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Determination of the Adipic Acid Solubility Curve in Acetone by Using ATR-FTIR and Heat Flow Calorimetry

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ABSTRACT: This contribution reports the determination of the solubility curve of adipic acid in acetone by using real-time ATR-FTIR and heat flow calorimetry. Focused beam reflectance measurement was used to detect the presence of insoluble adipic acid crystals. Theoretical evaluation based on the Nývlt equation was successfully used to achieve the temperature dependence of the solubility of adipic acid. The results obtained by evaluating the experimental and simulated data indicate that both procedures presented in this report can be used as process analytical tools to determine solubility curves.

INTRODUCTION

Crystallization is an important separation and purification technique used in a wide variety of industries. The availability of the solubility curves of solid materials is vital for developing crystallization processes.[1−3]

A primary limitation to the systematic modeling and control of crystallization processes is the difficulty in obtaining accurate in situ measurements of solids' concentrations in the dense slurries typical of industrial crystallization operations. High accuracy is needed because the nucleation and crystal growth kinetics are strongly dependent on the supersaturation, which is the difference between the actual amount of the solubilized material and its concentration in a saturated solution.[4]

The following techniques have been used to prepare solubility curves or to detect crystallization processes: isothermal method,[5] titration,[1,6] density,[7] calorimetry,[8,9] turbidity and video image analysis,[10] chord length counts,[11] HPLC,[12,13] ATR-FTIR spectroscopy,[4,14] and differential scanning calorimetry.[2,15] Theoretical evaluation of the Nývlt equation has been successfully used to achieve the temperature dependence of the solubility of solid materials.[1,16,17]

Adipic acid, a solid that presents several industrial applications[6] was chosen as a case study to evaluate the adequacy of ATR-FTIR and heat flow calorimetry as analytical tools for determining adipic acid solubility in acetone. Real time analysis of the total chord length counts were used to detect adipic acid crystals present in suspension.

EXPERIMENTAL SECTION

Apparatus. The ATR-FTIR measurements were performed in a Mettler-Toledo RC1e calorimeter by using a Mettler-Toledo ReactIR IC10 spectrometer. The base unit contains the Fourier transform mid-infrared source and the mercuric cadmium telluride (MCT) detector that should be cooled with liquid nitrogen. The sample interface module (SIM) is the interface on the instrument base unit where the K6 (16 mm diameter) conduit connects. It contains the optics that transfer the infrared source light from the base unit to the probe in contact with the chemical materials contained in the vessel, and then back to the detector.

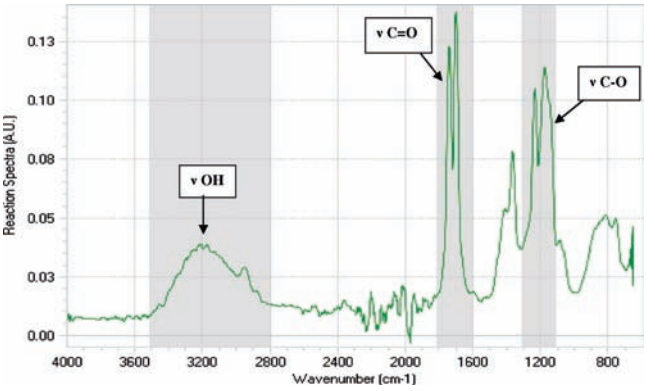

Figure 1. Absorbance spectra of adipic acid solution 10% (w/w) after subtracting the acetone absorptions, obtained at 44.8 °C.

Measurements are taken optically using a diamond sensor that uses a multiple reflection ATR element and a gold seal between the metal housing and the sensor.

The total chord length counts were obtained by using a Lasentec focused beam reflectance measurement (FBRM) that is a real-time measurement that tracks particle structures as they exist in-process. The Lasentec D600L probe consists of a Hastelloy C-22 tube with the sensor at one end with an optical diameter of 19 mm and a length of ∼406 mm. The FBRM laser provides a continuous beam of monochromatic light with a wavelength of 780 nm. The beam is located approximately 3 mm to the focal point.

Procedure. The experimental solubility of adipic acid in acetone was determined for nine different temperatures ranging from 24.9 to 49.8 °C. The solutions were prepared in an RC1e calorimeter by successive additions of adipic acid in a 1.8-L Hastelloy jacketed reactor vessel containing acetone at a stirring rate of 200 rpm. For measurements at 44.8 °C, the mass of acetone used was 594.7 g. The used mass for other temperatures are presented as Supporting Information in Table 3. The solubilization temperature was maintained constant during the whole process.

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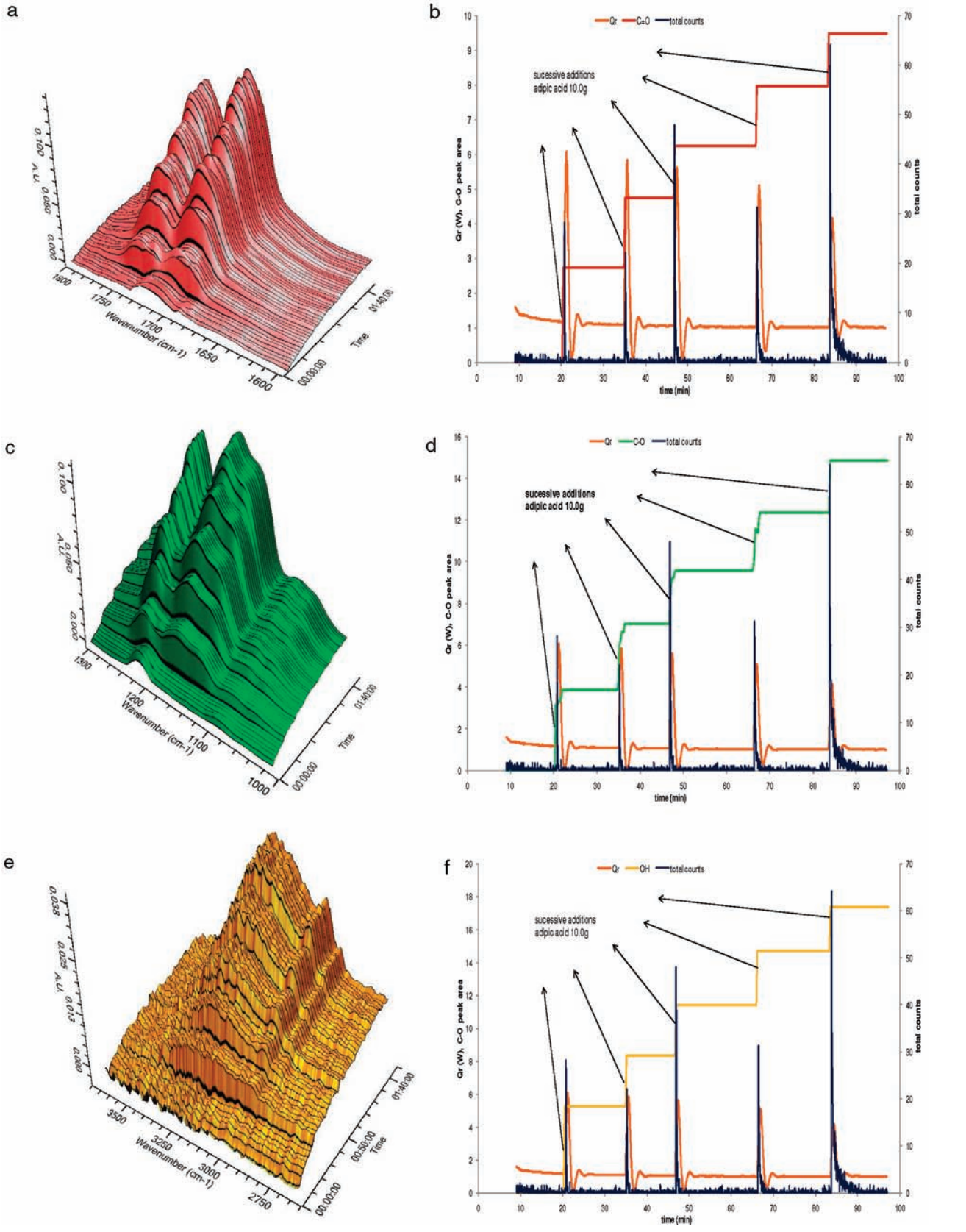

Figure 2. (a) C═O absorption (absorbance units). (b) C═O peak area and total chord length counts. (c) C−O absorption (absorbance units). (d) C−O peak area and total chord length counts. (e) O−H absorption (absorbance units). (f) O−H peak area and total chord length counts.

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ATR-FTIR and FBRM probes were kept immersed in the adipic acid solution 5 cm above the propeller stirrer. Infrared spectra obtained from 4000 to 650 cm^{-1} at 4 wavenumber resolution, were collected at 15 s intervals with each spectrum averaged over 30 scans.

RESULTS AND DISCUSSION

The solubility of adipic acid in acetone by ATR-FTIR was evaluated by analyzing the area of the C−O (1300−1100 cm^{-1}), C═O (1750−1600 cm^{-1}), and the O−H absorption bands (3600−2600 cm^{-1}) as presented in Figure 1. The split of the carbonyl absorption is due to the dimer association of carboxylic acids.[18]

The *X*, *Y*, and *Z* axes in the three-dimensional plots shown in Figure 2a,c,e correspond to wavenumbers, absorbance units, and experimental time respectively. The increased absorption peak areas observed after each addition of adipic acid, shown in Figure 2b,d,f, correspond to the increase in the adipic acid concentration in solution. The plateaus obtained after each addition indicate that the whole added material was made soluble. This indication obtained by FTIR analysis can be confirmed by the fact that the total chord length counts equal zero when the peak areas are constant in the plateaus (Figure 2b, d,f). All data presented in Figure 2 were obtained before the saturation of the solution.

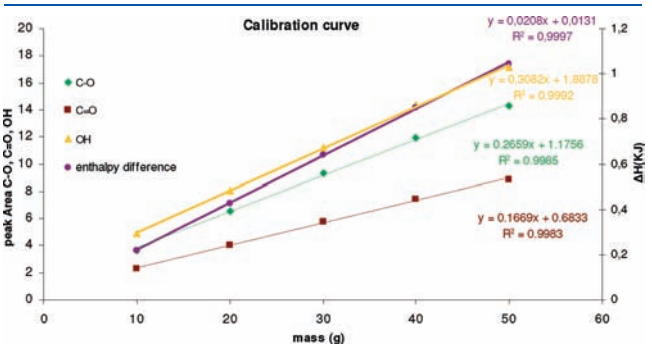

Figure 3. Calibration curves for the C−O (1300−1100 cm^{-1}), the C═O (1765−1660 cm^{-1}), the O−H (3500−2800 cm^{-1}) absorption bands and the enthalpy differences (ΔH) obtained at 317.8K.

The calibration curves that correlate the adipic acid added mass in acetone with the FTIR absorbance and the heat flow during the solubilization process are presented in Figure 3.

The peak areas of the C−O, C═O, and OH infrared absorption bands (Figure 2a,c,e) were used to construct the infrared calibration curves. The enthalpy differences (ΔH) between additions were obtained by calculating the heat flow peak areas (Figure 2b,d,f).

All analyses presented linear quadratic correlation coefficients (r^2) higher than 0.99, indicating a very good linear relationship with the adipic acid added mass.[20]

To make the determination of the solubility curve of adipic acid in acetone possible, similar experiments were performed at temperatures ranging from 29.9 to 49.8 °C. These calibration curves are presented in Table 4 in Supporting Information. These results are summarized in the data presented in Table 2.

When the saturation of the solution is achieved, the infrared absorption bands as well as the enthalpy variation should not present any change. The total chord length counts, after the saturation point, should present an increase indicating that the total added mass of adipic acid was not made completely soluble. These observations are presented in Figure 4.

The results presented in Figure 4 show clearly that the saturation point was reached only after five additions of adipic acid. The total chord length counts presented a measurable value only in the sixth addition. The last added portion was twice as big as the others. By analyzing the increased C−O peak area and the smallest solubilization enthalpy (ΔH) obtained in this addition,

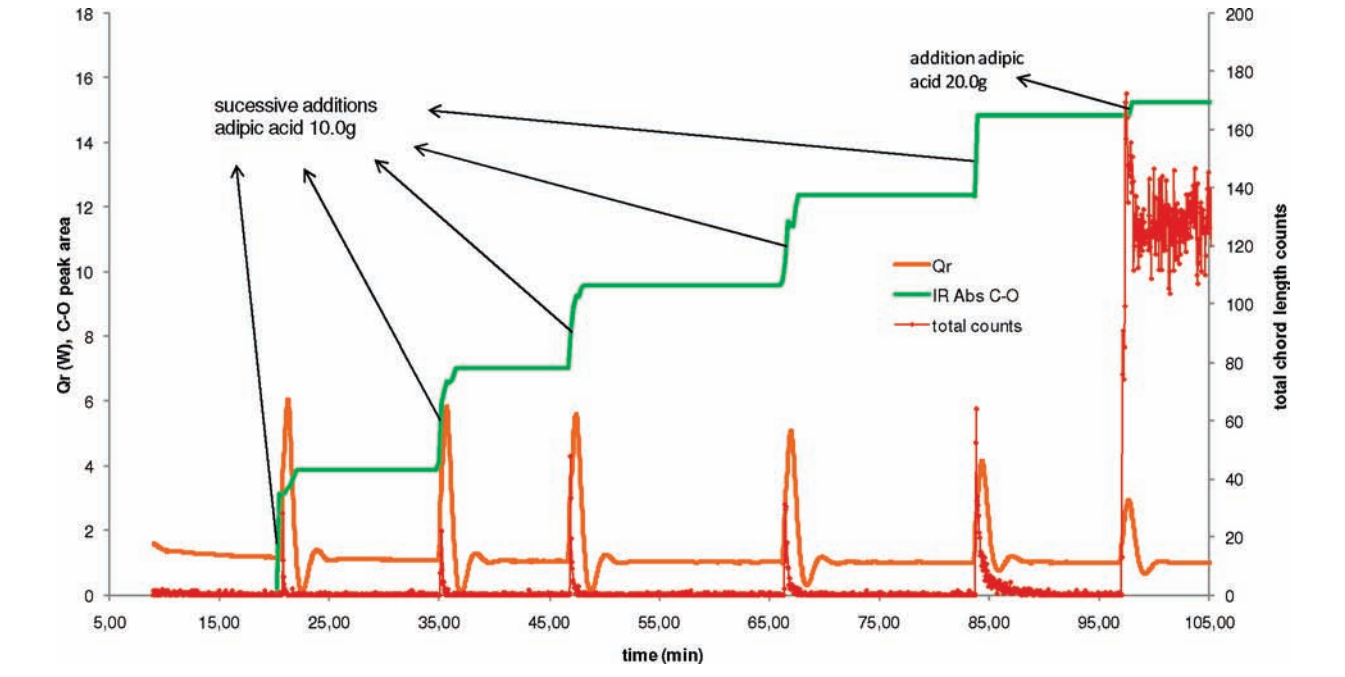

Figure 4. C−O peak area, heat flow curve, and total chord length counts obtained for additions of adipic acid that produce concentrations above saturation.

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Table 1. Comparison between FTIR and heat flow solubility data

temperature		adipic acid molar fraction (x_1)			
(K)	(°C)	FTIR	FTIR error (%)	ΔH(KJ)	ΔH error (%)
297.9	24.9	0.01681	1.34	0.01694	0.834
301.9	28.9	0.01903	1.15	0.01937	0.109
304	31.0	0.02027	0.593	0.02073	2.18
309.9	34.9	0.02387	0.651	0.02428	0.145
311.9	38.9	0.02603	0.326	0.02739	0.335
313.9	40.9	0.02795	0.050	0.02946	2.88
315.8	42.8	0.03081	0.183	0.03197	0.774
317.8	44.8	0.03300	0.621	0.03508	0.382
322.8	49.8	0.03867	0.859	0.04067	0.817

Table 2. Nývlt Parameters

	a	b	c	$\times 10^{-4}$ rmsd
Equation Parameters from FTIR Analysis				
C−O	−238.452	8014.13	36.4162	4.10405
C═O	−342.004	12828.8	51.7594	4.48804
OH	−456.582	18133.3	68.7532	6.01352
Equation Parameters from ΔH Analysis				
C−O	−465.160	18442.3	70.0786	5.92049
C═O				
OH				

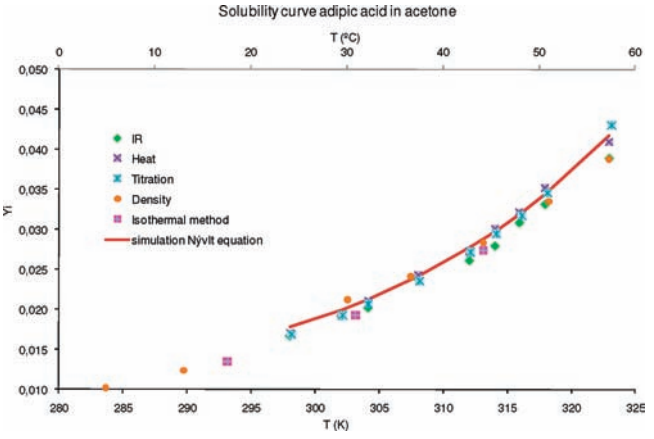

Figure 5. Solubility curves of adipic acid obtained by using ATR-FTIR, ΔH, density,[7] isothermic method,[5] and titration.[1].

it leaves no doubt that only a small part of the adipic acid was made soluble. If the total amount of adipic acid had been made soluble, a peak area of (0.40) should be found instead of the (0.10) which was found. The determination of the saturation point for each temperature was achieved by extrapolating the data furnished by the calibration equations. The molar fractions (x_1) obtained by FTIR and the enthalpy differences are presented in Table 1.

The determination of the saturation point for each temperature was achieved by extrapolating the data furnished by the equations, and these data are presented in Table 2.

Mathematical Modelling. The Nývlt model,[16,17,22] which makes the assumption that the enthalpy of the solution is directly proportional to the temperature, gives the expression obtained from the Clausius−Claperon equation.

By using the Nývlt procedure, the solubility of adipic acid may be obtained by eq 1.

$$\ln x_1 = a + \frac{b}{T} + c \ln T \qquad (1)$$

where T is the absolute temperature, the unit of which is K, and a, b, and c are empirical constants. The solubility data are correlated with eq 1.[13,17]

The values of the three parameters a, b, and c together with the root-mean-square deviations (rmsd) are listed in Table 2. The rmsd is defined as the following:

$$\text{rmsd} = \left\{ \frac{\sum_{i=1}^{N} [(x_{1,i} - x_{1,i}^{\text{calc}})]^2}{N-1} \right\}^{1/2} \qquad (2)$$

where N is the number of experimental points; x_1,i calculation is the solubility calculated from eq 2; and x_1,i is the experimental value of solubility.

The comparisons between the data presented herein and other published values[1,5,7] are presented in Figure 5

The close agreement between the solubility curves obtained by the real-time analysis used in this contribution (ATR-FTIR and heat flow calorimetry) and the literature data makes its utilization possible as a process analytical tool for determining solubility curves.

CONCLUSION

The solubility curve of adipic acid was determined by using real time, ATR-FTIR, and heat flow calorimetry analysis. The total chord length count was used to detect the presence of insoluble adipic acid crystals. Very good linear quadratic correlation coefficients were obtained for the FTIR and heat flow real time analyses were plot against the adipic acid added mass. The Nývlt equation was successfully used to achieve the temperature dependence of the solubility of adipic acid in acetone. The very close agreement between the solubility curves (obtained by ATR-FTIR and heat flow calorimetry) and previous literature data obtained by other techniques indicates that both procedures presented herein can be used as process analytical tools to determine solubility curves.

ASSOCIATED CONTENT

Supporting Information. Experimental details and calibration curve equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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