Visualization of High-Dimensional Phase Diagrams of Molecular and Ionic Mixtures

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A general method for visualizing high-dimensional phase diagrams of systems containing a mixture of molecular and ionic species is presented. Based on geometric modeling with homogeneous coordinates, canonical coordinates are developed to represent cuts and projections, which, being reaction-invariant, do not depend on the degree of ionization. Examples are provided to illustrate the application of this method for identifying useful transforms with potential applications in separation system synthesis.

Introduction

Visualization of phase equilibrium data in the form of phase diagrams is very useful in process design and synthesis. Synthesis procedures based on phase diagrams are available for distillation processes (Biegler et al., 1997), crystallization-based separations (Wibowo and Ng, 2000), extractive reaction processes (Samant and Ng, 1998), and hybrid systems (Berry and Ng, 1997; Pressly and Ng, 1999). However, all of these studies focused on systems with two- and three-dimensional (3-D) phase diagrams. Since many systems encountered in practice are multicomponent in nature, it is important to be able to visualize high-dimensional phase diagrams in a general way.

The only practical approach to view entities of dimensions four or higher is to take projections and cuts. There have been various attempts to use 2-D cuts and projections in the visualization of 4-D and 5-D phase diagrams (Purdon and Slater, 1946; Perel'man, 1966; Ricci, 1966; Hasse and Schönert, 1969). Although a single projection or cut only captures part of the system under consideration, a sequence of such projections and cuts can provide the user with a mental picture of the phase diagram in its entirety (Samant et al., 2000).

Representation of compositions in the projections and cuts can be simplified using a set of canonical, or transformed, coordinates. Such coordinates have been proposed for molecular systems (Ung and Doherty, 1995; Espinosa et al., 1996; Pérez Cisneros et al., 1997), as well as for ionic systems (Samant and Ng, 2001). Traditionally, the transformed coordinates are expressed in terms of mole fractions for molecular systems and in ionic molalities for ionic systems. Due to this apparent difference, it is not obvious how the canonical coordinates for systems involving both molecular and ionic species should be expressed.

The objective of this article is to provide a framework for the representation of high-dimensional phase diagrams of molecular and ionic mixtures as an illustration of multicomponent, multireaction systems. Specifically, based on geometric modeling with homogeneous coordinates, canonical coordinates are developed for viewing such phase diagrams through projections and cuts.

Projections and Canonical Coordinates

According to Gibbs phase rule, the number of degrees of freedom in a nonreactive C-component system with P phases co-existing in equilibrium is $f = C - P + 2$. It is common practice to represent the solid-liquid phase behavior of chemical systems as isobaric, polythermal or isobaric, isothermal phase diagrams (Ricci, 1966), in which temperature and pressure are not considered an independent variable. Since P is at least 1, there is a maximum of $(C-1)$ degrees of freedom in such diagrams. Therefore, they can be plotted using $(C-1)$ independent mol fraction coordinates, constituting an inhomogeneous coordinate system.

To utilize the concepts of geometric modeling in dealing with projections, it is advantageous to use homogeneous co-

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ordinates (Mortenson, 1997; Salomon, 1999; Hartley, 2000). In this coordinate system, objects in an n-dimensional space are described using mathematical expressions involving a set of $(n+1)$ coordinate axes. A point $P\ (x_1, x_2, \ldots, x_n)$ is described in homogeneous coordinates as $(y_1, y_2, \ldots, y_n, y_0)$, where $y_i = y_0 x_i$. For example, a point described as (2, 0, 4, 2) in homogeneous coordinates is written as (1, 0, 2) in inhomogeneous coordinates. The homogeneous coordinate representation for a C-component chemical system requires a total of C independent coordinates, which are chosen to be the number of moles of $(C-1)$ components $\{n_1, n_2, \ldots, n_{C-1}\}$ along with the total number of moles, n_{TOT}. By taking the total number of moles as y_o in the homogeneous system, normalized mol fractions appear naturally in the corresponding inhomogeneous coordinates.

When $n \geq 3$, it is impossible to plot an n-dimensional system in its entirety on a piece of paper. To get around this problem, a method has been developed to examine a set of lower dimensional subspace to form a mental picture of the system (Wibowo and Ng, 2002). This can be achieved in two ways: first, to view only a part of the system in an m-dimensional cut, which is basically the intersection between the original object with a subspace of dimension m. Second, all points in the n-dimensional system are projected to an m-dimensional projective subspace. For mathematical simplicity, we only consider linear subspaces. Such an m-dimensional subspace within the original n-dimensional space can be represented as the intersection of $(n-m)$ hyperplanes of dimension $(n-1)$

$$\boldsymbol{q}_i \cdot \boldsymbol{y} = 0; \quad i = 1, 2, \ldots, n-m \tag{1}$$

where $\boldsymbol{q}_i$ is the normal vector to each hyperplane. In other words, the subspace is defined by a set of normal vectors $\{\boldsymbol{q}_1, \boldsymbol{q}_2, \ldots, \boldsymbol{q}_{n-m}\}$ which are linearly independent.

To describe objects lying entirely in an m-dimensional subspace, it is both redundant and inconvenient to use the original set of $(n+1)$ coordinates. Instead, we can use a set of $(m+1)$ coordinates $\{Y_1, Y_2, \ldots, Y_m, Y_0\}$, which are referred to as the *canonical coordinates*. Once the relationship between the canonical and original coordinates is known, it is straightforward to plot the cut or projection of the original system using the new coordinates.

Graphical methods for synthesizing separation processes depend on the capability to track composition changes on the phase diagram, creating the so-called process paths. When the phase diagram is plotted in mole fraction coordinates, material balance lines are always linear and the lever rule, which is useful in constructing process paths, is always valid. It is desirable to preserve this feature when taking a projection, so that the process path can still be constructed in the same way on the resulting plot in canonical coordinates. Linear projection is preferable for this purpose, since linearity is preserved.

There are two classes of linear projection that are particularly useful to obtain projections of phase diagrams: central projection and orthogonal projection. In central projection, the projection rays originate from a single point and extend to all directions. Particularly useful is the unity-plane *projection*, which is a central projection with the origin as the center of projection, and $y_i = 1$ as the projective subspace. Specifically, a unity-plane projection with $y_0 = 1$ as the projective subspace transforms homogeneous into inhomogeneous coordinate system.

In orthogonal projection, projection rays are normal to the projective subspace. In a more general manner, we define *multiple orthogonal projection* from an n-dimensional space to an m-dimensional subspace as the one in which the directions of projection rays are parallel to the normal vectors $(\boldsymbol{q}_1, \boldsymbol{q}_2, \ldots, \boldsymbol{q}_{n-m})$ defining the projective subspace. Under this projection, a point is first projected in the direction of $\boldsymbol{q}_1$, then of $\boldsymbol{q}_2$, and so on. A convenient set of canonical coordinates describing the projective subspace is given by

$$Y_i = y_i - \boldsymbol{\theta}_i^T \boldsymbol{Q}_{\mathrm{ref}}^{-1} \boldsymbol{y}_{\mathrm{ref}}; \quad i = 0, 1, 2, \ldots, m \tag{2}$$

where

$$\boldsymbol{\theta}_i = [q_{1,i} \quad q_{2,i} \quad \cdots \quad q_{n-m,i}]^T; \quad i = 0, 1, 2, \ldots, m \tag{3}$$

$$\boldsymbol{Q}_{\mathrm{ref}} = \begin{bmatrix} q_{1,m+1} & q_{2,m+1} & \cdots & q_{n-m,m+1} \\ q_{1,m+2} & q_{2,m+2} & \cdots & q_{n-m,m+2} \\ \vdots & \vdots & \ddots & \vdots \\ q_{1,n} & q_{2,n} & \cdots & q_{n-m,n} \end{bmatrix} \tag{4}$$

$$\boldsymbol{y}_{\mathrm{ref}} = [y_{m+1} \quad y_{m+2} \quad \cdots \quad y_n]^T \tag{5}$$

Here, $q_{i,j}$ represents the j-th element of vector $\boldsymbol{q}_i$.

A special case of orthogonal projection in homogeneous space is the frequently used Jänecke projection, where one reference component is neglected and the composition of the remaining species is renormalized. As a special case of multiple orthogonal projection, we define *multiple Jänecke projection*, where the dimensionality is reduced directly to m. If components $(m+1)$ to $(C-1)$ are taken to be the reference components, the elements of the projection ray vectors $\{\boldsymbol{q}_1, \boldsymbol{q}_2, \ldots, \boldsymbol{q}_{C-m-1}\}$ are given by

$$q_{i,j} = \begin{cases} 1, & \text{if} \quad i = j+m \quad \text{or} \quad i = 0 \\ 0, & \text{otherwise} \end{cases} \tag{6}$$

This projection is equivalent to neglecting components $(m+1)$ to $(C-1)$, and normalizing the remaining mol fractions.

Another special case is the *reactive projection*. When chemical reactions are present, possible compositions are confined to a lower dimensional subspace. Consider a system involving C components and R independent reactions described as

$$\nu_{1j} A_1 + \nu_{2j} A_2 + \ldots + \nu_{Cj} A_C = 0; \quad j = 1, 2, \ldots, R \tag{7}$$

where ν_{ij} is the stoichiometric coefficient of component i in reaction j, which has a negative value for reactants and positive for products. Changes in composition due to these reactions are described by a set of equations

$$n_i = n_{i,0} + \sum_{j=1}^{R} \nu_{ij} \xi_j; \quad i = 1, 2, \ldots, C \tag{8a}$$

$$n_{\mathrm{TOT}} = n_{\mathrm{TOT},0} + \sum_{j=1}^{R} \nu_{\mathrm{TOT},j}\xi_j \tag{8b}$$

where ξ_j is the molar extent of reaction j. It can also be written as

$$\boldsymbol{n} = \boldsymbol{n}_0 + \xi_1\boldsymbol{q}_1 + \xi_2\boldsymbol{q}_2 + \ldots + \xi_R\boldsymbol{q}_R \tag{9}$$

where

$$\boldsymbol{q}_j = [\,\nu_{1,j}\ \nu_{2j}\ \cdots\ \nu_{C-1,j}\ \nu_{\mathrm{TOT},j}\,]^T;\quad j = 1, 2, \ldots, R \tag{10}$$

Equation 9 describes a linear *stoichiometric variety* of dimension R. A reactive projection is defined as a multiple orthogonal projection from a C-dimensional space to a $(C - R - 1)$-dimensional subspace, where the directions of the R projection rays follow the directions of $\{\boldsymbol{q}_1, \boldsymbol{q}_2, \ldots, \boldsymbol{q}_R\}$ defined in Eq. 10. Such projection causes the stoichiometric variety to disappear, leaving a reaction-invariant projection. The set of canonical coordinates defining the projective subspace can be found by substituting Eq. 10 into Eqs. 2–4.

Multiple orthogonal projection can also be performed from one subspace to another, and does not necessarily result in reduction of dimensionality. For example, after projecting an entity onto a subspace S_1 of dimension m_1, it may be desirable to perform further projection onto another subspace S_2 of dimension m_2, where $m_2 \le m_1$. The dimensionality is not reduced ($m_1 = m_2$) if all projection rays lie outside S_1.

Apart from linear projections, we can also take linear combinations of the coordinate axes to obtain a new set of coordinates, without affecting linearity of material balances. This is often useful if the resulting coordinates need to be put in a form which allows convenient mathematical manipulations, as will be illustrated later. The new set of coordinates is

$$Y_i' = \sum_{j=1}^{m} a_{i,j}Y_j;\quad i = 0, 1, 2, \ldots, m \tag{11}$$

where $a_{i,j}$ is an arbitrarily defined scaling factor. Note that this new set of coordinates still represents the same subspace.

Canonical Coordinates for Mixtures of Molecular and Ionic Species

Consider a solution containing s electrolytes (S_1, S_2, ..., S_s), which can dissociate completely or partially to form m cations (M_1, M_2, ..., M_m) and n anions (N_1, N_2, ..., N_n). There are also p nonelectrolytes (I_1, I_2, ..., I_p), which do not dissociate. The total number of components present in the system is $C = m + n + p + s$. Reactions among electrolytes can always be expressed as linear combinations of dissociation reactions of the molecular species into ions

$$S_k = \beta_{M_1,k}M_1 + \ldots + \beta_{M_i,k}M_i + \beta_{N_1,k}N_1 + \ldots + \beta_{N_j,k}N_j;\quad k = 1, 2, \ldots, s \tag{12}$$

where $\beta_{i,k}$ is the number of moles of ion i in one mole of electrolyte k. There may be chemical reactions among the nonelectrolytes, as well as between an electrolyte and a nonelectrolyte

$$\nu_{I_1,j}I_1 + \nu_{I_2,j}I_2 + \ldots + \nu_{I_p,j}I_p + \nu_{S_1,j}S_1 + \nu_{S_2,j}S_2 + \ldots + \nu_{S_s,j}S_s = 0;\quad j = 1, 2, \ldots, r \tag{13}$$

Thus, the total number of reaction is $R = r + s$. As will be seen, it is advantageous to write these reactions in the simplest dissociation form, since it leads to a more convenient set of coordinates. For example, the reaction $B + H^+X^- = BH^+X^-$ should be written as $BH^+ = B + H^+$, which is obtained by introducing the ionization reactions for HX and BHX. Obviously, writing in such a form is not possible for some reactions, such as $A + B = C + D$ where A, B, C, and D are all nonelectrolytes.

We are interested in plotting the polythermal projection or an isothermal cut of the isobaric phase diagram for representing solid-liquid equilibrium (SLE). The set of homogeneous coordinates to be used in such phase diagrams consists of the number of moles of $(m + n + p + s - 1)$ components, plus the total number of moles, n_{TOT}. It is convenient to choose the number of moles of an ion (which can be arbitrarily chosen to be one of the cations, say, M_m) as the one left out. Furthermore, there is an electroneutrality constraint

$$\sum_{i=1}^{m} z_{M_i}\left(n_{M_i} + \sum_{k=1}^{s}\beta_{M_i,k}n_{S_k}\right) = \sum_{j=1}^{n} z_{N_j}\left(n_{N_j} + \sum_{k=1}^{s}\beta_{N_j,k}n_{S_k}\right) \tag{14}$$

where z_i is the charge magnitude of ion i. Equation 14 means that regardless of the degrees of dissociation of the electrolytes, the solution must remain neutral at all times. This constraint implies that the number of mols of anion N_n can be expressed as a linear combination of the number of mols of the cations as well as anions N_1 to N_{n-1}. Therefore, it can also be left out, leaving the set $\{n_{M_1}, \ldots, n_{M_{m-1}}, n_{N_1}, \ldots, n_{N_{n-1}}, n_{S_1}, \ldots, n_{S_s}, n_{I_1}, \ldots, n_{I_p}, n_{\mathrm{TOT}}\}$.

According to the phase rule, the presence of reactions and electroneutrality condition reduces the number of degrees of freedom to $(m + n + p - r - 2)$, which would be the dimensionality of a reaction-invariant projection of the phase diagram. Such a projection can be obtained by eliminating the $(r + s)$ extents of reaction using multiple orthogonal (reactive) projection. From Eqs. 10, 12, and 13, the projection ray vectors are

$$\boldsymbol{q}_j = \lfloor 0\ \ldots\ 0\ 0\ \ldots\ 0\ \nu_{S_1,j}\ \ldots\ \nu_{S_s,j}\ \nu_{I_1,j}\ \ldots\ \nu_{I_p,j}\nu_{\mathrm{TOT},j}\rfloor^T;\quad j = 1, 2, \ldots, r \tag{15a}$$

$$\boldsymbol{q}_j = [\,\beta_{M_1,j-r}\ \ldots\ \beta_{M_{m-1},j-r}\ \ \beta_{N_1,j-r}\ \ldots\ \beta_{N_{n-1},j-r} - \delta_{1,j-r}\ \ldots\ -\delta_{s,j-r}\ \ 0\ \ldots\ \ 0\ \ \beta_{0,j-r}\,]^T;\quad j = r+1, r+2, \ldots, r+s \tag{15b}$$

where

$$\beta_{0,k} = \sum_{i=1}^{m}\beta_{M_i,k} + \sum_{j=1}^{n}\beta_{N_j,k} - 1 \tag{16}$$

$$\delta_{i,j} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{otherwise} \end{cases} \tag{17}$$

These are then substituted into Eqs. 2–5 to obtain for the mixture of molecular and ionic species a set of canonical coordinates, which cannot be written explicitly unless the r reactions are specified. Since each electrolyte corresponds to one reaction, it is convenient to pick all s electrolytes as reference components, along with r nonelectrolytes or ions. It is preferable to include all nonelectrolytes or complex ions corresponding to a dissociation reaction in these additional r reference components. For example, if we have a reaction $BH^+ = B + H^+$, then BH^+ should be selected as a reference component.

Without loss of generality, we discuss here a specific case where there is no reaction among nonelectrolytes ($r = 0$). A similar manipulation is applicable to systems where $r > 0$. The final expression of the set of independent canonical coordinates describing the $(m + n + p - 2)$-dimensional projective subspace can be explicitly expressed as

$$Y_i = n_i + \sum_{k=1}^{s} \beta_{i,k} n_{S_k}; \quad i = M_1, \ldots, M_{m-1}, N_1, \ldots, N_{n-1} \tag{18a}$$

$$Y_i = n_i; \quad i = I_1, \ldots, I_p \tag{18b}$$

$$Y_0 = n_{\mathrm{TOT}} + \sum_{k=1}^{s} \left(\sum_{i=1}^{m} \beta_{M_i,k} + \sum_{j=1}^{n} \beta_{N_j,k} - 1 \right) n_{S_k}. \tag{18c}$$

Not included here are two other coordinates Y_{M_m} and Y_{N_n}, which are not independent. After rearrangement, Eq. 18c can be written as

$$Y_0 = \sum_{i=1}^{m} \left(n_{M_i} + \sum_{k=1}^{s} \beta_{M_i,k} n_{S_k} \right) + \sum_{j=1}^{n} \left(n_{N_j} + \sum_{k=1}^{s} \beta_{N_j,k} n_{S_k} \right) + \sum_{l=1}^{p} n_{I_l} \tag{19}$$

It is interesting to note that each canonical coordinate gives the total number of mols of an ion, as if all other species that are capable to producing it completely dissociate. This reflects the independence of $\{Y_1, Y_2, \ldots, Y_0\}$ on the degree of ionization. For example, for $i = M_1$, Eq. 18a gives the total number of mols of ion M_1 that would be produced if all electrolytes containing that ion completely dissociate. The first (second) term of the righthand side of Eq. 19 denotes the total amount of cations (anions) that would be produced upon complete dissociation of all electrolytes.

After obtaining a reaction-invariant projection in a lower-dimensional projective subspace, we can perform further projections onto other subspaces, or simply using linear combination of coordinates to represent the same subspace, to obtain more convenient expressions. Let us now illustrate this point again using the special case where there is no reaction among nonelectrolytes. Two convenient expressions for the corresponding inhomogeneous coordinates are obtained by viewing the electrolytes as either ions or molecules. Of course, in reality they may exist partly as ions and partly as undissociated molecules, but it makes no difference since the degree of ionization has no effect on the location of any point in a reaction-invariant projection. The concentrations of molecules and ions in systems containing partially dissociated electrolytes can be readily calculated if the values of reaction equilibrium constants are given.

Molality coordinates

This set of coordinates is obtained by viewing all the electrolytes as ions such that the final expression is expected to involve concentrations of ions and nonelectrolytes only. Ionic concentrations are routinely expressed as molalities, that is, mols per gram of primary solvent (water).

Starting from Eq. 18b, the coordinate corresponding to the primary solvent (say, n_{I_1}) is multiplied with the molecular weight of the solvent W. Then, we perform a unity plane projection onto the hyperplane $W n_{I_1} = 1$. Neglecting the concentrations of electrolytes in Eqs. 18–19, we obtain a new set of independent coordinates

$$Y_{M_i} = [M_i]; \quad i = 1, 2, \ldots, m-1 \tag{20a}$$

$$Y_{N_j} = [N_j]; \quad j = 1, 2, \ldots, n-1 \tag{20b}$$

$$Y_{I_1} = 1 \tag{20c}$$

$$Y_{I_l} = [I_l]; \quad l = 2, 3, \ldots, p \tag{20d}$$

$$Y_0 = \sum_{i=1}^{m} [M_i] + \sum_{j=1}^{n} [N_j] + 1 + \sum_{l=2}^{p} [I_l] \tag{20e}$$

The square brackets indicate molalities. We show below that the same subspace can be defined by another set of coordinates obtained via linear combinations of the coordinate axes. Each of Eqs. 20a–b is multiplied by z_i, the charge magnitude of ion i. By adding $[(1/2)z_i - 1]$ times Y_{M_i} ($i = 1, 2, \ldots, m$) and Y_{N_j} ($j = 1, 2, \ldots, n$) to Eq. 20e, we obtain

$$Y_0 = \frac{1}{2} \sum_{i=1}^{m} z_{M_i} [M_i] + \frac{1}{2} \sum_{j=1}^{n} z_{N_j} [N_j] + 1 + \sum_{l=2}^{p} [I_l] \tag{21}$$

Such a linear combination allows the introduction of the electroneutrality constraint (Eq. 14), which implies that the first two terms on the righthand side of Eq. 21 are equal. Therefore, the expression Y_0 can be simplified in two different ways

$$Y_0 = \sum_{i=1}^{m} z_{M_i} [M_i] + 1 + \sum_{l=2}^{p} [I_l] = \sum_{j=1}^{n} z_{N_j} [N_j] + 1 + \sum_{l=2}^{p} [I_l] \tag{22}$$

From these equations, we obtain a set of inhomogeneous canonical coordinates

$$X(M_i) = \frac{z_{M_i} [M_i]}{\sum_{i=1}^{m} z_{M_i} [M_i] + 1 + \sum_{l=2}^{p} [I_l]}; \quad i = 1, 2, \ldots, m-1 \tag{23a}$$

$$X(N_j) = \frac{z_{N_j}[N_j]}{\sum_{j=1}^{n} z_{N_j}[N_j] + 1 + \sum_{l=2}^{p} [I_l]}; \quad j = 1, 2, \ldots, n-1 \tag{23b}$$

$$X(I_1) = \frac{1}{\sum_{i=1}^{m} z_{M_i}[M_i] + 1 + \sum_{l=2}^{p} [I_l]} = \frac{1}{\sum_{j=1}^{n} z_{N_j}[N_j] + 1 + \sum_{l=2}^{p} [I_l]} \tag{23c}$$

$$X(I_l) = \frac{[I_l]}{\sum_{i=1}^{m} z_{M_i}[M_i] + 1 + \sum_{l=2}^{p} [I_l]} = \frac{[I_l]}{\sum_{j=1}^{n} z_{N_j}[N_j] + 1 + \sum_{l=2}^{p} [I_l]}; \quad l = 2, \ldots, p \tag{23d}$$

This set of $(m + n + p - 2)$ coordinates is similar to the ionic coordinates defined in Samant and Ng (2001), but has the additional property that the numerical value of all coordinates is between 0 and 1. Samant and Ng's ionic coordinates can be recovered by another linear combination, that is, subtracting Eqs. 20c–20d from Eq. 22.

Mole fraction coordinates

An alternative way to obtain a set of canonical coordinates is to view the electrolytes as molecular species. All ionic concentrations are set to zero and mol fractions are used to express concentrations. After performing a linear combination of Eqs. 18–19, we obtain

$$Y_{M_i} = z_{M_i} \sum_{k=1}^{s} \beta_{M_i,k} n_{S_k}; \quad i = 1, 2, \ldots, m-1 \tag{24a}$$

$$Y_{N_j} = z_{N_j} \sum_{k=1}^{s} \beta_{N_j,k} n_{S_k}; \quad j = 1, 2, \ldots, n-1 \tag{24b}$$

$$Y_{I_l} = n_{I_l}; \quad l = 1, 2, \ldots, p \tag{24c}$$

$$Y_0 = \sum_{j=1}^{m} \left(z_{M_i} \sum_{k=1}^{s} \beta_{M_i,k} n_{S_k} \right) + \sum_{j=1}^{n} \left(z_{N_j} \sum_{k=1}^{s} \beta_{N_j,k} n_{S_k} \right) + \sum_{l=1}^{p} n_{I_l} \tag{24d}$$

Introducing the electroneutrality condition (Eq. 14), Eq. 24d can be simplified and written in two ways, similar to Eq. 22. Therefore, we arrive at a set of inhomogeneous coordinates

$$X(M_i) = \frac{z_{M_i} \sum_{k=1}^{s} \beta_{M_i,k} x_{S_k}}{\sum_{i=1}^{m} \left(z_{M_i} \sum_{k=1}^{s} \beta_{M_i,k} x_{S_k} \right) + \sum_{l=1}^{p} x_{I_l}}; \quad i = 1, 2, \ldots, m-1 \tag{25a}$$

$$X(N_j) = \frac{z_{N_j} \sum_{k=1}^{s} \beta_{N_j,k} x_{S_k}}{\sum_{j=1}^{n} \left(z_{N_j} \sum_{k=1}^{s} \beta_{N_j,k} x_{S_k} \right) + \sum_{l=1}^{p} x_{I_l}}; \quad j = 1, 2, \ldots, n-1 \tag{25b}$$

$$X(I_l) = \frac{x_{I_l}}{\sum_{i=1}^{m} \left(z_{M_i} \sum_{k=1}^{s} \beta_{M_i,k} x_{S_k} \right) + \sum_{l=1}^{p} x_{I_l}} = \frac{x_{I_l}}{\sum_{j=1}^{m} \left(z_{N_j} \sum_{k=1}^{s} \beta_{N_j,k} x_{S_k} \right) + \sum_{l=1}^{p} x_{I_l}}; \quad l = 1, 2, \ldots, p \tag{25c}$$

Note that since the coordinates in Eqs. 23 and 25 are derived via the same linear combinations from the same reaction-invariant coordinates (Eqs. 18–19), the plots of the projection of the phase diagram using both coordinates are identical.

The set of coordinates in Eq. 25 can also be obtained by identifying a set of independent reactions among the electrolytes without involving ions. Such a set of independent reactions can be obtained using the invariance matrix (Samant and Ng, 2001), in a way equivalent to the determination of a set of independent reactions among molecular species using atomic matrix (Aris and Mah, 1963; Amundson, 1966; Gadewar et al., 2001).

Example 1: Systems Involving Ampholytes

Ampholytes can donate or accept protons according to the environment. For example, an amino acid molecule AH dissociates in an alkaline condition, but accepts protons in an acidic environment,

$$AH = A^- + H^+ \tag{26a}$$

$$AH_2^+ = AH + H^+ \tag{26b}$$

Note that Eq. 26b has been reversed to put the reaction in dissociation form. This ampholytic behavior is possible because of the presence of both carboxylic and amine groups in a single molecule.

Consider a system containing an amino acid, water, and pH controlling agents (for example, HCl and NaOH). Because of potential reactions among hydrogen and hydroxyl ions, water is considered an electrolyte. Therefore, there are seven electrolytes (AH, AH_2Cl, NaA, NaOH, HCl, H_2O, NaCl), three cations (H^+, AH_2^+, Na^+), three anions (OH^-, A^-, Cl^-), giving a total of 13 components. There are a total of eight dissociation reactions, corresponding to the seven electrolytes as well as AH_2^+ (Eq. 26b). Taken into account the neutrality conditions, the dimensionality of the isobaric, isothermal phase diagram should be 3 ($= m + n - r - 2$).

To obtain a reaction-invariant projection, multiple orthogonal projection is performed. In addition to the molecular species, AH_2^+ is picked as the additional reference component. Equations 2–5 lead to the following set of independent canonical coordinates

$$Y_1 = n_{H^+} + 2n_{AH_2^+} + n_{AH} + 2n_{AH_2Cl} + n_{HCl} + n_{H_2O} \quad (27a)$$

$$Y_2 = n_{OH^-} + n_{NaOH} + n_{H_2O} \quad (27b)$$

$$Y_3 = n_{A^-} + n_{AH_2^+} + n_{AH} + n_{AH_2Cl} + n_{NaA} \quad (27c)$$

$$\begin{aligned} Y_0 &= n_{H^+} + 2n_{AH_2^+} + n_{Na^+} + n_{AH} + 2n_{AH_2Cl} \\ &\quad + n_{NaA} + n_{NaOH} + n_{HCl} + n_{H_2O} + n_{NaCl} \\ &= n_{OH^-} + n_{A^-} + n_{Cl^-} + n_{AH_2^+} + n_{AH} + 2n_{AH_2Cl} \\ &\quad + n_{NaA} + n_{NaOH} + n_{HCl} + n_{H_2O} + n_{NaCl} \end{aligned} \quad (27d)$$

Equation 27d is obtained after a similar manipulation as in Eq. 21 and an introduction of the neutrality condition. It can be observed that each expression in Eqs. 27a–c gives the total number of moles of an ion (or several ions), as if all electrolytes capable of producing it completely dissociate. This is in agreement with the condition previously mentioned, that is, all reactions are written in dissociation form and the dissociating species are taken as reference components.

Using the manipulation described in the previous section (Eqs. 20–23), a set of molality coordinates can be obtained

$$X(H^+) = \frac{[H^+] + 2[AH_2^+]}{[H^+] + 2[AH_2^+] + [Na^+]} \quad (28a)$$

$$X(OH^-) = \frac{[OH^-]}{[OH^-] + [A^-] + [Cl^-]} \quad (28b)$$

$$X(A^-) = \frac{[A^-]}{[OH^-] + [A^-] + [Cl^-]} \quad (28c)$$

In using this set of coordinates, it is convenient to assume that water completely dissociates, while at the same time serving as the basis of molality calculations. For example, a mixture of 1 mol NaOH and 1 mol water should be treated as a mixture of 1 mol Na^+, 1 mol H^+, and 2 mol OH^- in 18 g of solvent. A set of mole fraction coordinates can also be derived following Eqs. 24–25

$$X_1 = \frac{x_{AH} + 2x_{AH_2Cl} + x_{HCl} + x_{H_2O}}{x_{AH} + 2x_{AH_2Cl} + x_{NaA} + x_{NaOH} + x_{HCl} + x_{H_2O} + x_{NaCl}} \quad (29a)$$

$$X_2 = \frac{x_{NaOH} + x_{H_2O}}{x_{AH} + 2x_{AH_2Cl} + x_{NaA} + x_{NaOH} + x_{HCl} + x_{H_2O} + x_{NaCl}} \quad (29b)$$

$$X_3 = \frac{x_{AH} + x_{AH_2Cl} + x_{NaA}}{x_{AH} + 2x_{AH_2Cl} + x_{NaA} + x_{NaOH} + x_{HCl} + x_{H_2O} + x_{NaCl}} \quad (29c)$$

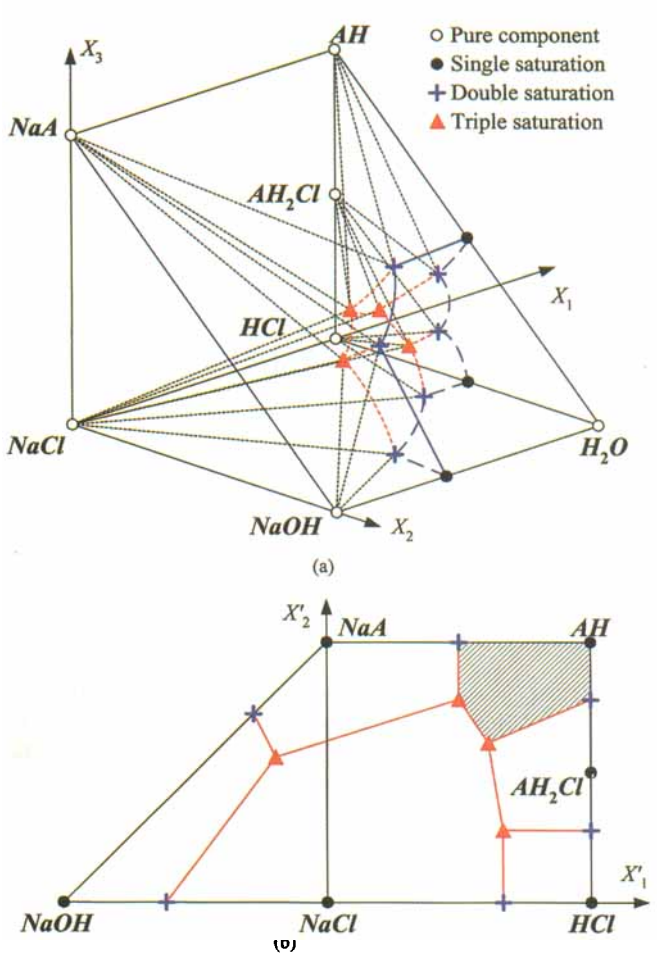

Figure 1. Isobaric isothermal SLE phase diagram of the ampholyte system (Example 1).

(a) Triangular prism diagram; (b) solvent-less projection.

Note that for dilute systems, the value of $X(H^+)$ and $X(OH^-)$ (or X_1 and X_2) are close to unity, while that of the other coordinate is very small, due to the large amount of water. As a result, the features in the phase diagram tend to cluster in a certain corner of the plot.

As an illustration of the use of canonical coordinates, Figure 1 depicts a plot of a hypothetical isobaric, isothermal SLE phase diagram of this system in mole fraction coordinates (X_1-X_2-X_3) showing all the saturation varieties. The procedures for theoretical identification and calculation of such varieties are available elsewhere (Samant et al., 2000; Samant and Ng, 2001) and will not be discussed here. Notice that the diagram takes the form of a triangular prism (Figure 1a). The solid and dashed blue lines are the intersections of the single saturation surfaces with the faces of the prism, while the dotted red lines represent double saturation lines in the prism's interior.

Figure 1b is a plot of a solvent-less (similar to the Jänecke) projection. It is obtained by taking an orthogonal projection in the direction $q = [-1 \quad -1 \quad 0 \quad 0]$ (that is, from H_2O apex to NaCl apex), followed by another orthogonal projection in the direction of the original n_{H_2O} axis. Note that the choice of q is completely arbitrary. Taking X_2 as the reference, the

first projection yields a 2-D projection defined by the set of canonical coordinates $\{(X_1 - X_2), X_3\}$. The second projection is mathematically equivalent to neglecting n_{H_2O} from the expressions for these coordinate axes. The final set of canonical coordinates obtained this way is

$$X_1' = \frac{x_{AH} + 2x_{AH_2Cl} - x_{NaOH} + x_{HCl}}{x_{AH} + 2x_{AH_2Cl} + x_{NaA} + x_{NaOH} + x_{HCl} + x_{NaCl}} \quad (30a)$$

$$X_2' = \frac{x_{AH} + x_{AH_2Cl} + x_{NaA}}{x_{AH} + 2x_{AH_2Cl} + x_{NaA} + x_{NaOH} + x_{HCl} + x_{NaCl}} \quad (30b)$$

Using this diagram, regions in which a component can be crystallized out of the solution in a pure form can be clearly identified. For example, the hatched region in Figure 1b indicates the region where pure AH can be crystallized out by evaporation of water.

Example 2: Separation of Chiral Molecules

Crystallization can be used to separate an aqueous solution of two enantiomers, (R)AH and (S)AH, using KOH and an amine B as resolving agents (Schroer et al., 2001). The amine initiates the formation of dissociable compounds BH(R)A and BH(S)A, which dissociate when reacting with KOH. A set of independent reactions is

$$(R)AH + B = BH(R)A \quad (31a)$$

$$(S)AH + B = BH(S)A \quad (31b)$$

$$BH(R)A + KOH = B + K(R)A + H_2O \quad (31c)$$

$$BH(S)A + KOH = B + K(S)A + H_2O \quad (31d)$$

Degree of freedom count indicates that the reaction-invariant phase diagram should be 4-D (9 components, 4 reactions). It is desirable to visualize the phase diagram.

Following our method, we consider the system as consisting of three cations (H^+, BH_2^+, K^+), three anions (OH^-, $(R)A^-$, $(S)A^-$), eight electrolytes, and one nonelectrolyte (B). There is a dissociation reaction for each electrolyte, while Eqs. 31a–d can be represented by one additional independent reaction

$$BH^+ = B + H^+ \quad (32)$$

Therefore, we have a total of 15 components and 9 independent reactions. From Eqs. 2–5, we obtain the set of independent canonical coordinates

$$Y_1 = n_{K^+} + n_{KOH} + n_{K(R)A} + n_{K(S)A} \quad (33a)$$

$$Y_2 = n_{(R)A^-} + n_{(R)AH} + n_{BH(R)A} + n_{K(R)A} \quad (33b)$$

$$Y_3 = n_{(S)A^-} + n_{(S)AH} + n_{BH(S)A} + n_{K(S)A} \quad (33c)$$

$$Y_4 = n_B + n_{BH^+} + n_{BH(R)A} + n_{BH(S)A} \quad (33d)$$

$$\begin{aligned} Y_0 = {} & n_{H^+} + 2n_{BH^+} + n_{K^+} + n_{(R)AH} + n_{(S)AH} + 2n_{BH(R)A} \\ & + 2n_{BH(S)A} + n_{K(R)A} + n_{K(S)A} + n_{KOH} + n_{H_2O} + n_B = n_{OH^-} \\ & + n_{(R)A^-} + n_{(S)A^-} + n_{BH^+} + n_{(R)AH} + n_{(S)AH} + 2n_{BH(R)A} \\ & + 2n_{BH(S)A} + n_{K(R)A} + n_{K(S)A} + n_{KOH} + n_{H_2O} + n_B \end{aligned} \quad (33e)$$

Again, Eq. 33 is obtained using a manipulation similar to the one used in deriving Eqs. 21–22. A set of transformed mole fraction coordinates can then be obtained by setting the number of moles of the ions to zero

$$X_1 = \frac{x_{KOH} + x_{K(R)A} + x_{K(S)A}}{x_{(R)AH} + x_{(S)AH} + 2x_{BH(R)A} + 2x_{BH(S)A} + x_{K(R)A} + x_{K(S)A} + x_{KOH} + x_{H_2O} + x_B} \quad (34a)$$

$$X_2 = \frac{x_{(R)AH} + x_{BH(R)A} + x_{K(R)A}}{x_{(R)AH} + x_{(S)AH} + 2x_{BH(R)A} + 2x_{BH(S)A} + x_{K(R)A} + x_{K(S)A} + x_{KOH} + x_{H_2O} + x_B} \quad (34b)$$

$$X_3 = \frac{x_{(S)AH} + x_{BH(S)A} + x_{K(S)A}}{x_{(R)AH} + x_{(S)AH} + 2x_{BH(R)A} + 2x_{BH(S)A} + x_{K(R)A} + x_{K(S)A} + x_{KOH} + x_{H_2O} + x_B} \quad (34c)$$

$$X_4 = \frac{x_B + x_{BH(R)A} + x_{BH(S)A}}{x_{(R)AH} + x_{(S)AH} + 2x_{BH(R)A} + 2x_{BH(S)A} + x_{K(R)A} + x_{K(S)A} + x_{KOH} + x_{H_2O} + x_B} \quad (34d)$$

To visualize the 4-D phase diagram, we can perform a 3-D projection. Arbitrarily taking a projection ray $q = [0 \quad -1 \quad -1 \quad -1 \quad 0]$ and normalizing with respect to water, we obtain a new set of independent coordinates

$$X_1' = \frac{x_{KOH} + x_{K(R)A} + x_{K(S)A}}{x_{(R)AH} + x_{(S)AH} + 2x_{BH(R)A} + 2x_{BH(S)A} + x_{K(R)A} + x_{K(S)A} + x_{KOH} + x_B} \quad (35a)$$

$$X_2' = \frac{x_{(R)AH} + x_{K(R)A} - x_{BH(S)A} - x_B}{x_{(R)AH} + x_{(S)AH} + 2x_{BH(R)A} + 2x_{BH(S)A} + x_{K(R)A} + x_{K(S)A} + x_{KOH} + x_B} \quad (35b)$$

$$X_3' = \frac{x_{(S)AH} + x_{K(S)A} - x_{BH(R)A} - x_B}{x_{(R)AH} + x_{(S)AH} + 2x_{BH(R)A} + 2x_{BH(S)A} + x_{K(R)A} + x_{K(S)A} + x_{KOH} + x_B} \quad (35c)$$

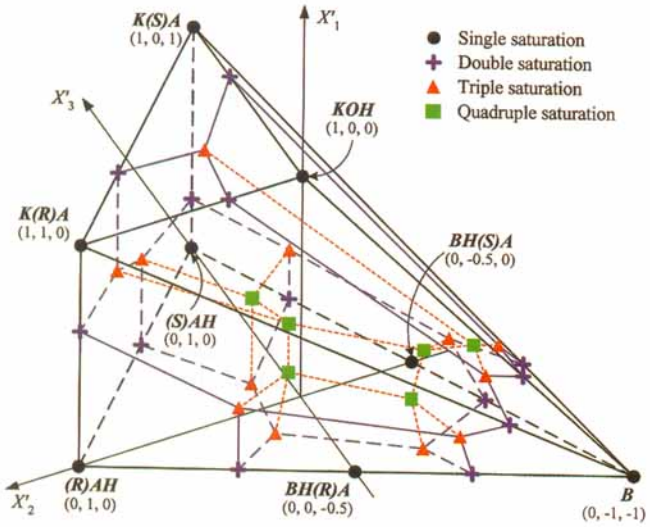

Figure 2. Solvent-less projection of the isobaric, isothermal SLE phase diagram of the chiral system (Example 2).

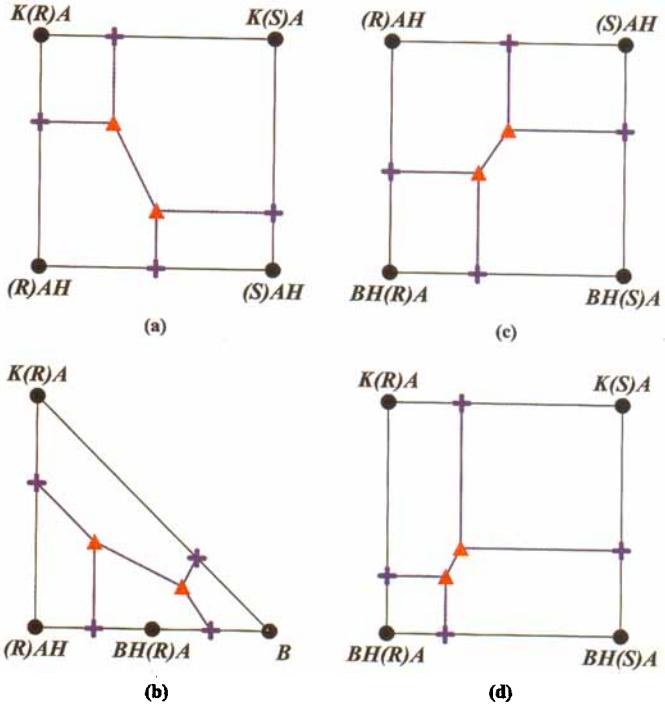

Figure 3. Cuts of the solvent-less projection (Example 2).

(a) Rectangular face; (b) front triangular face; (c) part of bottom face; (d) interior.

A plot of the phase diagram showing all saturation varieties is depicted in Figure 2. The phase diagram takes the shape of a six-faced object bordered by one rectangle and five triangles. The phase diagram has been greatly exaggerated in order to provide clarity. The regions where each pure component is obtainable via crystallization can be identified, although they are not easy to observe in such a 3-D plot.

In synthesizing the separation process, various cuts of this solvent-less projection are of great interest. Figure 3 shows various cuts of the phase diagram. Figure 3a is the rectangular face of the object in Figure 2. It represents a five-component system consisting of (R)AH, (S)AH, K(R)A, K(S)A, and water. It can be easily recognized that this is a typical plot of the phase diagram of a conjugate salt pair system. Figure 3b is the front triangular face, which represents the phase diagram of a three-solute system with compound formation. Figure 3c is part of the bottom face of the phase diagram, and Figure 3d is a cut taken through the interior of the phase diagram, passing through four vertices: BH(R)A, BH(S)A, K(R)A, and K(S)A. Both Figures 3c and 3d are typical phase diagrams of conjugate salt pairs.

With a phase diagram on hand, we can synthesize a process for separating (R)AH and (S)AH as their potassium salts, using techniques available in the literature (Berry and Ng, 1996; Wibowo and Ng, 2000; Schroer et al., 2001). The flowsheet is depicted in Figure 4, and the process path is drawn on various cuts depicted in Figure 5. The feed (F) is a racemic mixture of (R)AH and (S)AH (Figure 5a). A 50:50 mixture of KOH and B is then added in equimolar amounts. The reaction product is an aqueous mixture of K(R)A, K(S)A, BH(R)A, and BH(S)A, represented by point 1 in Figure 5b. Note that lever rule was not used, because a reaction product (water) is not present in the projection shown in Figure 2. The two sets of curves indicate the saturation varieties at two different temperatures T_1 and T_2. Point 1 is mixed with a recycle stream (point 5) to yield point 2, which is in compartment BH(S)A at T_1. This salt (point 6) is then removed in a crystallizer (C1). Water is added to the mother liquor (point 3) to prevent co-precipitation. The resulting stream (point 4) is fed to a cooling crystallizer (C2) operating at T_2, to remove K(R)A. The solid BH(S)A (point 6) is then dissolved in water and reacted with an equimolar amount of KOH. The product is a 1:1 mixture of B and K(S)A in an aqueous solution, represented by point 7 (Figure 5c), which is in compartment K(S)A. After mixing with a recycle stream (point 11), K(S)A is separated in a crystallizer (C3) operating at T_3. The mother liquor (point 9) is in compartment B at T_4, which allows sep-

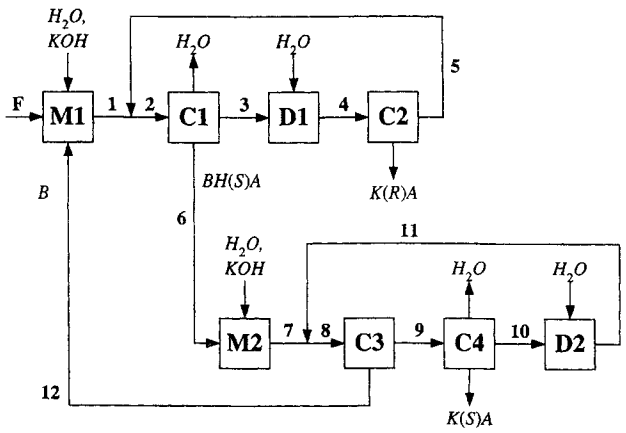

Figure 4. Flowsheet for separating (R)AH and (S)AH as their potassium salts (Example 2).

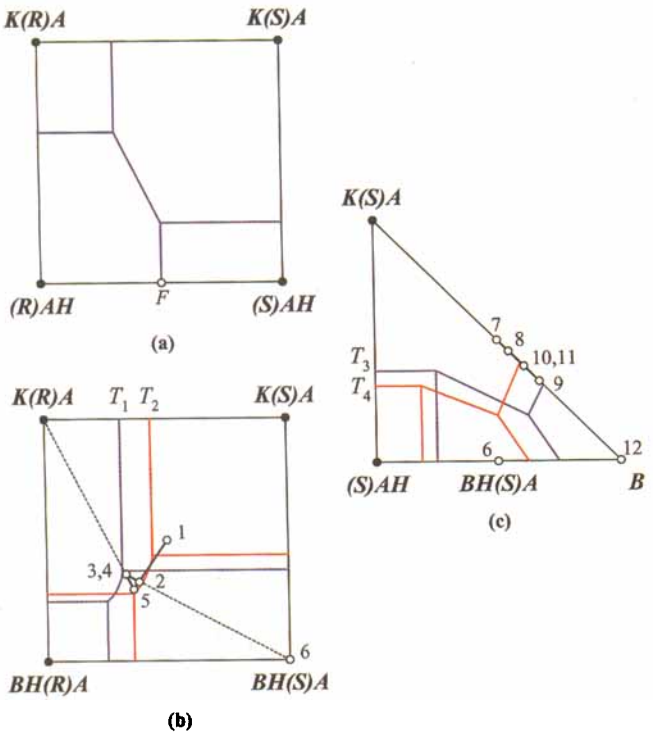

Figure 5. Process path for the separation of (R)AH and (S)AH (Example 2).

aration of B in an evaporative crystallizer (C4). B is then recycled to the first mixer (M1).

Conclusions

Visualization of high dimensional phase diagrams is very helpful in separations synthesis, where unit operations are represented as movements in composition space (Wibowo and Ng, 2000). Based on concept of geometric modeling with homogeneous coordinates, canonical coordinates are developed for facilitating the visualization of the phase diagrams of molecular and ionic mixtures using linear projections and cuts. In particular, a systematic way of obtaining reaction-invariant projections with a convenient set of reference components is presented. The same approach can be used to discover other useful transformed coordinates with potential applications.

The canonical coordinates describing a projective subspace can be obtained from the original coordinates via a linear transformation (Eq. 2), which is defined by the normal vectors to the subspace ($\boldsymbol{q}_i$). In other words, the choice of projective subspace determines the canonical coordinates. Depending on the application, it is preferable to choose one particular subspace over another. For example, the subspace defined by stoichiometric coefficients (Eq. 10) is chosen, because it leads to a reaction-invariant projection. Omitting the extent of reaction, such a projection is useful in the synthesis of reactive separation systems. Similarly, visual observation of solvent concentration is not a crucial part of crystallization system synthesis, and the solvent-free coordinates (Eqs. 30 and 35) provide a projection that is easier to visualize. In summary, the choice of transformations that would lead to useful phase diagrams or projections depends on the specific type of applications. Once a convenient projective subspace has been determined, the expression in Eq. 2 can be used to quickly identify the natural coordinates for representation.

Acknowledgment

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Notation

$a_{i,j}$ = scaling factor
C = number of components
f = number of degrees of freedom
i, j, k, l = indices
I_l = nonelectrolytes
m, n = dimension
m = number of cations
M_i = cations
n = number of anions
n_i = number of moles
N_j = anions
$\boldsymbol{q}_i = (q_{i,j})$ = normal vector to hyperplane i
$\boldsymbol{Q} = (q_{ij})$ = coefficient matrix, defined in Eq. 4
p = number of nonelectrolytes
P = number of phases
r = number of independent reactions involving nonelectrolytes
R = total number of independent reactions
s = number of electrolytes
S_k = electrolytes
x_i = mole fraction of component i, dimensionless
X_i = inhomogeneous canonical coordinate
Y_i = homogeneous canonical coordinate
z_i = magnitude of ionic charge
$\beta_{i,j}$ = number of moles of ion i in one mole of salt j
$\delta_{i,j}$ = Kronecker delta, defined in Eq. 17
$\boldsymbol{\theta}_i = (\theta_{i,j})$ = coefficient vector, defined in Eq. 3
ν_{ij} = stoichiometric coefficient of component i in reaction j
ξ = molar extent of reaction

Superscripts

T = transpose

Subscripts

ref = reference
TOT = total

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