Solvent Screening and Measurement of Phase Diagrams for the Yield Maximization of an Acrylic Acid Crystallization

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The yield of crystallization processes is mostly limited by the eutectic points as thermodynamic limits and the economically acceptable temperature level. In some cases it is possible to increase the yield and to improve the crystallization performance by the addition of a dedicated third component. Therefore, a structured solvent screening method is developed to rapidly identify possible solvents to increase the yield and to improve the performance of a crystallization unit if limiting factors are known. For a fast validation, an experimental stage gate process is developed to come up with the required information of each stage at a minimum workload. The developed stage gate process is based completely on thermal analysis using differential scanning calorimetry (DSC). The solvent screening approach and the stage gate process are successfully adopted to investigate the yield maximization of an acrylic acid crystallization from an aqueous melt by adding a third component. For three possible components complete ternary solid−liquid equilibrium diagrams are measured and evaluated.

1. Introduction

The recovery of acrylic acid by melt crystallization is limited in different ways. The yield is limited by the eutectic point at w_{AA} (mass fraction) = 0.62 and a temperature of 262.15 K. Additionally, the performance of the suspension crystallization unit is limited by the water content of the mother liquid. Increasing water content causes problems in the downstream solid−liquid separation, too.[1,2]

Therefore, the general scope of the present work is to increase the yield by the addition of a third component and therefore by altering the eutectic limit. Further, the performance of the crystallization should be improved in that way that the maximum recovery of acrylic acid should be achieved at low water content to reduce compressibility problems.[2]

The work flow should be divided into two stages to save time and money. This results in a dedicated solvent screening for the component identification and ends in a concerted experimental work flow using fast thermal analysis methods.

2. Solid−Liquid Equilibrium

2.1. Theoretical Prediction of a Solid−Liquid Phase Equilibrium. For the theoretical prediction of the solid−liquid equilibrium of an ideal system the van't Hoff equation can be used. The van't Hoff equation is presented by eq 1 below:

$$x_i^{\mathrm{L}} = \exp\left[-\frac{1}{RT}\cdot\Delta_{\mathrm{fus}}h_i\cdot\left(1-\frac{T}{T_{0i}^{\mathrm{SL}}}\right)\right] \qquad (1)$$

For the prediction of the solid−liquid equilibrium of acrylic acid and water, it is important to consider the aqueous milieu. Therefore, it is not possible to use the ideal van't Hoff equation without including the activity coefficients. The activity coefficients can be calculated by well-known thermodynamic models, that is, nonrandom two-liquid (NRTL) or universal quasichemical activity coefficient (UNIQUAC) models. Equation 2 represents the enhanced van't Hoff equation including the activity coefficients.

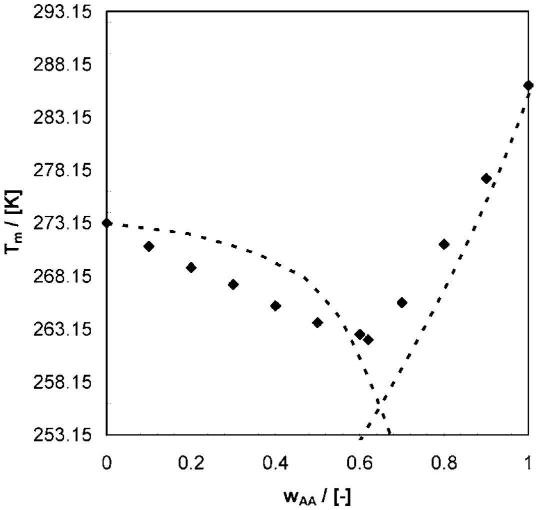

Figure 1. Solid−liquid equilibrium for acrylic acid and water; ◆, equilibrium temperatures for acrylic acid from literature;[3] - - -, calculated equilibrium temperatures via eq 2.

$$x_i^{\mathrm{L}} = \frac{1}{\gamma_i^{\mathrm{L}}}\exp\left[-\frac{1}{RT}\cdot\Delta_{\mathrm{fus}}h_i\cdot\left(1-\frac{T}{T_{0i}^{\mathrm{SL}}}\right)\right] \qquad (2)$$

For mixtures of acrylic acid and water eq 2 is used to predict solid−liquid equilibrium temperatures. The activity coefficients are calculated from ASPEN Software using model parameters fitted to VLE. The UNIQUAC model combined with the Hayden−O'Connell method was used. The results are presented in Figure 1.

It is obvious that the predicted solid−liquidus lines, which are represented by the dashed lines, differ significantly from

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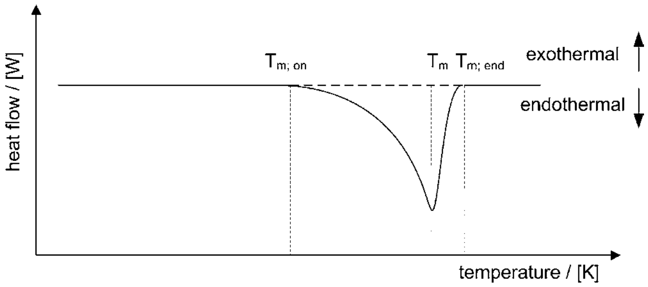

Figure 2. Heat flow of a solid to liquid phase change of a pure component.

literature data measured by Chubarov et al.[3] The temperature level of the liquidus line for water is much higher than the measured values, whereas the acrylic acid one is lower. Finally, the composition and temperature of the eutectic point differ.

This implies that the presented eq 2 based on activity coefficients is not useful to predict the solid−liquid equilibrium for the aqueous acrylic acid system. The authors' opinion is that in the near future experimental measurements of solid−liquid equilibria will still remain the preferred way to ensure reliable data for designing industrial applications. Therefore, this work is focused completely on rapid experimental procedures.

2.2. Thermal Analysis Methods for the Determination of Crystallization Thermodynamical Properties. Thermal analysis methods are generally used to quantify and qualify several kinds of phase changes and recalescence actions. For the design and the control of crystallization processes at a maximum yield, the knowledge of phase diagrams is essential. These limitations are given by the necessary operating temperature, the eutectic and peritectic points, respectively.[4]

In the past several techniques have been used to determine the solid−liquid equilibrium of a system: thermal microscopy, thermal analysis, zone melting, and single crystal growth.

These techniques are not all universally applicable, and some have only limited utility. The choice depends on a number of factors: availability of instrumentation, amount of material and time available, environmental sensitivity of the components, and temperature range.[4] In the present work, the thermal analysis, more precisely, differential scanning calorimetry (DSC), is used as a rapid measurement for temperatures and enthalpies of phase changes, requiring only very small amounts of chemical samples. This opens up a new high-throughput method to determine complete binary and ternary solid−liquid equilibrium phase diagrams.

Differential Scanning Calorimetry Principle. DSC is a thermo-analytical technique. Two crucibles—one containing the sample, the other one as a reference—are heated or cooled with the same rate. When the sample undergoes a (isothermal) phase change, unlike the reference it will not follow the heating and cooling program of the DSC device. To compensate the appearing temperature difference between sample and reference, the DSC device has to increase or decrease the heat flow to the sample crucible.

The result of a DSC experiment is a curve of heat flux versus temperature or versus time. The melting point and enthalpy of fusion of the sample material can be determined simultaneously from the DSC curve. An endothermic phase change gives a negative peak, whereas an exothermic phase changes results in a positive peak. The peak area quantifies the enthalpy of fusion. A pure sample gives a sharp peak, while an impure sample could show a broader peak, overlapping peaks, an indefinite start, and an unincisive maximum. As an example, Figure 2 represents a plot of an exothermic heat flow versus temperature. The temperature boundaries of the melting process are represented by $T_{m;on}$ and $T_{m;off}$. Whereas the index "m" represents the melting process, "on" represents the on-set and "end" the end-set, respectively. The peak represents the melting temperature T_m of the sample.

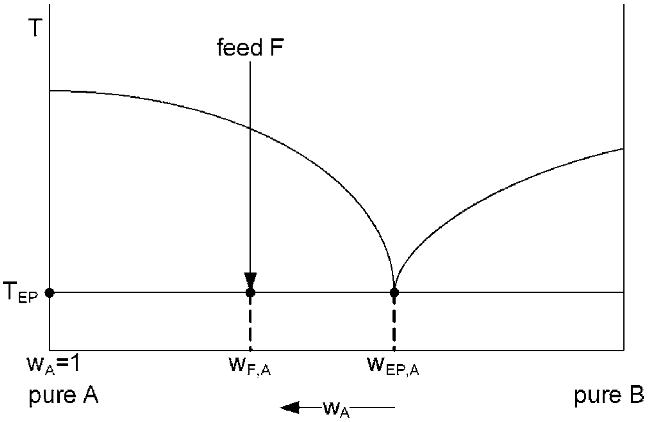

Figure 3. Calculation of the maximum yield of a crystallization unit.

T_m stands of course also for the equilibrium crystallization temperature. However, due to metastability effects, which are intrinsic to crystallization processes, it is not possible to measure the correct the phase change temperature by cooling the sample. Keeping all of these conditions in mind, the DSC provides a suitable technique to measure rapidly and exactly complete solid−liquid equilibrium phase diagrams, using the melting points of several samples at different concentrations. Additionally, the latent enthalpy of fusion can be obtained by measuring the area of the peak over time.

2.3. Determination of the Binary Eutectic Point and Equilibrium Diagram. For the industrial application of crystallization it is important to know two aspects of a solid−liquid system: (1) the maximum achievable yield and (2) the minimum operation temperature to reach an economical recovery yield.

These limits are given by the eutectic point. The eutectic point represents the minimum temperature at which a solid−liquid equilibrium exists. On the other hand, the eutectic concentration limits the possible yield of pure crystals. This becomes clear when applying the lever rule for calculating the yield of a crystallization step close to the eutectic temperature as shown in Figure 3. The mass yield of component A is then given by

$$\text{yield} = \frac{w_{F,A} - w_{EP,A}}{w_{F,A}(1 - w_{EP,A})} \qquad (3)$$

where A is the mass of pure crystals A, F is the mass of the feed with concentration $w_{F,A}$, and $w_{EP,A}$ is the mass fraction of A at the eutectic point. It is obvious that the higher $w_{EP,A}$ the more component A will remain in the mother liquor, and hence the yield will decrease.

For an extensive solvent screening it is necessary to identify the eutectic point by a standardized method. The determination of the eutectic temperature is possible by a single simple DSC experiment with only one composition of the binary system. Because of subcooling effects due to metastability, phase changes are performed from the completely solid state, hence heating up the sample.

In a binary mixture two exothermal peaks will occur. The first peak is caused by the phase change from a complete solid state into a two-phase system with solid A and liquid of eutectic

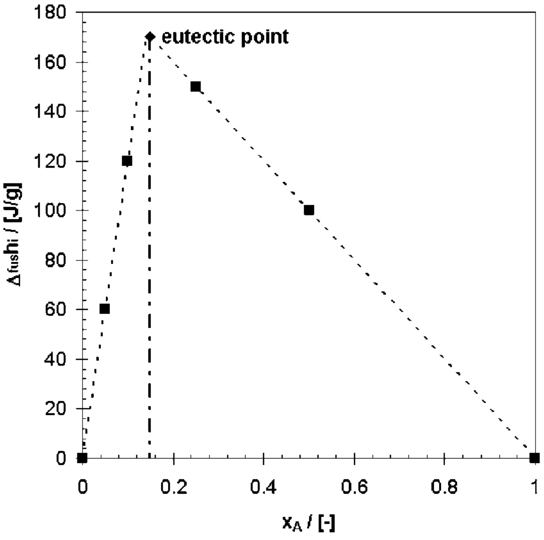

Figure 4. Method to determine the eutectic composition of the system methyl-4-hydroxybenzoate with *p*-hydroxybenzoic acid by the method of Burger;[5] ■, heat of fusion at different compositions; - - -, extrapolation lines to determine the intersection representing the eutectic point.

composition. The second peak represents the transition from a solid−liquid mixture to a complete melt.

For determination of the eutectic composition of a binary system Burger[5] proposed a simple and rapid method. The melting of samples at eutectic composition always occurs at the same temperature, but the enthalpy of fusion associated to the composition will increase with the amount of solids that can form at this certain point. For a mixture of eutectic composition, the DSC curve is similar to that of a pure component, that is, it shows only one peak. The enthalpy of fusion can be evaluated by integrating the peak area between the measured curve and a virtual or true baseline of a DSC plot.

The method of Burger[5] can be performed either via the isobaric phase diagram or via the mass related enthalpy of fusion of the eutectic peak. In the first case, the end melting temperature of the mixture is plotted against its composition. In the second case, the enthalpy of fusion per mass unit of the first peak [$J \cdot g^{-1}$] is plotted against the molar concentration x [mol %]. The second method proved to be the favorable one, because there is a linear relationship between the specific enthalpy of fusion and the concentration. Further, the integration of the first peak is easily possible for all mixtures. The end-set of the melting of the mixtures which composition lies near the eutectic can be determined only with difficulty and with little accuracy.

Figure 4 shows an example of the second method. The specific enthalpy of fusion of the first peak is plotted against the molar composition. The eutectic composition is then determined by a linear extrapolation. The intersection point characterizes the eutectic composition giving an additional point of the two-component phase diagram.[5]

2.4. Approach To Determine the Ternary Eutectic Point and Solid−Liquid Equilibrium. In analogy to a binary system, the feasibility of an industrial crystallization step depends mainly on the temperature level and limitation by the ternary point. Therefore, the proceeding described above to get rapid knowledge of the limits of a crystallization process is adapted to ternary diagrams.

The temperature level of the ternary eutectic point can also be determined by the analysis of a DSC. Figure 5 shows qualitatively a typical DSC plot of a melting process of a ternary solid system. The temperature level of the ternary point is marked with $T_{m;TEP}$.

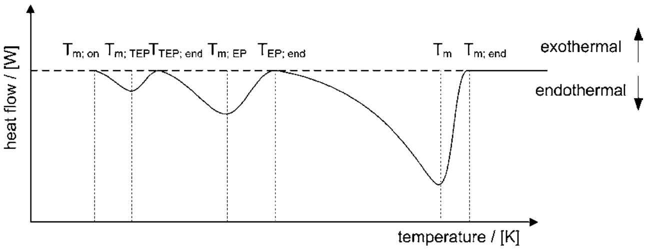

Figure 5. Enthalpy flow of a ternary system at different solid to liquid phase changes of a ternary system.

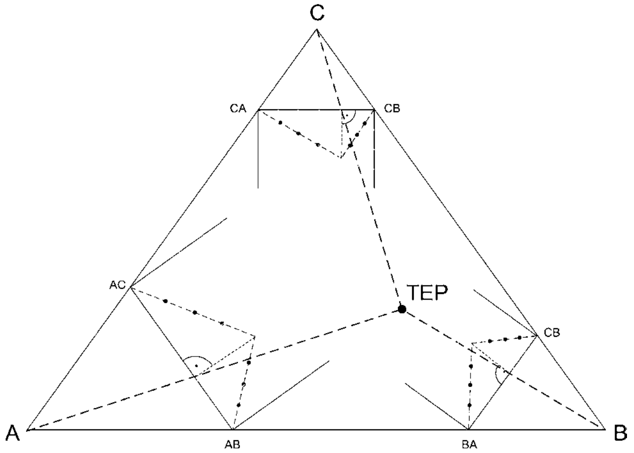

Figure 6. Determination of the triple eutectic point by adaption of the binary method of Burger.[5]

As is the case with the binary system, it is possible to calculate the enthalpy of fusion of the ternary eutectic point. The ternary eutectic point is obtained as follows and demonstrated in Figure 6:

1. $\Delta_{fus}H_{TEP}$ reaches its maximum at the ternary eutectic composition (TEP).

2. For pure components and binary mixtures $\Delta_{fus}H_{TEP}$ is zero, because in these cases the ternary eutectic point does not exist! Therefore, $\Delta_{fus}H_{TEP}$ is zero for compositions at the sides of the triangle.

3. Mixtures with compositions on the apparent lines between the ternary eutectic point and the pure components (represented by the lines A-TEP, B-TEP, and C-TEP) will exhibit only two peaks belonging to the crystallization of the pure components A, B, and C, respectively, and one peak representing the ternary eutectic point.

4. The maximum $\Delta_{fus}H_{TEP}$ of the pseudobinary system B−C at a constant mass fraction of A, for example, along AC−AB, is determined as described in Section 2.3. The connection between the respective composition and the pure component A results in a straight line. The same is done for the pseudobinary systems A−C and B−C. The intersection of the connecting lines represents the ternary eutectic point.

The approach is valid only for ternary systems, where the binary systems do not show any peritectic points. The melting behavior of peritectic systems is different from eutectic ones.

3. Approach of a Fast Solvent Screening Method

3.1. Approach for a Database Request for Fast Solvent Screening. In general the search for an additional solvent as a component to increase the yield of a crystallization process is quite difficult, because of the huge numbers of requirements and properties which have to be fulfilled, for example, nontoxicity, chemically inertness, crystalline behavior, and so forth.

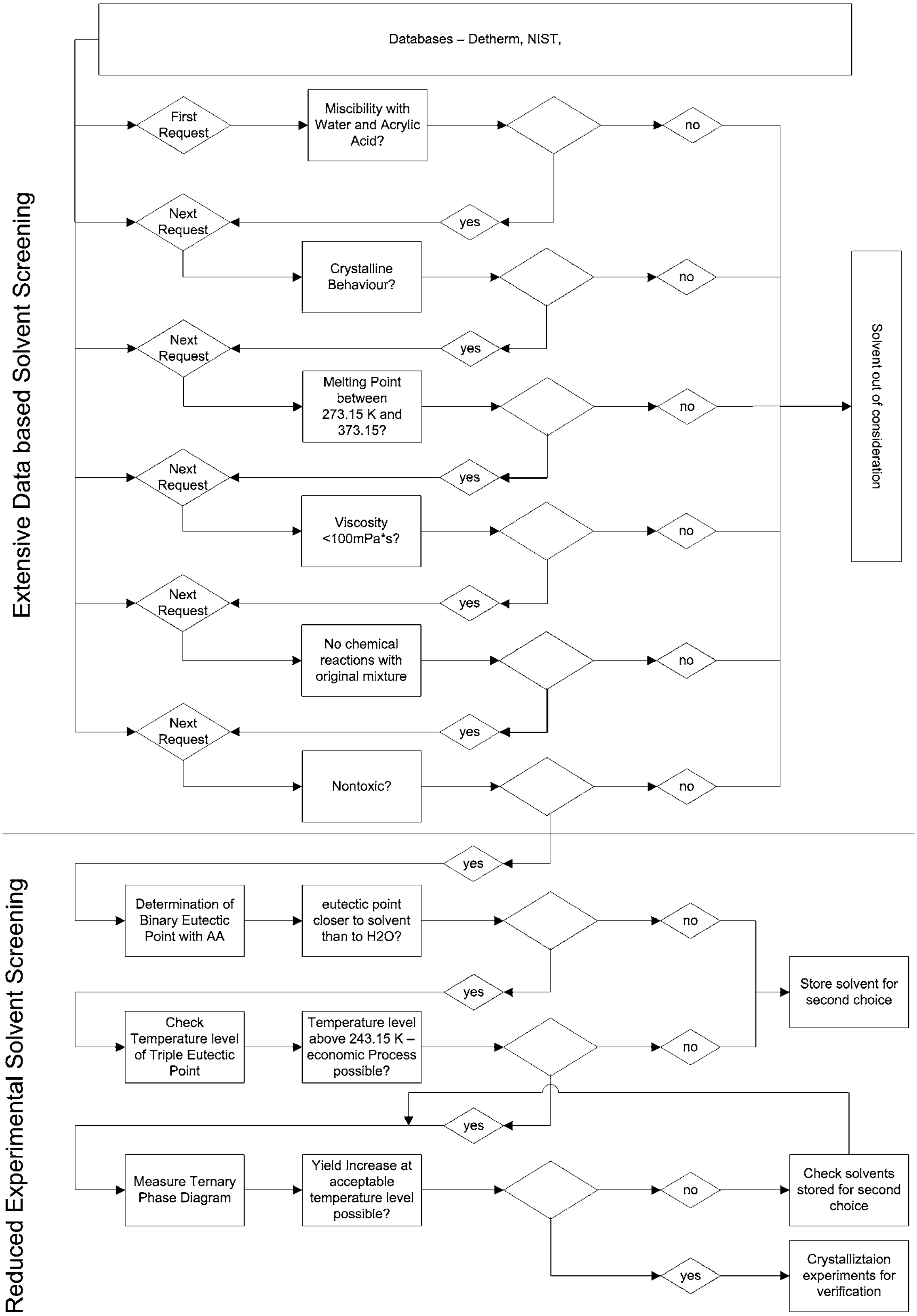

Figure 7. Database request for fast solvent screening.

On the basis of the scope of this work and the mentioned requirements, a two-stage solvent screening method was designed with the following objectives:

1. Reduce the number of necessary experiments to a minimum.

2. Consider the downstream requirements due to toxicity, product specifications, and so forth.

3. Use physical and chemical data to prepare a first rough estimation of the potential usage.

4. Use solid−liquid binary data for a first rough estimation of the location of the ternary eutectic point.

Mainly based on these four objectives a decision tree is developed for an automatic database request. The structure of the database request is shown in Figure 7.

3.2. State of the Art. The idea to increase the yield of a crystallization unit is a common industrial need. There are several approaches regarding special issues. Within the next two sections two well-known approaches will be presented shortly. There are many possible processes and substances published in patents and literature for aqueous systems of acrylic acid. However, because of the resulting process complexity, industrial applications using any of these processes are not known. Therefore, they will be presented for the sake of completeness, but the substance classes will not be considered in the solvent screening for acrylic acid.

3.2.1. Salting Out. Several approaches to increase the yield of an acrylic acid crystallization from aqueous solutions have been described in the past. In some cases, the limiting eutectic point has been removed successfully by the addition of certain salts to the aqueous solution.

Faerber[6] discloses in 1957 that calcium chloride (CaCl), sodium sulfate (Na_2SO_4), and dry metal salts such as nickel chloride ($NiCl_2$) and nickel bromide ($NiBr_2$) can be used as drying agents in combination with an aliphatic ketone. The salt dissolves in the aqueous phase and reduces the solubility of acrylic acid. The acrylic acid is transported into the organic phase. This displacement is called salting out. It was demonstrated that the acrylic acid could be concentrated from the aqueous solution up to a maximal 80 % in the organic phase.

Otsuki Susumu et al.[7] reported a method to accelerate the separation of an organic solvent phase from an aqueous phase to recover acrylic acid. They suggested adding an alkali metal salt or an ammonium salt $[NH_4]^+$ to the aqueous solution for accelerating the solvent separation. Rather than accelerating the phase separation or drying the aqueous solution, this patent discloses that the addition of such salts removes the eutectic point between acrylic acid and water. In this case the eutectic limitation can be overcome by forming a system of solid solutions.

One salt that eliminates the eutectic is sodium chloride. Other alkali metal salts like halides, nitrates and sulfates, and ammonium salts can remove the eutectic as well. However, it has been found that barium chloride, ferric chloride, and tin chloride have no significant effect upon the acrylic acid−water solid−liquid equilibrium.[8]

At the end, salts can be used to shift and remove the eutectic point, respectively. Therefore, it is possible to draw the following conclusion. The addition of salts opens up two types of processes: The first possibility is to use the salting out effect in a liquid−liquid extraction. Salts push acrylic acid into the organic phase, from which it can be crystallized. This requires further downstream units to recover and recycle at least the organic phase.

Second, salts can make the binary eutectic system become a solid solution. This always requires an extensive, economically unattractive multistage fractional crystallization. Hence, salts will be disregarded as potential third compounds.

3.2.2. Ionic Liquids (ILs). ILs are defined as liquid salts which are liquid below 100 °C.[9] ILs are organic salts and consist of large bulky and asymmetric organic cations and anions such as tetrafluoroborate $[BF_4]^-$, halides, nitrate $[NO_3]^-$, sulfate $[SO_4]^-$, aluminum chloride $[AlCl_4]^-$, and so forth.

The group of the cation is variable; typical cations are alkyl chains such as methyl, ethyl, butyl, and so forth, or other functional groups (e.g., fluoroalkyl, alkenyl, methoxy). The variability of the anions and residual groups in the imidazolium, pyridinium, pyrrolidinium, and ammonium or phosphonium cations are utilized to adjust the physical properties of the ILs such as melting point, viscosity, and density as well as the miscibility with water or organic solvents. Furthermore, they can be functionalized to act as acids or bases. The change of the anion dramatically affects the chemical behavior and stability of the IL.

The vast range of possible ILs makes a dedicated screening quite extensive. Additionally, in contrast to the use of common organic bulk chemicals, a complete recovery of the IL is required due to the high specific costs. Therefore, also ILs will be excluded from the solvent screening for a potential third component.

3.3. Screening Results. The increase of the crystallization yield requires certain properties as listed in Section 3.1. Especially organic components can fulfill these features. The screening shows that especially alcohols, ketones, and carboxylic acids should be considered. Especially carboxylic acids with a low number of carbons (1 to 4) could be attractive from the point of view of installation in an industrial process. In the end, the screening approach comes up with three components, which have to be investigated by simple lab experiments: propionic acid, butanoic acid, and acetic acid. Propionic and acetic acid are typical byproducts of the two-stage acrylic acid oxidation process,[10] so that a possible use would not change the complete production process generally:

1. Acetic acid shows properties in agreement with the requirements ($T_{EP} = 300.15$ K; $w_{AcA} = 0.58$; $T_{m,acetic} = 289.65$ K).

2. Butanoic acid shows good properties regarding the eutectic temperature and the eutectic composition in the binary system with water. The eutectic temperature is not too low ($T_{EP} = 259.75$ K), and the eutectic composition is $w_{BA} = 0.87$. The binary system with water shows a miscibility gap, which is not a fundamental problem, because the process would be operated at high acrylic acid concentrations.

3. Propionic acid shows good properties regarding the eutectic temperature and the eutectic composition in the binary system with water ($T_{EP} = 243.75$ K; $w_{PA} = 0.87$), as required. Besides, some solid−liquid equilibrium data of acrylic acid and propionic acid[11] are available ($T_{EP} = 262.15$ K, $w_{PA} = 0.7487$). However, propionic acid exhibits one major disadvantage. The system propionic acid−acrylic acid has a peritectic point[8] ($T_{PP} = 256.05$ K and $w_{AA} = 0.556$). A crystallization could result in the formation of a solid solution. Nevertheless, propionic acid will be considered as a possible component to increase the acrylic acid yield, even if a two-stage process would be necessary. The peritectic behavior has to be taken into account by applying the method of Burger[5] to determine the ternary eutectic point of the ternary system with propionic acid. The method of Burger is valid for eutectic systems only.

4. Experimental Section

4.1. Objectives. The objectives of the experiments are the general check to see if the identified components of the screening approach from Section 3.1 allow an increase of the crystallization yield of the binary system acrylic acid and water. For this purpose it is required that the location of an existing ternary eutectic point is high in relation to pure acrylic acid and has a low water content. This would offer the opportunity to separate pure acrylic acid at a high yield without getting in trouble with highly compressible acrylic acid crystals.

The temperature level of the ternary eutectic point is very important regarding crystallization and solid−liquid separation conditions like liquid viscosity and density. A temperature below 243.15 K makes an industrial crystallization process uneco-

Table 1. Feed Stock Qualities: Product Purity w, Melting Temperature T_m from DSC Measurements and Literature, and Heat of Fusion $\Delta_{fus}H$ from DSC Measurements and Literature

		melting temperature		heat of fusion	
	product purity	T_m(DSC)	T_m(literature[12])	$\Delta_{fus}H$ (DSC)	$\Delta_{fus}H$ (literature[12])
	w	K	K	$J \cdot mol^{-1}$	$J \cdot mol^{-1}$
water	fully desalinated	273.10	273.15	6014	5990 to 6030
acrylic acid	> 0.9997	286.35	260.15 to 286.65	11400	11126 to 12550
acetic acid	> 0.9995	289.65	289.25 to 289.75	11716	11116 to 11740
butanoic acid	> 0.999	267.55	267.05 to 267.75	7550	7520 to 7537
propionic acid	> 0.999	252.45	252.65 to 252.25	11252	11066 to 11590

Table 2. DSC Temperature Programs: Segment n, Time Period t, and Temperature Level or Temperature Gradients T_n to T_{n+1} for Three Different Ternary Systems

segment	time period	AA/H_2O/AcA	AA/H_2O/PA	AA/H_2O/BA
n	t	T_n to T_{n+1}	T_n to T_{n+1}	T_n to T_{n+1}
1	600 s	203.15 K	233.15 K	223.15 K
2	varied	(203.15 to 293.15) K	(233.15 to 293.15) K	(223.15 to 293.15) K
3	300 s	293.15 K	293.15 K	293.15 K
4	600 s	203.15 K	233.15 K	223.15 K
5	varied	(203.15 to 293.15) K	(233.15 to 293.15) K	(223.15 to 293.15) K

nomically. Crystal growth at low temperatures often leads to kinetic problems induced by limited heat and mass transfer. This may results in impure crystals, which could lead in a two-stage process. A high temperature difference between the operation temperature and the melting point could also lead to operating problems of wash column units for crystal separation and purification.

Therefore, the experiments are divided into three steps. First, the temperature level of the ternary eutectic point will be determined by simple and fast DSC measurements. For each system five mixtures of different compositions will be analyzed. Further, the ternary eutectic point and region will be determined via the advanced approach presented in Section 2.4. Finally, if the temperature of the ternary eutectic point is higher than 243.15 K, the complete phase diagrams will be measured.

4.2. Used Components. For the experiments the following materials from different suppliers were used. The feed stocks were analyzed by gas chromatography, and the melting points and heats of fusion were determined by DSC measurements. The results are listed in Table 1 and compared with data from literature.

The preparation of the different mixtures required for the measurements of the three ternary systems have been done similarly to reduce uncertainties between the different samples. Samples of a total weight of 5 g have been prepared on a laboratory balance providing a precision of 0.001 g. Taking the uncertainties of the feed stock qualities and of the laboratory balance into account, a total uncertainty of the mixture compositions of $w = 0.001$ can be stated.

4.3. Experimental Setup and Procedure. The experiments were carried out on a differential scanning calorimeter DSC 1400W combined with an automatic probe sampler and an external Intra Cooler from Mettler Toledo. The used DSC setup allows measurements in a temperature range from 188.15 K up to 973.15 K at a precision of 0.02 K. The generated raw data were evaluated with the Mettler Toledo Software STARe. The software enables us to calculate and analyze all system data like phase change temperatures (ternary, binary, and melting temperature) and specific enthalpy of fusion.

The ternary mixture samples were prepared from the pure components. The exact compositions were calculated after weighing. The measurements were carried out with hermetically closed crucibles to avoid changes of the sample compositions due to evaporation of the sample or inclusion of moisture. Additionally, the measuring cell was flushed continuously with nitrogen. All experiments were carried out with defined temperature programs using temperature gradients of (1 or 5) $K \cdot min^{-1}$, respectively. Generally, 5 $K \cdot min^{-1}$ is the preferred program. If an overlap of peaks occurs, a slower temperature gradient of 1 $K \cdot min^{-1}$ is required to obtain a decent baseline. The used temperature programs of the different compositions are summarized in Table 2.

4.4. Results. 4.4.1. Determination of the Ternary Eutectic Temperature and Concentration (TEP). For all three ternary systems different samples were analyzed by the presented DSC measurement programs. Afterward, the occurring curves were interpreted, and the peaks were related to the possible phase changes. As assumed, during the heating up, almost all samples of each system show a first peak at a certain temperature. This peak was identified to be the temperature of the ternary eutectic point called afterward "ternary peak temperature". The ternary mixture containing acetic acid shows an average ternary peak temperature of 237.05 K with a standard deviation of 0.5 K. Butanoic acid shows an average ternary peak temperature of 239.95 K with a standard deviation of 0.6 K. The system with propionic acid as a third component shows an average of around 241.95 K with a standard deviation of 0.9 K.

For all three systems the determination of the ternary eutectic points (TEP) has been carried out as described in Section 2.4. The analysis of all three systems shows good and clear results. The graphical constructions of the lines between the pure components and the local maxima of the enthalpy of fusion of the ternary eutectic point and their extrapolation result in one point. The absolute deviation of the intersection of the three lines of each system was about $\Delta w = 0.05$. Therefore, the precision of the determined ternary point is in a circular concentration range with a diameter of $\Delta w = 0.1$.

Figure 8 represents the results of the system acrylic acid, water, and acetic acid. The ternary eutectic point was identified at a concentration of $w_{AA} = 0.32$, $w_{H_2O} = 0.3$, and $w_{AcA} = 0.38$.

The system acrylic acid, water, and butanoic acid possesses the ternary eutectic point with the lowest water concentration. Figure 9 shows the graphical construction of the ternary eutectic point at $w_{AA} = 0.35$, $w_{H_2O} = 0.08$, and $w_{BA} = 0.57$.

Propionic acid shifts the ternary eutectic point away from acrylic acid and water. Figure 10 shows its location at $w_{AA} = 0.2$, $w_{H_2O} = 0.17$, and $w_{PA} = 0.63$. It was mentioned in Section 3.3 that applying the method of Burger to a peritectic system,

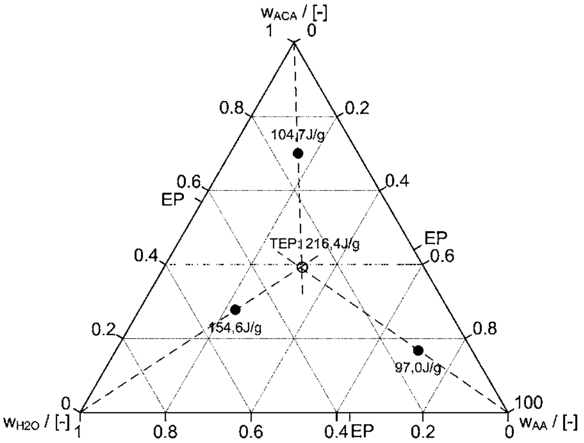

Figure 8. Determination of the ternary eutectic point of acrylic acid−water−acetic acid; ●, maxima of the heat of fusions of the pseudo binary systems along the three dotted lines; - - -, extrapolation lines for the determination of the intersection; ○, extrapolated ternary eutectic point.

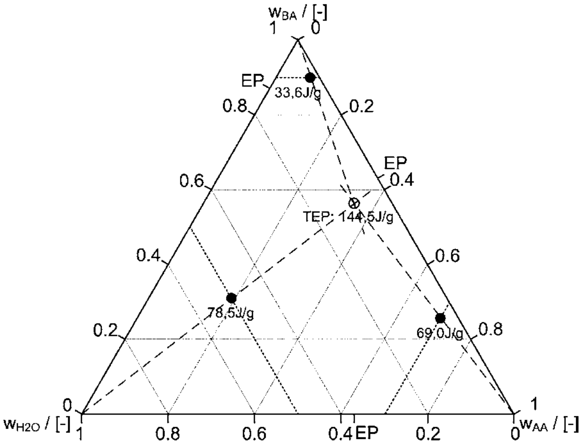

Figure 9. Determination of the ternary eutectic point of acrylic acid−water−butanoic acid; ●, maxima of the heat of fusions of the pseudo binary systems along the three dotted lines; - - -, extrapolation lines for the determination of the intersection; ○, extrapolated ternary eutectic point.

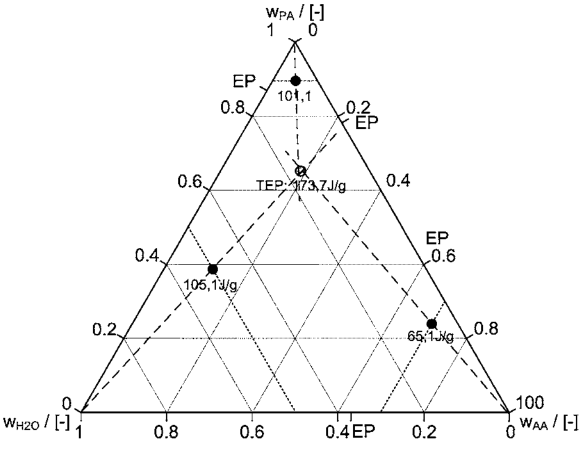

Figure 10. Determination of the ternary eutectic point of acrylic acid−water−propionic acid; ●, maxima of the heat of fusions of the pseudo binary systems along the three dotted lines; - - -, extrapolation lines for the determination of the intersection; ○, extrapolated ternary eutectic point.

like the binary system of propionic acid and acrylic acid, could cause problems. However, the determination of the ternary eutectic point of the system of propionic acid, water, and acrylic acid shows no irregularities.

Table 3. Compositions and Temperatures of the Ternary Systems

third component	w_{AA}	w_{H_2O}	$w_{\text{third component}}$	T_{TEP} / K
acetic acid	0.32	0.3	0.38	237.05
butanoic acid	0.35	0.08	0.57	239.95
propionic acid	0.2	0.17	0.63	241.95

Table 4. Equilibrium Data for Acrylic Acid−Water−Acetic Acid: Acrylic Acid Content w_{AA}, Water Content w_{H_2O}, Acetic Acid Content w_{AcA}, and Equilibrium Temperature T_m

w_{AA}	w_{H_2O}	w_{AcA}	T_m / K
0.329	0.265	0.406	237.75
0.299	0.253	0.448	239.75
0.300	0.224	0.476	241.55
0.317	0.283	0.400	242.05
0.301	0.314	0.385	242.75
0.164	0.437	0.399	242.85
0.292	0.301	0.407	244.65
0.399	0.270	0.331	244.95
0.218	0.381	0.401	245.75
0.234	0.334	0.432	246.15
0.324	0.305	0.371	246.25
0.496	0.197	0.307	248.35
0.227	0.271	0.502	248.55
0.300	0.349	0.351	250.65
0.036	0.364	0.600	251.35
0.278	0.372	0.350	251.55
0.240	0.399	0.361	252.55
0.073	0.328	0.599	252.55
0.270	0.250	0.480	253.15
0.255	0.445	0.300	254.35
0.250	0.250	0.500	255.95
0.200	0.359	0.441	260.05
0.066	0.630	0.304	260.75
0.025	0.275	0.700	260.85
0.146	0.654	0.200	261.35
0.057	0.242	0.701	262.15
0.150	0.382	0.468	262.65
0.160	0.240	0.600	263.35
0.438	0.363	0.199	263.75
0.490	0.210	0.300	266.65
0.295	0.605	0.100	266.95
0.182	0.018	0.800	271.75
0.730	0.071	0.199	272.55
0.640	0.160	0.200	273.45
0.060	0.185	0.755	273.65
0.663	0.237	0.100	274.65
0.714	0.131	0.155	276.35
0.766	0.109	0.125	278.25
0.792	0.098	0.110	279.05
0.012	0.098	0.890	282.15

The values in each diagram represent the values of the enthalpy of fusion of the ternary points related to the weight of the samples. For all three systems, the extrapolated enthalpy of fusions of the ternary point seems to be a function of the water content of this point. The higher the water contents of the ternary eutectic points, the higher the corresponding enthalpy of fusions. This goes along with the fact that the enthalpy of fusion of water (333 $J \cdot g^{-1}$) is around twice the value of a typical organic component (150 $J \cdot g^{-1}$).

The determination of the ternary eutectic points of each system has to be verified by the measurements of the complete solid−liquid equilibrium diagrams. Table 3 summarizes the measured ternary eutectic temperatures and concentrations.

4.4.2. Solid−Liquid Equilibrium Data. With the knowledge of the approximate location of the ternary eutectic point, it was possible to perform selective DSC experiments to measure the complete ternary phase diagram. For each system a dedicated sample table with at least 36 samples was worked out. With

Table 5. Equilibrium Data for Acrylic Acid−Water−Butanoic Acid: Acrylic Acid Content w_{AA}, Water Content w_{H_2O}, Butanoic Acid Content w_{AcA}, and Equilibrium Temperature T_m

w_{AA}	w_{H_2O}	w_{BA}	T_m/K
0.319	0.080	0.601	242.35
0.415	0.083	0.502	243.85
0.480	0.121	0.399	247.75
0.230	0.075	0.695	248.65
0.331	0.166	0.503	250.25
0.240	0.161	0.599	250.75
0.150	0.050	0.800	253.85
0.466	0.233	0.301	254.75
0.583	0.116	0.301	255.45
0.051	0.151	0.798	258.65
0.150	0.150	0.700	258.65
0.640	0.160	0.200	259.65
0.480	0.321	0.199	259.65
0.619	0.280	0.101	259.75
0.360	0.240	0.400	259.75
0.249	0.250	0.501	261.85
0.168	0.332	0.500	261.85
0.462	0.440	0.098	262.25
0.350	0.350	0.300	263.75
0.160	0.240	0.600	264.15
0.075	0.222	0.703	265.35
0.320	0.480	0.200	266.15
0.081	0.320	0.599	266.35
0.280	0.620	0.100	267.35
0.233	0.466	0.301	267.45
0.160	0.640	0.200	268.75
0.120	0.479	0.401	269.05
0.087	0.414	0.499	269.25
0.116	0.584	0.300	269.45
0.910	0.809	0.100	269.75
0.809	0.091	0.100	273.05

Table 6. Equilibrium Data for Acrylic Acid−Water−Propionic Acid: Acrylic Acid Content w_{AA}, Water Content w_{H_2O}, Propionic Acid Content w_{AcA}, and Equilibrium Temperature T_m

w_{AA}	w_{H_2O}	w_{PA}	T_m/K
0.233	0.117	0.650	241.75
0.250	0.250	0.500	242.25
0.293	0.059	0.648	243.65
0.125	0.125	0.750	244.15
0.336	0.166	0.498	244.15
0.187	0.063	0.750	244.35
0.175	0.174	0.651	245.65
0.313	0.137	0.550	246.25
0.267	0.183	0.550	246.85
0.063	0.188	0.749	248.45
0.381	0.069	0.550	248.95
0.419	0.083	0.498	248.95
0.117	0.233	0.650	249.85
0.076	0.075	0.849	250.05
0.226	0.224	0.550	250.05
0.469	0.231	0.300	250.35
0.359	0.241	0.400	251.85
0.183	0.267	0.550	252.85
0.166	0.332	0.502	253.65
0.480	0.320	0.200	253.95
0.059	0.291	0.650	255.05
0.481	0.120	0.399	255.75
0.350	0.350	0.300	256.85
0.240	0.361	0.399	257.75
0.068	0.380	0.552	258.15
0.582	0.116	0.302	258.15
0.621	0.279	0.100	260.25
0.084	0.416	0.500	260.75
0.641	0.160	0.199	261.55
0.452	0.448	0.100	261.85
0.233	0.467	0.300	262.45
0.121	0.479	0.400	262.55
0.321	0.480	0.199	262.85
0.128	0.575	0.297	264.65
0.280	0.620	0.100	265.75
0.165	0.632	0.203	265.85
0.747	0.150	0.103	267.75
0.090	0.810	0.100	268.75
0.809	0.091	0.100	272.45

this number of experiments the complete ternary diagram could be covered with a concentration raster of $\Delta w = 0.10$ width. The repetition of certain experiments shows an accuracy of the determination of phase change temperatures from DSC of 0.1 K.

The measured equilibrium data of the three ternary systems are listed in Tables 4, 5, and 6.

5. Discussion

The solvent screening—with the aim of finding a third component to increase the yield of an acrylic acid crystallization from aqueous mixtures—results in three potential components: acetic acid, propionic acid, and butanoic acid. All identified components reveal similar molecular structures. It is known that propionic acid forms a peritectic system. For further investigations, it would be useful to differ the screening criteria, so that components with higher melting points would be considered as well.

The determination of the ternary eutectic temperature by using the rapid technique explained in Section 2.4 shows that results correspond well to DSC measurements. There are deviations in the temperature values of up to 1 K. It was found by the analysis of the DSC plots that the determination of the eutectic temperature becomes more difficult with increasing distance from the TEP. This is due to the decreasing peak area.

The determination of the ternary eutectic concentration by the approach based on a method for binary eutectic systems shows apparently good results. It was found that the precision of this method is depending mostly on the accuracy of the pseudo binary measurements at a constant concentration of one of the three components. For both approaches, it is necessary that the DSC plots show a defined peak of the ternary eutectic point in relation to temperature determination and the calculation of the relative enthalpy of fusion. The best results are found, if the measurements are carried out at concentrations closer to the ternary eutectic point than to the pure components. A practical approach to ensure this was to set the constant concentration of one component close to one of its binary eutectic points.

The method of Burger is not applicable to binary peritectic systems. The binary system of propionic acid and acrylic acid has a peritectic point. However, applying the extended method of Burger to determine the ternary eutectic point of the system of water, propionic acid, and acrylic acid shows no irregularities. This might be caused by an overlap of the transaction peaks of the DSC plot. A detailed investigation on this context should be done for clarification in the future.

The measurement of the full ternary solid−liquid equilibrium by DSC measurements is quite comfortable if the samples are prepared once. For a useful interpretation of the measured solid−liquid equilibrium data a graphical presentation in a ternary diagram with isotherms would be helpful. Therefore, isotherms have to be calculated from an equilibrium state model. However, the authors do not have the software tool for the calculation of the isotherms.

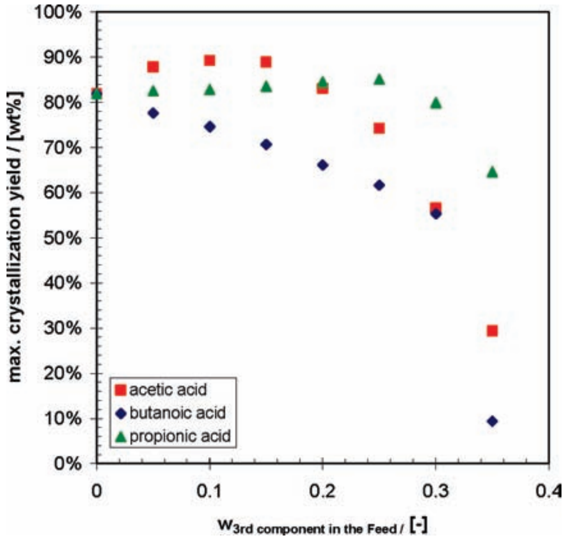

Figure 11. Maximum crystallization yield vs the addition of a third component to the feed with a water content of $w_{H_2O} = 0.1$.

6. Conclusion and Outlook

In consideration of the results presented in Section 4, it is possible to draw the several conclusions. All three components can be generally used to modify the crystallization process from an aqueous solution. Crystallization is always possible at a moderate and acceptable temperature level. However, the possible modifications and resulting advantages and disadvantages are different for all three systems.

For an aqueous melt of $w_{H_2O} = 0.1$ the maximum yield of the crystallization process is calculated exemplarily using the measured solid−liquid equilibrium data of Section 4.4.2. For the calculation it is assumed that the crystallization process is operating close to the ternary eutectic point. Figure 11 shows the theoretical crystallization yields, adding one of the chosen third components at different concentrations in the feed.

1. The addition of acetic acids results in an increasing crystallization yield. The maximum yield is reached at an acetic acid concentration in the feed of $w_{AcA} = 0.1$. The relative improvement of the yield is around 9 %. Passing this concentration, the crystallization yield decreases again. Nevertheless, if the crystallization process could be designed in that way that the mother liquor is at ternary eutectic composition, the crystals would grow from a water concentration of around $w_{H_2O} = 0.3$. This could cause problems due to the high compressibility of the acrylic acid crystals.[1,2]

2. The addition of butanoic acid to the aqueous feed does not result in any increase of the crystallization yield. However, due to the concentration of the ternary eutectic point, the addition of butanoic acid offers the possibility to crystallize acrylic acid at a low water concentration ($w_{H_2O} = < 0.1$). This results in a good solid−liquid separation performance and in small apparatus sizes.

3. The addition of propionic acid increases the crystallization yield. However, the relative improvement is 4 % only. Passing a concentration of $w_{PA} = 0.25$, the crystallization yield decreases again. Therefore, the performance of propionic acid ranks in-between the ones of acetic acid and butanoic acid if the required concentration range and the water content of the mother liquor are considered. Unfortunately, the peritectic point at $w_{AA} = 0.556$ cripples all advantages. Additionally, the further downstream processing could turn out to be very difficult, because the binary vapor−liquid equilibrium data are unfavorable. It will be quite impossible to separate the components by distillation because of an azeotropic point and a very close-boiling behavior!

Regarding the listed advantages and disadvantages, propionic acid should be neglected for further considerations. For the other two components a theoretical process should be designed, simulated, and benchmarked afterward in terms of the possible overall yield, energy consumption, and apparatus scale and process complexity.

Nomenclature

Symbols

$\Delta_{fus}H_i$	molar enthalpy of fusion of component i [$J\cdot mol^{-1}$]
H	molar enthalpy [$J\cdot mol^{-1}$]
R	gas constant [$J\cdot mol^{-1}\cdot K^{-1}$]
T	temperature [K]
w	mass fraction
x	mole fraction

Greek Symbols

γ	activity coefficient

Subscripts

end	end-set
i	component I
L	liquid phase
m	solid−liquid equilibrium/melting
on	on-set
S	solid phase

Abbreviations

A	component A
AA	acrylic acid
AcA	acetic acid
B	component B
BA	butanoic acid
C	component C
EP	binary eutectic point
F	feed
H_2O	water
PA	propionic acid
PP	peritectic point
TEP	ternary eutectic point

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