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Separation of Close-Boiling Mixtures of 4-Methoxyphenol/Catechol with *tert*-Butanol

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ABSTRACT

Solid–liquid equilibrium (SLE) behavior was observed for close-boiling mixtures of 4-methoxyphenol and catechol with *tert*-butanol. The experimental liquidus lines of binary systems showed that intermolecular complex compounds were formed in both *tert*-butanol/4-methoxyphenol and *tert*-butanol/catechol, implying that *tert*-butanol is a potential medium to serve as an adductive agent for separation of 4-methoxyphenol and catechol. A ternary SLE phase diagram for the *tert*-butanol/4-methoxyphenol/catechol system was thus prepared and, based on the diagram, the feasibility of such separation processes was discussed. Furthermore, the binary SLE data were correlated with the ideal-chemical model. The model with the determined parameters from binary mixtures was then applied to predict the equilibrium temperatures for the ternary system.

Key Words. Solid–liquid equilibrium; 4-Methoxyphenol; Catechol; *tert*-Butanol; Close-boiling compounds separation

INTRODUCTION

Adductive crystallization is a potent method for separating close-boiling mixtures (1, 2). With this method, one of the close-boiling compounds can be separated from the liquid mixture as an adducted solid and the other constit-

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uent left in the mother liquor. The information needed for process development is essentially to find a suitable adductive agent, the proper amount of the adductive agent to be used, and the favorable operating conditions.

This work was undertaken to study the separation of close-boiling 4-methoxyphenol (T_b = 516.0 K)/catechol (T_b = 518.0 K) mixtures. The mixtures may be encountered in producing 4-methoxyphenol from catechol via a catalytic reaction. Lee et al. (3) found that this binary system has a eutectic point at 0.6925 in the mole fraction of 4-methoxyphenol. To separate this close-boiling and eutectic mixture by the crystallization method, an appropriate auxiliary substance is added to the mixture in order to change its phase behavior. Any potential auxiliary agent must possess the characteristic of forming adducted compounds with at least one of the constituents of the close-boiling mixture. The solid–liquid eguilibrium (SLE) behavior of 4-methoxyphenol with two potential adductive agents, ethylenediamine and piperazine, was investigated previously (3). For this study, *tert*-butanol was selected as an auxiliary material. To gain insight into the intermolecular interactions between *tert*-butanol and the constituents of the close-boiling mixture, the liquidus lines were determined experimentally for binary systems of *tert*-butanol with 4-methoxyphenol and with catechol. Ternary SLE data for the system *tert*-butanol/4-methoxyphenol/catechol were also measured to construct an SLE phase diagram with which two conceptual separation processes are proposed.

Chemical effects should be taken into account for correlating the SLE data of complex formation systems. The ideal-chemical model (ICM) (4–6) assumes that the phase behavior is governed predominantly by the chemical equilibria of complex formations. Provided that the physical effects are also considered in the phase-equilibrium calculations, the treatment is called the chemical-physical method (4–6). This method calculates the physical contribution by using either a predictive activity coefficient model, such as the original regular solution model (7) and the UNIFAC (8), or a correlative activity coefficient model, such as the Wilson (9) and the NRTL (10). While the predictive activity coefficient models are able to estimate a component's activity coefficients without using any adjustable parameters, their reliability for adducted systems is still in doubt. When a correlative activity model is applied, the values of all interaction parameters associated with the model must be available. Therefore, even the chemical-physical model is theoretically more rigorous than the ICM; it can contain an excessive number of interaction parameters within the correlative activity coefficient model for a multicomponent adducted system, and some of these parameters cannot be determined from binary data only. Alternatively, the ICM is more practical, particularly for representing the SLE of multicomponent adducted systems when the chemical equilibrium constants are determined from binary data.

For this reason, the ICM is used illustratively in the present study to correlate the binary data. The validity of the ICM is further verified by comparing its predicted equilibrium temperatures with the experimental values of the ternary system.

EXPERIMENTAL SECTION

4-Methoxyphenol (99+%) and catechol (99+%) were purchased from Merck (Germany), and *tert*-butanol (99.7+%) was supplied by Fluka (Switzerland). The impurities in the chemicals are less than 0.5% according to gas chromatography analysis. All these substances were used without further purification.

The SLE phase boundaries were determined by the solid-disappearance method. The experimental procedure is detailed elsewhere (11). Each mixture sample (about 3 g) was prepared by weighting pure compounds to ±0.1 mg; that is, the accuracy of sample composition is better than ±0.0002 in mole fraction. The sample was sealed in a tiny vial and placed in a thermostated bath. A visual high-temperature thermostated bath (Neslab, TV-4000, stability ±0.03 K) connected with an external refrigeration circulator (Neslab, RTE-11A, stability ±0.01 K) was employed for phase behavior observations. The bath temperature was measured by a Hart Scientific Microtherm (Model 1506) with a thermistor probe to ±0.015 K. The accuracy of the reported solid-disappearance temperatures was estimated to be ±0.2 K under normal experimental conditions, and to be ±0.5 K in the vicinity of eutectic points.

In addition to two binary systems (*tert*-butanol/4-methoxyphenol and *tert*-butanol/catechol), nine pseudobinary systems were also investigated. The pseudobinary samples were prepared with constant molar ratios of 4-methoxyphenol:catechol = 2:8, 4:6, 6:4, 7:3, and 8:2; *tert*-butanol:4-methoxyphenol = 6.5:3.5 and 8:2; and *tert*-butanol:catechol = 5:5 and 7:3.

EXPERIMENTAL RESULTS

The experimental results of *tert*-butanol/4-methoxyphenol and *tert*-butanol/catechol are reported in Tables 1 and 2, respectively. The observed melting points of *tert*-butanol and catechol agree with the literature values to within ±0.3 K. The eutectic and the congruent points, as given in Table 3, were determined by interpolating the experimental SLE data. Figure 1 illustrates the SLE phase boundaries for *tert*-butanol/4-methoxyphenol and *tert*-butanol/catechol systems. Each liquidus line exhibits a congruent point that is located at 0.6667 in the mole fraction of *tert*-butanol, indicating that a 2:1 complex species was formed in each binary system. The congruently melting solids are (*tert*-butanol)$_2$-(4-methoxyphenol) and (*tert*-butanol)$_2$-

TABLE 1
Solid–Liquid Equilibria for *tert*-Butanol (1)/4-Methoxyphenol (2)

x_1	T (K)	δT (%)[a]	x_1	T (K)	δT (%)[a]
0.0	328.3	0.0	0.6194	283.5	0.1
0.2013	317.2	−0.2	0.6669	284.4	0.0
0.3313	306.8	−0.1	0.7088	283.8	0.0
0.4003	299.8	−0.2	0.7508	283.6	−0.3
0.5004	284.0	0.3	0.8296	280.1	−1.5
0.5105	281.9	0.4	0.8397	279.7	−0.7
0.5241	280.3	0.0	0.8496	280.8	−0.6
0.5322	281.1	−0.3	0.8803	284.0	−0.1
0.5504	281.9	−0.2	0.9500	291.9	0.3
0.5700	282.9	−0.2	1.0	298.5[b]	0.0

[a] $\delta T\% = 100 \times (T^{calc} - T^{expt})/T^{expt}$, where T^{calc} is the phase-equilibrium temperature calculated from the ICM.

[b] Melting temperature of *tert*-butanol is 298.8 K reported in the *TRC Thermodynamic Tables* (12).

(catechol). *tert*-Butanol is, consequently, considered a potential medium to serve as an adductive agent for separating the 4-methoxyphenol/catechol mixtures.

The experimental results of the nine pseudobinary systems are compiled in Tables 4–8. Figure 2 shows that the ternary SLE phase diagram is divided

TABLE 2
Solid–Liquid Equilibria for *tert*-Butanol (1)/Catechol (2)

x_1	T (K)	δT (%)[a]	x_1	T (K)	δT (%)[a]
0.0	377.7[b]	0.0	0.6198	303.3	0.3
0.0800	371.0	0.6	0.6660	304.8	0.0
0.1500	366.0	0.6	0.6998	303.5	0.3
0.2016	362.2	0.6	0.7503	301.8	0.3
0.2499	359.3	0.2	0.7998	298.2	0.3
0.3664	348.6	−0.5	0.8803	288.8	0.1
0.5000	328.8	−0.9	0.8994	284.7	0.3
0.5473	316.3	0.0	0.9199	287.8	0.3
0.5939	302.6	0.2	0.9500	291.8	0.3
0.6014	302.8	0.2	1.0	298.5	0.0

[a] As defined in Table 1.

[b] Melting temperature of catechol is 377.70 K as reported by Rai and Mandal (13) and 377.80 K by Sabbah and Buluku (14).

TABLE 3
Locations of Invariant Points

Type of invariant point	x_1	T (K)
tert-Butanol (1) + 4-methoxyphenol (2):		
Eutectic 1[a]	0.5241	280.3
Congruent[b]	0.6667	284.5
Eutectic 2[c]	0.8397	279.7
tert-Butanol (1) + catechol (2):		
Eutectic 1[d]	0.5939	302.6
Congruent[e]	0.6667	304.9
Eutectic 2[f]	0.8994	284.7

[a] {4-Methoxyphenol + (*tert*-butanol)$_2$-4-methoxyphenol}.
[b] {(*tert*-Butanol)$_2$-4-methoxyphenol}.
[c] {*tert*-Butanol + (*tert*-butanol)$_2$-4-methoxyphenol}.
[d] {Catechol + (*tert*-butanol)$_2$-4-methoxyphenol}.
[e] {(*tert*-Butanol)$_2$-catechol}.
[f] {*tert*-Butanol + (*tert*-butanol)$_2$-catechol}.

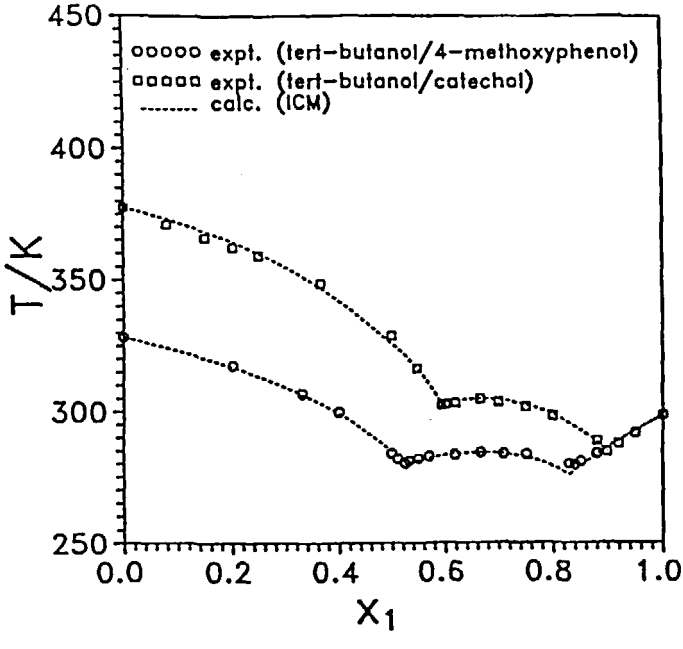

FIG. 1 SLE phase boundaries for *tert*-butanol/4-methoxyphenol and *tert*-butanol/catechol systems.

into five regions, marked respectively as A to E, by the loci of the ternary eutectic points. Each region corresponds to a solid that crystallizes from the mother liquor: *tert*-butanol in Region A, 4-methoxyphenol in Region B, catechol in Region C, adducted (*tert*-butanol)$_2$-(catechol) in Region D, and adducted (*tert*-butanol)$_2$-(4-methoxyphenol) in Region E. This phase diagram provides the basic information to find a proper amount of *tert*-butanol to be added and the feasible operating conditions for the separation process. Based on the phase diagram, two feasible methods for separating the binary eutectic mixture of 4-methoxyphenol/catechol by crystallization will be discussed in the following sections.

SEPARATION WITH ADDUCTIVE CRYSTALLIZATION

The first method, denoted as Method A, is operated as adductive crystallization. A conceptual flow diagram for this separation process is proposed in

TABLE 4
Solid–Liquid Equilibria for *tert*-Butanol (x_1') + (4-Methoxyphenol:Catechol = 2:8) (x_2') and *tert*-Butanol (x_1') + (4-Methoxyphenol:Catechol = 4:6) (x_2')

4-Methoxyphenol:catechol = 2:8			4-Methoxyphenol:catechol = 4:6		
x_1'[a]	T (K)	δT (%)[b]	x_1'[a]	T (K)	δT (%)[b]
0.5221	304.3	1.5	0.4612	292.7	4.3
0.5399	298.8	2.2	0.4730	290.0	4.6
0.5491	296.5[c]	2.4	0.4838	288.2[c]	4.7
0.5743	298.4	−0.2	0.4929	288.6	4.0
0.6296	300.2	−0.2	0.5007	289.0	3.4
0.6794	300.2[d]	−0.2	0.5196	289.9	2.0
0.7017	299.7	−0.1	0.5394	291.0	−0.2
0.7100	298.4	0.2	0.5553	291.6	−0.1
0.7817	293.9	0.5	0.5781	292.4	0.0
0.8799	285.1	−0.6	0.6208	292.9	0.2
0.8897	284.6[c]	0.0	0.6671	292.7[d]	0.3
0.8999	285.8	0.1	0.7994	285.8	0.6
0.9103	286.9	0.2	0.8401	281.8	0.5
0.9201	288.5	0.1	0.8553	279.8[c]	−0.2
0.9300	290.1	0.0	0.8700	282.4	−0.3
			0.9014	286.5	−0.1

[a] x_1' = mole of *tert*-butanol/(mole of *tert*-butanol + mole of 4-methoxyphenol + mole of catechol) in which the molar ratio of 4-methoxyphenol to catechol is 2:8.
[b] As defined in Table 1.
[c] Eutectic point.
[d] Congruent point.

TABLE 5
Solid–Liquid Equilibria for *tert*-Butanol (x_1') + (4-Methoxyphenol:Catechol = 6:4) (x_2') and *tert*-Butanol (x_1') + (4-Methoxyphenol:Catechol = 7:3) (x_2')

4-Methoxyphenol:catechol = 6:4			4-Methoxyphenol:catechol = 7:3		
x_1'	T (K)	δT (%)[a]	x_1'	T (K)	δT (%)[a]
0.3510	286.8	5.6	0.4016	283.8	1.3
0.3708	282.8	6.3	0.4493	279.7	0.5
0.3986	277.6	7.1	0.4726	275.1[b]	−1.0
0.4029	277.2[b]	7.1	0.4990	276.7	−0.7
0.4153	277.6	6.3	0.5293	277.3[c]	−0.2
0.4297	278.1	5.4	0.5623	277.2	0.4
0.4494	278.8	4.2	0.6000	277.2	0.8
0.5021	281.1	−0.3	0.6697	276.4	1.1
0.5998	283.5	0.5	0.7409	274.9	0.8
0.6676	284.1[c]	0.4	0.7897	273.7	0.1
0.7303	282.5	0.3	0.8006	273.4[b]	−0.2
0.7996	277.3	0.6	0.8500	279.3	−0.2
0.8062	276.3[b]	0.7			
0.8129	276.9	0.3			
0.8299	278.4	−1.1			
0.8301	278.9	−1.3			
0.8601	282.7	−0.9			

[a] As defined in Table 1. [b] Eutectic point. [c] Congruent point.

TABLE 6
Solid–Liquid Equilibria for *tert*-Butanol (x_1') + (4-Methoxyphenol:Catechol = 8:2) (x_2') and Catechol (x_1') + (*tert*-Butanol:4-Methoxyphenol = 6.5:3.5) (x_2')

4-Methoxyphenol:catechol = 8:2			*tert*-Butanol:4-methoxyphenol = 6.5:3.5		
x_1'	T (K)	δT (%)[a]	x_1'	T (K)	δT (%)[a]
0.3012	298.6	1.0	0.0927	277.1	0.2
0.5010	277.0	0.0	0.1101	275.3[b]	0.3
0.5244	274.0[b]	0.1	0.1286	277.6	0.2
0.5327	274.5	0.1	0.2005	283.1	−0.3
0.5602	275.7	0.4	0.2296	284.2	−0.5
0.6203	277.8	0.6	0.2504	284.6	−0.6
0.6673	278.5[c]	0.6	0.2805	284.9	4.8
0.7002	278.5	0.5	0.2902	284.6[b]	5.6
0.7500	276.8	0.7	0.3028	290.1	4.4
0.7605	276.9	0.5	0.3510	304.2	2.5
0.7900	276.2	0.1			
0.7982	275.8	0.1			
0.8005	275.9	0.0			
0.8102	275.0[b]	0.0			
0.8214	276.3	−0.8			
0.8499	280.1	−0.4			
0.8999	286.1	0.1			

[a] As defined in Table 1. [b,c] As noted in Table 5.

TABLE 7
Solid–Liquid Equilibria for Catechol (x_1') + (*tert*-Butanol:4-Methoxyphenol = 8:2) (x_2') and 4-Methoxyphenol (x_1') + (*tert*-Butanol:Catechol = 5:5) (x_2')

tert-Butanol:4-methoxyphenol = 8:2			*tert*-Butanol:catechol = 5:5		
x_1'	T (K)	δT (%)[a]	x_1'	T (K)	δT (%)[a]
0.0494	278.0	0.0	0.4065	300.1	3.7
0.0794	275.9[b]	0.3	0.4561	294.0	5.1
0.1010	279.1	1.0	0.4738	292.2[b]	5.4
0.1705	290.0	0.1	0.5075	295.1	3.8
0.2022	291.8	0.2	0.5492	298.9	1.3
0.2500	293.4	0.2	0.5994	303.2	1.0
0.2993	293.9	0.1	0.6540	307.8	0.6
0.3401	294.5[b]	−0.5	0.7022	311.6	0.4
0.3519	302.0	1.0	0.7998	318.8	−0.2

[a] As defined in Table 1.
[b] As noted in Table 5.

Fig. 3. Figure 2 illustrates its corresponding separation path. The operation procedure of this method is summarized as follows.

1. Adding *tert*-butanol into the binary eutectic mixture of 4-methoxyphenol/catechol until the composition of the ternary mixture is

TABLE 8
Solid–Liquid Equilibria for 4-Methoxyphenol (x_1') + (*tert*-Butanol:Catechol = 7:3) (x_2')

x_1'	T (K)	δT (%)[a]
0.0250	303.4[b]	−0.2
0.0509	302.1	−0.3
0.0753	299.0	0.2
0.2016	291.1	−0.5
0.2793	283.3	−0.4
0.3196	280.0	−0.8
0.3296	279.2	−1.0
0.3508	277.4[c]	−0.1
0.3646	279.2	0.1
0.3999	283.4	0.4

[a] As defined in Table 1.
[b] Congruent point.
[c] Eutectic point.

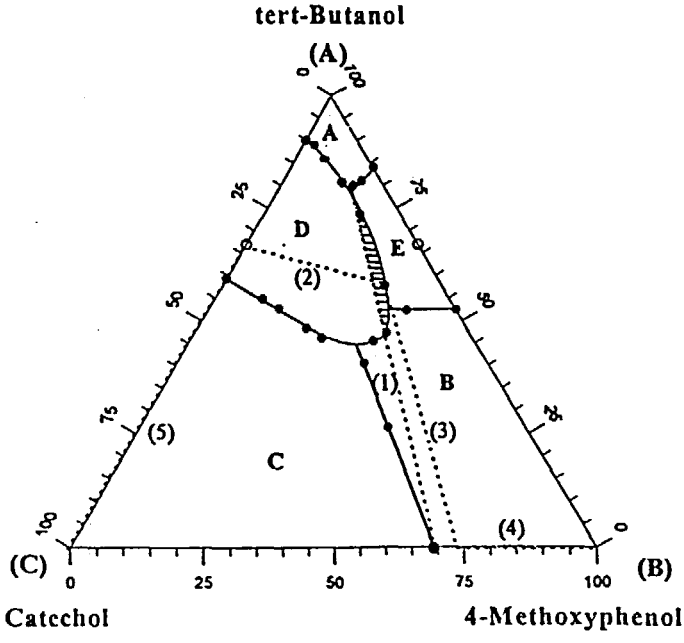

FIG. 2 Solid–liquid phase diagram (in mole fractions) for *tert*-butanol (A)/4-methoxyphenol (B)/catechol (C) ternary system (●, eutectic point; ○, congruent point).

located in adducted Area D, where the mole fractions of *tert*-butanol in the mixture are within the 47 to 77 mol% range. The preferable composition of *tert*-butanol is around 60 mol%.

2. Cooling the mixture down to about 275 K in crystallizer C_1 in which adducted solid, (*tert*-butanol)$_2$-catechol, will be formed, causing the mother liquor composition to lie in the shaded area as shown in Fig. 2. In this shaded area the mole fraction of 4-methoxyphenol (on the *tert*-butanol-free basis) becomes greater than its composition in the binary eutectic mixture of 4-methoxyphenol/catechol. The adducted solid is then separated from the magma via the separator S_1.
3. Distilling the mother liquor in distillation column D_1. *tert*-Butanol can be recovered from the top of D_1 and 4-methoxyphenol/catechol-rich mixture effluents from the bottom.
4. Cooling the bottom stream down to about 309 K in crystallizer C_2. Pure 4-methoxyphenol solid will be formed and next removed from the separator S_2.

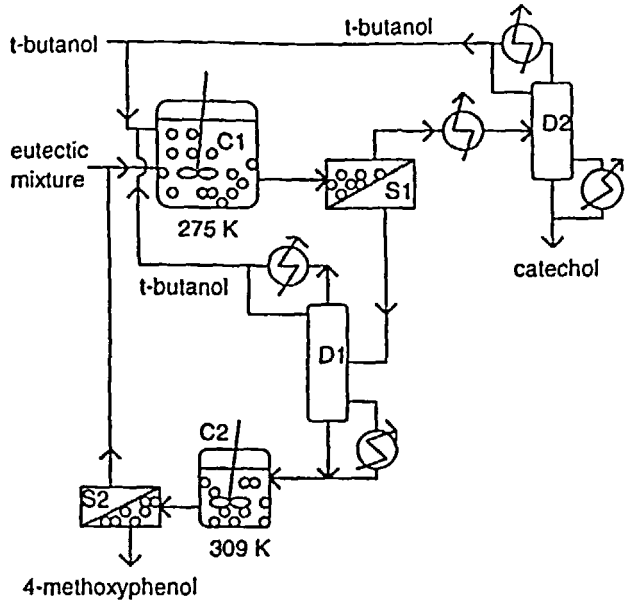

FIG. 3 Conceptual flow diagram for the separation process with Method A.

5. Melting and dissociating the adducted solid, (*tert*-butanol)$_2$-catechol, by heat, followed by vacuum distillation (D_2). Catechol is obtained from the bottom and *tert*-butanol is recovered as the distillate.

SEPARATION WITHOUT ADDUCTED SOLID BEING CRYSTALLIZED

Although the above adductive crystallization method is capable of separating the binary eutectic mixture, it has shortcomings; e.g., a large amount of *tert*-butanol is required, the operable range (the shaded area in Region D) of the process is rather narrow, and various unit operations are often needed. An alternative separation process (Method B) is further suggested in this section. As shown in Fig. 2, the 4-methoxyphenol composition on the ternary eutectic locus of the 4-methoxyphenol/catechol branch appears to decrease when the amount of *tert*-butanol is increased. A conceptual flow diagram of

Method B is presented in Fig. 4 by taking advantage of this phase behavior to overcome the separation barrier imposed on the binary eutectic mixture. The path of separation is shown in Fig. 5. The entire process is operated within the nonadducted areas of B and C. Unlike the adductive crystallization method, this method does not need to crystallize any adducted solid. The separation procedure is described as follows.

1. Adding *tert*-butanol into the binary eutectic mixture of 4-methoxyphenol/catechol up to about 40 mol% *tert*-butanol.
2. Cooling the mixture down to about 278 K in the crystallizer C_1 to produce pure 4-methoxyphenol solid, while the mother liquor composition will approach the intersection of Areas B, C, and D in the process. The mole fraction of 4-methoxyphenol (on the *tert*-butanol-free basis) in this region of intersection becomes lower as compared with its composition in the binary eutectic mixture of 4-methoxyphenol/catechol. Removing the pure 4-methoxyphenol solid from the magma via the separator S_1.
3. Distilling the mother liquor in the distillation column D_1, where *tert*-butanol is recovered from the top and the 4-methoxyphenol/catechol-rich mixture is collected from the bottom.

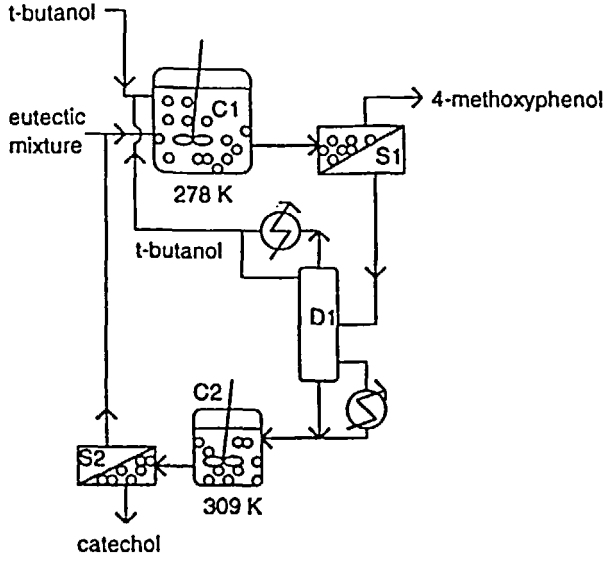

FIG. 4 Conceptual flow diagram for the separation process with Method B.

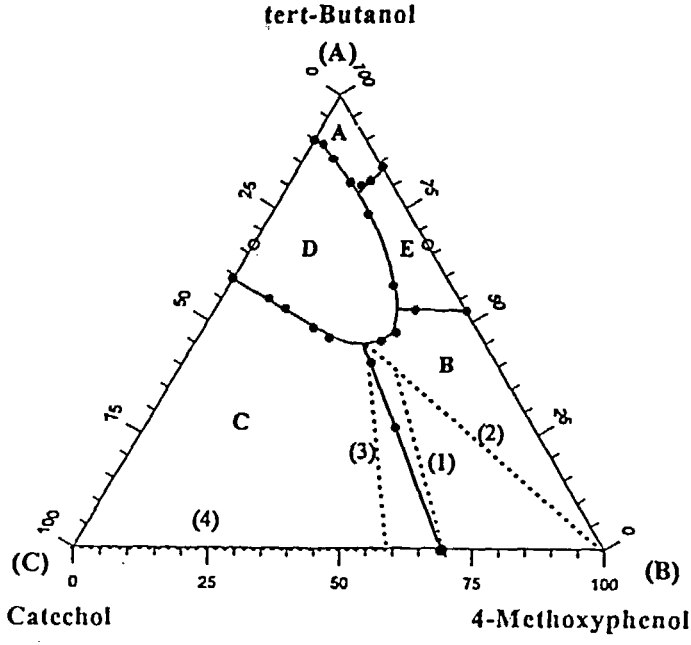

FIG. 5 Path for the separation process with Method B (●, eutectic point; ○, congruent point).

4. Cooling the bottom stream down to about 309 K in the crystallizer C_2. Pure catechol solid is obtained from the separator S_2.

In comparison with Method A, Method B cuts the requirement for *tert*-butanol by one-third and reduces the required distillation columns by one. As a result, Method B is more favorable economically than Method A.

CORRELATION FOR BINARY SYSTEMS

It is vital to engineering applications to estimate the phase behavior of multicomponent systems from knowledge of the related binary systems via a mathematical model. The following calculations illustrate a simple method, the ideal-chemical model (ICM), to meet this demand. The ICM is frequently applied to describe the SLE behavior of complex formation systems (3, 5, 6). In the ICM, the solid–liquid equilibrium criterion for a complex formation system can be expressed approximately as (4)

$$\ln(a_i) = \ln(z_i) = \frac{\Delta H_i^{fus}}{R}\left(\frac{1}{T_{m,i}} - \frac{1}{T}\right) \quad (1)$$

where a_i, z_i, ΔH_i^{fus}, and $T_{m,i}$ are the activity, "true" mole fraction, molar enthalpy of fusion, and melting temperature for the species i, respectively, and T is the phase-equilibrium temperature. The "true" mole fractions for all species at a given "apparent" composition (x_i) are calculated by simultaneously solving the chemical equilibria of adducted formations and the material balance equations. The mechanism of adducted species formation should be assigned prior to implementing chemical equilibrium calculations. Since the "real" mechanism of complex formations is not known, the mechanism of A_2B formation in the solutions of *tert*-butanol/4-methoxyphenol and *tert*-butanol/catechol was empirically assumed to be

$$A + B \leftrightarrow AB \quad (2)$$

$$AB + A \leftrightarrow A_2B \quad (3)$$

where AB is a hypothetical intermediate species. Under the above assumptions, the material balance and the chemical equilibrium equations for a binary system are given by

$$K_{AB} = \frac{z_{AB}}{(z_A)(z_B)} \quad (4)$$

$$K_{A_2B} = \frac{z_{A_2B}}{(z_{AB})(z_A)} \quad (5)$$

$$x_A = \frac{z_A + 2z_{A_2B} + z_{AB}}{z_A + z_B + 2z_{AB} + 3z_{A_2B}} \quad (6)$$

and

$$z_A + z_B + z_{AB} + z_{A_2B} = 1 \quad (7)$$

where K_i is the chemical equilibrium constant for complex i formation. Its temperature dependence is represented by the van't Hoff relationship,

$$\ln K_i = K_{0,i} + \frac{K_{1,i}}{T} \quad (8)$$

where $K_{0,i}$ and $K_{1,i}$ are constants and treated in this study as model parameters.

If the "apparent" composition of solutions is located between two eutectic points, the solid compound is A_2B and the $T_{m,i}$ in Eq. (1) accordingly corresponds to the "true" melting temperature of the complex (T_{m,A_2B}). The value of T_{m,A_2B} was calculated by Eq. (1) by replacing T with the congruently melting temperature T'_{m,A_2B}:

$$T_{m,A_2B} = T'_{m,A_2B}\{1 - [R \ln(z_{A_2B})/\Delta S^{fus}_{A_2B}]\} \quad (9)$$

The molar entropy of fusion for the adducted compound A_2B, $\Delta S^{fus}_{A_2B}$, was estimated by the method of Beardmore et al. (15), i.e.,

$$\Delta S^{fus}_{A_2B} = \frac{2}{3}\Delta S^{fus}_A + \frac{1}{3}\Delta S^{fus}_B - R\left[\frac{2}{3}\ln\left(\frac{2}{3}\right) + \frac{1}{3}\ln\left(\frac{1}{3}\right)\right] \quad (10)$$

with

$$\Delta S^{fus}_i = \Delta H^{fus}_i / T_{m,i} \quad (11)$$

where i represents species A, B, or A_2B. The molar enthalpies of fusion are 6.79 kJ·mol^{-1} (16), 18.30 kJ·mol^{-1} (3), and 22.54 kJ·mol^{-1} (3) for *tert*-butanol, 4-methoxyphenol, and catechol, respectively.

For each complex formation binary system, the ICM contains four model parameters: $K_{0,AB}$, $K_{1,AB}$, K_{0,A_2B}, and K_{1,A_2B}. While the values of the model parameters are specified, the solid-disappearance temperature (T) at a given "apparent" solution composition, x_A, is calculated by the following procedure:

1. Determine the species of solid formation (i.e., A, B, or A_2B) corresponding to x_A based on the experimental eutectic compositions.
2. If solid A_2B is formed, estimate T_{m,A_2B}, $\Delta S^{fus}_{A_2B}$, and $\Delta H^{fus}_{A_2B}$ from Eqs. (9)–(11), respectively.
3. Guess a solid-disappearance temperature, T.
4. Calculate chemical equilibrium constants K_{AB} and K_{A_2B} at T from Eq. (8).
5. Solve "true" mole fractions z_A, z_B, z_{AB}, and z_{A_2B} from Eqs. (4)–(7) simultaneously.
6. Calculate the "new" equilibrium temperature T from Eq. (1).
7. Check the convergence of T. If T does not converge, go to Step 4 with a new T.

The optimal values of model parameters are obtained by minimizing the average absolute percent deviation (AAD%) of calculated equilibrium temperatures from experiment over the entire range of the liquidus line, i.e.,

$$\text{AAD\%} = \frac{100}{n_p}\sum_{j=1}^{n_p}\frac{|T_j^{calc} - T_j^{expt}|}{T_j^{expt}} \quad (12)$$

Table 9 reports the correlated results from the ICM. The calculated values

TABLE 9
Results of Binary SLE Data Reduction with the ICM

Mixture (A) + (B)	Complex solid	$K_{0,AB}$	$K_{1,AB}$ (K)	K_{0,A_2B}	K_{1,A_2B} (K)	AAD%[a]
tert-Butanol + 4-methoxyphenol	A_2B	−8.754	2729.8	−5.175	1067.0	0.31
tert-Butanol + catechol	A_2B	−1.661	984.0	−7.682	2041.4	0.33

[a] AAD% is defined in Eq. (12).

are presented in Fig. 1 as dashed lines. They show good agreement with the experimental data.

PREDICTION FOR TERNARY SYSTEM

The phase-equilibrium temperature surface of *tert*-butanol (A)/4-methoxyphenol (B)/catechol (C) ternary system can be predicted from the ICM with the optimized values of model parameters determined from the binary data. The validity of the assumptions made in the previous section will be tested by the experimental ternary data. For the ternary system, the chemical equilibrium and the material balance equations are

$$K_{AB} = \frac{z_{AB}}{(z_A)(z_B)} \tag{13}$$

$$K_{AC} = \frac{z_{AC}}{(z_A)(z_C)} \tag{14}$$

$$K_{A_2B} = \frac{z_{A_2B}}{(z_{AB})(z_A)} \tag{15}$$

$$K_{A_2C} = \frac{z_{A_2C}}{(z_{AC})(z_A)} \tag{16}$$

$$z_A + z_B + z_{AC} + z_{AB} + z_{A_2B} + z_{A_2C} = 1 \tag{17}$$

$$x_B = \frac{z_B + z_{AB} + z_{A_2B}}{z_A + z_B + z_C + 2z_{AB} + 2z_{AC} + 3z_{A_2B} + 3z_{A_2C}} \tag{18}$$

and

$$x_C = \frac{z_C + z_{AC} + z_{A_2C}}{z_A + z_B + z_C + 2z_{AB} + 2z_{AC} + 3z_{A_2B} + 3z_{A_2C}} \quad (19)$$

The algorithm for ternary SLE calculations is similar to that reported by Lee and Lien (2). The ICM predicts the phase-equilibrium temperatures to a grand AAD% of 1.3. Figure 6, as an illustrative graph, compares the predicted results with the experimental values for some pseudomixtures. In general, the ICM developed in this study makes reasonable predictions of the phase boundaries for the ternary system; however, the deviations are relatively large in the region of the eutectic points in some instances.

CONCLUSIONS

Solid–liquid equilibrium behavior was observed for binary and ternary mixtures composed of *tert*-butanol, 4-methoxyphenol, and catechol at tem-

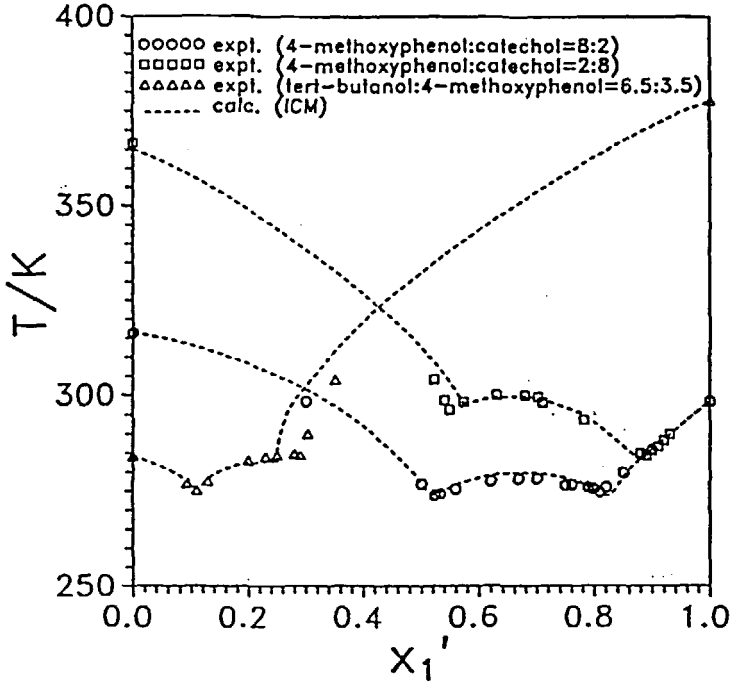

FIG. 6 Comparison of the predicted equilibrium temperatures from the ICM with the experimental values for some pseudobinary systems.

peratures ranging from 273 to 378 K. It was indicated that a 2:1 adducted compound was formed in both *tert*-butanol/4-methoxyphenol and *tert*-butanol/catechol systems. *tert*-Butanol was thus considered a feasible auxiliary agent for separating the close-boiling and eutectic mixture of 4-methoxyphenol/catechol with the crystallization method. Two different paths for the separation process (Methods A and B) were suggested on the basis of the phase behavior of *tert*-butanol/4-methoxyphenol/catechol ternary mixtures. Method B is preferable to Method A (adductive crystallization method) from an economic viewpoint. The experimental equilibrium data were correlated with the ICM, which was found to represent well the binary data and to be capable of qualitatively predicting the SLE phase boundaries for the ternary system.

NOTATION

a	activity
AAD%	average absolute percent deviations
A, B, C	pure compounds
AB, AC	1–1 complex compounds
A_2B, A_2C	2–1 complex compounds
ΔH	change of molar enthalpy ($kJ \cdot mol^{-1}$)
K	equilibrium constant of complex formation
n_p	number of data points
R	gas constant ($kJ \cdot mol^{-1} \cdot K^{-1}$)
ΔS	change of molar entropy ($kJ \cdot mol^{-1} \cdot K^{-1}$)
T	temperature (K)
T_m	melting temperature (K)
T_{m,A_2B}	"true" melting temperature for A_2B (K)
T'_{m,A_2B}	congruently melting temperature for A_2B (K)
x	"apparent" mole fraction
x'	"apparent" mole fraction in a pseudobinary system
z	"true" mole fraction

Superscripts

calc	calculated value
expt	experimental value
fus	fusion

Subscript

i	component i

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