On the Design of Crystallization-Based Separation Processes: Review and Extension

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An analysis is given of various aspects of the design of crystallization-based separation processes. A literature review is included for each of the different themes treated in the study. Special emphasis is placed on the usefulness of the relative composition diagram as a tool for identification of possible flow sheets for separations based on fractional crystallization. A series of rules are derived that may be of practical value in the use of the relative composition diagram. Illustrative examples are included that present the advantages and limitations of this methodology. Results are compared with those obtained from the literature where available. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 1754–1769, 2006

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Introduction

Crystallization is extensively used in different industrial applications, including the production of a wide range of materials such as fertilizers, detergents, foods, and pharmaceutical products, as well as in the treatment of waste effluents. In spite of the popularity of this operation, exceeded in scope only by distillation processes, the development of new methodologies for design and operation of crystallization-based separation processes has become of interest to the chemical process sector only in the last 15 years. Following the outstanding work of Fitch[1] in 1970, there were practically no other studies on this topic until the early 1990s, when different research groups began to investigate problems in this area and produce important advances.

Difficulties in the design of these processes occur with respect to various factors, including the following:

(1) The crystallization stages are usually accompanied by other separation techniques such as leaching, which represent phenomena different from crystallization.

(2) Various types of crystallization exist, including crystallization by cooling, evaporation, reactions, and drowning-out, with differing operating conditions, costs, and product quality. For any given separation there are usually several flow sheet alternatives, which may combine different methods of crystallization.

(3) The characteristics of the product, especially the size and size distribution of the crystals, affect a series of other associated operations, such as filtration and washing.

(4) The separation is limited by multiple saturation points, among these the eutectic points, which require the search for pathways that can overcome the composition of these points by using temperature change or the use of external chemical agents.

(5) Kinetic factors and metastability may affect the design of the separation route, the governing factors of which may require experimental study for resolution.

Because crystallization is a phenomenon limited by solid–liquid equilibrium conditions, all studies in this field have considered this factor in design. The supposition of equilibrium is adequate for most of the operations because they usually

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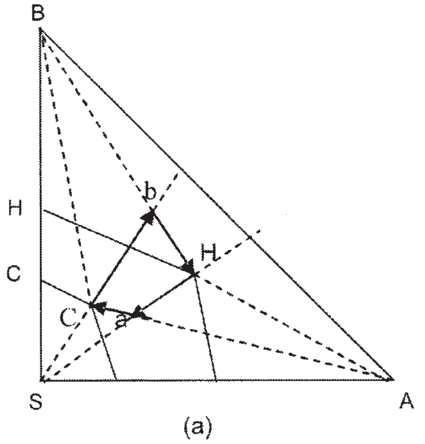


Figure 1. Isothermal sections and a partial separation cycle.

operate nearly under these conditions. As a consequence, various studies use the phase diagram as a tool for process design.

Over the last few years, various studies have been published on the design of crystallization-based separation processes. The objective of the present study is to review the topic, identifying the advances achieved and difficulties still present. Special attention is given to the application of relative composition as a tool for identifying attractive conceptual designs.

Separation of Simple Systems

The simplest problem, from the perspective of the design of separation processes using fractional crystallization is represented by the separation of two solid components A and B, the stable solid phases of which remain the same over the range of different conditions (generally temperature and pressure) desired for the process. Examples of this kind of systems are KCl + NaCl + H_2O, KNO_3 + $NaNO_3$ + H_2O, and L-serine acid + L-aspartic acid + water under atmospheric conditions. It is well known that maximum precipitation of the solids is obtained at the multiple saturation point (MSP). Because the MSP limits the complete separation of the solids, it is important to find pathways that can overcome the MSP. The most common way to achieve this objective is to use temperature changes in the operation. For example, Figure 1 shows two isothermal sections, with multiple saturation points C and H at the temperatures T^C and T^H, respectively. A partial separation cycle (a cycle either not including feeds or having feeds with compositions similar to C or H) is included in Figure 1. With a solution of composition H, the temperature is changed to T^C and solvent is added, such that the composition changes to that of point a. Under these conditions the solid A is crystallized to produce a pulp with a solution composition identical to that of point C. Once the crystals of A are separated, solution C is raised to temperature T^H and the solvent is removed, reaching point b. There B crystallizes and the solution reaches point H. Optimization of the process requires that the distances Cb and Ha are the smallest possible such that the removal and addition of solvent are the smallest possible, and that the distances bH and aC are the largest possible so that the crystallization ratios of solids/saturated solution are the largest possible to maximize the recovery of solids. Because C and H are saturated in both solids, it would appear that points C and H may be used for crystallization of either of the solids. However, as shown in Figure 1, the solid B is crystallized at point H, whereas solid A is crystallized at point C. The contrary is not possible, as will be subsequently demonstrated. The diagram of relative compositions is of great help in understanding this.

The relative composition (R) is defined as the composition ratio of the two solutes that require separation.[2] Here, in the case of a ternary system containing a solvent and two solutes, this ratio represents the relative composition in terms of the dry weight of the solutes. The relative composition diagram is a representation of the states that are important from the perspective of the process design. For example, Figure 2a is a reconstruction of Figure 1 that includes lines of constant values of relative composition through points C and H. As can be observed, the ratio between the composition of species B over species A has been used, which is an arbitrary choice and does not affect the results to be obtained. Also included are the relative composition lines representing the pure solid species. Figure 2b shows the "relative composition diagram" (RCD), which contains the values of R, ordered from maximum to minimum, and the relations between the phases in equilibrium, that is, each multiple saturation point is united with its corresponding solid phases. This diagram shows that two zones exist in the phase diagram at temperature T^C, one of which goes from line R^B to R^C (where it is possible to crystallize B) and the other from line R^C to R^A (where it is possible to crystallize A). At temperature T^C there is no way to cross from one zone to the other, given that the movements allowed by solvent adjustment follow lines of constant relative composition. Similarly, the diagram shows the temperature zones for T^H, one from R^B to R^H and another from R^H to R^A. The challenge for separation of B from A consists basically in transferring from one zone to another by making use of changes in temperature. Thus it can be observed in Figure 2b that once the limit of separation is reached in the R^B–R^H region at temperature T^H (this is point H), by changing the temperature to T^C it is possible to pass to the R^C–R^A region. This signifies that A will be crystallized at T^C and B at T^H. The reverse is not possible.

The relative compositions diagram (RCD) can be modified by eliminating the zones that cannot be used for crystallization of a given solute. For example, it can be noted in the diagram of Figure 2b that it is not possible to use the R^B–R^C zone for crystallization of B, given that there is no other potential source operating point at either temperature having an R value between R^B and R^C, whereas crystallizing B would move R in the direction of R^B. The same is valid for the R^H–R^A zone in relation to the crystallization of A. Therefore, if these parts of the diagram are eliminated, Figure 2c is obtained, which we term the "feasible pathways diagram" (FPD). This diagram shows that beginning from MSP H it is possible to crystallize A using temperature T^C, given that MSP H is within the zone in which it is possible to crystallize A at T^C, whereas beginning from MSP C it is possible to crystallize B using temperature T^H, given that MSP C is in the zone in which it is possible to crystallize B at T^H. Figure 2d is a possible scheme for this process, where circles C and H represent operation at the multiple saturation points at temperatures T^C and T^H, respectively. The solid lines represents the saturated solutions, whereas the double lines represent the solid products. The solvent (S), which can be added or removed from the system,

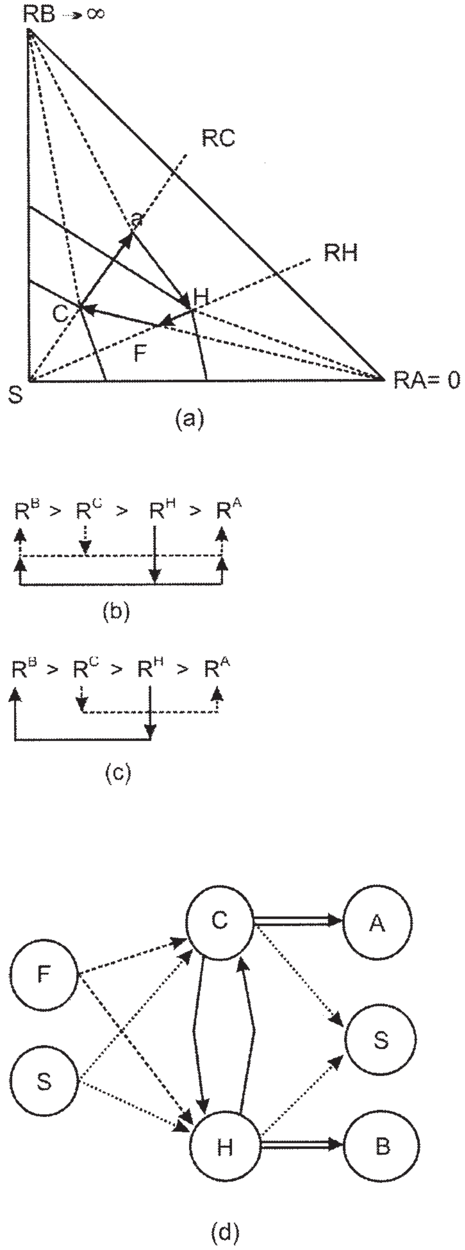


Figure 2. Design of a separation sequence for a simple system.

(a) Relative compositions, (b) relative composition diagram (RCD), (c) feasible pathways diagram (FPD), (d) process scheme.

requires adjustment based on mass balances in the system, and is represented by dotted lines. The feed F may be mixed in at point(s) C and/or H, depending on the characteristics of the systems. The choice of the mixing point for the feed is indeed very important, given that significant differences in volumetric flow rate recycled and consumption of solvent result according to the choice. This point will be further analyzed below.

In summary, to identify possible separation pathways, the following needs to be done:

- Calculate relative compositions between the two solutes to be separated for all potential points of operation, arbitrarily selecting the divisor component in the mass concentration ratio. The potential points are multiple saturation points, products, and others that will be presented below (intermediate products, feeds, other saturation points).
- Order the relative compositions from maximum to minimum (or vice versa) and unite the multiple saturation points with their corresponding solid phases. This diagram is termed the relative composition diagram (RCD).
- Construct the feasible pathways diagram (FPD), eliminating the infeasible pathways. That is, eliminate the paths between multiple saturation points (MSPs) and their solid phases if no point exists having an *R* value between the *R* values of the MSP and its solid phase.

At this point it is necessary to clarify that the objective of introducing the RCD and FPD is to structure the information available in the phase diagram to facilitate the identification of possible pathways for fractional crystallization. The concept of relative composition was introduced by Cisternas and Rudd,[2] who used the concept to classify different types of phase diagrams and identify potential designs for separation processes. Relative composition diagrams were introduced by Cisternas[3] in 1999 as a way of constructing a superstructure of equilibrium states on which to search for an optimum separation pathway using mathematical programming. On the other hand, it is important to note that other studies exist that analyze this type of system, such as the work of Ng[4] and Dudczak.[5] The work of Ng is limited to certain specific characteristics in the phase behavior, however, and it is difficult to expand this method to include more complex systems. Dudczak used a search strategy within a space of defined states.

Furthermore, it is important to recognize that although phase diagrams are widely used for the design of these processes, these also possess a series of limitations as design tools. Among these are the following:

(1) For systems with more than three components it is necessary to use isobaric isothermal projections, usually on the basis of dry and/or saturated bases of some of the components, which could easily lead to inadequate design decisions. For example, if the solvent is excluded from the diagram, it is not possible to know the level of its recirculation, and thus alternatives might be selected that use excessively high solvent levels.

(2) It is usually possible to plot only two isotherms for systems of three or more components, which does not provide for observation of all the alternatives. For example, many saline systems tend to form double salts, the existence of which is a function of temperature. Thus in the Na_2SO_4–$MgSO_4$–H_2O system at 18°C no double salts are formed, although at 50°C the double salt $Na_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$ is formed, whereas at 97°C the salts $MgSO_4{\cdot}Na_2SO_4$ and $MgSO_4{\cdot}3Na_2SO_4$ are formed. Also, in the case where various isotherms are simultaneously plotted, identification of processes would be a difficult task based on the existence of a large number of possible alternatives.

(3) Although some material balances have an uncomplicated presentation in the phase diagram, others require greater effort. For example, if a recirculation stream exists, the procedure becomes complex[1] and, if more than one recirculation stream exists, no procedure has been described in the literature. Another example is the possibility of stream splitters, where an input stream along with output streams are all represented by

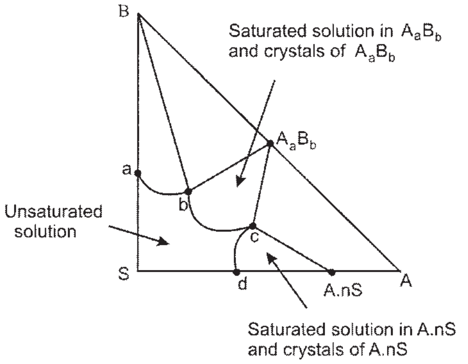


Figure 3. Phase diagram for a system with compound formation.

points located in the same area in the diagram. The exclusion of stream splitters is an error, given that it has been shown that optimum flow diagrams may involve stream splitters.[6] For these reasons several researchers have used simulation and optimization techniques for the design of crystallization-based processes.[3,7-9] The use of the phase diagram as a design method for separation processes has been widely analyzed in the literature.[1,2,10,11]

Separation of Systems with Formation of Compounds

Many systems tend to form compounds having various solid phases that are made up of the individual species. For example, Figure 3 shows a system forming two compounds, one between solutes A and B (A_aB_b) and another between solute A and the solvent (A·nS). If the system forms compounds with the solvent, the design procedure would be exactly the same as that previously described for simple systems. There now exists a new region in the diagram, however, where a compound crystallizes that is formed by the two solutes (which may or may not be solvated). This situation is common in many systems where different compounds may exist depending on the temperature. Thus in the Na_2SO_4–$MgSO_4$–H_2O system at 18°C no double salts are formed, but at 50°C the double salt $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$ is formed, whereas at 97°C two double salts are formed, including $MgSO_4 \cdot Na_2SO_4$ and $MgSO_4 \cdot 3Na_2SO_4$. Such compounds are not necessarily formed by increasing the temperature, given that the inverse behavior is observed in the Na_2SO_4–$(NH_4)_2SO_4$–H_2O system, which forms the double salt $Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$ at 25°C, but does not form double salts at 60°C. It should be noted in Figure 3 that more multiple saturation points (b and c) now exist. The number of these points is equal to the number of solid species, minus one. Thus in the Na_2SO_4–$MgSO_4$–H_2O system at 97°C, three MSPs could exist.

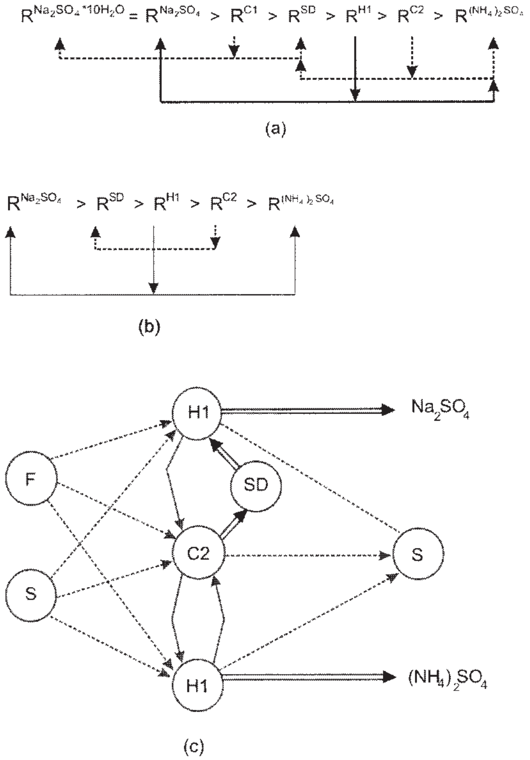


Figure 4. Na_2SO_4 + $(NH_4)_2SO_4$ + H_2O system.

(a) RCD, (b) FPD, (c) separation scheme.

The procedure for design of these systems is analogous to the procedure described previously, except that the compound formed could be an intermediate or final product based on the objectives. For example, consider the Na_2SO_4–$(NH_4)_2SO_4$–H_2O system at 25 and 60°C, which, as already indicated, tends to form double salts at low temperature that disappear at higher temperatures, such as 60°C. Consider also that separation of a mixture of these components into their pure form is desired. Table 1 presents the solubility data for this system. Values of R have been included for the MSPs and for the intermediate product as well. Figure 4a presents the RCD in which dotted lines depict the system at 25°C and solid lines depict the system at 60°C. It should be observed that the sodium sulfate may precipitate as the decahydrated form at 25°C and as an anhydrous form at 60°C, whereas both compounds have the same R value. There are three infeasible pathways.

It is not possible to crystallize ammonium sulfate at 25°C (point C2), given that in the zone that goes from R^{C2} to its solid

Table 1. Equilibrium Data for $(NH_4)_2SO_4$–Na_2SO_4–H_2O System at 25 and 60°C[47] *

T		Saturated Solution (wt %)				
(°C)	Key	% Na_2SO_4	% $(NH_4)_2SO_4$	% H_2O	Solid Phase	R
25	C1	25.76	14.10	60.14	A + SD	1.82
25	C2	8.00	38.70	53.30	SD + C	0.20
60	H1	16.33	36.91	46.76	B + C	0.44
	SD	41.04	38.15	20.81	—	1.07

*A = $Na_2SO_4 \cdot 10H_2O$; B = Na_2SO_4; C = $(NH_4)_2SO_4$; SD = $Na_2SO_4 \cdot (NH_4)_2SO_4 \cdot 4H_2O$.

Table 2. Equilibrium Data for LiCl–$MgCl_2$–H_2O System at 30 and 102°C[47] *

T		Saturated Solution (wt %)				
(°C)	Key	% LiCl	% $MgCl_2$	% H_2O	Solid Phase	R
30	C1	39.90	6.27	53.83	A + SD	6.36
30	C2	26.60	16.60	56.80	SD + B	1.60
102	H	17.40	35.60	47.00	B + C	0.49
	SD	16.08	36.12	47.80	—	0.45

*A = $LiCl \cdot H_2O$; B = $MgCl_2 \cdot 6H_2O$; C = LiCl; SD = $LiCl \cdot MgCl_2 \cdot 7H_2O$.

phase $R^{(NH4)2SO4}$ there are no other potential points of operation. In the case of point C1, which is saturated with the double salt and sodium sulfate decahydrate, it cannot be used to produce any of its solid species in equilibrium, and thus not only the infeasible pathways but also point C1 are eliminated. The resultant FPD is shown in Figure 4b, where it is clear that the double salt would be produced at point C2 from the saturated solution H1. The sodium sulfate and ammonium sulfate would be produced in conditions near the MSP H1, but starting from different mixtures. The sodium sulfate is produced starting from the double salt, whereas the ammonium sulfate would be produced starting from the C2 saturated solution. The process diagram is shown in Figure 4c. The meaning of the lines is the same as that used in Figure 2d. Operating between the selected temperatures, it is not possible to produce sodium sulfate decahydrate, nor is it possible to avoid precipitation of the double salt intermediate product. Now the feed may be mixed with the streams supplying the operations at the two H1 points and at point C2. These possibilities represent a range of alternatives, including the possibility for division of the feed stream. The amount of solvent to be added or removed at each operating point may be determined by mass balance.

We will now consider a more complex example. Suppose we seek to separate a mixture that contains both lithium and magnesium chloride. The values of the MSP compositions at 30 and 102°C are given in Table 2. The system forms the compound $LiCl \cdot MgCl_2 \cdot 7H_2O$. The values of R for this system have been included in the table. The RCD is shown in Figure 5a, where it can be observed that the only pathway for producing LiCl is point H when starting at C1, and that C2 is a MSP that is incongruently soluble because the value of R^{C2} is not found among the values of its solid phases in equilibrium, as occurs in the MSPs that are congruently soluble. Apparently the problem is similar to that described above, although two alternatives exist for producing magnesium chloride, C2 and H, and two alternatives for producing a double salt, C1 and C2. As previously mentioned, when there is a need to optimize the separation process from the perspective of reducing the recirculation flows, the distance between the composition of the initial mixture and that of the saturated solution must be the greatest possible. For example, in Figure 1 it is required that the distances bH and aC be the greatest possible. This means that of the two alternatives C2 and H for producing magnesium chloride, C2 must be chosen, given that the distance between R^{C2} and $R^{MgCl2 \cdot 6H2O}$ is greater than the distance between R^H and $R^{MgCl2 \cdot 6H2O}$. In the same way, between the two alternatives C1 and C2 for producing the double salt, C1 must be chosen. Figure 5b shows the FPD including the decisions taken here.

In this case it is possible to identify various separation pathways. Considering that our objective is the separation of a mixture of lithium and magnesium chlorides, it is necessary to analyze the possibility of direct separation of these compounds without producing the intermediate double salt. Thus in Figure 5c the double salt has been eliminated as a potential operation state (as well as R^{C1}) and it can be observed that it is completely feasible to separate the mixture without passing through the double salt intermediate. The separation pathway is shown in the phase diagram of Figure 5e for clarification. It should be observed that if the objective had been, say, the production of lithium chloride and the double salt, it would have been necessary to eliminate the magnesium chloride as a product (as well as R^{C2}), obtaining the diagram presented as Figure 5d. Also observe that in the example given in Figure 4b, if the double salt is eliminated (as well as R^{C2}) the separation is not

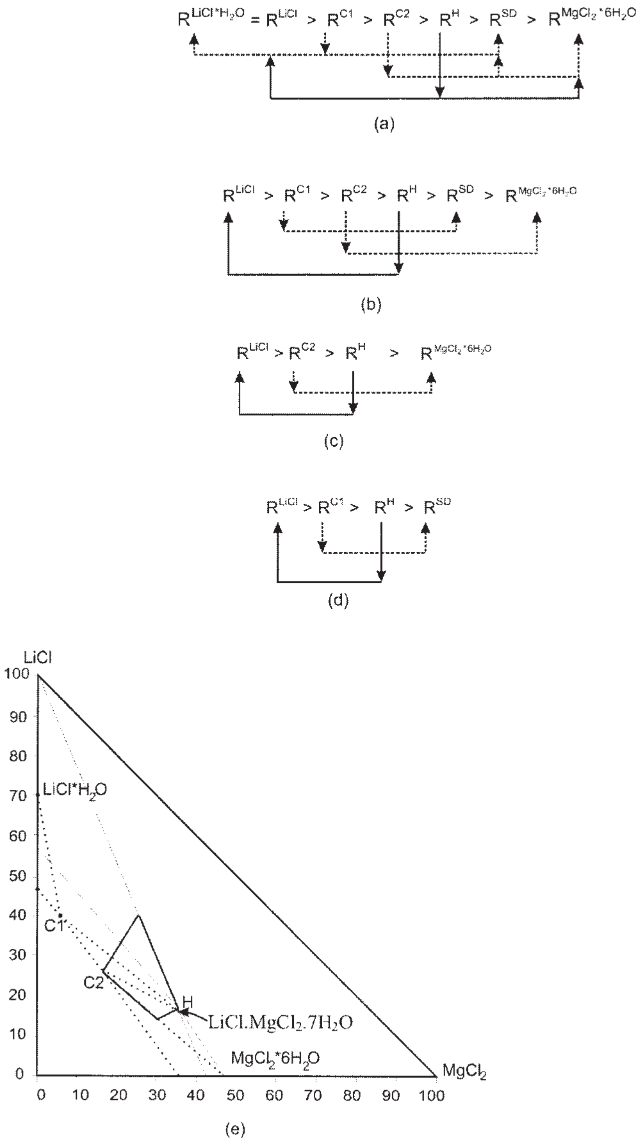


Figure 5. Lithium chloride and magnesium chloride system.

(a) RCD, (b) FPD, (c) FPD without double salt, (d) FPD without magnesium chloride, (e) process shown as a phase diagram.

feasible, and so in the previous example direct separation is not possible. Finally, we need to determine whether our decision was correct, and for this we observe that in the FPD of Figure 5b for producing $MgCl_2{\cdot}6H_2O$ using MSP C2, either H or the double salt (DS) can be used. The values $R^{C2} = 1.6$, $R^{H} = 0.49$, $R^{DS} = 0.45$, $R^{MgCl2{\cdot}6H2O} = 0$. Because the maximum production of $MgCl_2{\cdot}6H_2O$ is desired, the best starting point would be the double salt rather than point H (the $R^{C2} - R^{DS}$ is greater than the $R^{C2} - R^{H}$ difference). However, the difference between R^{H} and R^{DS} is very small (also the quantity of solvent is similar) and the pathway that uses the double salt requires more processing steps, showing that the choice to eliminate the production of intermediate double salt has been correct.

We reach the following conclusions from the examples studied:

- In systems with the formation of compounds between the solutes, the procedure for selection of pathways for fractional crystallization is the same, except that now it is necessary to include the compounds as potential products or intermediate products.
- When the MSP cannot be used to produce any of the solid species found in equilibrium, this MSP should be eliminated from the analysis.
- When two or more alternatives exist for producing a given product, favor MSPs that show the highest difference between the *R* value of the solid product and the *R* value of the MSP.
- When two or more alternatives exist as an initial point for producing a given product, favor the initial point that shows the maximum difference between the value of *R* of the MSP that produces the product and the value of *R* of the initial point.
- Study the FPD using only the solid phases that are desired because, in some cases, they may be obtainable by direct separation methods, avoiding passing through intermediate products or producing products that are not desired.

It should be observed that some of these conclusions are general, and thus are applied to systems with formation of compounds as well as systems without the formation of compounds. For example, the third conclusion may be used for the selection of the operating temperature in a system without the formation of compounds, that is:

- Among the various temperatures yielding the same solid phase, select the temperature at which the distance between the value of *R* of the solid product and the value of *R* of the MSP is greatest.

Table 3. Equilibrium Data for $MgSO_4 + Na_2SO_4 + H_2O$ System[47] *

T (°C)	Key	Saturated Solution (wt %) MgSO$_4$	Saturated Solution (wt %) Na$_2$SO$_4$	Solid Phase	*R*
18.7	C	20.57	11.80	$Mg_7 + Na_{10}$	1.7
25	D1	21.15	13.00	Mg_7 + SD1	1.6
25	D2	16.60	17.80	DS1 + Na_{10}	0.9
50	E1	31.32	4.74	Mg_6 + DS1	6.6
50	E2	11.98	23.25	DS1 + Na	0.5
97	F1	32.20	5.55	Mg_1 + DS2	5.8
97	F2	14.40	19.15	DS2 + DS3	0.8
97	F3	5.88	26.90	DS3 + Na	0.2
	DS1	35.99	42.48		0.8
	DS2	45.86	54.14		0.8
	DS3	22.02	77.98		0.3

*$Mg_7 = MgSO_4 \cdot 7H_2O$; $Mg_1 = MgSO_4 \cdot 1H_2O$; $Mg_6 = MgSO_4 \cdot 6H_2O$; $Na_{10} = Na_2SO_4 \cdot 10H_2O$; $Na = Na_2SO_4$; DS1 = $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$; DS2 = $Na_2SO_4 \cdot MgSO_4$; DS3 = $MgSO_4 \cdot 3Na_2SO_4$.

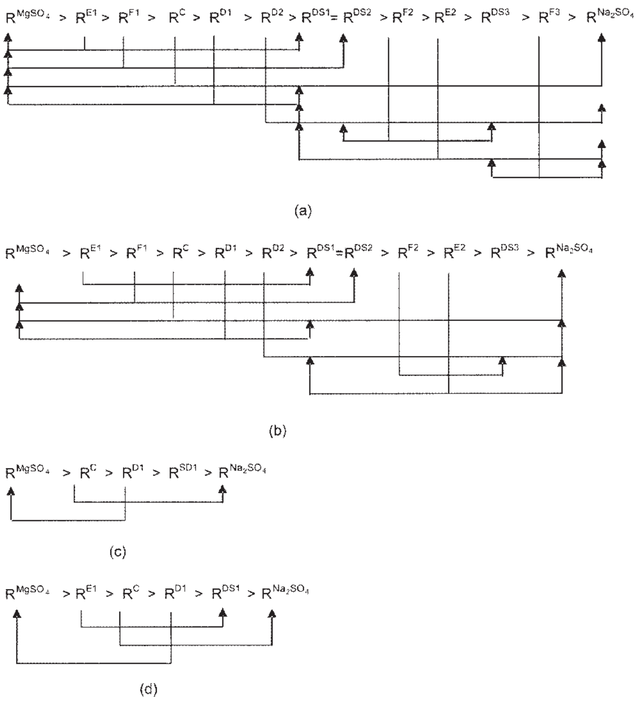


Figure 6. $MgSO_4 + Na_2SO_4 + H_2O$ system.

(a) RCD, (b) FPDs, (c) simplified FPD, (d) FPD with recycling of double salt.

As a further example we consider the $MgSO_4 + Na_2SO_4 + H_2O$ system because, as mentioned earlier, it presents various solid phases according to the temperature, and is therefore a more difficult problem to approach. The compositions of the multiple saturation points are presented in Table 3. This system was studied by Cisternas[3] with the objective of decomposing the double salt DS1, termed astrakanite, into magnesium and sodium sulfates.

Figure 6 shows the RCD for this example, showing that the different solid phases of sodium and magnesium sulfate have not been differentiated to simply the RCD. The MSP F3 can be eliminated because it is not possible to use it either in producing sodium sulfate or for production of the double salt DS3. For MSPs E1, D2, and F2, it is possible to eliminate one of the separation pathways. Thus, the resulting FPD shown in Figure 6b is still complex. Because the objectives are to produce sodium sulfate and magnesium sulfate we must evaluate each of the possibilities. To produce sodium sulfate, MSPs E2, D2, and C may be used, with later preference for MSP C, given that it is the MSP that has the greatest difference between the value of *R* of the MSP and the value of R^{Na2SO4}. Similarly, to produce magnesium sulfate we can use the MSPs F1, C, and D1. The choice in this case would be point D1. Following these options, the diagram in Figure 6c is obtained, where the value of R^{DS1} is retained, given that it is the feed. The pathway proposed allows separation of the double salt DS1 into its components without the need for recycling this salt. However, the values of *R* of MSPs C and D1 are similar, so the process would have large recirculation flows. For example, in the precipitation of magnesium sulfate the $R^{C} - R^{D1}$ difference is 0.1 compared

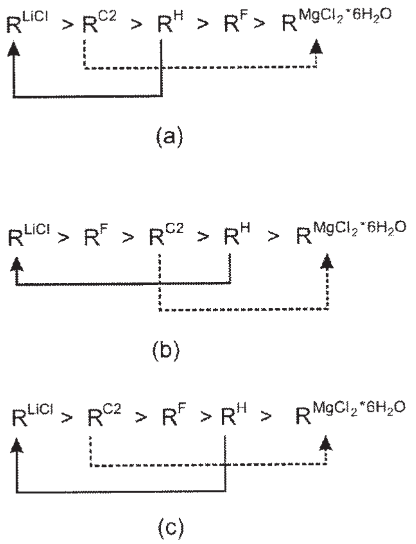


Figure 7. Different feed regions for the example in Figure 5.

with ∞ for the $R^{\mathrm{MgSO4}} - R^{D1}$ difference. If we then consider a certain level of recycling of DS1 or DS2 (Figure 6b), there remain two alternatives, MSPs E1 and F1, with MSP E1 favored because it shows a greater difference between R values, resulting in the diagram of Figure 6d. The process in this case would be as follows: The precipitated DS1 and the feed are adjusted to the conditions of MSP C, producing $Na_2SO_4 \cdot 10H_2O$ and saturated solution C. The saturated solutions C and D1, having similar R values, are mixed and brought to the conditions of MSP E1, precipitating the double salt DS1 and producing the saturated solution E1. The latter solution is raised to the conditions of MSP D1, crystallizing $MgSO_4 \cdot 7H_2O$, and obtaining saturated solution D1.

Although not considered here, in some cases the product of interest is the compound. In these cases the procedure is exactly the same, except that the objectives are different. The reader interested in this type of systems may consider different studies such as those of Cisternas and Swaney[6] or Thomsen et al.,[7] which include the formation of compounds, or specific studies of these types of systems such as that of Dudczak.[12]

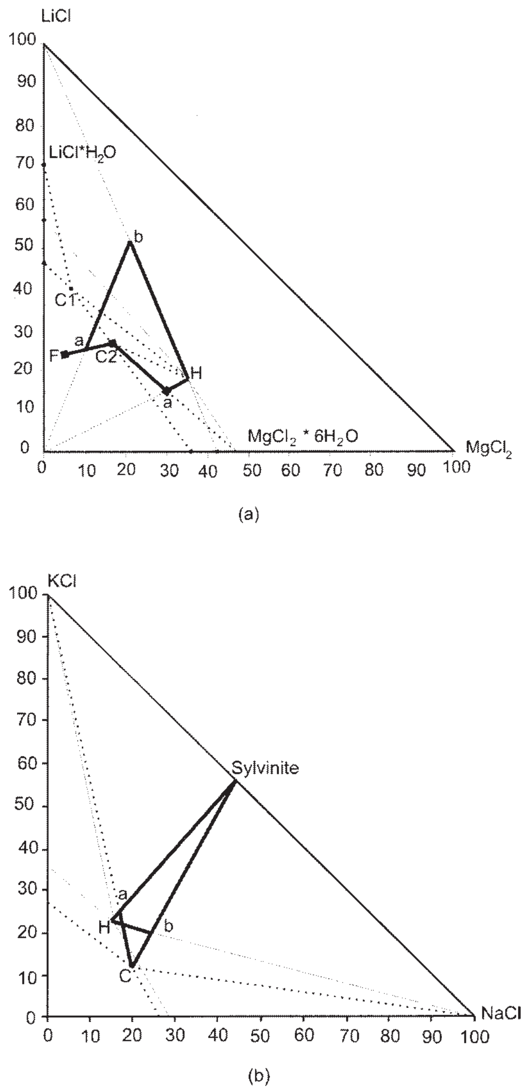
Incorporating One or More Feeds

The composition of the feed plays an important role in making decisions about which streams to mix. In general the feed may be mixed with other streams and taken to any of the MSP conditions selected in the FPD, or may be divided before being mixed and raised to the conditions of any of the selected MSPs. In this section we will discuss how to select the mixing point for the feed. Here we again consider the example in which we seek to separate a mixture of lithium chloride and magnesium chloride into their pure salts. As can be seen in Figure 5c, there are three regions in which the feed may occur: between R^{LiCl} and R^{C2}, between R^{C2} and R^{H}, and between R^{H} and $R^{\mathrm{MgCl2 \cdot 6H2O}}$. These three possibilities are shown in Figure 7. If the feed R value, R^{F}, lies between R^{H} and $R^{\mathrm{MgCl2 \cdot 6H2O}}$ (where only magnesium chloride is crystallized; Figure 7a), then it should be mixed with the saturated solution H at the conditions of MSP C2. This would permit an increase in the amount of magnesium chloride precipitated relative to the quantity of solution C2.

This decision is also in accord with the widely known rule of thumb: "separate the highest quantity component first, " which in this case says to separate the magnesium chloride first, given that the feed occurs in the crystallization zone of this component. Similarly, if the feed has a value of R^{F} between R^{C2} and R^{LiCl} (region of lithium chloride crystallization; Figure 7b), then mixing should be done with saturated solution C2 at the conditions of MSP H, which would permit an increase in the quantity of lithium chloride precipitated relative to the quantity of solution H. In these first two cases, the relative quantity of salt precipitated would increase compared with the quantity obtained in a partial cycle (without feed, or with feed having a composition equal to one of the MSP). In the third case, when the feed has a value of R^{F}, which occurs between R^{C2} and R^{H} (Figure 7c) then the feed occurs in the region used for the crystallization of both products and, whatever feed is mixed, the relative quantity of salt will be reduced. In general we can say that the best mixing point is the one with a value of R most distant from the R^{F} value of the feed. However, the latter is not always true because there are cases where the best option is to divide the feed and mix a given quantity with each saturated solution of the MSPs.

Figure 8 illustrates two examples that clarify these rules. Figure 8a shows an example that represents the example of Figure 7b, where the feed occurs in the LiCl crystallization zone. In this case the feed must be mixed with solution C2, giving solution a, and then the resultant mixture is moved to the conditions of MSP H, where the solution is heated to evaporate solvent until reaching point b. Under these conditions crystals of LiCl are produced, plus a saturated solution H. The rest of the process consists of cooling solution H and adding solvent to reach point a, where crystals of $MgCl_2 \cdot 6H_2O$ are produced as well as saturated solution C2. Figure 8b shows an example well studied in the literature,[2,6,13,14] which includes the separation of KCl and NaCl starting with sylvinite. The diagram represents two isothermal cuts at 30 and 100°C. The sylvinite feed is found between the R values of MSPs C and H, with the specific values $R^{H} = 1.4$, $R^{F} = 0.9$, and $R^{C} = 0.6$, in the zone in which two solutes crystallize, including KCl and NaCl. According to the rule the feed should be mixed with the streams that operate at the MSP conditions having an R value that is the most distant from the R^{F} value, that is, the feed should be mixed with solution C and carried to the conditions of MSP H (the value of R^{F} is further from R^{H} than from R^{C}). The optimal solution,[6] however, is to mix 83.4% of sylvinite with solution C, to reach point b arriving at the conditions of point H, to produce NaCl crystals and solution H (Figure 8b). Once solution H is separated it is mixed with 16.6% of the remaining feed to reach point a. This feed splitting permits separating the salts without removing or adding solvent (water) to the system, other than the losses in the process of purging and the occlusion in the cakes. Although the application of the rule does not produce the best solution, it is close to being an optimal solution. Also, the optimal solution does not consider that the process includes leaching of part of the sylvinite, producing KCl as a product that is less pure than that obtained by crystallization.

Let us finally consider a last example with multiple feeds, a topic scarcely treated in the literature. In general, the studies that use some algorithm in search of separation pathways[3,5,6]



(a)

(b)

Figure 8. (a) Management of feed in the example in Figure 7b for the lithium chloride and magnesium chloride system; (b) management of the feed in the separation of sylvinite.

may include multiple feeds. Suppose that there are two sylvinites, one with 47.7% KCl (52.3% NaCl) and another with 25% KCl (75% NaCl and 5% H_2O). In this case the values of R are as follows: $R^H = 1.4$, $R^{F1} = 0.9$, $R^C = 0.6$, and $R^{F2} = 0.4$. Thus the first feed, which is identical to that in the previous example, again lies in the crystallization zone of the two salts, and so the same rule is applied as before: mix the first feed with solution C, carrying it to the conditions of MSP H. This example has been studied by Cisternas and Swaney[6] (corresponding to their example 1.2) with the result that this feed must be split, sending 77.4% to the conditions of MSP H, so for this case our decision nears the optimal conditions. The second feed occurs in the zone of NaCl crystallization (Figure 9) and thus needs to be mixed with solution C and carried to the conditions of MSP H. This is precisely the result found in Cisternas and Swaney.[6]

In summary:

- If the feed occurs within the crystallization zone of only a single product, it should be mixed with the streams that operate under MSP conditions for which the product occurs in equilibrium.
- If the feed occurs within the crystallization zone of two products, choose mixing with streams that operate at MSP conditions having a value of R that is the most distant from the R^F value. In some cases, however, depending on the management of the solvent, it may be better to split the feed and operate at the two MSPs of the products that crystallize in this zone.

To verify whether our rules provide adequate solutions, studies were carried out to compare our results with the optimal solution obtained by the procedure developed by Cisternas and Swaney.[6] The following systems were included in the study: LiCl + $MgCl_2$ + H_2O (30 and 102°C), KNO_3 + $NaNO_3$ + H_2O (30 and 100°C), Na_2CO_3 + Na_2SO_4 + H_2O (20 and 50°C), $MnSO_4$ + K_2SO_4 + H_2O (25 and 97°C), $MgSO_4$ + K_2SO_4 + H_2O (25 and 50°C), and Na_2SO_4 + $(NH_4)_2SO_4$ + H_2O (25 and 60°). These examples include systems that operate without the formation of compounds, systems with formation of compounds at a single temperature, and systems that form compounds at both temperatures. The FPD was constructed for each of these systems and for each crystallization zone the separation pathways were identified using the previously described rules if the feed was found in this zone. (It should be noted that each separation pathway includes various types of process depending on the management of solvent, dilution, or evaporation, which is determined by mass balance.) Later an automated computer procedure was implemented using GAMS, which randomly generated 200 feeds to scan within each specific zone. An optimal separation scheme was obtained for each of these feeds following the method of Cisternas and Swaney[6] and was compared with that obtained using the rules developed here. In most cases, the solutions obtained both by the computer optimization and by the cited rules were in agreement. Differences were observed in cases when the feed was found in a two-product crystallization zone. In these cases the solvent balances played an important role, and thus some did not agree with the pathway solutions obtained. In each case the differences observed were small, affirming that the solutions obtained following the rules were optimal or near optimal. For greater reliability in these cases, it is recommended that three possible alternatives be studied, including feeds under MSP conditions, feeds under conditions of the alternative MSP, and splitting of the feeds using both MSPs.

Multicomponent Systems

When a system has more than three components, including one or more solvents, the synthesis of the separation system becomes complicated because the representation of the behavior of the equilibrium cannot be given in a single diagram.

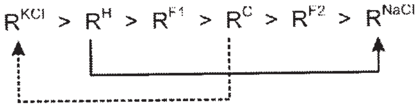


Figure 9. FPD with multiple feeds for the example of Figure 8b.

Different strategies approaching the solution of this problem include constructing diagrams on a dry basis, the use of projections of systems saturated with one component, or the use of auxiliary diagrams.[15,16] Important advances in the representation of these systems have been achieved by Ng and coworkers. The representation of the phase diagram using hyperplanes for linear systems or by a set of hyperplanes for nonlinear systems allows identifications of limits and regions of the system, facilitating identification of possible separation pathways.[17] This type of tool allows one to work with any type of phase diagram, and thus includes hybrid processes such as distillation–crystallization.[18] On the other hand, the use of digraphs allows one to analyze multicomponent systems by means of different projections and sections, whether these are molecular[19] or ionic systems,[20] including the formation of compounds and polymorphs.[21] These advances have been embodied in the commercial software SLEEK (Solid–Liquid Equilibrium Engineering Kit, Clear Water Bay Technology Inc.). Searching for separation pathways for multicomponent systems, Cisternas and Rudd[2] identified separation pathways based on phase diagram characteristics. Cisternas[3] proposed a methodology based on the search for an optimal separation path within a superstructure of potential states of operation.

The previously discussed strategy based on the use of the relative composition diagram (RCD) and the feasible pathways diagram (FPD) can be used in the identification of feasible separation pathways in various multicomponent systems. A primary concept is the identification of pairs of components within the set of components to be separated, the separations of which are then put into a hierarchy. Once a pair of components has been selected, the remaining components are considered to be pseudosolvents, in the sense that they can be added to or removed from the system. To select the order of separation of the pairs of components we return to the heuristics "remove most plentiful component next " or "remove corrosive, hazardous compounds early " or "do the difficult separations last," and the like. Furthermore, the classification of components as desired products, subproducts, wastes, and contaminants may be useful. For example, it may not be recommendable to use a product or a contaminant as a pseudosolvent. Once a potential separation path has been identified, the phase diagram may be useful in adapting the process to certain specific requirements, such as the purity of the salt.

Let us consider an example of how to use the RCD and the FPD with multicomponent systems. Let us suppose that we desire to separate KNO_3 from a mixture formed by KNO_3 (14.25%), $Mg(NO_3)_2$ (25.69%), $NaNO_3$ (3.25%), and water (56.81%). The possible separation pairs are KNO_3–$Mg(NO_3)_2$, KNO_3–$NaNO_3$, and $Mg(NO_3)_2$–$NaNO_3$. Because the KNO_3 is the desired product, it must be considered as part of the pair of components that should be separated first. The $Mg(NO_3)_2$ and the $NaNO_3$ can be pseudosolvents and, because the $Mg(NO_3)_2$ occurs in the greatest quantity, its separation should be prioritized. The problem is then proposed of how to separate the $Mg(NO_3)_2$ from the KNO_3, in which the $NaNO_3$ acts as a pseudosolvent. Table 4 shows the equilibrium values of this system at 20 and 80°C; the points of interest are the MSPs C and H. The relative composition, defined as $\%KNO_3/\%Mg(NO_3)_2$, has a value of 0.3 in the MSP at 20°C and 0.9 in the MSP at 80°C. The RCD is shown in Figure 10a, where it is clear that the separation of KNO_3 is not possible at MSP H, whereas the separation of $Mg(NO_3)_2$ is not possible at MSP C. Then, eliminating these pathways, the FPD shown in Figure 10b is obtained. Because the value *R* of the feed is 0.6 (between the *R* values of MSP C and H), in principle the feed could be mixed with either of the MSPs or even be split to mix with both MSPs.

Table 4. Equilibrium Data for $KNO_3 + NaNO_3 + Mg(NO_3)_2 + H_2O$ System at 25 and 100°C[47] *

T (°C)	Key	Saturated Solution (wt %) KNO_3	$Mg(NO_3)_2$	$NaNO_3$	Solid Phase	*R*
20	C	21.15	64.68	14.16	K + N + M	0.3
80	H	40.34	46.07	13.59	K + N + M	0.9

*K = KNO_3; N = $NaNO_3$; M = $Mg(NO_3)_2 \cdot 6H_2O$.

For example, Figure 10c shows the case in which the feed (point A) is mixed with saturated solution H and carried to the conditions of MSP C, which requires adding a certain quantity of $NaNO_3$ (salting-out) to reach point b. Saturated solution C is carried to the conditions of MSP H, which produces the cocrystallization of $Mg(NO_3)_2$ and $NaNO_3$. This alternative achieves the separation of pure KNO_3, but requires a certain quantity of $NaNO_3$ representing added cost, either because it is necessary to separate the mixture of $Mg(NO_3)_2$ and $NaNO_3$ or buy $NaNO_3$. Figure 10d shows the case in which the feed is mixed with saturated solution C and carried to conditions of MSP H. In this case the KNO_3 is not obtained by salting-out with $NaNO_3$, but is coprecipitated with $NaNO_3$, and this is clearly not the best option because it requires a second step to separate the resulting mixture. Nevertheless, both alternatives can be modified to overcome these difficulties. For example, the option presented in Figure 10c may be modified to avoid the use of $NaNO_3$ as a salting-out agent as observed in Figure 10e. The option of Figure 10d can be modified as shown in Figure 10f to avoid the coprecipitation of $KNO_3 + NaNO_3$. The level of separation difficulty of a system can be evaluated from the difference between the values of *R* of the MSP used, where the smaller difference represents the greater difficulty.[2] It is therefore clear that the latter two options are less optimal from the perspective of the levels of recycled flows in the system, but they avoid certain characteristics that may not be desired. In the four options presented it is clear that the $NaNO_3$ acts as a pseudosolvent and that, because it occurs in small quantity in the system, its recycling is also small. In any case, if no attractive alternative can be identified it is still possible to consider the $Mg(NO_3)_2$ as a pseudosolvent and study the alternatives generated. Figures 10c to 10f are Jänecke projections.

Let us now consider as an example a more complex system that forms compounds, and for which it is thus more difficult to identify separation pathways. Table 5 shows equilibrium data at 0 and 25°C for the $H_3BO_3 + K_2SO_4 + MgSO_4 + H_2O$ system, whereas Figure 11a shows its phase diagram (Jänecke projection). Because there are no metathetic reactions between the cations and anions at these temperatures it is possible to use this cut of the entire phase diagram; otherwise, all cations and anions must be considered.[19] Note that this system forms the compound shoenite. Among the solid species K_2SO_4, $MgSO_4$, and $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$, two multiple saturation points exist at each temperature: H1 and H2 at 25°C; C1 and C2 at 0°C. This signifies that in some MSPs the salt in equilibrium is not

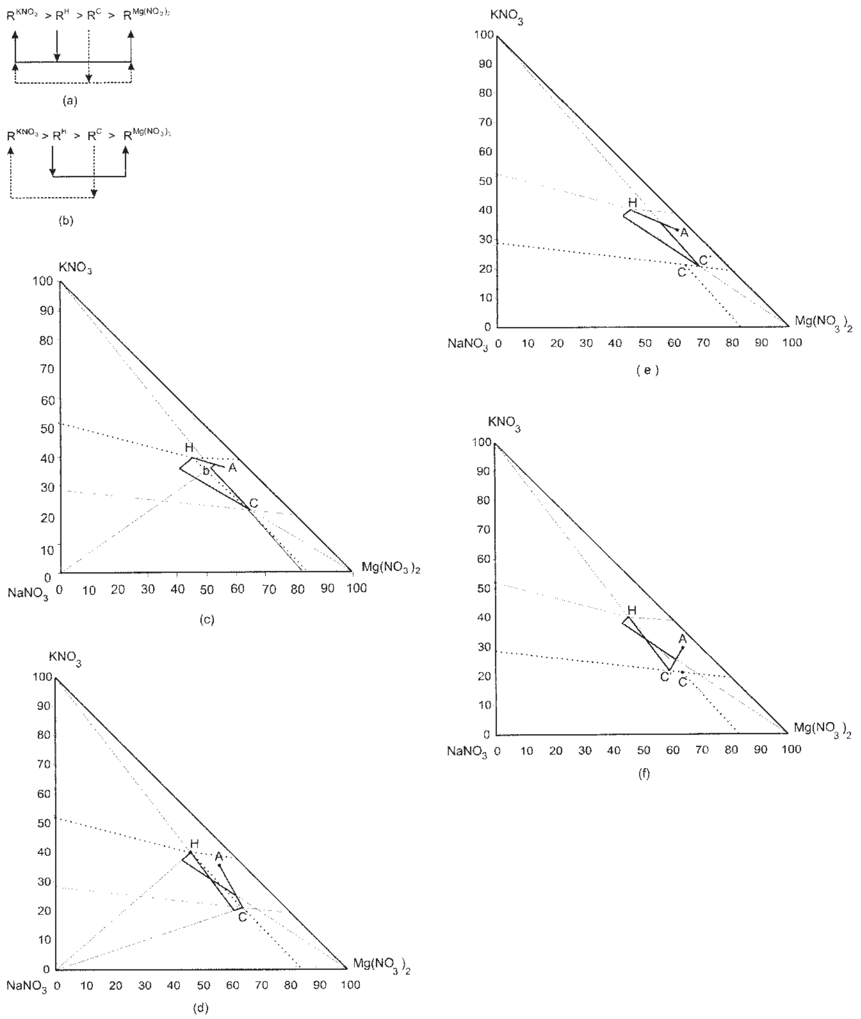


Figure 10. KNO_3 + $Mg(NO_3)_2$ + $NaNO_3$ + water system.

(a) RCD for the separation of the KNO_3 + $Mg(NO_3)_2$ pair, (b) FPD for the separation of the KNO_3 + $Mg(NO_3)_2$ pair, (c) process when the feed is mixed with H, (d) process when the feed is mixed with C, (e) modification of process 10c without salting-out, (f) modification of process 10d without coprecipitation.

K_2SO_4 or $MgSO_4$ but is the compound $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. Under these circumstances it is not possible to consider these species as pseudosolvents in our method, given that they do not coprecipitate together with the other solutes. This limits the application of the RCD and FPD with these types of systems, although it is still possible to apply them for the solutes that do not form compounds with other solutes.

Let us consider, for example, that the pseudosolvent is the H_3BO_3, that is, that the pair of solutes to be separated is K_2SO_4 and $MgSO_4$. The *R* values are presented in Table 5 and the RCD is given in Figure 11b. Once the infeasible pathways are eliminated, that is, the precipitations of $MgSO_4$ and $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ under conditions of H1 and H2, respectively, and considering that the best condition for the precipitation of shoenite is H1 and the best condition for the crystallization of K_2SO_4 is C2, we obtain the diagram of Figure 11c. According to this diagram the magnesium sulfate should crystallize under conditions of MSP C1, starting from saturated solution H1; the shoenite should crystallize under conditions of MSP H1, starting from solutions C1 and C2; and the potassium sulfate should crystallize under conditions of MSP C2, starting from the decomposition of the shoenite. To identify the participation of the boric acid as a pseudosolvent it is necessary to present the process in a phase diagram or carry out mass balances (in which the participation of water as solvent also becomes known). Figure 11a also shows the pathway described, without considering any feed. In carrying solution H1 to the conditions of MSP C1, coprecipitated boric acid and

Table 5. Equilibrium Data for H_3BO_3 + K_2SO_4 + $MgSO_4$ System at 0 and 25°C[47] *

T (°C)	Key	Saturated Solution (g/100 g H_2O) H_3BO_3	K_2SO_4	$MgSO_4$	Solid Phase	*R*
0	C1	0.7	2.8	19.1	M12 + S + H	0.25
	C2	2.0	8.2	9.9	H + K + S	0.24
25	H1	1.77	2.9	25.26	M7 + S + H	0.61
	H2	4.3	11.3	10.5	K + S + H	0.38

*M7 = $MgSO_4 \cdot 7H_2O$; M12 = $MgSO_4 \cdot 12H_2O$; S = $K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$; H = H_3BO_3; K = K_2SO_4.

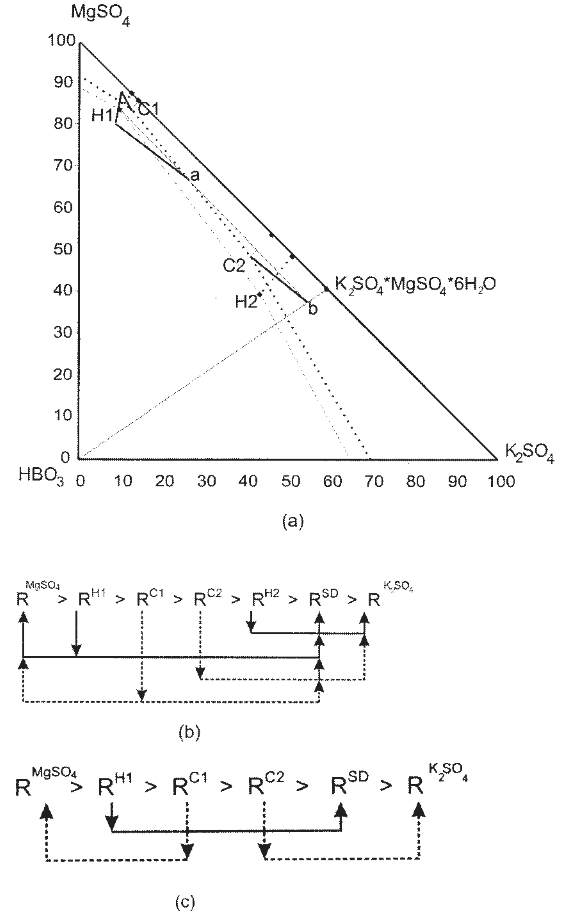


Figure 11. $H_3BO_3 + K_2SO_4 + MgSO_4 + H_2O$ system.

(a) Phase diagram, (b) RCD, (c) FPD.

magnesium sulfate are produced; solution C1 is mixed with solution C2, giving the mixture at point a, which under the conditions of MSP H1 would produce coprecipitation of shoenite; and boric acid as represented by point b. The decomposition of point b under conditions of MSP C2 produces crystallization of potassium sulfate and the solution C2, which is recycled to the process. The final pathway will depend on the location of the feed and the objectives sought.

In summary:

- The previously discussed strategy based on the use of the relative composition diagram (RCD) and feasible pathways diagram (FPD) can be used for the identification of feasible pathways for separation in some multicomponent systems.
- The basic concept consists of identifying pairs among a set of components to be separated and setting a hierarchy for their separation. Once a pair of components has been selected, the remaining components are considered as pseudosolvents (in the sense that they could be added to or removed from the system). If a given solute forms a compound with another solute, it cannot be considered as a pseudosolvent in applying the RCD.
- For selecting the order of separation of the pairs of components, widely recognized general precepts are applied, including "first favor separation of components that are present in the highest quantity," "remove corrosive components as early as possible," "leave the more difficult separations for last," and so forth. Also, classification of the components into products desired, subproducts, wastes, and contaminants may be of great usefulness.
- Once a potential separation path is identified using the FPD, the phase diagram may be of help in adapting the process to certain specific requirements, such as the elimination of coprecipitation.

Systems with Chemical Reactions

In many cases, fractional crystallization is a process following a chemical reaction, or the solute crystallizes during the occurrence of a chemical reaction, given that the solute product may be of low solubility. Berry and Ng[22] presented a systematic method for synthesizing reactive crystallization processes where the reaction occurs in the liquid phase, although some products may precipitate. These use coordinate transformations that permit the visualization of the problem for three or fewer degrees of freedom. Subsequently, Kelkar and Ng[23] included the kinetics of the crystallization and reaction together with the effects of mass transfer in the design of systems for reactive crytallization. Although these effects are important, and may indeed affect the crystallization pathway, they are difficult to take into account from the outset because of the amount of data necessitated, and therefore their incorporation is more appropriate once the separation route for a mixture of solutes has been selected. Combined kinetic and metastability effects may also produce complications in the operation and design of these processes.[24]

The RCD and the FPD may be used in the search for separation processes by fractional crystallization undergoing chemical reaction. Let us consider the following chemical reaction:

$$\nu_A A + \cdots \rightarrow \nu_C C + \cdots \tag{1}$$

where A and C represent components to be separated by fractional crystallization. Here A is a reagent and C is a product, although this is not a requirement; that is, A and C could also be two products. The quantity of A and C after the chemical reaction may be expressed as

$$n_A = n_{iA} + \nu_A \varepsilon \qquad n_C = n_{iC} + \nu_C \varepsilon \tag{2}$$

where n_A and n_C are the moles of A and C; n_{iA} and n_{iC} are the initial moles; and ε represents the extent of the reaction. The relative composition of the product of the reaction, R^R, can be defined as

$$R^R = \frac{n_A MW_A}{n_C MW_C} = \frac{MW_A}{MW_C}\frac{(n_{iA} + \nu_A \varepsilon)}{(n_{iC} + \nu_C \varepsilon)} \tag{3}$$

where MW_i represents the molecular weight of species i. Note that if A is a reagent and the initial quantity of C is zero, then R^R varies from ∞ (when the reaction extent is zero) to zero (when the reaction extent equals $\varepsilon = -n_{iA}/\nu_A$). After considering the operating conditions required for the chemical reaction as well as the thermodynamic limitations on the reaction and the R values of the MSP, an adequate value for R^R can be chosen.

Considering, for example, the production of boric acid from ulexite, $Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$, the chemical reaction would be

$$\begin{aligned}Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O + 3H_2SO_4 \rightarrow Na_2SO_4 \\ + 2CaSO_4 + 10H_3BO_3 + 4H_2O\end{aligned}$$

The reaction occurs in the aqueous phase and the $CaSO_4$ precipitates because it is practically insoluble in the solution. Then the resulting solution contains sodium sulfate and boric acid, whose separation is desired through fractional crystallization. In this case the value of R^R can be defined as

$$R^R = \frac{MW_{Na_2SO_4}(n_{iNa_2SO_4} + \varepsilon)}{MW_{H_3BO_3}(n_{iH_3BO_3} + 10\varepsilon)} \tag{4}$$

Considering that the initial quantities of sodium sulfate and boric acid are zero, we have

$$R^R = \frac{MW_{Na_2SO_4}}{10MW_{H_3BO_3}} \tag{5}$$

and thus the value of R^R is 0.23. Table 6 gives the equilibrium data for the sodium sulfate + boric acid + water system. The RCD is shown in Figure 12a, in which it is clear that the boric acid cannot be produced under the conditions of MSP H, whereas it is not possible to crystallize the sodium sulfate under the conditions of MSP C. The FPD including the feed is shown in Figure 12b. It is clear from this diagram that the reaction product, represented by point R^R, must be brought to the conditions of MSP C, and the sodium sulfate must be crystallized under the conditions of MSP H. Figure 12c shows the scheme for the process. The reagents plus saturated solution H are sent to the reactor.

The resulting solution, after filtration removal of solid residues, has an R value between R^H and R^R and is brought to conditions of MSP C, producing crystallization of the boric acid. Once saturated solution C is separated from the boric acid crystals it is brought to the conditions of MSP H, producing the crystallization of sodium sulfate. The scheme obtained is in agreement with that proposed by Pocovi et al.[25] for fractional crystallization of boric acid and sodium sulfate in the treatment of ulexite.

In summary:

- For systems with chemical reactions, a determination is made of the value or range of values of the relative composition R^R of the solutes that are to be separated. The value of R^R is a function of the extent of reaction, and thus its value must be treated as a function of the operating conditions, the R value of the MSP, and the thermodynamic limits on reaction extent.

Table 6. Equilibrium Data for Na_2SO_4 + H_3BO_3 + H_2O System at 20.5 and 75°C[47] *

T		Saturated Solution (wt %)			
(°C)	Key	Na_2SO_4	H_3BO_3	Solid Phase	R
20.5	C	19	5.7	H + N10	3.3
75	H	28.2	17.1	H + N	1.6

*H = H_3BO_3; N10 = $Na_2SO_4 \cdot 10H_2O$; N = Na_2SO_4.

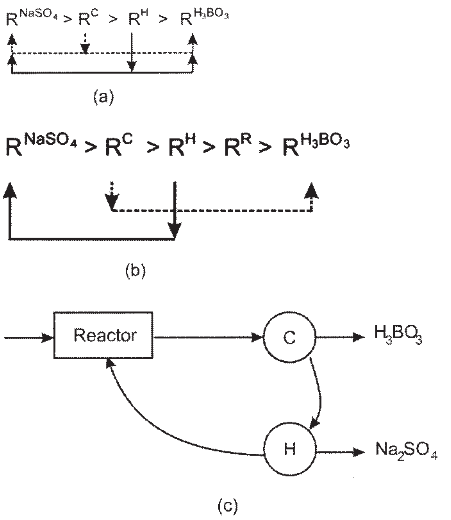


Figure 12. Production of boric acid starting with ulexite.

(a) RCD, (b) FPD, (c) process scheme.

- The RCD and the FPD are constructed by considering that R^R represents the feed to the separation system.

Exploiting Other Separation Strategies

Until now we have used changes in both temperature and quantity of solvent, and used some of the components as pseudosolvents (salting-out) to obtain the desired separation. The use of other agents such as solvents or gases for decreasing the solubility has also awakened interest in this method for obtaining separation of some species, a technique known as *drowning-out*. The basic concept is to add another chemical agent to affect the solubility of the species of interest and then seek a strategy for recovery of the chemical agent, usually by distillation or liquid–liquid separation. Although the size of the crystal typically decreases in this type of procedure, complicating the subsequent separation and management of the product, there is interest in using this strategy not only in systems that require high degrees of evaporation, but also in systems in which the crystallized product is not the final product desired. Significant levels of evaporation are generally required when the solubility of the species in question changes little with change in temperature.[26,27] In other cases, if the components crystallize in hydrated form, calcination may be necessary to obtain decomposition of the component and thus reduce the quantity of hydrates. It has been observed that in some systems the addition of an external agent changes the hydration number of the species. For example, Taboada et al.[28] observed that the addition of polyethylene glycol reduced the quantity of hydrates in the crystallization of sodium carbonate.

Berry et al.[29] presented a method for synthesizing separation schemes based on crystallization by drowning-out. Different alternatives were identified based on the characteristics of the phase diagrams. Their analysis centered on the conditions required in the equilibrium behavior for recovery of the separation agent. The method is useful in separation of binary systems of solvent + solute. The application of drowning-out to separate solutes (that is, at least two solutes) has not been well studied in the literature. In general, there are few experimental data treating these types of systems, and methodologies for the synthesis of separation processes by fractional crystallization by drowning-out have not been proposed in the literature.

The RCD and the FPD can be used in the identification of separation pathways when there are two or more solutes. Consider the separation of sylvinite using ammonia as a potential agent for drowning-out. Table 7 presents equilibrium data for this system with and without ammonia, as well as the values for *R*, defined as %KCl/%NaCl. This example was studied by Cisternas and Swaney.[6] Figure 13a shows the RCD for this system, where it should be noted that NaCl cannot be precipitated at the MSP with NH_3, whereas KCl cannot be precipitated at MSP H. By elimination of these two pathways, the FPD of Figure 13b is obtained in which it is observed that NaCl can be obtained under conditions of both MSPs H and C. Using the heuristics developed, we must favor the use of MSP H over C because the difference between its *R* value and the *R* of NaCl is greatest. Similarly, as in Figure 13b, it can be observed that KCl can be crystallized under the conditions of MSPs C and CA, where CA stands for the MSP with ammonia. Using the same heuristic we must favor MSP CA over MSP C. In the FPD in Figure 13c we have included the feed, which lies between MSP H and MSP CA; the feed could be placed at the closer MSP point or divided into two streams. Figure 13d shows the general scheme of the process. It should be observed in this case that to go from MSP CA to MSP H the removal of the NH_3 (possibly by distillation) is required, a situation that in previous examples without drowning-out signified changes in the temperature. In the diagram of Figure 13d, addition or removal of water has not been included and must be determined by mass balance. The result obtained is the same obtained by Cisternas and Swaney[6] using optimization. The use of the RCD and FPD is validated, delivering solutions near the optimum, without losing the possibility of analyzing other alternatives. This procedure can be applied to other similar systems, such as the separation of ampicillin from potassium chloride from aqueous solution using ethanol.[9]

Another alternative for separating a mixture of solutes that—to our knowledge—has not been reported in the literature is to change the oxidation level of the ionic species to favor their separation. For example, the $FeSO_4 + Al_2(SO_4)_3 +$ water system has a very small crystallization region for aluminum sulfate, whereas the $Fe_2(SO_4)_3 + Al_2(SO_4)_3 +$ water system has a larger region. If separation of aluminum sulfate is desired, it is possible to oxidize the Fe^{+2} to Fe^{+3} and then work under the modified conditions. In this case the external agent consists of the components that produce the oxidation. To find useful conditions for the change in level of oxidation, potential-pH diagrams may be used.

Table 7. Equilibrium Data for KCl + NaCl + H_2O + NH_3 System at 25, 30, and 100°C[47]

T (°C)	Key	Saturated Solution (wt %) KCl	NaCl	H_2O	NH_3	Solid Phase	*R*
30	C	11.70	20.25	68.05	0	KCl + NaCl	0.6
100	H	22.20	15.90	61.90	0	KCl + NaCl	1.4
25	CA	1.0	16.2	42.8	40.0	KCl + NaCl	0.06

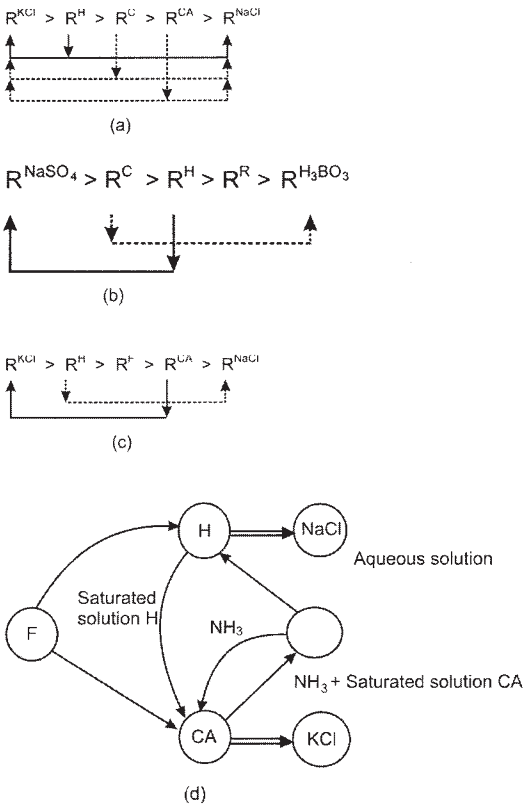


Figure 13. Separation of silvinite using ammonia as a drowning-out agent.

(a) RCD, (b) FPD, (c) analysis of the feed, (d) process scheme.

Some systems show the formation of solid solutions and, in these cases, a cascade of equilibrium steps must be used that can be determined using the methods of McCabe–Theile or Ponchon–Savarit.[30] However, some of these systems show congruent points where the solid solution occurs in equilibrium with a liquid solution of the same composition. These congruent points demarcate the limit of enrichment arising from countercurrent stages.

Separation of these systems is possible by using cascades at different temperatures.[2] To identify a separation path, these congruent points need to be considered in a manner analogous to that of the MSPs and then the method is applied to obtain the RCD and FPD.

Chiral crystallization plays an important role in the separation of enantiomers in the pharmaceutical and agrochemical industry. The separation of this type of component may be difficult, given that the composition of the solid phase (which can be a racemic compound) or an equimolar solid solution (pseudoracemic) is the same as the composition of the liquid phase.

One method of separating these components consists in the formation of a dissociable compound using a chemical agent, which is removed from the system once the separation has been achieved. The separation of soluble species can be carried out with the aid of the RCD and FPD. The synthesis of separation processes for this type of component was analyzed by Schroer et al.,[31] who carried out a complete analysis of the problem and presented a procedure based on hierarchical decision steps.

In summary:

- When considering drowning-out processes for the separation of two or more solutes, the RCD and FPD may be used, including the MSP with the drowning-out agent as another MSP in the system.
- Once the separation path is selected—if it includes drowning-out—it must be understood that the drowning-out agent must be removed from the system. The manner in which it is removed cannot be determined using the RCD or the FPD. If the oxidation level is exploited as a means of surpassing solubility limits, the RCD must be constructed using the MSPs at the different oxidation levels. The system is then analyzed in a form analogous to the above-cited studies.
- In systems that form solid solutions with congruent points, these points should be treated as if they were MSPs, and then the RCD and FPD are used to identify the separation pathway. Each separation step must be replaced by a cascade of equilibrium stages.

Other Effects

Another series of factors related to fractional crystallization exist, which can influence the selection of separation pathways, and are briefly discussed in this section.

Effluent treatment

When fractional crystallization is desired as a methodology for the treatment of effluents, this activity is generally integrated within a strategy that includes other operations. On the other hand it may be of interest only for the elimination of certain elements by crystallization, without concern over whether the crystals are obtained in pure form or as mixtures. What is required under these conditions is to identify the interception of the task and its location within the network of effluent treatments. Parthasarathy et al.[32-34] worked on integration of crystallization in effluent treatment networks. These authors used phase diagrams to identify the conditions of operation in their studies. The use of the RCD may be of aid in this strategy, especially in systems more complex than those analyzed in their studies.

Stages complementary to the crystallizer

Crystallization does not occur as an isolated stage in the process, and a series of other operations are necessary, such as solution concentration, filtration, washing, drying, and recrystallization. Thus, studies must be included on the effects of the crystallization step on the other complementary stages when selecting a separation pathway.

Chan and Ng[35] developed a systematic procedure for the synthesis of a processing system, both upstream and downstream of the crystallizer. The procedure included five hierarchical steps that allowed construction of a flow diagram. Although the result will not necessarily be optimal, the approach is useful in selecting the unit operations required and their interconnection in association with the crystallizer. The procedure, which considers aspects such as solvent management and product characteristics, can be a valuable complement to other procedures that consider the overall process. An important group of aspects to consider in crystallization processes, which affect the other operations, are the characteristics of the solids produced, especially the particle size distribution. This aspect has been analyzed, together with other factors, in the studies of Wibowo et al.[36] and Wibowo and Ng.[37] These studies present a series of heuristics that allow prediction of operating problems in the design associated with the interactions between crystallization and downstream operations. One aspect not considered in these studies is that fractional crystallization may include leaching steps that require complementary stages of a different type.

On the other hand, Cisternas and co-workers[13,38] included energy integration for the system and treatment of the solid (filtration, washing) together with the process synthesis for fractional crystallization. The strategy of these authors included the use of mathematical programming, including disjunctions for decision making. It can be observed from these studies that ancillary factors had little effect on the selection of a separation pathway. However, nonideal solid–liquid separation affects the flow rates and concentration of all streams.[13,39,40] These authors, however, did not include the distribution of particle size as part of their analysis, a factor that may have a more significant effect.

Metathetic salts

A *reciprocal salt pair* is defined as a pair of salts that produce a metathetic reaction. Various processes used this type of reaction to produce a specific type of product; some separation systems include metathetic reactions. Although the concept still applies of separation systems design using changes of temperature and solvent for overcoming compositions at final crystallization points, diagrams of relative composition cannot be applied to this type of system. Separation schemes can be identified following indications presented by Fitch,[1] Dye et al.,[41] and Berry and Ng.[42] These studies use projections based on dry weight to identify possible separation pathways. For complex systems in which we seek to include analyses at various temperatures, the difficulty with this strategy lies in the fact that there may be a large number of alternatives that may be difficult to identify. Also, exclusion of the solvent may lead to errors in the selection of the best alternative. Cisternas et al.[43] developed a methodology based on the identification of potential stages of operation to form a superstructure upon which to search for the most useful separation pathway. This procedure allows resolution, at least in part, of the above-mentioned problems.

Simulation as a design tool

There is no doubt that simulation of these processes may be of great help, both in the selection of crystallization pathways and in the validation and optimization of a selected route. Here, modeling of the solid/liquid equilibria of multicomponent systems is of the utmost importance; difficulties are associated with the capacity to predict the number, stability, and phase of components, and their capacity to form complexes in the solution.[44] Ji et al.[45] developed a methodology for the simulation of crystallization processes for electrolyte solutions, predicting liquid–solid equilibria and automatically identifying the number of phases and their identities. This method can be used to construct phase diagrams and crystallization pathways. Thomsen et al.[7,8] and Takano et al.[9] worked on the development of methods for the determination of phase diagrams of mixtures of electrolytes using thermodynamic models such as UNIQUAC, as well as their application to conceptual design for separation by crystallization with electrolytes, including aspects such as analysis, design, and simulation. Furthermore, simulation appears to be an important tool for improving already existing processes.[46]

Conclusions and Comments

Over the last 15 years significant advances have been achieved in methods for the design and improvement of separation processes based on fractional crystallization. These advances have addressed the separation of simple systems, systems involving the formation of compounds, drowning-out, metathetic salts, hybrid processes, and multicomponent systems. Important advances have been made in the use of phase diagrams as design tools, especially with respect to the visualization of multicomponent systems. Procedures for the conceptual design of these systems have been divided into two schools of thought. One group of researchers used hierarchical procedures based on rules, whereas others used superstructures that represent different possibilities for processing, applying a mathematical model for identification of the most useful approach to each problem.

It has been demonstrated that relative composition diagrams (RCDs) and feasible pathway diagrams (FPDs) are simple tools that allow identification of separation processes that may be feasible and nearly optimal. The effort required for application of RCDs and FPDs is minimal and allows identification of conceptual designs that can be used as starting points for larger analyses, such as simulations or laboratory studies. Laboratory studies are a major issue because crystallization is a kinetic process and operates in a metastable region where molecular interactions between solute, solvent, and impurities can be critical. The FPDs and RCDs have been applied to simple systems, systems with compound formation, multicomponent systems, systems with multiple feeds, and in some cases to more complex systems such as those including chemical reactions, drowning-out, and solid solutions. In these cases, various rules have been derived for correct application and analysis, complemented by a group of examples demonstrating the advantages and limitations of this strategy.

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