.

The main aims of our work is the study of the crystallization behaviour of Li salts with applications as ionic conductor and piezoelectric materials from bulk aqueous solutions and gels. Particular interest is devoted to Lithium sulphate and the double salts LiKSO_4 and LiNaSO_4 . In the case of Li_2SO_4 , crystals have been obtained using different methods (melting, hydrothermal or water/sulfuric acid solvents) [1]. Starting from the melt it is not possible to obtain high quality single crystals in the monoclinic phase because the large discontinuous volume change at the cubic-monoclinic transition which provokes a great number of cracks in the crystals. Within this general framework, one of our goals is the growth of these salts at low temperatures. For this we use mixture solvents, mainly methanol/water and ethanol/water mixtures.

In the present work we report some data on the following steps of the crystallization process of Li-sulphates.

1. The study of the growth media by a) the phase diagrams and macroscopic properties at different temperatures of the systems Li_2SO_4 , $\text{Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ and $\text{Li}_2\text{SO}_4\text{-K}_2\text{SO}_4$ in water and in mixed methanol/water solvents and b) a structural study of these systems at different concentrations and temperatures by means of Raman and IR spectroscopy.

2. The study of the mass transport of the reactants in aqueous solutions and in gels by means of the Raman spectroscopy.

A crucial point in these items is the connection between the data obtained at molecular level and the macroscopic properties. We will focus the attention in this paper on the discussion on the relation between

the spectroscopic results and the macroscopic data. To achieve this, some parameters with macroscopic (thermodynamic) significance should be obtained from the spectra. Among these, association parameters (K_{ass} , ΔH and ΔS) and mass transport parameters (relaxation times and diffusivity coefficients) are, in our opinion, of particular importance.

2. EXPERIMENTAL

Details on the experimental set-up for phase diagrams and macroscopic properties measurements can be found in [2]. The Raman spectra of aqueous solutions were taken in a Ramanor HG2S double monochromator and in a SPEX spectrophotometer both coupled to a computer and in the usual 90° scattering configuration.

As excitation the 514.5 nm and the 488.0 nm lines of an argon ion laser were used. The incident power at the sample was about 300 mW. Spectra at different temperatures in the range 5° to 80° C were obtained on samples with different concentrations thermostated to $\pm 0.1^\circ$ C in fused silica cells using a circulating water bath.

In the case of the spectroscopic mass transport measurements, experimental arrangements were specially constructed based on diffusion phenomena along glass tubes with very large length/diameter ratios (a capillary of 25 μ internal diameter and 20 cm length and a vertical tube of 3 mm internal diameter and 60 cm length). Finally, the transport in gel was monitored by using vertical tubes of 8 mm internal diameter and 12 cm length. In these tubes the silica gel occupies about 3/4 of the total and in the remain volume at the top are placed the different liquid systems.

Because of the presence of fluorescence under 514.5 and 488.0 nm exciting lines a FT-Raman spectrometer with laser excitation in the IR region (1100 nm) was in this case used.

3. RESULTS AND DISCUSSION

3.1. Association processes

Although there are some limitations in sensitivity at low concentrations, Raman spectroscopy is a powerful tool for examine the nature of ion association in aqueous electrolyte solutions when the solute contains polyatomic ions. In the case of sulphates the profile modification of the $\nu_1(\text{SO}_4)$ symmetric stretching band has been taken for some authors as an evidence of the ion association [3]

For Li_2SO_4 the modification consist in an asymmetry in the high wavenumber side of the band which appears as a shoulder when concentration and temperature increases.

The estimation of the band parameters of this shoulder is dependent on some subjective criteria when curve resolving programs are used. In order to overcome this limitation we have developed a general method of self-deconvolution band profile using Fourier transform analysis.[4]. The advantage of this method is that it allow the estimation of the number and band parameters of the possible components contained under a complex band profile without any previous assumption about them. The data thus obtained are used as input in a curve-fitting program which allow the optimisation of the band parameters by means of least-squares routines. Figure 1 illustrates the method for a saturated Li_2SO_4 solution at room temperature .

If we assume the component B_1 at 982 cm^{-1} correspond to the sulphate ions non participating in ionic association with Lithium ions and the 989 cm^{-1} component B_2 correspond to the associates sulphates and we assume the same molar scattering coefficient for the two species of sulphate we can calculate the association constant for the reaction

$$K_{ass} = \frac{1-\alpha}{\alpha(\alpha+1)m} \frac{\gamma_{\pm 11}^2}{\gamma_{\pm 12}} \approx Q_c \cdot Q_\gamma \quad (2)$$

where $\alpha = I_{982}/I_{tot}$, $1-\alpha = I_{989}/I_{tot}$, m is the molality and Q_γ is assumed to be $(1/\gamma_{\pm 12})^2$ [5]. The data for $\gamma_{\pm 12}$ were taken from Holmes and Mesmer [6]. In the range 0.5 to 2.5 m where the activity coefficient is practically constant Q_c is found to be also constant. The average values of Q_c and $K_{ass}(sp)$ in these interval are respectively 0.09 kg mol^{-1} (standard error 0.004) and 1.24 (standard error 0.041). This last value is lower than the one obtained from macroscopic measurements $K_{ass} = 5$ [7].

This difference is interpreted on the basis the Li-SO_4 association is a multistage process. The macroscopic measurements will reflect all interactions taking place in the solution (from short to long range distances) but the Raman spectra only those acting over short range distances. The long distance interactions can be calculated on the basis of electrostatic forces using the Bjerrum equation [8]. The summation of the value thus calculated and the spectroscopic one is in a good agreement with the macroscopic obtained value.

The dependence of the spectroscopically obtained $\ln K_{ass}(sp)$ with $1/T$ is presented in Figure 2. The points can be fitted by a straight line (regression coefficient 0.97). From this plot the enthalpy and entropy for the association were calculated $\Delta H = 20 \text{ KJ/mol}$, $\Delta S = 70 \text{ J/mol K}$.

Figure 1

Figure 2

3.2 Transport properties

Figure 3 shows the evolution of the integrated intensity of the Raman spectra of $\nu_1(\text{SO}_4)$ in a 2 m Li_2SO_4 aqueous solution diffusing along the closed vertical tube for times up to 25 days and the axial profile at this time. Together with these results are shown the computer simulation of the process where C/C_0 is the concentration quotient obtained from the measured intensity ratio at different positions of the tube to the position $L=0$ (which is taken in our case 2 cm apart from the reservoir).

From these data, the time evolution is fitted by a D_a value ranging between 0.43×10^{-5} and $0.45 \times 10^{-5} \text{ cm}^2/\text{s}$ and the axial profile by a value of $0.37 \times 10^{-5} \text{ cm}^2/\text{s}$. The data obtained from the capillary can not be fitted by the same D_a value except if a convective flow rate of about $5 \times 10^{-2} \text{ cm/hour}$ is introduced in the model. We assume in consequence a D_a value of $0.41 \times 10^{-5} \text{ cm}^2/\text{s}$ for Li_2SO_4 in aqueous solution (at 2 m concentration) which is found to be in good agreement with the values obtained for other sulphates (MgSO_4 : $0.39 \times 10^{-5} \text{ cm}^2/\text{s}$; CuSO_4 : $0.58 \times 10^{-5} \text{ cm}^2/\text{s}$) from macroscopic measurements [9].

In Figure 4 we present the evolution of the integrated area of the $\nu_1(\text{SO}_4)$ band for a 1 m Li_2SO_4 aqueous solutions diffusing along the gel tube, and in Figure 5 we show the results of the computer simulation of process. Because the aqueous solution reservoir can not to be assumed as infinite and there is some water in the gel, the model become rather complicated but the experimental data can be fitted with an acceptable accuracy by a diffusivity coefficient $0.3 \times 10^{-5} \text{ cm}^2/\text{s}$ which is not far from the obtained in bulk solutions. That mean the diffusion properties in gels do not differ appreciably from those in bulk solutions.

The differences in transport properties from gel and bulk solution arise from the fact that in the gel, convection is strongly suppressed.

Figure 3

Figure 4

Figure 5

4. CONCLUSIONS

Raman Spectroscopy provide a method which complements the clasical macroscopic methods in the characterisation of the growth media. Some times the Raman spectra contains unique data which will lead to a deeper understanding of the thermodynamic properties of the system.

The use of self-deconvolution band profile methods allow the estimation of the Raman band parameters without any previous assumption about these. The data thus obtained can be related in a more objective way with the species presents, their populations and the chemical process taking place. From these the ionic association and their dependence with concentration and temperature has been calculated. It has been also possible to measure (for the first time in our knowledge) the diffusivity coefficients of Li_2SO_4 in bulk aqueous solutions and in gels using Raman spectroscopy.

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