

A Kinetic Study of the Intercalation of Ethanol into Vanadyl Phosphate

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Abstract. The course of intercalation of ethanol into VOPO₄ has been studied by X-ray diffraction, thermomechanical analysis and a volumetric method. In all cases the kinetic curves were observed to have a sigmoidal shape. A model, based on the Avrami equation, has been proposed for description of the kinetic behavior. The activation energy of intercalation based on this model has been determined. The existence of the advancing phase boundary in the system during intercalation has been confirmed.

Key words. Intercalation, X-ray powder diffraction, thermomechanical analysis, volumetry, vanadyl phosphate, ethanol, kinetics.

1. Introduction

Although there have been numerous studies of the kinetics and mechanism of the intercalation of atoms and ions [1], little is known about the kinetics and mechanism of the intercalation of molecular guests.

Intercalation of cobaltocene from dimethoxymethane solution into SnS₂ was studied by real-time, *in situ* X-ray diffraction using a synchrotron as the source of radiation [2]. A model is presumed in which the crystal of the host contains intercalated and nonintercalated parts. A two-phase system is consequently formed, with a transition area which was referred to as an advancing phase boundary [3]. The mechanism of the intercalation can be divided into two parts. Firstly, nucleation of the guest at the edge of the host crystals; followed by penetration of the guest inside the crystals, i.e. the growth of the intercalated part. A reaction mechanism of non-integral order, intermediate between an Avrami first and second order kinetics, was suggested. The reaction mechanism is described by the rate expression for nuclei-growth reactions of non-integral order

$$\alpha = 1 - e^{-(kt)^n}, \quad (1)$$

where α is the extent of the reaction, k is the rate constant, t is the time of reaction, and the exponent n is equal to 1.5. The authors determined the activation energy of the above-mentioned reaction as $47 \pm 3 \text{ kJ mol}^{-1}$.

A similar method was employed in a study of the intercalation of water into anhydrous vanadyl phosphate [4]. Diffractograms of VOPO_4 powder, exposed to a flow of wet air, were measured repeatedly. In contrast to deintercalation [5], the intercalation of water does not proceed via the formation of VOPO_4 monohydrate. A reaction mechanism was proposed, based on the shifts of the positions and the widths of the (001) lines. Formation of a Hendricks–Teller disordered layered lattice was presumed, composed of α_1 - VOPO_4 and $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ layers.

The change of the basal spacing during intercalation results in the change of the dimension of the host crystal along the c -axis. A method called thermomechanical analysis (TMA) is based on this fact. This method was also employed for the study of the intercalation of water into VOPO_4 . The TMA measurements of the VOPO_4 crystal exposed to wet air at room temperature revealed that the intercalation of water followed an exponential course [4].

The fact that the guest molecules, which are liquid under ambient conditions, possess a smaller volume in the intercalate than in the original liquid form, is the principle of the volumetric method for following the rate of the intercalation [6]. The method was employed for the measurement of the kinetics of intercalation of liquid 1-butanol into solid VOSO_4 in the temperature range 25 – 60°C . The value of the activation energy (54.6 kJ mol^{-1}) was determined. In the same work, water was observed to have an accelerating effect in the VOPO_4 -wet ethanol system.

Vanadyl phosphate is a compound which is very easily intercalated by molecular guests having Lewis base character (amines [7, 8], pyridine and its derivatives [9], pyrazole, pyrazine, pyrrole, phenazine [10], methylpyrroles [11, 12]). Aliphatic alcohols, which form a bilayer in the van der Waals space of the host [13], are also examples of such guests. The host–guest ratio is roughly 1 : 2 in this intercalate.

This paper gives the results of the study of the kinetics of intercalation of ethanol into anhydrous vanadyl phosphate. For this purpose, X-ray diffraction, thermomechanical analysis, and the volumetric method were used.

2. Experimental

Vanadyl phosphate dihydrate was prepared by prolonged boiling of a mixture of vanadium pentoxide and phosphoric acid in water [14]. The polycrystalline product was separated by sieve analysis and the fraction of particle size 0.1 – 0.2 mm was used for the XRD and the volumetric measurements. For the thermomechanical analysis, $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was recrystallized from the mother solution by allowing it to stand for 30 days at room temperature [5]. In this way, square flat crystals were prepared with dimensions of $1 \times 1 \text{ mm}$ and thickness about 0.05 mm .

Powder data were obtained with an HZG-4 X-ray diffractometer (Freiberger Präzisionsmechanik, Germany) using CuK_α radiation with discrimination of CuK_β

radiation by a Ni filter. Diffraction angles were measured from 5 to 25 °C (2θ). Every cycle of measurement lasted 8 min. The time scale of the kinetic data obtained by XRD was recalculated according to the delay needed to achieve the right position of the goniometer corresponding to the maxima of the (001) lines of the starting material and the product. The positions and the linewidths of the diffraction lines were determined by a Lorentz function fit. The measurements were carried out on a heated corundum plate with a thermocouple. The $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ powder was placed on the plate, heated up to 250 °C, and kept at this temperature for about 1 h to obtain dehydrated α_1 - VOPO_4 . The sample was then cooled to 25 °C using a flow of dry air (0.5 L min^{-1}). The kinetic measurements were carried out in a flow of air saturated with ethanol vapor (air was bubbled through ethanol at 22 °C and at the same flow rate). The sample temperature was kept 3 °C warmer than the flowing air temperature to avoid condensation of alcohol on the sample.

The thermomechanical measurements were carried out by means of a TMA CX03R dilatometer described previously [15], equipped with a differential capacitance probe detector. The parent monocrystal of $\text{VOPO}_4 \cdot 2\text{H}_2\text{O}$ was placed in a cylindrical quartz crucible with diameter 5 mm and height 7 mm. The sample was then heated up to 200 °C to prepare anhydrous VOPO_4 , followed by rapid cooling to room temperature. After cooling, the crucible was filled with liquid ethanol and the time dependence of the thickness of the crystal was then followed at room temperature. The level of ethanol was such that the crystal was immersed in the liquid at all times. The force applied to the sample was 50 mN during the experiment.

The principle of the volumetric method and the description of the apparatus used are given in the previous paper [6] in detail. The amount of anhydrous VOPO_4 used for the experiment was about 0.25 g. The kinetics measurements were carried out at 11.2, 14.2, 19.6, and 24.7 °C.

The extent of reaction, α_1 , was calculated according to an equation

$$\alpha_1 = B/B_\infty, \quad (2)$$

where B is the change of an appropriate property measured at time t and B_∞ is the change of this property at infinite time (i.e. when the property followed remains constant for about one hour). According to the method used for following the course of the reaction, B corresponds to: (i) the intensity of the (001) lines of the intercalate; (ii) the change of the thickness of the crystal (the thermomechanical measurements); (iii) the change of the volume of the reaction system (the volumetric method).

In case of XRD measurements, a decrease of the intensity of the (001) line of the starting vanadyl phosphate was also followed. The reaction extent α_H is then given by an equation

$$\alpha_H = 1 - A/A_0, \quad (3)$$

where A is the intensity of the (001) line of anhydrous vanadyl phosphate at time t and A_0 is this intensity at time $t = 0$.

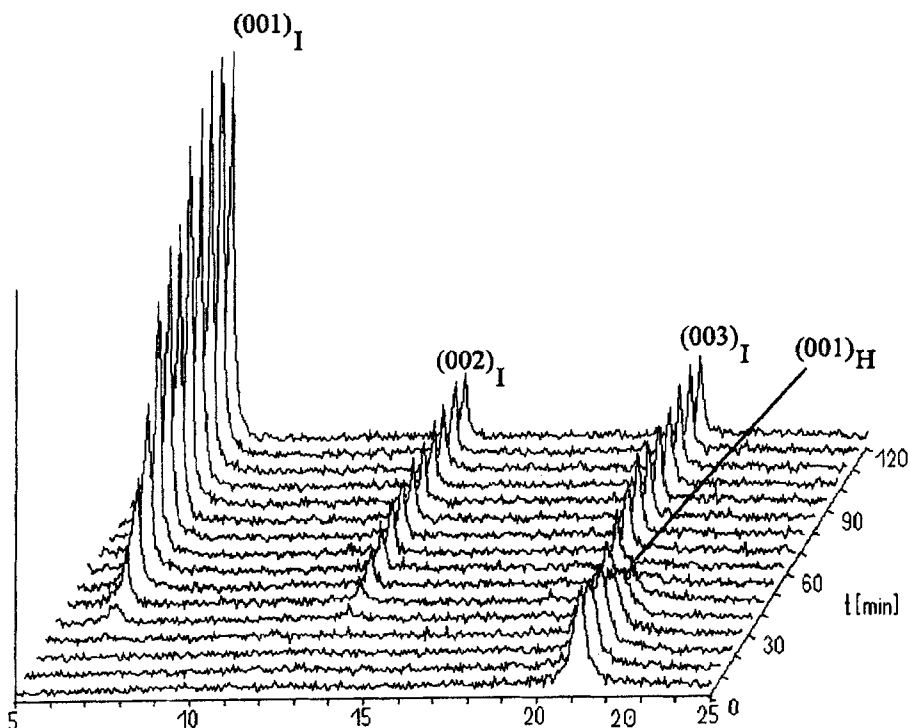


Figure 1. The changes of the diffractograms during intercalation of ethanol into α_1 -VOPO₄ (index 'H' stands for anhydrous vanadyl phosphate, index 'I' for VOPO₄·2C₂H₅OH).

3. Results and Discussion

Changes of the diffractograms during intercalation of ethanol into α_1 -VOPO₄ are given in Figure 1. As seen from this figure, the original α_1 -VOPO₄ (basal spacing 4.2 Å) is changed to VOPO₄·2C₂H₅OH (basal spacing 13.17 Å). In the region investigated, three sharp (001) lines of the intercalate were observed giving the same value of the basal spacing. The lines observed belong to either anhydrous VOPO₄ or intercalated vanadyl phosphate, which indicate that there is no intermediate product like VOPO₄·C₂H₅OH. As the shifts of the positions of the lines and the increase of the linewidths were not observed, it is assumed that the intercalate is formed in a greater part of the crystals directly, without the occurrence of the random stacking of the layers (the Hendricks–Teller effect, which was observed in the case of intercalation of water [4]). Formation of the regular alteration of the intercalated and nonintercalated galleries (staging) was also not found.

The dependence of the extent of reaction of anhydrous VOPO₄ and the ethanol intercalate on reaction time are given in Figure 2. The curves were observed to have a sigmoid shape corresponding to a decrease of concentration of VOPO₄ and an increase of concentration of VOPO₄·2C₂H₅OH, respectively. A delay of formation of the product in comparison with the decrease of the pristine host was observed.

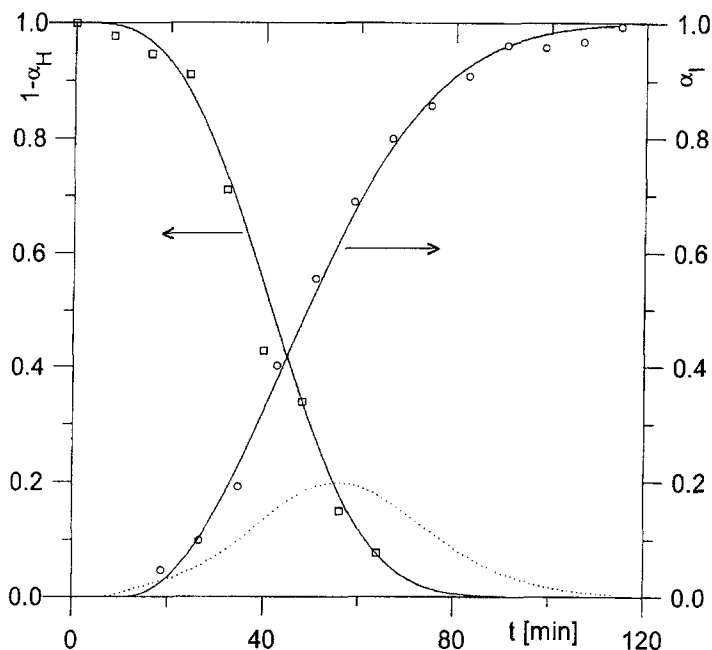


Figure 2. Dependence of the extent of reaction of the parent host α_H (\square) and the product α_1 (\circ), on time t obtained by XRD during intercalation of ethanol into α_1 -VOPO₄. The difference $\alpha_H - \alpha_1$ (dotted line) corresponds to the amount of the advancing phase boundary in the system.

This delay is about 9 min as determined by Avrami function fit. This phenomenon can be explained by the existence of a so-called advancing phase boundary [3] as depicted in Figure 3. The advancing phase boundary (APB) is an area of the crystal which is formed immediately at the beginning of the reaction, thus decreasing the amount of the pristine host present. From the point of view of X-ray diffraction, APB has a disordered structure and is shown as a slight increase of the baseline of the diffractogram only. During intercalation, APB spreads and shifts in the crystals, being replaced by the intercalate formed. The amount of this non-diffracted APB corresponds to a difference of $\alpha_H - \alpha_1$, which is shown in Figure 2 as a dotted line. The reaction rate ($3.68 \times 10^{-4} \text{ s}^{-1}$) calculated for the decrease of the host is in agreement with the reaction rate ($3.63 \times 10^{-4} \text{ s}^{-1}$) found for formation of the intercalate.

A thermomechanical measurement of the thickness of the crystal gives a similar sigmoid shape of the curve expressing the dependence of the degree of the reaction conversion on time as found for the intercalation of VOPO₄ by liquid ethanol (Figure 4).

The results of the volumetric measurements for four different temperatures are given in Figure 5. As seen from this figure, the reaction rate is dependent on the

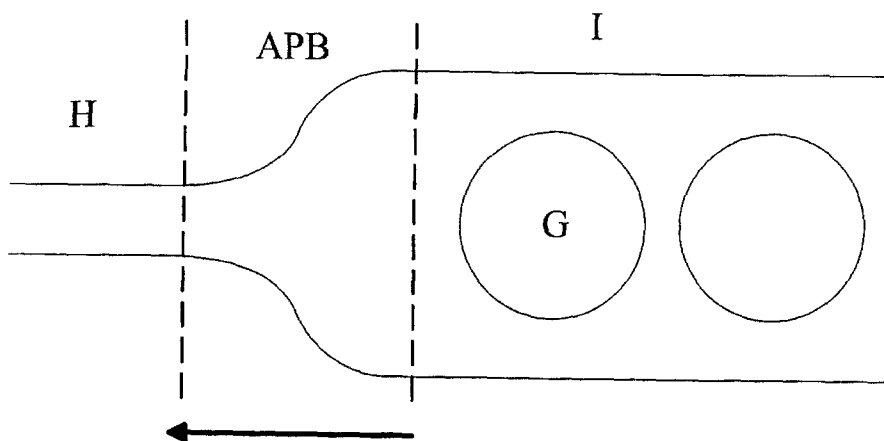


Figure 3. Schematic drawing of the advancing phase boundary. H = pristine host layer, I = intercalated layer, APB = advancing phase boundary, G = guest molecule; arrow indicates the direction of the shift of APB.

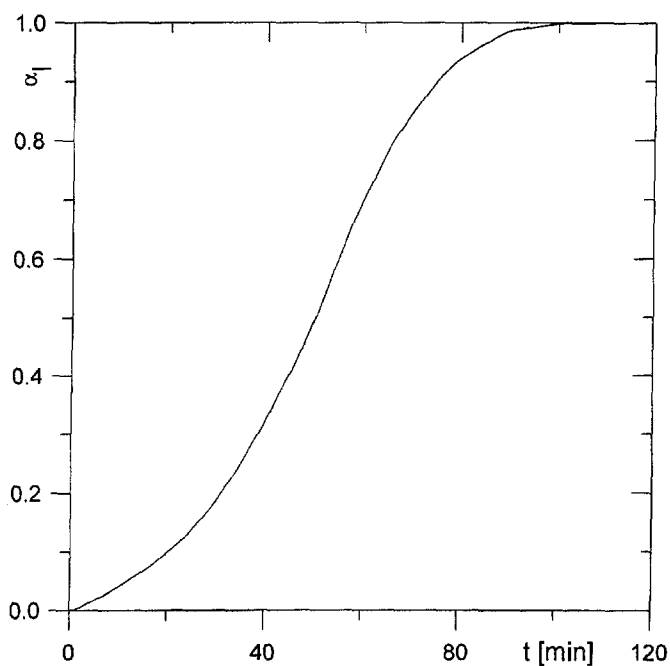


Figure 4. The dependence of the extent of reaction α_1 on time t obtained by thermomechanical analysis.

temperature. Also in this case, a sigmoid shape is apparent for all three kinetic curves.

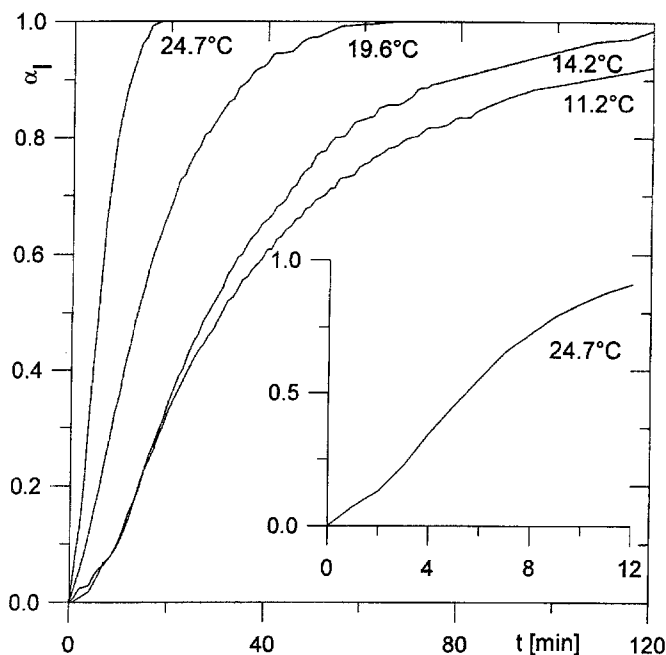


Figure 5. Kinetic curves for intercalation of liquid ethanol into vanadyl phosphate at various temperatures obtained by the volumetric method.

The shape of the kinetic curves is the same and does not depend on the method of measurement used. The result is the same regardless of whether the alcohol is used in the liquid (TMA, volumetric measurement) or vapor phase (XRD). One of the plausible explanations of the sigmoid shape of the kinetic curves is a two-step mechanism of the intercalation mentioned above. The first step is entering of the ethanol molecules into the interlayer space at the edge of the crystals which is accompanied by drawing of the neighboring layers of $(\text{VOPO}_4)_\infty$ away (the nucleation). In the second step, the intercalate zone spreads into the internal parts of the crystals (the growth). According to Clark *et al.* [2], the kinetic data can be fitted by an Avrami equation for nuclei-growth reactions of non-integral order. In this case, the values obtained from volumetric measurements were used for calculation of the rate constants. An Arrhenius-type dependence of these rate constants on temperature (Figure 6) gives the preexponential factor of $6.9 \times 10^{14} \text{ s}^{-1}$ and the value of the activation energy of $100 \pm 14 \text{ kJ mol}^{-1}$. This value is higher than the value found for the intercalation of butanol into VOSO_4 , which can be explained by the fact that alcohols are less easily intercalated into VOPO_4 , as follows from our previous work [13]. In contrast to VOSO_4 , it is not possible to intercalate aliphatic alcohols with more than four carbon atoms into anhydrous VOPO_4 .

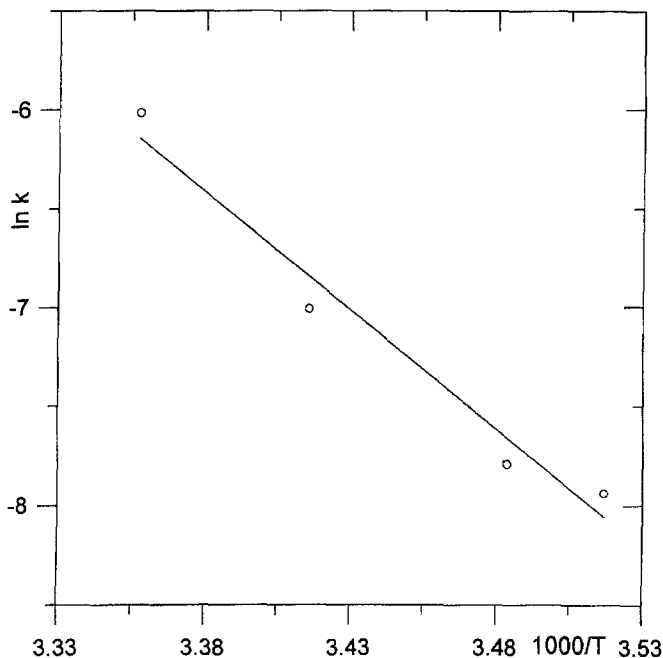


Figure 6. Arrhenius-like dependence of rate constants calculated from the data obtained by the volumetric method.

4. Conclusions

The kinetics of the intercalation of VOPO_4 with ethanol have been followed by three different independent methods. In all cases, a sigmoid shape of the kinetic curves was observed.

During this intercalation, only the fully intercalated phase is generated in contrast to the intercalation of water, where the disordered layered lattice composed of intercalated and nonintercalated layers is formed. A delay of formation of the intercalate in comparison with the decrease of the starting host material is explained by the existence of the advancing phase boundary. A presumed mechanism has two steps – the nucleation and the growth. For the description of this mechanism, a kinetic model was proposed employing the Avrami equation. The activation energy determined is higher than those found for the intercalation of cobaltocene into SnS_2 probably due to the splitting of $\text{V}=\text{O} \cdots \text{V}$ bonds between layers of the guest.

Acknowledgment

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