Determination of the Solid−Liquid Phase Diagram of the Binary System Acrylic Acid + Propionic Acid

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ABSTRACT: In this work, the solid−liquid equilibrium of the binary system acrylic acid (AA) + propionic acid (PA) has been determined by two different methods: analytical and synthetic methods. The phase diagram of AA + PA we obtained exhibits an eutectic behavior, a peritectic point, and a peritectic compound which has never been identified before. Current crude biobased AA contains a higher proportion of PA than AA from petrochemical origin. The determined phase diagram is favorable to the implementation of melt crystallization, and good theoretical yields can be assumed for the production of AA with a high purity.
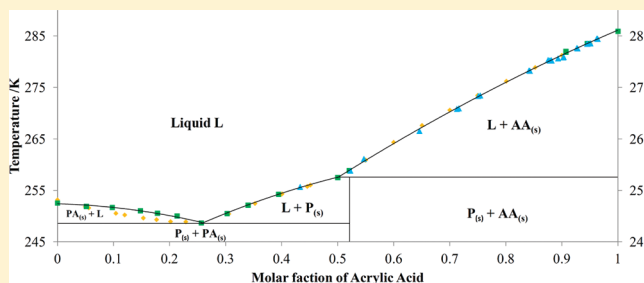
INTRODUCTION

With a global market exceeding four million tons per year, acrylic acid (AA) is a major intermediate chemical. Acrylic acid and esters are very versatile building blocks which are used in polymer and copolymer forms. They can be used in a variety of fields such as superabsorbent polymers, detergents, paint formulation, adhesive, water treatment, paper, and textile, to name a few. The current AA synthesis is based on propylene, which is obtained by the steam cracking of oil fractions. Today, AA is fully dependent on the oil market.

To diversify the feedstocks for AA production, a novel production route is envisioned, based on glycerol, a green byproduct of oleochemistry and biodiesel production. However, its current applications are limited. To synthesize bio-AA, glycerol is dehydrated to acrolein, which is then oxidized. The impurity profile of crude biobased AA is different to that of classical propylenebased AA. In particular, an impurity, propionic acid (PA), could be produced significantly. This component could be undesirable for applications of the monomer. Classical purification techniques of AA cannot efficiently separate these two chemicals since their carbon chains are similar, their chemical functions are almost identical, and their boiling points are extremely close. However, melting points differ significantly, allowing melt crystallization to be a promising separation technique.

To be competitive and to respect new environmental regulations, chemical industries in Europe have to design new processes. Melt crystallization is not a widespread purification technique, whereas it has many advantages over other separation techniques such as distillation, absorption, and adsorption:

- low energy consumption,
- production of high-purity products,
- high environmental safety, since operations are done at lower temperatures,
- reduced maintenance costs,

- no need for additional substances, since it is free from solvent,
- thermosensitive products can be purified.

Melt crystallization permits the separation of compounds with less energy and fewer subsidiary compounds such as solvent.[1] This purification technique takes place in process intensification. Moreover, melt crystallization is sometimes one of the only purification techniques to be able to separate products such as isomeric compounds.

The solid−liquid phase diagram provides fundamental thermodynamic data necessary for the purification by melt crystallization. First of all, it verifies the absence of areas of miscibility at the solid state of the chemicals to be separated. Indeed, the separation of compounds that form solid solutions is almost impossible by melt crystallization.

Moreover, the liquidus curve is an essential piece of information that the phase diagram brings. This curve delimits regions of solid−liquid equilibrium and the liquid state. It allows us to know the temperature at which a mixture starts to crystallize, for an ideal system without supercooling, and it gives the composition of the liquid phase in a system in thermodynamical equilibrium at a fixed temperature. Therefore, for an initial mixture to purify with a given proportion of PA, the phase diagram allows us to determine the temperature at which the process must be operated, to reach a desired yield.

Solid−liquid equilibrium AA + PA data in the engineering literature are restricted. Lohmann et al.[2] worked on the solid−liquid equilibrium of several organic binary systems, and they proposed some points of the liquidus curve AA + PA. An eutectic point has been observed by extrapolation, and a peritectic behavior
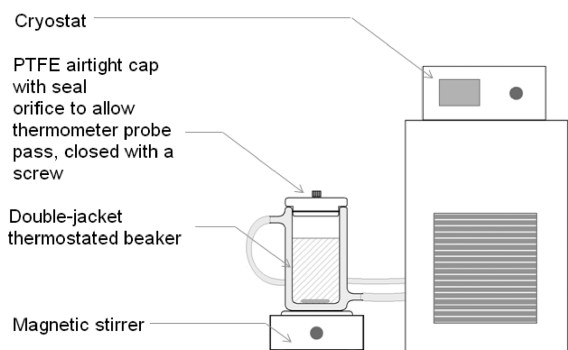
Figure 1. Experimental apparatus for analytical measurements of solid—liquid equilibria.

has been presumed. Thus, since the purification of AA is strongly dependent on these thermodynamical data, the phase diagram AA + PA had to be established with precision. Therefore, two different experimental techniques have been used: analytical and synthetic methods.

METHODS OF PHASE DIAGRAM DETERMINATION

Analytical Method. To determine the phase diagram, several methods and techniques exist. Some are based on thermal analysis, and they can use differential thermal analysis (DTA) or differential scanning calorimetry (DSC) to detect phase transitions. Others rely on chemical analysis of phases in thermodynamical equilibrium, as the analytical method does, a technique we used. This method[3,4] consists of measuring one of the component concentrations in the liquid phase in a sample with an excess amount of the solid phase at a given temperature.

Moreover, we studied the time required for establishment of thermodynamic equilibrium, and it was shown that, after six hours, the system was at stationary state; the proportion of PA in the liquid phase did not vary significantly. Experimentally, the liquid phase was analyzed using a gas chromatograph (GC) Agilent-6890N, equipped with a flame ionization detector. The chromatographic column was a FFAP-HP (50 m × 0.32 mm × 0.50 μm), heated at 503 K. In our experimental conditions, the retention times for AA and PA were respectively 4.60 min and 4.37 min, with an injected volume of 1 μL and a split-ratio of 10. Each sample is analyzed three times. Glacial AA was supplied by Arkema, and PA was obtained from a commercial source (Acros). Gas chromatography analysis gave a purity of 0.9995 in mass fraction for AA and 0.9980 for PA.

Thermodynamical equilibria were established in the experimental apparatus represented in Figure 1. The device consists of a double jacket beaker where the medium is homogenized by a magnetic stirrer. The system is airtight and thermostatted by circulating water—glycol which temperature is fixed by a cryostat. It should be noted that, below 273 K, the whole system is heat-insulated. Using this device, experiments between 245 K and 300 K can be performed. The uncertainty in the determination of the temperature is given by the thermometer used. In this case, the calibrated thermometer EBRO used provides an uncertainty of ± 0.02 K.

After six hours, stirring is stopped, and a good liquid—solid separation phase allows us to sample easily the liquid phase

which is analyzed three times by gas chromatography, to measure the quantities of both acids. The absolute uncertainty in mole fraction is assumed to be ± 0.0001.

Synthetic Method. Another technique to determine the phase diagram is the synthetic method.[2,5,6] In this method, a sample, previously quenched, with a known composition, is heated up at a defined rate (0.2 K·h^{-1}). This temperature increase must be particularly slow to let the establishment of thermal equilibrium. The liquidus point is the temperature at which all solid phase just disappears.

The mixtures are prepared using Class A material such as a measuring pipet and measuring phial. The uncertainty of the given composition is assumed as ± 0.0001 in mole fraction. It should be noticed that the temperature of disappearance of any solid phase in suspension is detected visually with an evaluated uncertainty within ± 0.02 K. This good precision is due to the low reheating rate of the system and to a very good solid—liquid separation phase. The reproducibility of the results was controlled by determining five times the liquidus temperature of a mixture AA/PA 90:10 (vol/vol) where the standard deviation was within ± 0.065 K. The experimental device is the same as the one used for the analytical method. The average time necessary to establish a point of the liquidus curve was eight hours. Unlike the analytical method, the determination of the points of liquidus does not require us to titrate the liquid phase.

Table 1. Experimental Solid—Liquid Equilibrium Data for the Binary System Acrylic Acid (AA) + Propionic Acid (PA) Using the Analytical Method

T/K	x_{AA}	T/K	x_{AA}
284.45	0.9638	280.25	0.8815
284.50	0.9623	280.25	0.8781
283.55	0.951	278.30	0.8412
283.55	0.9502	278.25	0.8428
283.50	0.9456	273.45	0.7543
283.50	0.9449	273.35	0.7507
282.65	0.9266	270.95	0.7161
282.60	0.9277	270.85	0.7126
280.90	0.9033	266.55	0.6458
280.85	0.9023	261.15	0.5467
280.65	0.8931	258.85	0.5225
280.35	0.8753	255.70	0.4329
280.30	0.8805		

Analysis of the Peritectic Compound. Binary mixtures containing between (0.3697 ± 0.0001) mol/mol and (0.4207 ± 0.0001) mol/mol of AA are thermostatted in the experimental apparatus represented in Figure 1, to establish thermodynamical equilibrium. Samples are prepared with Class A material and analyzed by gas chromatography. Systems are kept at a temperature comprised between $(250.65$ and $254.35)$ K. After two days, the solid and the liquid phase are separated to be analyzed. Then, the crystals are partially molten to wash the solid surface from the liquid phase. The residual solid is totally molten and analyzed by gas chromatography.

■ RESULTS

Tables 1 and 2 contain the experimental results obtained using the two techniques previously described. The set of our experimental

Table 2. Experimental Solid−Liquid Equilibrium Data for the Binary System Acrylic Acid (AA) + Propionic Acid (PA) Using the Synthetic Method

T/K	x_{AA}	T/K	x_{AA}
285.90	1.0000	254.25	0.3943
283.50	0.9450	252.15	0.3400
282.00	0.9071	250.50	0.3026
282.00	0.9071	249.05	0.2658
281.95	0.9071	248.65	0.2565
281.85	0.9071	249.05	0.2450
281.90	0.9071	249.35	0.2345
258.85	0.5204	250.05	0.2134
258.25	0.5107	250.55	0.1783
257.50	0.5000	251.05	0.1479
257.45	0.4956	251.70	0.0979
257.05	0.4806	252.00	0.0515
255.75	0.4403	252.55	0.0000
255.10	0.4200		

liquidus points is represented in Figure 1. Results obtained by analytical and synthetic method are identical, as shown in Figure 2. Besides, the time of experiment and accuracy are similar. The main difference concerns the necessity for titrating the liquid phase.

Table 3 gives the composition of the solid phase formed at a temperature comprised between $(250.65$ and $254.35)$ K from binary mixtures. This crystalline phase corresponded to a peritectic compound, which contained on average 0.5214 mol/mol of AA with a standard deviation within $\pm$ 0.0004 mol/mol.

■ DISCUSSION

By extrapolation of points of liquidus curve, we propose the phase diagram represented in Figure 2.

The experimental points can be represented by the following correlating equations:

$$T = -(21.63/K) \cdot (x_{AA})^2 + (89.69/K) \cdot x_{AA}$$
$$+ (218.07/K) \qquad \text{for} \quad 0.5000 < x_{AA} < 1.0000$$

$$T = -(38.12/K) \cdot (x_{AA})^2 + (65.72/K) \cdot x_{AA}$$
$$+ (234.24/K) \qquad \text{for} \quad 0.2565 < x_{AA} < 0.5000$$

$$T = -(44.73/K) \cdot (x_{AA})^2 - (2.72/K) \cdot x_{AA} + (252.43/K)$$
$$\text{for} \quad 0.0000 < x_{AA} < 0.2565$$

The determination coefficients are respectively 0.999, 0.999, and 0.992.

As shown in Figure 2, the experimental results were compared to literature data.[2]

The experimental liquidus curve fits well with the one obtained by Lohmann et al.[2] from $(0.2565$ to $1.000)$ mol/mol of AA. However, between $(0$ and $0.2565)$ mol/mol the curvatures are opposite. Indeed, our results led to an equation $T = f(x_{AA})$, for which the second derivative is negative while results of Lohmann et al.[2] give a positive second derivative. More commonly, the
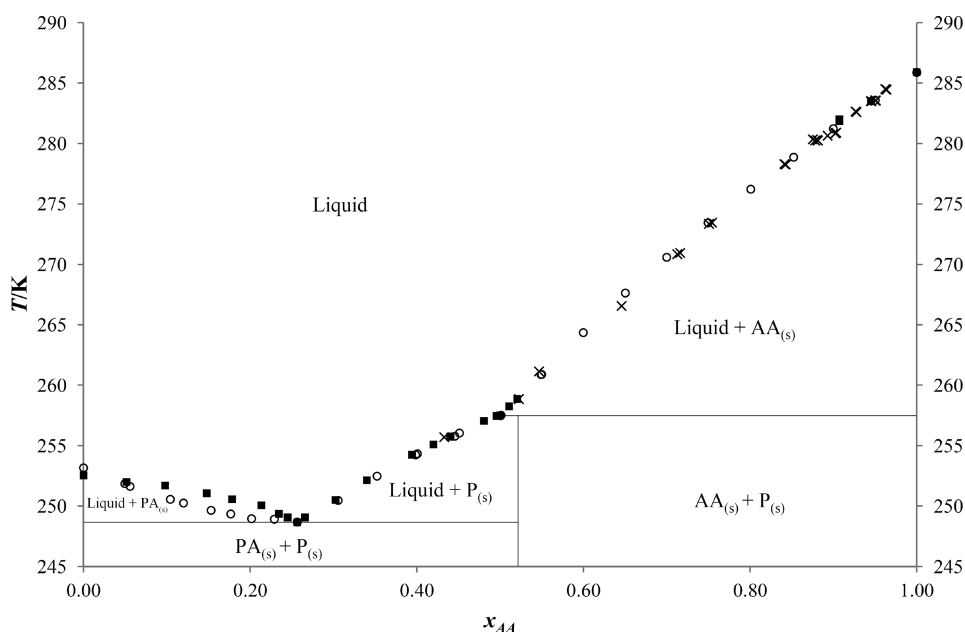

Figure 2. Experimental solid−liquid equilibrium of the binary system acrylic acid (AA) + propionic acid (PA): literature data, ○; results obtained with the analytical method, ×, and synthetic method, ■. $P_{(s)}$ corresponds to the solid peritectic compound at the solid state, and $AA_{(s)}$ and $PA_{(s)}$ stand for, respectively, acrylic acid (AA) at the solid state and propionic acid (PA) at the solid state. The composition of the system in AA is given by x_{AA} in mole fraction.

Table 3. Experimental Measurements of the Solid Phase x^S_{AA} Formed from Initial Binary Systems Acrylic Acid (AA) + Propionic Acid (PA) with a Given Composition x^0_{AA} at Temperature T

T/K	x^0_{AA}	x^S_{AA}
254.35	0.4207	0.5216
254.35	0.3697	0.5215
252.15	0.4207	0.5213
252.15	0.3953	0.5209
250.65	0.3953	0.5210
250.65	0.3697	0.5221

concavity of liquidus curves corresponds to a negative second derivative. Besides, melting points of pure PA from our work and the one of Lohmann et al.[2] differ, as shown in Table 4.

Table 4. Melting Points T/K of Pure Compounds

	T/K			
	results	Lohmann et al.[2] (1998)	Lebedev et al.[8] (1999)	Haynes[7] (2011)
PA	252.55 ± 0.02	253.17 ± 0.015		252.65
AA	285.90 ± 0.02	285.87 ± 0.015	286.71 ± 0.01	285.65

The value of the melting point we obtained for PA was very close to the value referred by Haynes.[7] As for AA, our measurements and the results of Lohmann et al.[2] correspond to similar melting points, close to the literature value.[7,8] Besides, our experimental device allowed carrying out experiments at low temperatures such as 250 K and led to accurate results.

This diagram shows immiscibility at the solid state of both acids, moving away from the problematic case of solid solutions. Specifically, the part of the diagram between (0.5000 and 1.0000) mol/mol of AA shows that AA crystallizes purely during cooling while the liquid phase is being enriched in PA. This region of the phase diagram makes crystallization favorable to separate these acids.

A peritectic compound, which contained (0.5214 ± 0.0004) mol/mol of AA, has been identified for the first time, which confirmed the assumed peritectic behavior of the binary system AA + PA.

Besides, the eutectic behavior was confirmed at (0.2565 ± 0.0001) mol/mol of AA, at (250.05 ± 0.02) K, and the peritectic point at (0.5000 ± 0.0001) mol/mol of AA, at (257.50 ± 0.02) K. This point constitutes the thermodynamical limit during purification: indeed, the maximal enriching limit of mother liquor in PA is 0.5000 mol/mol.

CONCLUSION

The solid−liquid phase diagram AA + PA has been determined now with precision, by two different experimental techniques which led to results strictly identical. Besides, a peritectic compound (0.5214 ± 0.0004) mol/mol of AA has been crystallized and identified. Eutectic behavior and peritectic point have been identified, respectively at (0.2565 ± 0.0001) mol/mol of AA and at (0.5000 ± 0.0001) mol/mol of AA. It was also shown that AA crystallized with a theoretical 100 % purity when the liquid phase contained from (0.5000 to 1.0000) mol/mol of AA. These thermodynamical data constitute basic knowledge, necessary for optimal implementation of the purification of AA by melt crystallization. Clearly, this diagram is favorable to the purification of AA. Moreover, crude bio-AA is not a binary

system but a multicomponent mixture. The impact of these impurities on the phase diagram AA + PA has to be evaluated.

These results allow tackling serenely the purification of AA by melt crystallization. A stainless steel tube-calender crystallizer will be used for purification tests of AA+PA. The device will allow a recirculation of the liquid phase to improve mass and heat transfers. Besides, many surface defects of steel promote nucleation surfaces (primary heterogeneous), which severely limits the problems caused by supercooling. Indeed supercooling generates too-rapid growth of crystals and increases risks of inclusions of the mother liquor.

Finally, cavities that AA crystals presented[9] retain the impure liquid, which reduces the purity of the final product. Thereby, their growth must be mastered by optimizing the operating conditions.

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Ulrich, J. Is melt crystallization a green technology? *Cryst. Growth Des.* **2004**, *4*, 879−880.

(2) Lohmann, J.; Röpke, T.; Gmehling, J. Solid-liquid equilibria of several binary systems with organic compounds. *J. Chem. Eng. Data* **1998**, *43*, 856−860.

(3) Kurosama, I. Solid-Liquid equilibrium in multi-solute systems. Ph.D. Dissertation, Georgia Institute of Technology, Atlanta, GA, 2004.

(4) Cohen-Adad, R.; Cohen-Adad, M. T. Solubilities of Solids in Liquids. In *The Experimental Determination of Solubilities*; Hefter, G. T., Tomkins, R. P. T., Eds.; John Wiley & Sons: Chichester, 2004.

(5) Jakob, A.; Joh, R.; Rose, C.; Gmehling, J. Solid−Liquid equilibria in binary mixtures of organic compounds. *Fluid Phase Equilib.* **1995**, *113*, 117−126.

(6) Fiege, C.; Joh, R.; Petri, M.; Gmehling, J. Solid−Liquid Equilibria for Different Heptanones with Benzene, Cyclohexanone, and Ethanol. *J. Chem. Eng. Data* **1996**, *41*, 1431−1433.

(7) Haynes, W. M. Physical constant of organic compounds. *Handbook of Chemistry and Physics*, 91st ed.; CRC Press, Inc.: Boca Raton, FL, 2011.

(8) Lebedev, B. V.; Kulagina, T. G.; Veridusova, V. V. Thermodynamics of acrylic acid from T = 5 K to T = 330 K. *J. Chem. Thermodyn.* **1999**, *31*, 1077−1084.

(9) Beilles, S.; Franke, R.; Nordhoff, S. Influence of water as an impurity on acrylic acid melt crystallization. *Chem. Eng. Trans.* **2002**, *1*, 725−730.