**Separation Science and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Phase Behavior of Separating m-Cresol/p-Cresol Mixtures with Ethylenediamine

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**To cite this Article** Lee, Ming-Jer and Lien, Pei-Jung(1995) 'Phase Behavior of Separating m-Cresol/p-Cresol Mixtures with Ethylenediamine', Separation Science and Technology, 30: 19, 3697 — 3713
**To link to this Article: DOI:** 10.1080/01496399508014153
**URL:** http://dx.doi.org/10.1080/01496399508014153

SEPARATION SCIENCE AND TECHNOLOGY, **30**(19), pp. 3697–3713, 1995

# Phase Behavior of Separating *m*-Cresol/*p*-Cresol Mixtures with Ethylenediamine

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## ABSTRACT

Solid–liquid equilibrium (SLE) data were measured experimentally for the ternary system *m*-cresol + *p*-cresol + ethylenediamine. These data form a phase diagram in which seven areas were distinguished by the loci of eutectic points. Each region corresponded to a pure or a complex solid that could crystallize from the mother liquor. The phase diagram provided us with the favorable operating conditions for separating *m*-cresol/*p*-cresol mixtures by using ethylenediamine as a neutralizing agent. The separation strategy was discussed. Moreover, the ideal-chemical model (ICM) and the regular solution-chemical model (RSCM) were applied, respectively, in this study to correlate the binary data and predict the phase behavior of the ternary mixtures.

*Key Words.* Solid–liquid equilibrium; *m*-Cresol; *p*-Cresol; Ethylenediamine; Close boiling compounds separation

## INTRODUCTION

Adductive crystallization is an attractive method for separating a compound from close boiling mixtures. For instance, Gaikar et al. (1) reported that 91% of *p*-cresol could be recovered from a *m*-cresol/*p*-cresol mixture by using piperazine as a neutralizing agent and dibutyl ether as a solvent. In the present study, the phase behavior is investigated for the ternary

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system *m*-cresol + *p*-cresol + ethylenediamine where ethylenediamine serves as a neutralizing agent. Since the melting point of ethylenediamine is much lower than that of piperazine, a solvent may not be necessary in this case. As reported by Lee and Chi (2) and Lee et al. (3), four kinds of intermolecular complexes could form in the ternary mixtures of *m*-cresol + *p*-cresol + ethylenediamine. These complex compounds are $(m\text{-cresol})_2$–*p*-cresol, $(m\text{-cresol})_2$–ethylenediamine, $(p\text{-cresol})_2$–ethylenediamine, and $(p\text{-cresol})_6$–ethylenediamine. One of the solids (a pure substance or a complex compound) will crystallize from the ternary solutions, depending on the feed compositions. To explore the feasible operating conditions for the separation process, a solid–liquid equilibrium (SLE) phase diagram of the ternary system is needed. In this work, solid-disappearance temperatures of the ternary system (actually eight pseudo-binary systems) are observed to determine the loci of eutectic and congruent points. On the basis of this phase diagram, the separation strategy is discussed as well.

In addition to SLE measurements, development of appropriate models for the phase equilibrium calculations is also necessary for the separation process design. Stoicos and Eckert (4) and Feng et al. (5) showed that physical-chemical models could be applied successfully to describe the SLE behavior of the systems involving complex formations. Recently, Lee et al. (3) employed an ideal-chemical model (ICM) that correlated well the SLE data of *m*-cresol + ethylenediamine and *p*-cresol + ethylenediamine systems. In the present study, both the ICM and a regular solution-chemical model (RSCM) were adopted. These two models with the determined binary parameters are used respectively for predicting the phase boundaries of the ternary system of *m*-cresol + *p*-cresol + ethylenediamine.

## EXPERIMENTAL SECTION

Ethylenediamine (99 wt%), *m*-cresol (99 wt%), and *p*-cresol (99 wt%) were purchased from Aldrich, USA. The purity of these compounds was checked by gas chromatographic analysis. All these substances were used without further purification. The SLE phase boundaries for the ternary system *m*-cresol + *p*-cresol + ethylenediamine were determined by a solid-disappearance method. The experimental procedure has been described elsewhere (2) in detail. Each mixture sample (2–3 g) was prepared by weighing pure compounds to ±0.1 mg. A visual high-temperature thermostated bath (Neslab, TV-4000, stability ±0.03 K) connected to an external refrigeration circulator (Neslab, RTE-11A, stability ±0.01 K) was used for observing the phase behavior of samples at temperatures above

273 K. Another visual low-temperature bath (Neslab, LTV-70, stability ±0.05 K) was employed when the observed temperatures were below 273 K. Bath temperature was measured by a Hart Scientific Microtherm (Model 1506) with a platinum RTD probe to ±0.02 K. In general, the uncertainty of the reported solid-disappearance temperatures was estimated to be ±0.1 K.

In order to construct an SLE phase diagram for the ternary mixtures of *m*-cresol + *p*-cresol + ethylenediamine, the solid-disappearance points of eight pseudo-binary systems were observed at atmospheric pressure. The samples include the ternary mixtures with constant molar ratios of *m*-cresol:*p*-cresol = 2:8, 3:7, 4:6, 5:5, 7:3, and 8:2, ethylenediamine:*p*-cresol = 4:6, and ethylenediamine:*m*-cresol = 3:7.

## EXPERIMENTAL RESULTS AND DISCUSSION

Tables 1–4 report the observed results for the respective pseudo-binary systems. Projections of eutectic and congruent points are shown in Fig. 1. This phase diagram is divided into seven regions, marked respectively as "A" to "G" by the loci of the eutectic points. Each region corresponds to a solid that will crystallize from the mother liquor, such as region "A" for *m*-cresol, region "B" for *p*-cresol, region "C" for ethylenediamine, region "D" for $(m\text{-cresol})_2$–*p*-cresol, region "E" for $(m\text{-cresol})_2$–ethylenediamine, region "F" for $(p\text{-cresol})_2$–ethylenediamine, and region "G" for $(p\text{-cresol})_6$–ethylenediamine. Among these seven areas, region "E" is of particular interest for the separation process. This region covers two eutectic compositions of the *m*-cresol + *p*-cresol system wherein neither pure *m*-cresol nor pure *p*-cresol can be separated directly by using a conventional crystallization method (without adding the third compound). According to the phase diagram, separation becomes possible by using the adductive crystallization method when a proper amount of ethylenediamine is added to the cresol mixtures; i.e., a feed composition of the ternary mixture should be located within the area confined by the dashed lines as shown in Fig. 1. If the crystallization temperature is low enough, the $(m\text{-cresol})_2$–ethylenediamine solid may form and the mother liquor possibly locates in the shaded area where the compositions of ethylenediamine-free mixtures are lower than the first eutectic point of the *m*-cresol + *p*-cresol system. Under the circumstances, pure *p*-cresol is likely to be separated from the mother liquor via the conventional crystallization method. For example, adding 26–30 mol% ethylenediamine is preferable when the original molar ratio of *m*-cresol to *p*-cresol is 7:3. A complex solid of $(m\text{-cresol})_2$–ethylenediamine could form provided that the solutions are cooled down to about 258 K. After dissociating the solid with

TABLE 1
SLE for (*m*-Cresol:*p*-Cresol = 2:8) ($x'_1$) + Ethylenediamine ($x'_2$) and (*m*-Cresol:*p*-Cresol = 3:7) ($x'_1$) + Ethylenediamine ($x'_2$)

| *m*-Cresol:*p*-cresol = 2:8 | | | | *m*-Cresol:*p*-cresol = 3:7 | | | |
|---|---|---|---|---|---|---|---|
| $x'_1$ | $T$ (K) | ICM dev. $T$[a] (%) | RSCM dev. $T$[a] (%) | $x'_1$ | $T$ (K) | ICM dev. $T$[a] (%) | RSCM dev. $T$[a] (%) |
| 0.283 | 266.4 | 0.8 | 0.8 | 0.288 | 271.0 | −1.1 | −0.6 |
| 0.309 | 261.4 | 2.0 | 2.0 | 0.309 | 265.8 | 0.2 | 0.8 |
| 0.310 | 257.8[b] | 3.4 | 3.4 | 0.331 | 255.2[b] | 3.8 | 4.4 |
| 0.333 | 262.0 | 4.2 | 5.0 | 0.361 | 272.0 | −0.3 | 0.2 |
| 0.357 | 270.8 | 2.3 | 3.0 | 0.378 | 283.6 | −3.5 | −3.0 |
| 0.367 | 274.4 | 1.5 | 2.3 | 0.401 | 287.5 | −3.6 | −3.1 |
| 0.438 | 296.0 | −2.2 | −1.7 | 0.438 | 294.3 | −4.1 | −3.5 |
| 0.582 | 316.7 | −3.1 | −2.8 | 0.470 | 299.1 | −4.2 | −3.6 |
| 0.627 | 319.7 | −3.1 | −2.8 | 0.501 | 302.9 | −4.1 | −3.4 |
| 0.658 | 320.8 | −3.1 | −2.8 | 0.527 | 306.5 | −4.3 | −3.5 |
| 0.665 | 321.1[c] | −3.1 | −2.9 | 0.552 | 308.4 | −4.0 | −3.2 |
| 0.673 | 321.1 | −3.1 | −2.8 | 0.598 | 310.5 | −3.4 | −2.4 |
| 0.710 | 318.5 | −2.6 | −2.3 | 0.624 | 312.2 | −3.4 | −2.4 |
| 0.752 | 310.8 | −1.3 | −1.0 | 0.647 | 312.9[c] | −3.3 | −2.3 |
| 0.773 | 285.8 | 6.3 | 6.6 | 0.672 | 312.1 | −3.0 | −1.8 |
| 0.782 | 280.4[b] | 7.8 | 8.1 | 0.690 | 310.9 | −2.6 | −1.4 |
| 0.798 | 282.7 | 5.9 | −10.9 | 0.709 | 309.2 | −2.3 | −1.1 |
| 0.803 | 282.9 | 5.4 | −10.4 | 0.725 | 291.5 | 3.4 | 4.6 |
| 0.817 | 283.3[c] | −10.8 | −9.2 | 0.731 | 284.2 | 5.9 | 7.2 |
| 0.822 | 283.1 | −10.3 | −8.7 | 0.742 | 275.3[b] | 9.0 | 10.3 |
| 0.842 | 281.7 | −8.4 | −6.8 | 0.767 | 280.6 | 6.0 | 7.2 |
| 0.855 | 280.8 | −5.5 | −4.8 | 0.794 | 287.8 | 2.0 | 3.1 |
| 0.885 | 278.2[b] | −2.5 | −1.9 | 0.820 | 288.5 | −20.1 | −17.0 |
| 0.911 | 288.8 | −4.3 | −3.8 | 0.844 | 286.8 | −17.3 | −14.2 |
| | | | | 0.867 | 277.4[b] | −8.1 | −5.2 |
| | | | | 0.881 | 282.4 | −9.3 | −6.4 |
| | | | | 0.894 | 288.8[c] | −11.1 | −8.2 |
| | | | | 0.915 | 284.5 | −9.4 | −6.4 |
| | | | | 0.923 | 274.3 | −2.0 | −0.6 |
| | | | | 0.941 | 278.7 | −2.3 | −1.0 |

[a] dev. $T$ (%) = 100 $(T^{calc} - T^{expt})/T^{expt}$.
[b] Eutectic point.
[c] Congruent point.

heat, *m*-cresol and ethylenediamine are separated from the melt by distillation. Furthermore, any trace of ethylenediamine can be removed from the mother liquor by distillation, and *p*-cresol is obtained from the residues by subsequently using a conventional crystallization method.

TABLE 2

SLE for (*m*-Cresol:*p*-Cresol = 4:6) ($x'_1$) + Ethylenediamine ($x'_2$) and (*m*-Cresol:*p*-Cresol = 5:5) ($x'_1$) + Ethylenediamine ($x'_2$)

| *m*-Cresol:*p*-cresol = 4:6 | | | | *m*-Cresol:*p*-cresol = 5:5 | | | |
|---|---|---|---|---|---|---|---|
| $x'_1$ | $T$ (K) | ICM dev. $T$ (%) | RSCM dev. $T$ (%) | $x'_1$ | $T$ (K) | ICM dev. $T$ (%) | RSCM dev. $T$ (%) |
| 0.324 | 266.2 | −0.4 | 0.4 | 0.338 | 263.2 | 0.4 | 1.3 |
| 0.356 | 264.8 | −0.8 | 0.1 | 0.355 | 261.4 | 0.5 | 1.5 |
| 0.401 | 254.6 | 1.6 | 2.6 | 0.379 | 260.1 | 0.2 | 1.3 |
| 0.418 | 251.2[a] | 2.3 | 3.4 | 0.400 | 256.3[a] | 0.9 | 2.2 |
| 0.439 | 257.0 | 6.9 | 0.2 | 0.417 | 258.5 | −0.6 | 0.6 |
| 0.471 | 262.5 | 6.2 | −3.2 | 0.454 | 262.7 | −3.7 | −2.3 |
| 0.500 | 270.2 | 4.4 | 5.4 | 0.628 | 278.3 | −10.7 | −7.1 |
| 0.624 | 310.2 | −5.6 | −4.3 | 0.644 | 279.1 | −10.8 | −7.3 |
| 0.648 | 311.5[b] | −5.7 | −4.3 | 0.668 | 280.1[b] | −11.1 | −7.2 |
| 0.673 | 277.4[a] | −14.2 | −10.4 | 0.676 | 280.0 | −11.1 | −7.8 |
| 0.689 | 310.9[b] | −23.7 | −20.4 | 0.689 | 279.2 | −11.1 | −7.7 |
| 0.716 | 307.2 | −23.6 | −20.3 | 0.716 | 278.2 | −11.3 | −8.1 |
| 0.733 | 282.6 | −17.6 | −14.2 | 0.737 | 277.1 | −11.0 | −9.0 |
| 0.816 | 282.4 | −9.5 | −7.0 | 0.816 | 273.7 | −5.2 | −2.9 |
| 0.851 | 279.3 | −6.9 | −4.3 | 0.900 | 269.6 | 0.1 | 2.6 |
| 0.873 | 266.9[a] | −1.8 | 1.0 | 0.910 | 268.4[a] | 0.9 | 3.5 |
| 0.892 | 275.2 | −4.0 | −1.3 | 0.930 | 274.4 | −0.6 | 2.0 |
| 0.918 | 275.8 | −3.5 | −0.7 | | | | |
| 0.932 | 277.1[b] | −3.7 | −0.8 | | | | |
| 0.952 | 275.4 | −2.7 | 0.2 | | | | |

[a] Eutectic point.

[b] Congruent point.

Gaikar et al. (1) reported that the complex solid of ($p$-cresol)$_2$–piperazine, rather than ($m$-cresol)$_2$–ethylenediamine as in the present study, was produced from the mother liquor at 253 K. It is implied that the ($p$-cresol)$_2$–piperazine region is dominant in the SLE phase diagram of the *m*-cresol + *p*-cresol + piperazine system, and the locus of the congruently melting compound ($p$-cresol)$_2$–piperazine would extend to near the binary edge of *m*-cresol + piperazine. As a consequence, the separation strategy is crucially dependent on the chemical nature of the neutralizing agent, and the phase diagram of the multicomponent systems can provide useful information for the separation process design.

Determination of phase diagrams for multicomponent systems is a time-consuming task. If phase behavior can be estimated from knowledge of

TABLE 3

SLE for (*m*-Cresol:*p*-Cresol = 7:3) ($x_1'$) + Ethylenediamine ($x_2'$) and (*m*-Cresol:*p*-Cresol = 8:2) ($x_1'$) + Ethylenediamine ($x_2'$)

| *m*-Cresol:*p*-cresol = 7:3 | | | | *m*-Cresol:*p*-cresol = 8:2 | | | |
|---|---|---|---|---|---|---|---|
| $x_1'$ | *T* (K) | ICM dev. *T* (%) | RSCM dev. *T* (%) | $x_1'$ | *T* (K) | ICM dev. *T* (%) | RSCM dev. *T* (%) |
| 0.331 | 263.0 | 0.7 | 1.2 | 0.307 | 261.4 | 2.1 | 3.2 |
| 0.358 | 260.8 | 0.7 | 2.1 | 0.337 | 260.1 | 1.6 | 3.0 |
| 0.378 | 257.3 | 1.4 | 2.9 | 0.357 | 256.4 | 2.5 | 3.9 |
| 0.387 | 258.1[a] | 0.7 | 2.3 | 0.366 | 255.7[a] | 2.4 | 4.0 |
| 0.399 | 258.8 | 0.1 | 1.6 | 0.378 | 257.7 | 1.2 | 2.8 |
| 0.420 | 262.1 | −2.0 | −2.0 | 0.400 | 260.3 | −0.6 | 1.1 |
| 0.580 | 279.4 | −5.9 | −2.8 | 0.441 | 266.2 | −4.3 | −2.7 |
| 0.642 | 284.1 | −5.4 | −2.6 | 0.499 | 270.9 | −3.2 | −2.3 |
| 0.675 | 284.3[b] | −6.0 | −3.3 | 0.589 | 278.8[b] | −2.7 | −2.5 |
| 0.728 | 283.6 | −6.4 | −3.0 | 0.645 | 279.4 | −1.6 | −1.8 |
| 0.828 | 280.9 | −5.4 | −3.9 | 0.681 | 279.6 | −1.5 | −1.8 |
| 0.864 | 278.9 | −3.4 | −1.2 | 0.718 | 279.3 | −1.7 | −2.2 |
| 0.903 | 276.9 | −0.9 | 1.3 | 0.823 | 276.4 | −0.4 | −6.0 |
| 0.912 | 275.9 | −0.2 | 2.1 | 0.897 | 274.3 | 3.5 | 2.1 |
| 0.925 | 280.9 | −1.5 | 0.8 | 0.910 | 277.5 | 2.8 | 1.4 |

[a] Eutectic point.

[b] Congruent point.

TABLE 4

SLE for (Ethylenediamine:*p*-Cresol = 4:6) ($x_1'$) + *m*-Cresol ($x_2'$) and (Ethylenediamine:*m*-Cresol = 3:7) ($x_1'$) + *p*-Cresol ($x_2'$)

| Ethylenediamine:*p*-cresol = 4:6 | | | | Ethylenediamine:*m*-cresol = 3:7 | | | |
|---|---|---|---|---|---|---|---|
| $x_1'$ | *T* (K) | ICM dev. *T* (%) | RSCM dev. *T* (%) | $x_1'$ | *T* (K) | ICM dev. *T* (%) | RSCM dev. *T* (%) |
| 0.301 | 275.5 | −0.9 | 0.3 | 0.101 | 278.1 | −1.7 | −1.5 |
| 0.318 | 270.5[b] | 0.1 | 1.3 | 0.113 | 277.1 | −1.8 | −1.5 |
| 0.337 | 287.1[a] | −6.6 | −5.5 | 0.131 | 276.4 | −2.3 | −2.0 |
| 0.361 | 282.8 | −6.4 | −5.2 | 0.153 | 275.1 | −2.9 | −2.5 |
| 0.376 | 279.8 | −8.5 | −5.5 | 0.178 | 273.3 | −3.7 | −3.1 |
| 0.405 | 270.4 | −4.7 | −1.7 | 0.207 | 264.1[a] | 0.2 | 2.6 |
| | | | | 0.223 | 267.3 | −0.1 | 2.2 |

[a] Eutectic point.

[b] Congruent point.

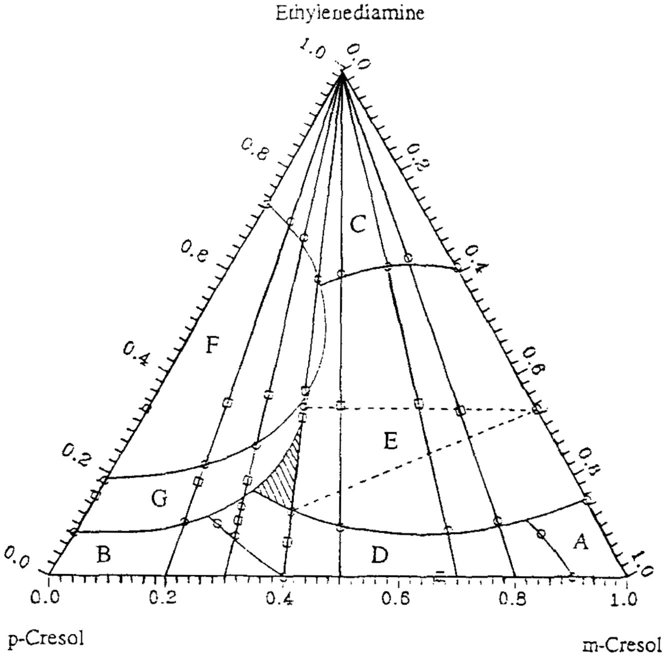

FIG. 1 Solid–liquid phase diagram (in mole fractions) for *m*-cresol + *p*-cresol + ethylenediamine system (○, eutectic point; □, congruent point).

the related binary systems via an appropriate model, it would be valuable information and of particular interest. In the following section, SLE calculations for both binary and ternary systems are presented.

## SOLID–LIQUID EQUILIBRIUM CALCULATION

Solid–liquid equilibrium criterion for a complex formation system can be expressed approximately as (4)

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

where $a_i$, $z_i$, $\alpha_i$, $\Delta H_i^{\text{fus}}$, and $T_{\text{m}i}$ are activity, "true" mole fraction, "true" activity coefficient, molar heat of fusion, and melting temperature of compound *i*, respectively. The "true" mole fractions of a mixture at given apparent compositions ($x_i$s) are determined by solving the chemical equilibria of complex formations and material balance equations simultaneously. Each chemical equilibrium constant, $K_i$, is evaluated from the van't Hoff relationship by assuming that the heat of complex formation is independent of temperature over the entire range of the liquidus line, i.e.,

$$\ln K_i = \frac{-\Delta H_i^{\mathrm{cpx}}}{RT} + \frac{\Delta S_i^{\mathrm{cpx}}}{R} \tag{2}$$

where constants $\Delta H_i^{\mathrm{cpx}}$ and $\Delta S_i^{\mathrm{cpx}}$ represent the enthalpy and the entropy change of complex $i$ formation, respectively. In the present study, these two constants are treated as model parameters instead of determining the adduction constants by the gas chromatography method (5) or by the NMR chemical-shift method (6).

The "true" activity coefficient $\alpha_i$ in Eq. (1) accounts for the nonideality of component $i$ in the liquid phase. Any suitable solution model can be applied to calculate the activity coefficient. However, a predictive model such as the regular solution method or the group-contribution method (e.g., ASOG and UNIFAC) would be preferable because there are no extra undetermined parameters involved in this type of model. If $\alpha_i$ is simply assumed to be unity, the model is designated as the ICM. Provided that $\alpha_i$ is calculated from the regular solution theory, the method is designated as the RSCM. In this work, the applicability of the ICM and the RSCM is investigated for the $m$-cresol + $p$-cresol + ethylenediamine system. When the RSCM is employed, the "true" activity coefficient of component $i$ is calculated from

$$\alpha_i = \exp\{[V_i(\delta_i - \bar{\delta})^2]/(RT)\} \tag{3}$$

where $\delta_i$ is the solubility parameter of compound $i$ and $\bar{\delta}$ is the volume fraction average of the solubility parameters of all species. The solubility parameter of the congruently melting compounds is estimated from the values of reactants by the method proposed by Harris and Prausnitz (7) and Stoicos and Eckert (4). For example, the solubility parameter of the complex $A_2B$ could be estimated from

$$\delta_{A_2B} = \sqrt{\frac{\delta_{AB}^2 V_{AB} + \delta_A^2 V_A}{V_{A_2B}}} \tag{4}$$

with

$$\delta_{AB} = \sqrt{\frac{\delta_A^2 V_A + \delta_B^2 V_B}{V_{AB}}} \tag{5}$$

and

$$V_{A_mB}(\mathrm{cm^3/mol}) = mV_A + V_B - m \cdot 6.0 \tag{6}$$

where $V_i$ represents the liquid molar volume of compound $i$. The solubility parameters and liquid molar volumes for the related compounds are listed in Table 5.

While the SLE criterion is applied to complex $i$, $T_{mi}$ in Eq. (1) should be the "true" melting temperature of the congruently melting solid instead of the observed congruent temperature ($T'_{mi}$). The "true" melting point can be estimated from Eq. (1) by replacing $T$ with $T'_{mi}$, i.e.,

$$T_{mi} = T'_{mi}\{1 - [R \ln(z_i \alpha_i)/\Delta S_i^{\text{fus}}]\} \tag{7}$$

Since the experimental entropy of fusion for a complex is unavailable, the value is estimated approximately from information about the monomers by the following equation (10):

$$\begin{aligned}\Delta S^{\text{fus}}_{\text{A}_m\text{B}_n} = {} & [m/(m+n)]\Delta S^{\text{fus}}_{\text{A}} \\ & + [n/(m+n)]\Delta S^{\text{fus}}_{\text{B}} \\ & - R[m/(m+n)] \ln[m/(m+n)] \\ & + [n/(m+n)] \ln[n/(m+n)]\end{aligned} \tag{8}$$

with

$$\Delta S_i^{\text{fus}} = \Delta H_i^{\text{fus}}/T_{mi} \tag{9}$$

where $\Delta H_i^{\text{fus}}$ of pure *m*-cresol, *p*-cresol, and ethylenediamine have been reported (3).

## Correlation for Binary Systems

In order to determine the model parameters, including $\Delta H_i^{\text{cpx}}$ and $\Delta S_i^{\text{cpx}}$, the constituent binary data should be correlated with the ICM

TABLE 5
Solubility Parameter, Liquid Molar Volume, and Heat of Fusion for the Pure Compounds

| Substance | $\delta_i$ (J·cm$^{-3}$)$^{0.5}$ | $V_i^{a,b}$ (cm$^3$·mol$^{-1}$) | $\Delta H_i^{\text{fus}\ b}$ (J·mol$^{-1}$) |
|---|---|---|---|
| *m*-Cresol | 20.9[c] | 105.0 | 8,670 |
| *p*-Cresol | 24.4[d] | 105.2 | 9,140 |
| Ethylenediamine | 25.2[c] | 67.3 | 10,620 |

[a] At 298.15 K.

[b] Reported in Lee et al. (3).

[c] Reported in Brandrup and Immergut (8).

[d] Solubility parameter of *p*-cresol was estimated from $\{[(\Delta H_i^{\text{sub}} - \Delta H_i^{\text{fus}}) - RT]/V_i\}^{0.5}$, where $\Delta H_i^{\text{sub}} = 73{,}986$ J·mol$^{-1}$ (9).

and the RSCM, respectively. As mentioned earlier, an $A_2B$ complex compound is formed in *m*-cresol (A) + *p*-cresol (B) and *m*-cresol (A) + ethylenediamine (B) systems, whereas both $A_2B$ and $A_6B$ complex compounds may form in a *p*-cresol (A) + ethylenediamine (B) system. The former two systems are treated as ternary mixtures containing A, B, and $A_2B$. At a given apparent composition ($x_A$), the "true" mole fractions ($z_A$, $z_B$, and $z_{A_2B}$) are computed from the following simultaneous equations:

$$K_{A_2B} = \frac{z_{A_2B}\alpha_{A_2B}}{(z_A\alpha_A)^2(z_B\alpha_B)} \tag{10}$$

$$X_A = \frac{z_A + 2z_{A_2B}}{z_A + z_B + 3z_{A_2B}} \tag{11}$$

with

$$1 = z_A + z_B + z_{A_2B} \tag{12}$$

The equilibrium temperature is subsequently solved from Eq. (1) through an iterative procedure while $\Delta H^{\text{cpx}}_{A_2B}$ and $\Delta S^{\text{cpx}}_{A_2B}$ are specified and $T_{mi}$, $\alpha_{A_2B}$, and $\Delta H^{\text{fus}}_{A_2B}$ are evaluated by the method described in the previous section. With an optimization algorithm, the optimal values of $\Delta H^{\text{cpx}}_{A_2B}$ and $\Delta S^{\text{cpx}}_{A_2B}$ are obtained by minimizing the average absolute deviation (AAD) of calculated equilibrium temperatures over the entire range of liquidus line.

$$\text{AAD} = \frac{100}{n_p}\sum_{j=1}^{n_p}\frac{|T_j^{\text{calc}} - T_j^{\text{expt}}|}{T_j^{\text{expt}}} \tag{13}$$

After optimization, the "true" melting point of complex $A_2B$ is readily determined from Eq. (7). The calculated results from the ICM and the RSCM are listed in Table 6, where the results of the ICM for *m*-cresol + ethylenediamine are taken from Lee et al. (3). Figures 2 and 3 illustrate comparisons of calculated and experimental values for *m*-cresol + *p*-cresol and *m*-cresol + ethylenediamine systems, respectively. It appears that both the ICM and the RSCM correlate those SLE data to within reasonable accuracy, while relatively large errors are exhibited around the regions near the eutectic points.

For the *p*-cresol (A) + ethylenediamine (B) binary system, the mixture is considered to be a quaternary system containing A, B, $A_2B$, and $A_6B$. The "true" mole fraction of a mixture is determined from the following simultaneous equations:

$$K_{A_2B} = \frac{z_{A_2B}\alpha_{A_2B}}{(z_A\alpha_A)^2(z_B\alpha_B)} \tag{14}$$

TABLE 6
Results of the SLE Calculations from the ICM and the RSCM Models for the Binary Systems[a]

| Mixture (A) + (B) | Complex $i$ | $T_{mi}$ (K) | $-\Delta H_i^{cpx}/R$ (K) | $-\Delta S_i^{cpx}/R$ | AAD[b] (%) |
|---|---|---|---|---|---|
| | | *ICM* | | | |
| Ethylenediamine + *m*-cresol[c] | $AB_2$ | 364.2 | 722.47 | 0.124 | 1.2 |
| Ethylenediamine + *p*-cresol[c] | $AB_2$ | 422.5 | 950.00 | 0.900 | 0.8 |
| | $AB_6$ | 512.2 | 1040.00 | 0.710 | |
| *p*-Cresol + *m*-cresol | $AB_2$ | 427.0 | 2001.12 | 6.504 | 0.8 |
| | | *RSCM* | | | |
| Ethylenediamine + *m*-cresol | $AB_2$ | 368.2 | 612.81 | 0.309 | 1.7 |
| Ethylenediamine + *p*-cresol | $AB_2$ | 421.6 | 950.00 | 0.900 | 0.8 |
| | $AB_6$ | 509.2 | 1040.00 | 0.710 | |
| *p*-Cresol + *m*-cresol | $AB_2$ | 436.8 | 1562.24 | 5.526 | 0.4 |

[a] Experimental data source for *p*-cresol and *m*-cresol.: Lee and Chi (2).

[b] $\text{AAD}\,(\%) = \dfrac{100}{n_p}\displaystyle\sum_{j=1}^{n_p}\dfrac{|T_j^{calc} - T_j^{expt}|}{T_j^{expt}}$.

[c] Calculated results have appeared in Lee et al. (3).

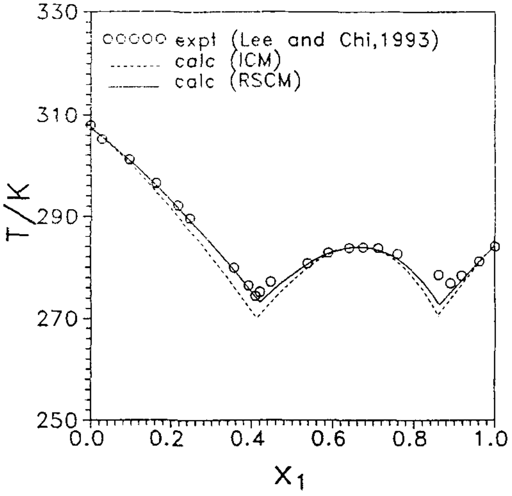

FIG. 2 Phase boundary of *m*-cresol + *p*-cresol system.

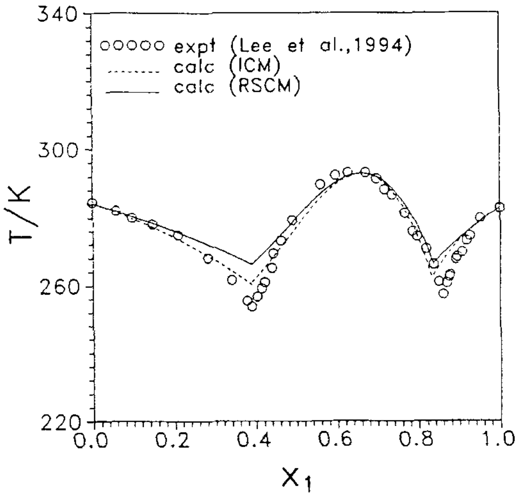

FIG. 3 Phase boundary of *m*-cresol + ethylenediamine system.

$$K_{A_6B} = \frac{z_{A_6B}\alpha_{A_6B}}{(z_A\alpha_A)^6(z_B\alpha_B)} \tag{15}$$

$$x_A = \frac{z_A + 2z_{A_2B} + 6z_{A_6B}}{z_A + z_B + 3z_{A_2B} + 7z_{A_6B}} \tag{16}$$

$$1 = z_A + z_B + z_{A_2B} + z_{A_6B} \tag{17}$$

with

$$\ln K_{A_2B} = \frac{-\Delta H^{cpx}_{A_2B}}{RT} + \frac{\Delta S^{cpx}_{A_2B}}{R} \tag{18}$$

$$\ln K_{A_6B} = \frac{-\Delta H^{cpx}_{A_6B}}{RT} + \frac{\Delta S^{cpx}_{A_6B}}{R} \tag{19}$$

The model parameters $\Delta H^{cpx}_{A_2B}$, $\Delta S^{cpx}_{A_2B}$, $\Delta H^{cpx}_{A_6B}$, and $\Delta S^{cpx}_{A_6B}$ are determined by an algorithm similar to the one described above. The calculated results are presented in Table 6 where the results of the ICM are those reported by Lee et al. (3). Figure 4 shows that the agreement between calculated and experimental liquidus lines is generally good except for the region around the last eutectic point, and the calculated results from these two models are not much different. The optimized parameters determined

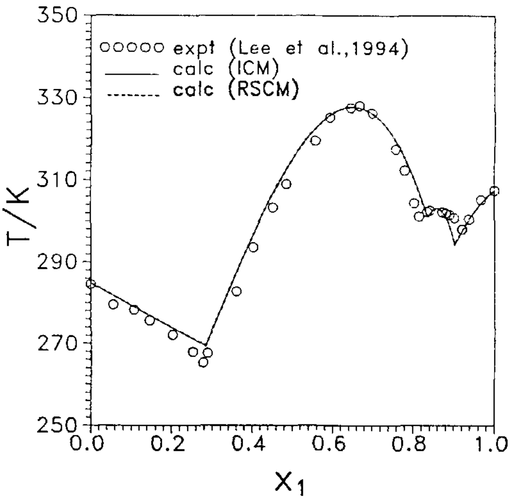

FIG. 4 Phase boundary of *p*-cresol + ethylenediamine system.

from the binary SLE data are useful for predicting the SLE behavior of the multicomponent system.

## Prediction for Ternary System

As noted earlier, four complexes [(*m*-cresol)$_2$–*p*-cresol ($A_2B$), (*m*-cresol)$_2$–ethylenediamine ($A_2C$), (*p*-cresol)$_2$–ethylenediamine ($B_2C$), and (*p*-cresol)$_6$–ethylenediamine ($B_6C$)] may form in the ternary solution of *m*-cresol (A) + *p*-cresol (B) + ethylenediamine (C). The "true" compositions in the mixture are solved from the following simultaneous equations:

$$K_{A_2B} = \frac{z_{A_2B}\alpha_{A_2B}}{(z_A\alpha_A)^2(z_B\alpha_B)} \tag{20}$$

$$K_{A_2C} = \frac{z_{A_2C}\alpha_{A_2C}}{(z_A\alpha_A)^2(z_C\alpha_C)} \tag{21}$$

$$K_{B_2C} = \frac{z_{B_2C}\alpha_{B_2C}}{(z_B\alpha_B)^2(z_C\alpha_C)} \tag{22}$$

$$K_{B_6C} = \frac{z_{B_6C}\alpha_{B_6C}}{(z_B\alpha_B)^6(z_C\alpha_C)} \tag{23}$$

with

$$z_A + z_B + z_C + z_{A_2B} + z_{A_2C} + z_{B_2C} + z_{B_6C} = 1 \tag{24}$$

$$x_A = \frac{z_A + 2z_{A_2B} + 2z_{A_2C}}{z_A + z_B + z_C + 3z_{A_2B} + 3z_{A_2C} + 3z_{B_2C} + 7z_{B_6C}} \tag{25}$$

and

$$x_B = \frac{z_B + z_{A_2B} + 2z_{B_2C} + 6z_{B_6C}}{z_A + z_B + z_C + 3z_{A_2B} + 3z_{A_2C} + 3z_{B_2C} + 7z_{B_6C}} \tag{26}$$

The chemical equilibrium constants, $K_i$s, at a given $T$ are evaluated from Eq. (2) with the optimized parameters reported in Table 6.

In the SLE calculation, solid component $i$ is dependent on the apparent composition of the feed. A congruently melting solid is produced through a crystallization process if the apparent composition is located within regions "D," "E," "F," and "G" as shown in Fig. 1. By using the ICM and the RSCM along with the determined model parameters, the solid-disappearance temperature of a ternary mixture can be predicted from Eq. (1) via the following procedure:

(a) Determine the compound of solid formation (component $i$) with the aid of Fig. 1.
(b) Assume an equilibrium temperature $T$.
(c) Calculate the chemical equilibrium constants at $T$.
(d) Guess the "true" mole fractions, $z_k$s.
(e) Calculate the "true" activity coefficients ($\alpha_k = 1$ for the ICM or $\alpha_k$s are evaluated from the regular solution model for the RSCM).
(f) Solve the system of simultaneous equations (Eqs. 20–26) to obtain new $z_k$s.
(g) Check the convergence of $z_k$s. If $z_k$s do not converge, go to Step (e) and use the new $z_k$s.
(h) Introduce $T_{mi}$, $\Delta H_i^{\text{fus}}$, $z_i$, and $\alpha_i$ into Eq. (1) and calculate the new $T$.
(i) Check the convergence of $T$. If $T$ does not converge, go to Step (c) with the new $T$.

The deviations of predicted equilibrium temperatures for the pseudo-binary systems were presented in Tables 1–4. Table 7 shows that the results from the RSCM (grand AAD = 3.6%) is slightly better than those from the ICM (grand AAD = 4.2%). Figure 5 compares the experimental equilibrium temperatures with those predicted from the RSCM. Similar

TABLE 7
Predicted Results for the Ternary System *m*-Cresol + *p*-Cresol + Ethylenediamine

| *m*-Cresol:*p*-cresol | $n_p$ | ICM AAD[a] (%) | RSCM AAD[a] (%) |
|---|---|---|---|
| 2:8 | 24 | 4.3 | 4.5 |
| 3:7 | 30 | 5.2 | 4.4 |
| 4:6 | 20 | 7.3 | 5.2 |
| 5:5 | 17 | 5.3 | 4.4 |
| 7:3 | 15 | 2.7 | 2.3 |
| 8:2 | 15 | 2.1 | 2.7 |
| 4:6[b] | 6 | 1.8 | 2.2 |
| 3:7[c] | 7 | 4.5 | 3.3 |
| Total $n_p$ | 134 | | |
| Grand AAD (%) | | 4.2 | 3.6 |

[a] $\mathrm{AAD}(\%) = \frac{100}{n_p} \sum_{j=1}^{n_p} \frac{|T_j^{\mathrm{calc}} - T_j^{\mathrm{expt}}|}{T_j^{\mathrm{expt}}}$.

[b] Ethylenediamine:*p*-cresol.

[c] Ethylenediamine:*m*-cresol.

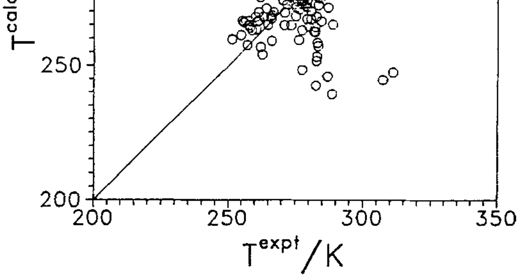

FIG. 5 Comparison of the predicted equilibrium temperatures from the RSCM with the experimental values for the ternary system.

to the binary systems, the predictions become worse around the eutectic regions, especially for the pseudo-binary system of *m*-cresol:*p*-cresol = 4:6 due to the complexity of the liquidus line.

## CONCLUSION

The solid–liquid equilibrium behavior was observed for the ternary system composed of *m*-cresol, *p*-cresol, and ethylenediamine at temperatures ranging from 251 to 321 K. The phase equilibrium diagram determined from the observations provided us with favorable operating conditions for separating *m*-cresol and *p*-cresol by using ethylenediamine as a neutralizing agent. This study also showed that the RSCM correlated well with the binary data and was capable of estimating the SLE phase boundaries of the ternary system to within reasonable accuracy, except for the region near the eutectic points. The models developed are useful for separation process design.

## ACKNOWLEDGMENT

Financial support from the National Science Council, ROC (NSC84-2214-E011-003), is gratefully acknowledged.

## NOTATION

| | |
|---|---|
| $a$ | activity |
| $AB_2$ | 1–2 congruently melting compound |
| $AB_6$ | 1–6 congruently melting compound |
| $c$ | number of components |
| $H$ | enthalpy ($J \cdot mol^{-1}$) |
| $K$ | equilibrium constant of complex formation |
| $m$, $n$ | constants |
| $n_p$ | total number of data points |
| $R$ | gas constant ($J \cdot mol^{-1} \cdot K^{-1}$) |
| $S$ | entropy ($J \cdot mol^{-1} \cdot K^{-1}$) |
| $T$ | solid-disappearance temperature (K) |
| $T_m$ | melting temperature (K) |
| $T_{mAB_2}$ | "true" melting temperature for $AB_2$ (K) |
| $T'_{mAB_2}$ | apparent melting temperature for $AB_2$ (K) |
| $V$ | liquid molar volume ($cm^3 \cdot mol^{-1}$) |
| $x$ | (apparent) mole fraction |
| $z$ | "true" mole fraction |

| | |
|---|---|
| $\alpha$ | "true" activity coefficient |
| $\delta$ | solubility parameter $(\mathrm{J \cdot cm^{-3}})^{0.5}$ |

### *Superscripts*

| | |
|---|---|
| calc | calculated value |
| cpx | complex formation |
| expt | experimental value |
| fus | fusion |
| sub | sublimation |

### *Subscripts*

| | |
|---|---|
| $i$ | component $i$ |

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*Received by editor April 6, 1995*