

# Vapor-Liquid Equilibrium Modeling of Associated Systems using a Linear Solvatochromic Approach

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## Abstract

A modified linear solvation energy relation (LSER) has been proposed to estimate the properties and vapor-liquid equilibria (VLE) of associated systems. The model combines the solvatochromic parameters of solvation energy of solution with the thermodynamic factors derived from a group contribution method, i.e., the UNIFAC-original activity coefficient model. The reliability of the model has been analyzed against the VLE data of three alcohol-containing binary systems given in the literature, namely, methyl propanoate + 1-butanol (I), 1-butanol + 2-methyl-1-butanol (II) and cumene + benzyl alcohol (III), where system III exhibits extremely nonideal behaviors. The proposed log-basis equation (METLER) is expected to be an improvement in data fit clarifying the simultaneous impact of hydrogen bonding, solubility and thermodynamic factors of components on vapor-liquid equilibria. The model matches the experimental data reasonably over the entire composition range, yielding a mean relative error of 9.6 % for all the systems considered.

**Key Words:** Vapor-liquid equilibria; Associated system; Modified LSER model

## Lineer Solvatokromik Yaklaşımı ile Asosiye Sistemlerin Buhar-Likid Dengesinin Modellenmesi

### Özet

Alkol veya benzeri *H*-bağ oluşumuna yatkın komponentler içeren asosiye bir karışımın buhar-sıvı dengesi ve sistem özelliklerini tanımlayabilecek modifiye lineer solvatokromik yaklaşımı (METLER) teklif edilmektedir. Lineer serbest enerji prensibine dayalı bu modelde UNIFAC orijinli termodinamik faktörler, çözünürlük ve solvatokromik parametreler yer almaktadır. Model güvenilirlik analizi ise, alkol kapsamlı asosiye ikili karışımları temsilen üç nümerik örnek ile değerlendirilmiştir, sırası ile, metil propanoat + 1-butanol (I), 1-butanol + 2-metil-1-butanol (II) ve izopropil benzen (kumen) + benzil alkol (III). Teklif edilen METLER modeli, aşırı ve düzensiz sapmaların gözlemlendiği III. sistem de dahil olmak üzere tüm deneysel buhar-sıvı denge verilerini ortalama % 9.6 hassasiyetle temsil etmektedir.

**Anahtar Sözcükler:** Buhar-sıvı dengesi; Asosiye sistem; Modifiye LSER modeli

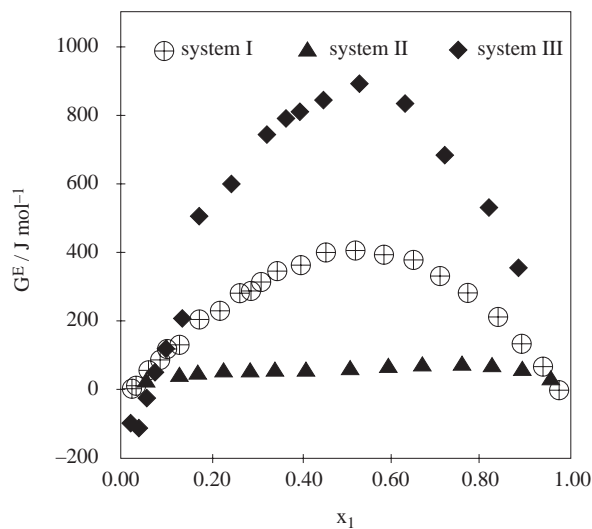
## Introduction

Modeling the thermodynamic properties and phase equilibria of a mixture involving associating components capable of hydrogen bonding such as alcohols remains a challenging problem since such systems show extremely nonideal behavior. Many attempts have been made to describe the vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) of alcohol-containing mixtures using the concept of multiscale association (Brandani and Evangelista, 1987), as well as applying a generalized solvatochromic approach with linear solvation energy relationship, LSER (Kamlet et al., 1988; Marcus, 1991). Theoretically-based approaches such as NRTL and UNIQUAC activity coefficient models (Prausnitz et al., 1980), ASOG (Tochigi et al., 1990) and UNIFAC-Dortmund (Gmehling et al., 1993) group-contribution methods, and Peng-Robinson and Redlich-Known-Soave cubic equations of state (EOS) derived from molecular-statistical theory, have been applied widely to these systems. Apart from these methods, there are three basic versions of EOS, including the family of “chemical interaction” equations which are expected to improve the accuracy of phase equilibrium calculations for systems with multiple associating sites, i.e., the associated perturbed anisotropic chain theory (APACT), the statistical associating fluid theory (SAFT), and the lattice quasichemical hole model (HM) (Economou and Donohue, 1992; Prikhodko et al., 1997).

The group contribution methods can estimate quantitatively the VLE behavior of associating systems using many temperature- and density-dependent adjustable parameters, but the strong local composition effects caused by hydrogen bonding and dipole-dipole interactions are not accounted for explicitly in the models. Many of these problems can be eliminated by combining the group-contribution concepts with the linear free energy principle. In this study, attempts have been made to estimate the properties and vapor-liquid equilibria of associated mixtures on the basis of a newly proposed approach, METLER (modified expansion terms for linear energy relation), which combines the modified solvatochromic parameters of LSER with the thermodynamic factors (of activity coefficients) derived from UNIFAC-original model (Fredenslund et al., 1977) in a relation including expansion terms.

## Testing Binary Systems

The model consistency was tested against the isobaric VLE data for the alcohol-containing binary systems, methyl propanoate + 1-butanol (I) at 101.32 kPa (Susial and Ortega, 1993), 1-butanol + 2-methyl-1-butanol (II) at 100 kPa (Aucejo et al., 1994) and cumene + benzyl alcohol (III) at 10 kPa (Resa et al., 1994), respectively. All the mixtures exhibit positive deviations from ideality with a range that may be attributed to interactions leading to the formation of various associated aggregates. Observed nonideal behavior is indicative of the magnitude of experimental activity coefficients  $\gamma_i$ , as well as of the variation of excess Gibbs function,  $G^E$ , with composition, as depicted in Figure 1. The obtained  $G_{\max}^E$  values for systems I, II and III are 400, 70 and 885 J·mol<sup>-1</sup>, respectively. Owing to the need for limiting the scope of this work, only three systems will be thoroughly evaluated representing both the association through hydrogen-bond formation (systems I and II) and dipole-dipole (or induced dipole) interaction between aromatic  $\pi$  system and the substituent of aromatic ring (system III).



**Figure 1.** Variation of excess Gibbs energy,  $G^E$ , with liquid phase composition  $x_1$ : I, methyl propanoate (1) + 1-butanol (2); II, 1-butanol (1) + 2-methyl-1-butanol (2); III, cumene (1) + benzyl alcohol (2)

Referring to Figure 1, it will be observed that the largest deviation is found for the mixture cumene + benzyl alcohol, reflecting probably a strong dipole-dipole (or induced dipole) interaction of components

(dipole moments,  $\mu = 5.67 \times 10^{-12}C \cdot m$  for benzyl alcohol and  $\mu = 2.64 \times 10^{-12}C \cdot m$  for cumene; Reid et al., 1987; Riddick et al., 1986) accompanying the multiple associating effects at the substituent and aromatic ring (aromatic  $\pi$  system) of benzyl alcohol; i.e., for aromatics with substituents that are strong  $\pi$ -electron donors to the aromatic ring, it is suggested the multiple hydrogen bonding effects at substituent and ring appear. In fact, the solvatochromic parameters of  $H$ -bond formation for benzyl alcohol are evaluated by summations of those for benzene and methanol (Table 2). The same remark holds for cumene including propane and benzene in the structure. At a composition range of a dilute cumene solution, an extremely divergent behavior, that of changing from the negative region to the positive one, is observed, which may be attributed to an association between a cumene molecule and a “packet”-like aggregated segment of alcohol molecules. The segment structure is presumably deactivated at a lower alcohol composition range. The Gibbs function  $G^E$  for systems I and II is remarkably smaller, indicating that the weaker interactive forces through hydrogen bonding appear in both systems with the interaction effect slightly predominant in the more polar ester + alcohol mixture ( $\mu = 5.80 \times 10^{-12}C \cdot m$  for methyl propanoate and  $\mu = 5.54 \times 10^{-12}C \cdot m$  for 1-butanol), as compared to the mixture of two alcohols ( $\mu = 5.67 \times 10^{-12}C \cdot m$  for 2-methyl-1-butanol).

### Thermodynamic Factors by UNIFAC-original Model

In the design practice of distillation applying a new class rate based algorithm, thermodynamic factors,  $\Gamma_L^{ij}$ , are essential for considering the liquid phase nonideality of the mixture. The definition of  $\Gamma_L$  for a  $n$ -component system is given by Taylor and Kooijman (1991). Mori et al. (1996) extended the application of this approach to ASOG and UNIFAC-Dortmund group contribution methods.

$$\Gamma_L^{ij} = \delta_{ij} + x_i \left. \frac{\partial(\ln \gamma_i)}{\partial x_j} \right|_{T,P,\Sigma} \quad (1)$$

where the symbol  $\Sigma$  (constrained condition) means that the differentiation with respect to liquid-phase composition  $x_j$  is to be carried out while keeping all other mole fractions  $x_k$  ( $k \neq j$ ,  $k = 1 \dots n - 1$ ) constant except the  $n$ th, and  $\delta_{ij}$  is the Kronecker delta, 1 if  $i = j$ , and 0 if  $i \neq j$ . The mole fraction of species  $n$  must be eliminated making use of the fact that the  $x_i$  sum to unity, when the partial derivative

of  $\ln \gamma_i$  is evaluated. For a two-component system  $\Gamma_L$  is obtained from Eq. (1) as follows:

$$\Gamma_L = 1 + x_1 \left. \frac{\partial(\ln \gamma_1)}{\partial x_1} \right|_{\Sigma} \quad (2)$$

The constrained (by  $\sum_i x_i = 1$ ) partial derivative of  $\ln \gamma_1$  needed in the evaluation of  $\Gamma_L$  is related to the unconstrained derivatives by

$$\left. \frac{\partial(\ln \gamma_1)}{\partial x_1} \right|_{\Sigma} = \left. \frac{\partial(\ln \gamma_1)}{\partial x_1} \right|_{x_2} - \left. \frac{\partial(\ln \gamma_1)}{\partial x_2} \right|_{x_1} \quad (3)$$

The application of Eq. (2) to ASOG and UNIFAC-Dortmund models has been described elsewhere (Senol, 1998). In this study,  $\Gamma_L$  values estimated from the UNIFAC-original model (Fredenslund et al., 1977, Gmehling et al., 1982) using the residual  $\gamma_i$  approach of Mori will be thoroughly evaluated. For proceeding the UNIFAC-original algorithm, the following unconstrained  $\gamma_i$  derivatives in terms of the combinatorial part and a slightly modified approach of Mori et al. (1996) for the residual one should be used.

$$\begin{aligned} \left. \frac{\partial(\ln \gamma_i^C)}{\partial x_j} \right|_{T,P,\bar{\Sigma}} = & -V_j + 5q_i(V_j - F_j) + \quad (4) \\ & + V_i(V_j \sum x_j l_j - l_j) \end{aligned}$$

where,

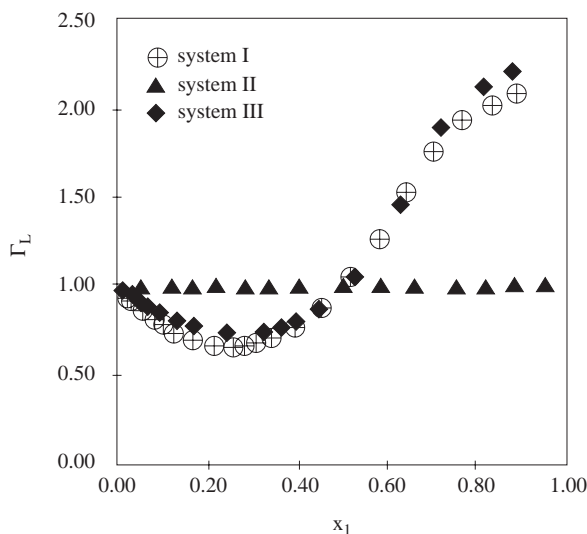
$$\begin{aligned} V_i = \frac{\Phi_i}{x_i} = \frac{r_i}{\sum_j r_j x_j}; \quad F_i = \frac{\theta_i}{x_i} = \frac{q_i}{\sum_j q_j x_j}; \\ l_i = 5(r_i - q_i) - r_i + 1 \quad (4a) \end{aligned}$$

$\bar{\Sigma}$  means the unconstrained  $\gamma_i$  derivatives when all the  $x_n$  ( $n \neq j$ ) are kept constant, and  $r_i$  and  $q_i$  are the UNIFAC parameters. The variation of  $\Gamma_L$  with composition is shown in Figure 2.

### Fitting VLE Data by METLER

The vapor phase mole fraction ( $y_1$ ), the boiling temperature of mixture (T/K), and the ratio of activity coefficients data, defined as  $Pr$ , can be fitted using a log - basis equation consisting of two liquid phase-composition depended parts, i.e., the part accounting for the properties at the composition limits ( $Pr_o$ ), and the second one, considering the influence

of an overall interaction in liquid phase and its non-ideality, covering the expansion terms with respect to the thermodynamic factor ( $\Gamma_L$ ), the Hildebrand solubility parameter ( $\delta_H/(\text{J}\cdot\text{cm}^{-3})^{0.5}$ ), and the modified solvatochromic parameters  $\pi'$ ,  $\alpha'$ , and  $\beta'$ .



**Figure 2.** Variation of thermodynamic factors,  $\Gamma_L$ , with liquid phase mole fraction  $x_1$ : I, methyl propanoate (1) + 1-butanol (2); II, 1-butanol (1) + 2-methyl-1-butanol (2); III, cumene (1) + benzyl alcohol (2)

$$Pr = Pr_o + \prod_i x_i \times \sum_k (C_{\Gamma,k}(\Gamma_L)^k + C_{H,k}(\delta'_H)^k + C_{\pi,k}(\pi')^k + C_{\beta,k}(\beta')^k + C_{\alpha,k}(\alpha')^k) \quad (5)$$

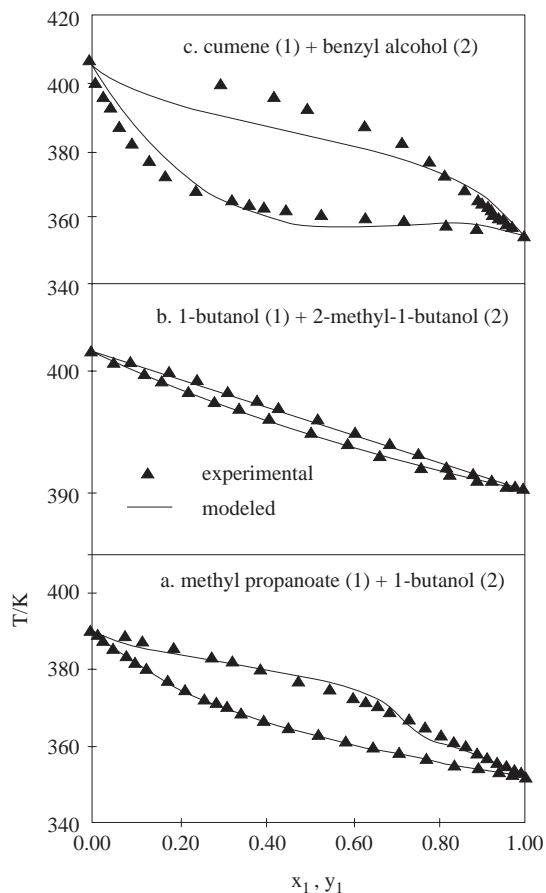
in which the modified terms are evaluated as follows:

$$\delta'_H = \delta_{H,1} \times \delta_{H,m}/1000; \quad \pi' = (\pi_1 - 0.35\delta_1) \times \pi_m; \\ \beta' = \beta_1 \times \beta_m; \quad \alpha' = \alpha_1 \times \alpha_m \quad (6)$$

Estimates were performed assuming the degree of expansion  $k = 1$ . Index “1” designates the light component properties. The subscript “ $m$ ” denotes the parameters related to the mixture in terms of  $x$  composition, assuming the following additional parameter estimation rule:

$$\delta_{H,m} = \sum_i x_i \delta_{H,i}; \quad \pi_m = \sum_i x_i (\pi_i - 0.35\delta_i); \\ \beta_m = \sum_i x_i \beta_i; \quad \alpha_m = \sum_i x_i \alpha_i \quad (7)$$

$\delta_H$  is the Hildebrand solubility parameter.  $\pi$  and  $\delta$  are the solvatochromic parameters that measure the component dipolarity/polarizability, i.e., the dipole-dipole and dipole-induced dipole interactions of component in mixture, respectively. The hydrogen-bonding terms  $\alpha$  and  $\beta$  measure the  $H$ -bond donating and  $H$ -bond accepting abilities of the component, respectively (Table 1). Thus, the implication for the complementary effects of hydrogen bonding, solubility and thermodynamic factors assuming a mean value estimation rule for the solvatochromic parameters will proceed. The boiling temperatures ( $T_i$ ) at operating pressure and the constants of the Antoine vapor pressure equation for pure components are given in Table 2.



**Figure 3.** Phase diagram representation of equilibrium temperature  $T$  vs liquid-phase  $x_1$  and vapor-phase  $y_1$  mole fractions: experimental, a (Susial and Ortega, 1993), b (Aucejo et al., 1994), c (Resa et al., 1994); modeled by METLER (Eq. 5)

**Table 1.** Hildebrand Solubility Parameter ( $\delta_H$ ), and Solvatochromic Parameters of Compounds

Compound	$\pi^{a,b}$	$\beta^{a,b}$	$\alpha^{a,b}$	$\delta_H^{c,d}$ MPa <sup>0.5</sup>	$\delta^{a,b}$
methyl propanoate	0.55	0.45	0.00	18.205	0.0
1-butanol	0.40	0.45	0.33	23.300	0.0
2-methyl-1-butanol	0.40	0.45	0.33	23.532	0.0
cumene	0.51	0.12	0.00	17.400	1.0
benzyl alcohol	0.99	0.52	0.35	24.750	1.0

<sup>a</sup> Kamlet et al. (1988); <sup>b</sup> Marcus (1991); <sup>c</sup> Barton (1975); <sup>d</sup> Riddick et al. (1986).

**Table 2.** Boiling Temperatures ( $T_i$ ) at Operating Pressure and Constants of the Antoine Vapor Pressure Equation<sup>e</sup> for Pure Components

Compound	$T_i/K$	$A_i$	$B_i$	$C_i$
methyl propanoate <sup>a</sup>	351.77	15.1713	3383.33	-30.99
1-butanol <sup>a</sup>	390.23 <sup>d</sup>	15.3763 <sup>b</sup>	3253.99 <sup>b</sup>	-88.124 <sup>b</sup>
2-methyl-1-butanol <sup>b</sup>	401.55	14.8958	3107.20	-99.883
cumene <sup>c</sup>	354.05	6.37499	1671.459	-43.15
benzyl alcohol <sup>c</sup>	406.85	6.70690	1904.299	-73.15

<sup>a</sup> Susial and Ortega (1993),  $T_i$  at 101.32 kPa; <sup>b</sup> Aucejo et al. (1994),  $T_i$  at 100 kPa;

<sup>c</sup> Resa et al. (1994),  $T_i$  at 10 kPa; <sup>d</sup>  $T_i = 390.15$  K at 100 kPa;

<sup>e</sup>  $\ln(P_i^o/\text{kPa}) = A_i - B_i/(C_i + T/K)$  (Antoine equation).

The coefficients  $C_i$  of Equation (5) were obtained by the application of the multivariable regression procedures of the Linpack algorithm (Kuo, 1972; Himmelblau, 1989), using the parameters from Tables 1 and 2, and the thermodynamic factors according to the Taylor and Kooijman (1991) approach for the unconstrained derivatives of activity coefficient ( $\gamma_1$ ) applied to the UNIFAC model. The resulting  $C$  coefficients and corresponding properties ( $Pr$  - log mean) as well as a comparison with the observed performance using the root mean square deviation ( $\sigma$ ) are presented in Table 3.  $T_i(K)$  is the boiling point of pure component  $i$  at operating pressure.  $P_1^o$  and  $P_2^o$  (kPa) are the vapor pressures of pure components estimated by the Antoine equation at the normal boiling point of the light component,  $T_{b1}(K)$ .  $\gamma_1^\infty$  and  $\gamma_2^\infty$  are activity coefficients at infinite dilution estimated by the UNIFAC-original model with group-interaction parameters from Gmehling et al. (1982).

Table 4 presents a quantitative assessment of the predictions achieved for the existing model with respect to the mean relative error ( $\bar{\epsilon}$ ) and standard deviation ( $S$ ) of the properties considered, as well as a comparison with the statistical results of indi-

rectly estimated  $y_1$  depending on the modeled  $\gamma_1/\gamma_2$  value. Referring to the  $Pr$  (log-basis) definition from Table 3, the present model reproduces the  $y_1$  data with an average error  $\bar{\epsilon}(y_1) = 12.76\%$  and root mean square deviation  $\sigma(y_1) = 0.0846$ . Conversely,  $y_1$  evaluated through incorporating the predicted  $\gamma_1/\gamma_2$  by METLER into the Raoult law and neglecting pressure effect on the liquid phase fugacity, matches the experimental data less accurately with  $\bar{\epsilon}(y_1) = 16.86\%$  and  $\sigma(y_1) = 0.0915$ .

The convenience of the proposed model was also studied through a plot of the observed properties against the  $Pr$  (log-basis) estimates of Eq.(5) as defined in Table 3 in terms of liquid- and vapor-phase mole fractions  $x_1$  and  $y_1$  (Figure 3). Figure 3 illustrates that the new model coincides with the experimental results appropriately for the whole  $x$  concentration range, except for system III due to its strong divergent behavior overly sensitive to the composition range. In fact, besides the accuracy of the model prediction, an important concern is whether the proposed model actually tracks the trend of vapor liquid equilibria relative to the  $T$ ,  $y$  and  $\gamma$  properties, especially for system III divergently deviating from

ideality. However, there is no doubt that this phenomenon will have a significant impact on the implementation of a rate-based simulation algorithm incorporating the prediction by METLER. Consequently, the proposed approach, Eq. (5), reflecting the simultaneous effect of hydrogen bonding, solu-

bility and thermodynamic factors, appears to be an improvement in data fit for the associated systems. The model proved to be reasonably accurate, yielding a mean error of 9.6% for all the mixtures and properties considered.

**Table 3.** Coefficients  $C_i$  of Equation (5) and Root Mean Square Deviation  $\sigma$  Evaluated for Different Properties  $Pr$

Binary system <sup>a</sup>	$C_\Gamma$	$C_H$	$C_\pi$	$C_\beta$	$C_\alpha$
$Pr = \ln(T/K); Pr_o = \sum_i x_i \ln(T_i); \sigma(T/K)$					
methyl propanoate/1-butanol ( $\sigma = 0.1056$ )	-0.0015	0.3950 $\times 10^{-4}$	1.2667	-2.0267	0.0
1-butanol/2-methyl-1-butanol ( $\sigma = 0.1489$ )	0.7322	-0.2705 $\times 10^{-5}$	-1.0253	-1.1559	-3.1834
cumene/benzyl alcohol ( $\sigma = 4.0235$ )	0.0240	-0.2449 $\times 10^{-2}$	-1.7094	-4.0365	0.0
$Pr = \ln(y_1/y_2); Pr_o = \ln\left(\frac{x_1}{x_2}(1+q)\right); q = \left(\frac{P_2^o}{P_1^o}\right)_{T_{b1}}; \sigma(y_1)^b$					
methyl propanoate/1-butanol <sup>d,1</sup> ( $\sigma = 0.0381$ )	8.2020	-0.1839 $\times 10^{-2}$	-345.87	424.41	0.0
1-butanol/2-methyl-1-butanol <sup>d,2</sup> ( $\sigma = 0.0050$ )	9.9601	0.3085 $\times 10^{-3}$	10.523	5.7960	-121.92
cumene/benzyl alcohol <sup>d,3</sup> ( $\sigma = 0.2109$ )	1.2617	0.2039	-367.14	901.22	0.0
$Pr = \ln(\gamma_1/\gamma_2); Pr_o = x_2 \ln(\gamma_1^\infty) - x_1 \ln(\gamma_2^\infty); \sigma(\gamma_1/\gamma_2)^c$					
methyl propanoate/1-butanol ( $\sigma = 0.4890$ )	-2.0045	0.1195 $\times 10^{-2}$	206.33	-256.41	0.0
1-butanol/2-methyl-1-butanol ( $\sigma = 0.1619$ )	103.90	0.2670 $\times 10^{-2}$	92.799	33.013	-1146.9
cumene/benzyl alcohol ( $\sigma = 0.6780$ )	0.8649	0.9644 $\times 10^{-2}$	-0.8404	31.682	0.0

<sup>a</sup> Binaries are presented as component (1) / component (2); <sup>b</sup>  $P_1^o$  and  $P_2^o$  are the vapor pressures of pure components estimated by the Antoine equation at  $T_{b1}$ , kPa; <sup>c</sup>  $\gamma_1^\infty$  and  $\gamma_2^\infty$  are activity coefficients at infinite dilution estimated by UNIFAC-original, <sup>d</sup> For  $Pr = y_1$  and  $Pr_o = x_1$  the coefficients are: 1.  $C_\Gamma = 0.465$ ,  $C_H = -0.269 \times 10^{-3}$ ,  $C_\pi = -42.104$ ,  $C_\beta = 57.73$ , ( $\sigma(y) = 0.0085$ ); 2.  $C_\Gamma = 9.235$ ,  $C_H = -0.283 \times 10^{-3}$ ,  $C_\pi = 10.89$ ,  $C_\beta = 8.167$ ,  $C_\alpha = -112.34$ , ( $\sigma(y) = 0.0113$ ); 3.  $C_\Gamma = -0.081$ ,  $C_H = 0.023$ ,  $C_\pi = -404.71$ ,  $C_\beta = 733.12$ , ( $\sigma(y) = 0.174$ )

**Table 4.** Comparison of Mean Errors  $\bar{e}(\%)^a$ , and Standard Deviations  $S$  Obtained in the Prediction of Properties ( $T, y_1$  and  $\gamma_1/\gamma_2$ ) by METLER

System	$T/K$		$y_1^b$		$\gamma_1/\gamma_2$	
	$\bar{e}, \%$	$S$	$\bar{e}, \%$	$S$	$\bar{e}, \%$	$S$
methyl propanoate/1-butanol	0.02	0.1080	10.95	0.0389	25.99	0.50
1-butanol/2-methyl-1-butanol	0.03	0.1545	1.18	0.0052	13.55	0.168
cumene/benzyl alcohol	0.93	4.1473	26.14	0.2174	8.02	0.697

<sup>a</sup>,  $\bar{e}(Q) = (100/N) \sum_{N=1}^N |(Q_{\text{exp}} - Q_{\text{cal}})/Q_{\text{exp}}|$  where  $Q \equiv T, y_1$  or  $\gamma_1/\gamma_2$  and a modeled value due to the  $Pr$  (log-basis) definition from Table 3; <sup>b</sup> for the estimated  $y_1$  in terms of Raoult law including the modeled  $\gamma_1/\gamma_2$  by METLER, the mean error and standard deviation of  $y_1$  are defined as:  $\bar{e}\% = 13.56$  and  $S = 0.0422$  (system I),  $\bar{e}\% = 6.91$  and  $S = 0.0224$  (system II), and  $\bar{e}\% = 30.10$  and  $S = 0.218$  (system III), respectively.

**Nomenclature**

$C$	: constant, Eq.(5)
$\bar{\epsilon}$	: mean relative error (%)
$G^E$	: excess Gibbs energy (J/mol)
$P^o$	: vapor pressure of pure component (kPa)
$Pr$	: property as defined in Table 3 and Eq. (5)
$Pr_o$	: property as defined in Table 3 and Eq. (5)
$Q$	: referred to quantities given in Table 4
$S$	: standard deviation, Table 4
$T$	: equilibrium temperature (K)
$T_b$	: normal boiling point of component (K)
$x$	: liquid-phase mole fraction
$y$	: vapor-phase mole fraction

**Greek letters**

$\alpha'; \alpha$	: solvatochromic parameters, Eq. (6)
$\beta'; \beta$	: solvatochromic parameters, Eq. (6)
$\Gamma_L$	: thermodynamic factor
$\gamma_i$	: activity coefficient of component $i$
$\delta$	: solvatochromic parameter, Eq. (6)
$\delta_L$	: Hildebrand solubility parameter (MPa <sup>0.5</sup> )
$\delta_{ij}$	: Kronecker delta, 1 for $i = j$ , 0 for $i \neq j$
$\mu$	: dipole moment (C·m)
$\pi'; \pi$	: solvatochromic parameters, Eq. (6)
$\sigma$	: root-mean-square-deviation

**Subscript**

m	: mixture
cal	: calculated
exp	: experimental

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