



**HAL**  
open science

# Modeling of highly nonideal systems: 1. A generalized version of the NRTL equation for the description of low-pressure equilibria

Evelyne Neau, Joan Escandell, Christophe Nicolas

## ► To cite this version:

Evelyne Neau, Joan Escandell, Christophe Nicolas. Modeling of highly nonideal systems: 1. A generalized version of the NRTL equation for the description of low-pressure equilibria. *Industrial and engineering chemistry research*, 2010, 49 (16), pp.7580-7588. 10.1021/ie100121c . hal-01025255

**HAL Id: hal-01025255**

**<https://hal.science/hal-01025255v1>**

Submitted on 29 Dec 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Modeling of Highly Nonideal Systems: 1. A Generalized Version of the NRTL Equation for the Description of Low-Pressure Equilibria

Evelyne Neau,<sup>\*,†</sup> Joan Escandell,<sup>†</sup> and Christophe Nicolas<sup>‡</sup>

Laboratory M2P2, UMR 6181, and Laboratory LMGEM, UMR 6117, University of Méditerranée, Faculty of Sciences of Luminy, 13288 Marseille, France

The topic of the present work is the development of a simple model for the description of phase equilibria occurring in nonideal systems, such as those containing size-asymmetric components or mixtures made of polar or associating compounds with hydrocarbons, that are capable of strong demixing. The generalized NRTL model presented in this first part derives from the lattice two-fluid theory and differs from the original model by considering the size asymmetry of mixture components; results obtained for the modeling of phase equilibria in hydrocarbon, polar, and highly immiscible systems are compared with other literature models, such as the van Laar, NRTL, and UNIQUAC models. In the second part of this work, this model is associated with the Peng–Robinson EoS using the EoS/ $G^E$  approach based on a generalized reference state, and a new group contribution is proposed for the prediction of the binary interaction parameters.

## 1. Introduction

The topic of the present article is the development of a new excess Gibbs energy model for the description of phase equilibria in highly nonideal systems, such as those containing size-asymmetric components or mixtures made of polar substances or water with hydrocarbons that are capable of strong demixing. These systems are of great interest not only in chemical engineering under atmospheric conditions, but also for process design under high pressure; in particular, the modeling of complex systems, including petroleum fluids with associating compounds such as water or glycol, has become increasingly important with the exploitation of petroleum reservoirs under extreme conditions.

A first way to handle such systems is to consider equations of state (EoS) derived from theoretical expressions for the excess Helmholtz energy. A first category of equations is based on the association approach proposed by Wertheim,<sup>1,2</sup> among them, the SAFT (statistical associating fluid theory) model<sup>3</sup> or the CPA (cubic plus association) equation<sup>4</sup> have acquired great popularity, because of the wide range of applications involved and the satisfactory description of phase equilibria. A second class of models, especially suitable for polymers, is derived from the lattice theories of Guggenheim<sup>5</sup> and Barker,<sup>6</sup> taking into account the presence of vacant sites, or holes, and leading to Sanchez–Lacombe-type equations.<sup>7</sup> The lattice-fluid hydrogen-bonding (LFHB) model of Panayiotou and Vera<sup>8,9</sup> and, in particular, the predictive quasichemical group contribution equation of state (QC-GCEoS) model of Smirnova and Victorov<sup>10</sup> allow very successful estimations of phase equilibria in mixtures containing associating components.

An alternative method for modeling these complex mixtures is to consider the EoS/ $G^E$  approach, which assumes that, in a given reference state, the excess properties estimated from an EoS are equal to those obtained from a “low-pressure” excess Gibbs energy model,  $G^E$ . This assumption should, in principle, allow for the definition of more physically meaningful EoS mixing rules on the condition that liquid solution models be

appropriate to the description of the mixture considered. Two approaches are usually associated with cubic EoS. In the first, excess Gibbs energy parameters previously determined at low pressure using the activity coefficient technique are directly introduced into the EoS; the most popular mixing rules thus obtained are MHV1<sup>11</sup> (modified Huron–Vidal first-order), MHV2<sup>12</sup> (modified Huron–Vidal second-order), Wong–Sandler,<sup>13</sup> and LCVM<sup>14</sup> (linear combination of Vidal and Michelsen). The second approach consists of estimating the excess Gibbs energy parameters directly from the EoS, usually by means of group contribution methods; predictive models developed in this framework lead to the well-known VTPR<sup>15</sup> (volume-translated Peng–Robinson) and UMR-PRU<sup>16</sup> (universal mixing rule Peng–Robinson UNIFAC) models based on UNIFAC group contributions or to the PPR78<sup>17</sup> (predictive Peng–Robinson 1978) and NRTL-PR<sup>18–20</sup> (nonrandom two-liquids-Peng–Robinson) equations obtained from the generalized van Laar and NRTL models, respectively.

The main purpose of the first part of this work is to propose a liquid solution model based on the lattice fluid theory that is able to represent the mixing properties of size-asymmetric systems and mixtures containing polar and non polar substances. The generalized NRTL model presented herewith derives from the lattice two-fluid theory and differs from the original model by considering the differences in size and shape between mixture components. In the second part of this work,<sup>20</sup> this model is associated with the Peng–Robinson EoS using the EoS/ $G^E$  approach based on the generalized reference state,<sup>21</sup> and a new group contribution estimation is proposed for the calculation of the binary interaction parameters.

Results obtained for the modeling of phase equilibria are compared with other literature models, such as the van Laar, NRTL and UNIQUAC (universal quasichemical) models. The knowledge of the strong points and limitations of each low-pressure  $G^E$  model is crucial for the further development of equations of state based on the EoS/ $G^E$  concept. Indeed, the use of an EoS will neither cancel the theoretical limitations inherent in a given equation nor improve its ability to describe mixing properties.

\* To whom correspondence should be addressed. E-mail: evelyne.neau@univmed.fr.

<sup>†</sup> Laboratory M2P2, UMR 6181.

<sup>‡</sup> Laboratory LMGEM, UMR 6117.

## 2. Generalized NRTL Model

Lattice models suggest that deviations from ideality in liquid solutions are due to the two main following effects: First, the differences in size and shape between molecules give rise to a nonideal entropy of mixing described as the combinatorial part. Second, the different forces of attraction between molecules are responsible for mixing energies and entropic effects, called the residual part. The Helmholtz energy of mixing at constant volume,  $A^{\text{MV}}$ , is expressed as

$$A^{\text{MV}} = -TS^{\text{MV}} + U^{\text{MV}} \quad (1)$$

which leads to the excess Helmholtz energy at constant volume

$$A^{\text{EV}} = -TS^{\text{EV}} + U^{\text{EV}} \quad \text{with} \quad S^{\text{EV}} = S^{\text{MV}} + R \sum_i n_i \ln x_i, \quad U^{\text{EV}} = U^{\text{MV}}(2)$$

where  $S^{\text{EV}}$  and  $U^{\text{EV}}$  are the excess entropy and energy, respectively, and are described in the next two sections.

**2.1. Combinatorial Part.** The entropic effects are represented by the general Staverman–Guggenheim equation for athermal mixtures of molecules of arbitrary size and shape

$$S^{\text{EV}} = -R \left( \sum_i n_i \ln \frac{\phi_i}{x_i} + \frac{z}{2} \sum_i n_i q_i \ln \frac{\theta_i}{\phi_i} \right) \quad (3)$$

$\phi_i$  and  $\theta_i$  are the volume and surface fractions of a molecule  $i$ , respectively, given by

$$\phi_i = \frac{x_i r_i}{r}, \quad \theta_i = \frac{x_i q_i}{q} \quad \text{with} \quad r = \sum_l x_l r_l, \quad q = \sum_l x_l q_l \quad (4)$$

where  $r_i$  and  $q_i$  are the volume and surface area factors, respectively, and  $z$  is the coordination number, usually fixed as  $z = 10$ .

**2.2. Residual Part.** As described by Guggenheim<sup>5</sup> and Prausnitz et al.,<sup>22</sup> the energy of mixing can be expressed as

$$U^{\text{EV}} = U^{\text{MV}} = U^{\text{Conf}}(T, V, n) - \sum_i U_i^{\text{Conf}}(T, V_i, n_i) \quad (5)$$

where  $U^{\text{Conf}}$  and  $U_i^{\text{Conf}}$  are the configurational energies of the mixture and pure compound  $i$ , respectively; they are estimated from the configurational energies  $U_{ji}$  and  $U_{ii}$  of the pair interactions between two nearest components of different types ( $j$  and  $i$ ) and of the same type ( $i$  and  $i$ )

$$U^{\text{EV}} = \frac{1}{2} \sum_i \sum_j N_{ji} (U_{ji} - U_{ii}) \quad \text{with} \quad N_{ji} = n_i q_i z \theta_{ji} \quad (6)$$

$N_{ji}$  is the number of pair interactions between a component  $j$  about a central molecule  $i$ ; it is calculated by assuming that a molecule  $i$  has  $q_i z$  external contacts and that  $\theta_{ji}$  is the local fraction of component  $j$  about molecule  $i$ .

The determination of  $\theta_{ji}$  is the key point of lattice theories, because it represents the probability that a contact starting from  $i$  be a  $j$ – $i$  contact. In classical models, it is estimated:

(i) Either by assuming a completely random mixture ( $G_{ji} = 1$  in eq 7), which leads to a one-fluid lattice model, such as the van Laar<sup>23,24</sup> equation.

(ii) Or, as in this work and in the NRTL,<sup>25</sup> UNIQUAC,<sup>26</sup> and Wilson<sup>27</sup> models, by using the concept of local composition

$$\frac{\theta_{ji}}{\theta_{ii}} = \frac{\theta_j G_{ji}}{\theta_i G_{ii}}, \quad G_{ji} \neq G_{ij} \quad (7)$$

$G_{ji}$  is the molecular repartition coefficient; it is assumed independent of the molar composition and is expressed by the relation

$$G_{ji} = \exp[-(z/2)\alpha_0(U_{ji} - U_{ii})/RT] \quad (8)$$

where  $\alpha_0$  is the nonrandomness factor proposed by Renon and Prausnitz for the NRTL model. The same relation is also used with the UNIQUAC or Wilson models, except that those models assume  $\alpha_0 = 1$ .

By taking into consideration the conservation equation

$$\sum_l \theta_{li} = \frac{\theta_{ii}}{\theta_i} \sum_l \theta_l G_{li} = 1 \quad (9)$$

and the definition of surface fractions  $\theta_j$  (eq 4), the local fraction  $\theta_{ji}$  (eq 7) and therefore the number  $N_{ji}$  of pair interactions (eq 6) are expressed as follows

$$\theta_{ji} = \frac{\theta_j G_{ji}}{\sum_l \theta_l G_{li}} = \frac{x_j q_j G_{ji}}{\sum_l x_l q_l G_{li}}, \quad N_{ji} = n x_i q_i z \frac{x_j q_j G_{ji}}{\sum_l x_l q_l G_{li}} \quad (10)$$

so that the excess energy at constant volume  $U^{\text{EV}}$  (eq 6) is given by the final expression

$$U^{\text{EV}} = n \sum_i x_i q_i \frac{\sum_j x_j q_j G_{ji} \Gamma_{ji}}{\sum_l x_l q_l G_{li}} \quad \text{with} \quad \Gamma_{ji} = \frac{z}{2} (U_{ji} - U_{ii}) \quad (11)$$

$\Gamma_{ji}$  represents the configurational energy required for replacing  $z/2$  pair interactions  $i$ – $i$  by  $z/2$  pair interactions  $j$ – $i$ .

By substituting, at low pressure, the molar Helmholtz excess energy at constant volume,  $A^{\text{EV}}/n$  (eq 2), by the molar excess Gibbs energy at constant pressure,  $g^{\text{E}}$ , given by

$$g^{\text{E}} = g_{\text{combinatorial}}^{\text{E}} + g_{\text{residual}}^{\text{E}} \quad (12)$$

with

$$g_{\text{combinatorial}}^{\text{E}} = -TS^{\text{EV}}/n, \quad g_{\text{residual}}^{\text{E}} = U^{\text{EV}}/n \quad (13)$$

we obtain, according to the expressions of the combinatorial term (eq 3) and the residual contribution (eq 11), the final formulation of the generalized NRTL model

$$g^{\text{E}} = RT \left[ \sum_i x_i \ln \frac{r_i}{r} + \frac{z}{2} \sum_i x_i q_i \ln \frac{q_i r}{q r_i} \right] + \sum_i x_i q_i \frac{\sum_j x_j q_j G_{ji} \Gamma_{ji}}{\sum_l x_l q_l G_{li}} \quad (14)$$

In addition, as is shown in Figure 1, the ratios  $q_i/r_i$  become rapidly constant and small for long alkane chains, so that this contribution is usually canceled in the Staverman–Guggenheim combinatorial term (eq 3), which leads to the generalized NRTL model expressed as

$$g_{\text{NRTL\_gen}}^{\text{E}} = RT \sum_i x_i \ln \frac{r_i}{r} + \sum_i x_i q_i \frac{\sum_j x_j q_j G_{ji} \Gamma_{ji}}{\sum_l x_l q_l G_{li}},$$

$$G_{ji} = \exp(-\alpha_0 \Gamma_{ji}/RT) \quad (15)$$

The interaction parameters  $\Gamma_{ji}$  are usually determined by correlating experimental vapor–liquid equilibrium (VLE) and excess enthalpy ( $h^{\text{E}}$ ) data.

The volume and surface area factors of pure compounds,  $r_i$  and  $q_i$ , respectively, are estimated from the values of the UNIFAC<sup>28</sup> subgroup parameters  $R_k$  and  $Q_k$  according to the equations

$$r_i = \sum_k \nu_{ik} R_k, \quad q_i = \sum_k \nu_{ik} Q_k \quad (16)$$

where  $\nu_{ik}$  is the number of subgroup  $k$  in a molecule  $i$ .

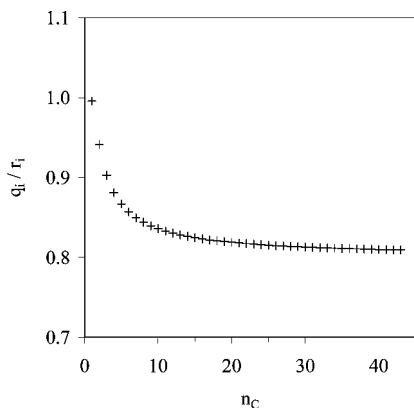
The nonrandomness factor,  $\alpha_0$  (eq 15), is assumed to be constant; it can be fixed as  $\alpha_0 = 0.2$ , as in the original NRTL model<sup>25</sup> or as  $\alpha_0 = -1$ , as suggested by Marina and Tassios<sup>29</sup> for mixtures leading to strong demixing.

### 3. Results and Discussion

The aim of the present work is to study the ability of lattice fluid models to describe nonideal systems, such as those containing size-asymmetric components and polar substances or water with hydrocarbons. For this purpose, results obtained with the proposed generalized NRTL model were compared with those of well-known literature equations, such as the van Laar, NRTL and UNIQUAC versions presented in Table 1. Examination of the various expressions of the excess Gibbs energy leads to the following conclusions:

(i) van Laar models, especially the generalized version with a combinatorial term, also called a “zeroth-order approximation of lattice models” (Guggenheim),<sup>5</sup> are close to the proposed NRTL model, except that they assume, in eqs 7 and 15, that  $G_{ji} = 1$ . Therefore, these models based on the one-fluid lattice theory presuppose that molecular interactions are sufficiently small not to disturb the random distribution of molecules.

(ii) Contrary to the other two-fluid NRTL models, the UNIQUAC equation does not estimate the Helmholtz energy,  $A^{\text{EV}}$ , directly from the excess energy (eq 2), but integrates  $U^{\text{EV}}$  with respect to the inverse of temperature,  $1/T$ , the integration constant being expressed from the excess entropy,  $-TS^{\text{EV}}$  (eq 3). This procedure yields a residual contribution,  $g_{\text{residual}}^{\text{E}}$ , rather similar to that of the Wilson equation, although the latter model



**Figure 1.** Variations of the ratio  $q_i/r_i$ , estimated from the UNIFAC model,<sup>28</sup> with respect to the length,  $n_c$ , of the alkane chain.

**Table 1.** Literature Excess Gibbs Energies Derived from the Lattice Fluid Theory

Original van Laar <sup>23,24</sup>
$g_{\text{van Laar}}^{\text{E}} = \frac{A_{21}A_{12}x_1x_2}{A_{12}x_1 + A_{21}x_2}$
Original NRTL <sup>25</sup>
$g_{\text{NRTL}}^{\text{E}} = \sum_i x_i \frac{\sum_j x_j G_{ji} \Gamma_{ji}}{\sum_l x_l G_{li}}, \quad G_{ji} = \exp(-\alpha_0 \Gamma_{ji}/RT), \quad \Gamma_{ji} \neq \Gamma_{ij}, \quad \alpha_0 = 0.2$
HV-NRTL <sup>30</sup>
$g_{\text{NRTL\_HV}}^{\text{E}} = \sum_i x_i \frac{\sum_j x_j b_j G_{ji} \Gamma_{ji}}{\sum_l x_l b_l G_{li}}$
Generalized van Laar <sup>5</sup>
$g_{\text{van Laar\_gen}}^{\text{E}} = RT \left( \sum_i x_i \ln \frac{r_i}{r} \right) + \frac{1}{2} \sum_i x_i q_i \sum_j \frac{x_j q_j E_{ji}}{q}$ , $E_{ji} = E_{ij}, \quad r = \sum_i x_i r_i, \quad q = \sum_i x_i q_i$
Generalized NRTL
$g_{\text{NRTL\_gen}}^{\text{E}} = RT \left( \sum_i x_i \ln \frac{r_i}{r} \right) + \sum_i x_i q_i \frac{\sum_j x_j q_j G_{ji} \Gamma_{ji}}{\sum_l x_l q_l G_{li}}$
UNIQUAC <sup>26</sup>
$g_{\text{UNIQUAC}}^{\text{E}} = RT \left( \sum_i x_i \ln \frac{r_i}{r} + \frac{z}{2} \sum_i x_i q_i \ln \frac{q_i r}{q r_i} \right) -$ $RT \sum_i x_i q_i \ln \left( \sum_j \frac{q_j}{q} G_{ji} \right), \quad G_{ji} = \exp(-\Delta u_{ji}/RT)$

is known to be mathematically unable to represent liquid–liquid equilibria (LLE).

(iii) The original NRTL model is theoretically consistent, except that it assumes that all molecules have similar sizes and shapes ( $r_i = q_i \approx 1$ ), which yields a zero combinatorial term (eq 3) and a simplified expression for the residual energy (eq 11). On the contrary, the HV-NRTL equation, proposed by Huron and Vidal<sup>30</sup> with the infinite-pressure reference state associated with the Peng–Robinson equation of state, has no theoretical background; indeed, even if no combinatorial term is considered ( $r_i \approx 1$ ), surface fraction factors equal to the covolumes of the EoS ( $q_i \approx b_i \approx T_{ci}/P_{ci}$ ) are arbitrarily and partially introduced in the residual term of the excess function,  $g_{\text{NRTL\_HV}}^{\text{E}}$  (see Table 1).

In view of their introduction in cubic EoS as excess Gibbs free energy ( $G^{\text{E}}$ ) models, all of these equations were studied from the point of view of their ability to describe the VLE of hydrocarbons and polar–hydrocarbon mixtures, as well as the LLE of water–hydrocarbon systems. Special attention was paid to the physical meaning of the estimated parameters, which is

**Table 2. Values of Model Parameters<sup>a</sup>**

compounds		$T$ range (K)		original van Laar	original NRTL	HV-NRTL	generalized van Laar	generalized NRTL	UNIQUAC	ref(s)
1	2	$N_p$ <sup>b</sup>	$T_{\min}$ – $T_{\max}$	$A_{12}, A_{21}$	$\Gamma_{12}, \Gamma_{21}$	$\Gamma_{12}, \Gamma_{21}$	$E_{12}$	$\Gamma_{12}, \Gamma_{21}$	$\Delta u_{12}, \Delta u_{21}$	
cyclohexane	hexane*	25	298–313	0.1535 0.1461	22.56 372.43	53.99 312.71	0.0452	26.72 88.74	62.14 23.67	31
cyclohexane	eicosane	27	306–317	–0.3706 –0.7283	3137.75 –3562.24	–5881.89 1017.49	0.0451	–532.87 675.89	–251.18 382.50	32
benzene	hexane*	173	298–333	0.5018 0.6672	2246.62 –539.54	196.91 1163.09	0.2109	–492.89 1095.27	–154.60 629.87	33–37
benzene	hexadecane	73	298–333	0.0310 0.6319	3801.34 –2790.25	193.31 71.85	0.2028	–230.39 1573.08	–155.60 636.02	38–40
acetone	pentane*	32	238–298	1.7239 1.6557	1999.05 2619.34	379.47 3994.79	0.6077	–1101.41 3080.46	–67.95 1988.56	41
acetone	tetradecane	23	313–333	1.1536 2.3881	7330.93 –1124.68	–12070.41 10971.87	0.6205	–1551.98 3709.53	–316.80 2306.69	42
methanol	benzene	139	293–333	2.3052 1.7277	1036.50 5108.51	–3749.83 8646.36	1.2441	–1759.01 6521.46	–379.31 934.82	43–50
2-propanol	decane	7	363	1.3390 1.6874	4261.99 896.27	–9223.98 10135.43	0.4536	–2110.34 4318.16	–312.10 2747.64	51
water	hexane*	43	273–425	–	–	–4842 + 3641512/ $T$ –346.8 + 5453313/ $T$	–5.040 – 3265/ $T$	11330 – 1839541/ $T$ –2002 + 3965100/ $T$	–4292 + 55369/ $T$ –6921 + 1224702/ $T$	52
water	benzene	276	273–350	–	–	–4930 + 1945457/ $T$ 4023 + 2998734/ $T$	–3.270 + 2348/ $T$	13688 – 2535909/ $T$ –3940 + 3513531/ $T$	–3809 + 39505/ $T$ –7320 + 1188029/ $T$	53

<sup>a</sup> All parameter values in J/mol. <sup>b</sup>  $N_p$  = number of experimental bubble points used for the fitting of parameters.

the condition that must be addressed for the development of further predictive equations of state. This the case for the group contribution versions of the generalized van Laar, NRTL, and UNIQUAC models, which led, respectively, to the PPR78,<sup>17</sup> NRTL-PR<sup>18–20</sup> and VTPR,<sup>15</sup> and UMR-PRU<sup>16</sup> equations of state.

Table 2 lists the mixtures considered, together with the ranges of temperatures and numbers of data points used for fitting the model parameters; all binary interaction parameters were assumed to be temperature-independent, except for the LLE of the water–hexane and water–benzene systems. Parameters were obtained by minimizing the objective function built from deviations in the bubble point and vapor mole fractions for VLE and in the mole fractions of the dilute components in the aqueous and hydrocarbon phases for LLE.

**3.1. Hydrocarbon Mixtures.** Four binary systems were chosen to illustrate the VLE of hydrocarbon mixtures: cyclohexane with hexane and eicosane and benzene with hexane and hexadecane. The interest in such systems is that they can be characterized by moderate excess Gibbs energies and a given size asymmetry; they can therefore be considered as test systems for the evaluation of the combinatorial impact on the various modelings considered in Table 1.

Figure 2 shows that, once the parameters are fitted to the experimental data, all models provide exactly the same description of the VLE. However, because the excess properties of these mixtures are mainly governed by entropic effects, only consistent models with a combinatorial term should, in principle, provide parameter estimations that are really representative of molecular interactions. This point is discussed further below.

All systems considered in Figure 2 are formed by molecules,  $i$  and  $j$ , that contain only one functional group each,  $K$  and  $L$ , respectively, corresponding to cycloalkane and paraffin for cyclohexane–hexane and cyclohexane–eicosane mixtures and to aromatic and paraffin for benzene–hexane and benzene–hexadecane mixtures. Hence, the interaction parameters between molecules ( $A_{ij}$ ,  $\Gamma_{ij}$ , and  $E_{ij}$  in Table 2) should be equal to the interaction parameters between groups ( $A_{KL}$ ,  $\Gamma_{KL}$ , and  $E_{KL}$ ) and should, therefore, lead to the same residual term for each series of mixtures considered. To check this assumption, the binary systems cyclohexane–eicosane and benzene–hexadecane were modeled using the interaction parameters fitted to the VLE of

cyclohexane–hexane and benzene–hexane, respectively [values denoted with asterisks (\*) in Table 2]. Figure 3 presents the predictions obtained for these two systems with these parameters. The following observations can be made:

(i) The original models (van Laar and NRTL) yield identical, unsatisfactory predictions. Results obtained with the HV-NRTL model, especially for the benzene–hexadecane system (Figure 3b), evidence that the excess Gibbs energy proposed by the authors suffers from a strong inconsistency, mainly because of the introduction of covolumes in only one part of the residual term (Table 1).

(ii) Successful, similar predictions are obtained with all generalized models (van Laar, NRTL, and UNIQUAC) from the sole correlation of the binary cyclohexane–hexane and benzene–hexane systems. This confirms that only models that take the entropic effects into account allow, for these systems, meaningful estimations of binary interaction parameters.

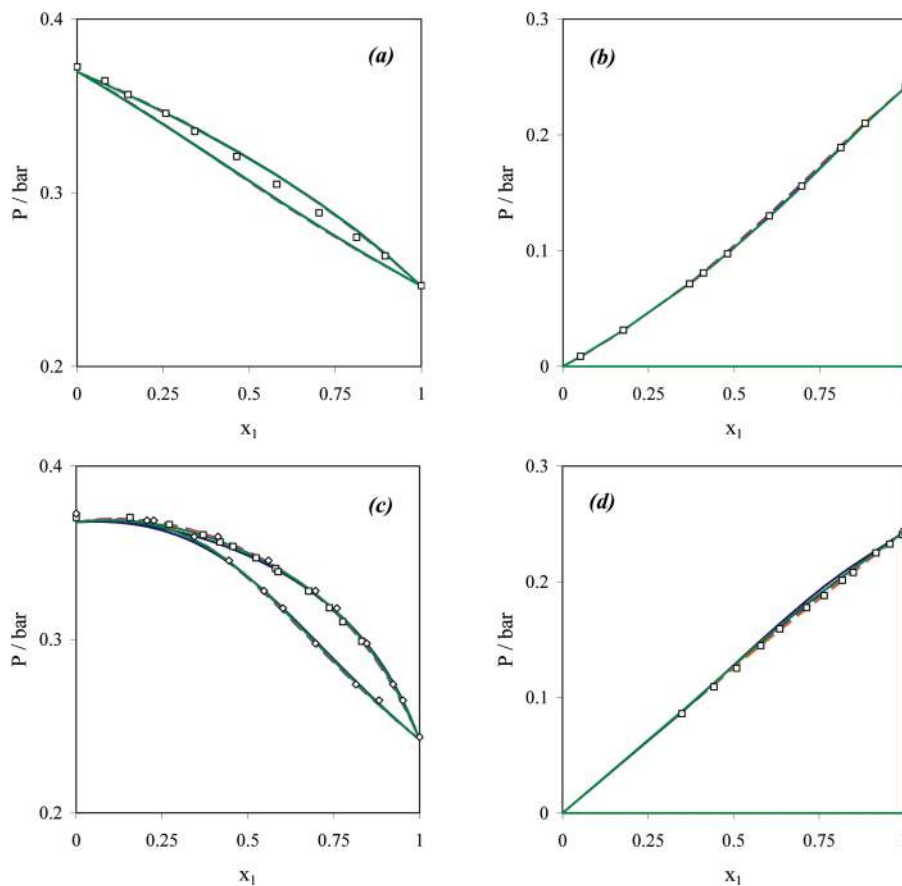
**3.2. Hydrocarbons with Polar Components.** The purpose of this section is to study the ability of the various lattice fluid equations to model asymmetric systems made of polar and hydrocarbon substances. Figure 4 shows the descriptions obtained with the van Laar, NRTL, and UNIQUAC models for the acetone–pentane, acetone–tetradecane, methanol–benzene, and 2-propanol–decane systems. Examination of the various modeling results yields the following conclusions:

(i) The generalized van Laar model yields the worst results for all of the binary mixtures considered. Although this model takes entropic effects into account, its main drawback is that it is derived from the one-fluid lattice theory, which means that it is based on the hypothesis of a completely random molecular distribution. As a consequence, the excess Gibbs energy depends, for a binary mixture (Table 1), on only one interaction parameter (the interchange energy  $E_{12}$ ), which is not appropriate for the modeling of this kind of system.

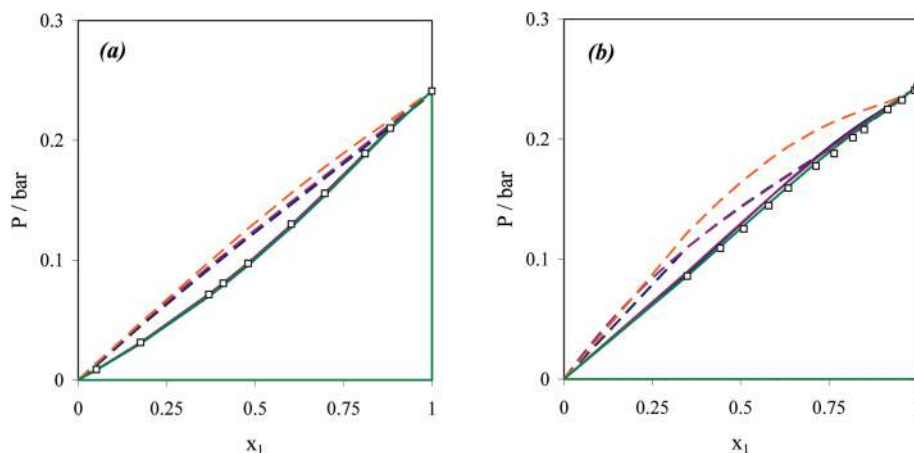
(ii) All of the other equations, which depend on two binary interaction parameters, provide identical, satisfactory representations of the experimental VLE data. This explains why these models are commonly used for the correlation of this kind of asymmetric system at low pressures.

From the conclusions of the study of hydrocarbon mixtures, it can be expected that only the generalized NRTL and





**Figure 2.** Hydrocarbon mixtures. Modeling of VLE, using model parameters detailed in Table 2, with the (blue dashed line) original van Laar, (purple dashed line) original NRTL, (orange dashed line) HV-NRTL, (blue solid line) generalized van Laar, (purple solid line) generalized NRTL, and (green solid line) UNIQUAC models. (a) Cyclohexane (1)–hexane (2) system ( $\square$ )<sup>31</sup> at  $T = 313$  K, (b) cyclohexane (1)–eicosane (2) system ( $\square$ )<sup>32</sup> at  $T = 313$  K, (c) benzene (1)–hexane (2) system ( $\square$ ,  $\diamond$ )<sup>33,35</sup> at  $T = 313$  K, (d) benzene (1)–hexadecane (2) system ( $\square$ )<sup>40</sup> at  $T = 313$  K.

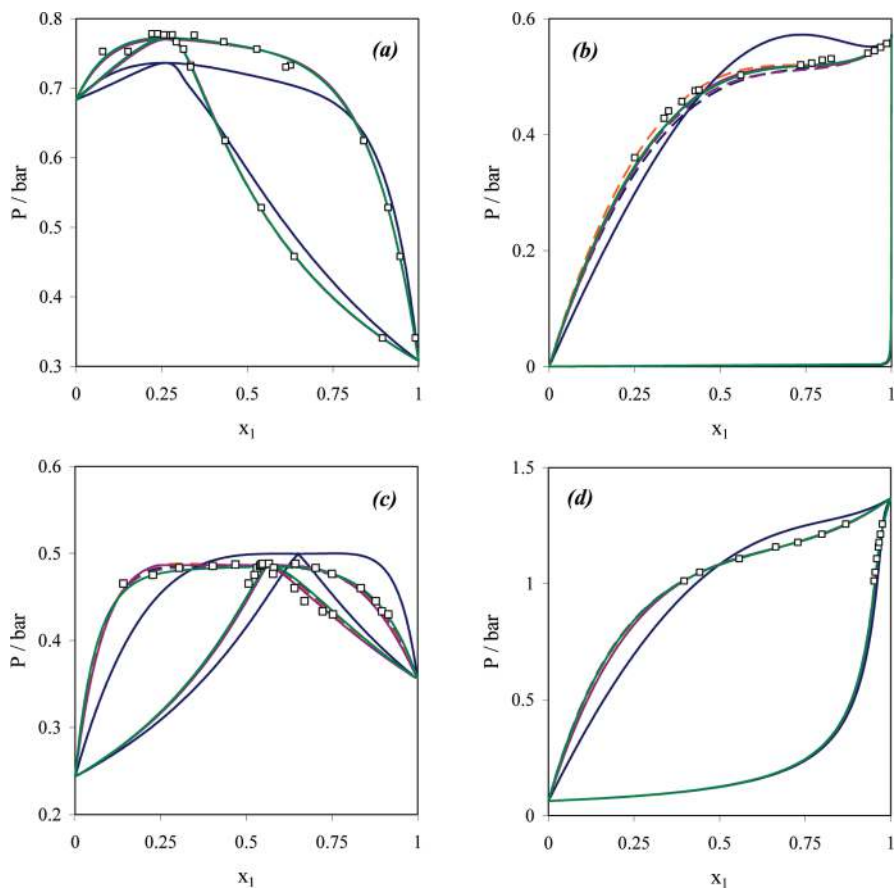


**Figure 3.** Hydrocarbon mixtures. Prediction of VLE, using model parameters listed in Table 2 for cyclohexane–hexane\* and benzene–hexane\*, with the (blue dashed line) original van Laar, (purple dashed line) original NRTL, (orange dashed line) HV-NRTL, (blue solid line) generalized van Laar, (purple solid line) generalized NRTL, and (green solid line) UNIQUAC models. (a) Cyclohexane (1)–eicosane (2) system ( $\square$ )<sup>32</sup> at  $T = 313$  K, (b) benzene (1)–hexadecane (2) system ( $\square$ )<sup>40</sup> at  $T = 313$  K.

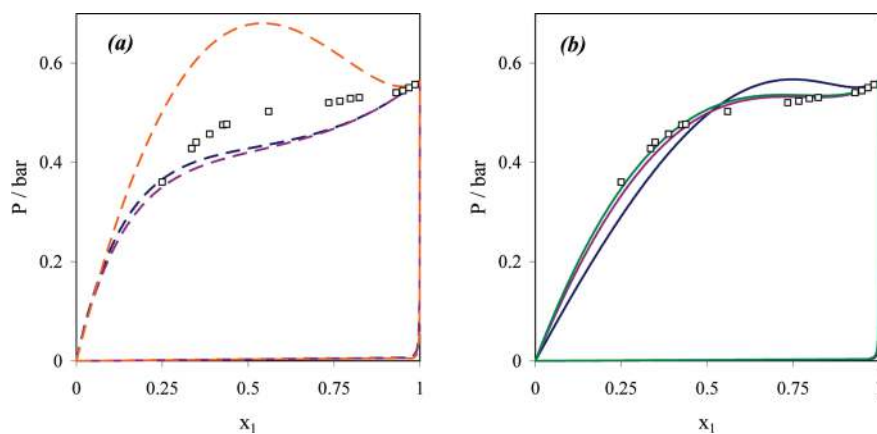
UNIQUAC models would be able to yield satisfactory representation of the asymmetries due to the size and polarity of substances with significant estimated parameters. Following the same procedure as in the case of hydrocarbon mixtures, we predicted the VLE of the acetone–tetradecane mixture with the parameters [values denoted with asterisks (\*) in Table 2] fitted to the acetone–pentane experimental data. Figure 5 shows that, exactly as for hydrocarbon mixtures, the original van Laar and

NRTL models, together with the empirical HV-NRTL equation, yield inconsistent predictions (Figure 5a). In contrast, except for the generalized van Laar equation, the other generalized models, NRTL and UNIQUAC, are able (Figure 5b) to satisfactorily account for asymmetries due to the size and polarity of substances with meaningful parameter values.

**3.3. Water–Hydrocarbon Mixtures.** According to the conclusions for the two preceding types of systems, the modeling



**Figure 4.** Hydrocarbons with polar compounds. Modeling of VLE, using model parameters detailed in Table 2, with the (blue dashed line) original van Laar, (purple dashed line) original NRTL, (orange dashed line) HV-NRTL, (blue solid line) generalized van Laar, (purple solid line) generalized NRTL, and (green solid line) UNIQUAC models. (a) Acetone (1)–pentane (2) system ( $\square$ )<sup>41</sup> at  $T = 298$  K, (b) acetone (1)–tetradecane (2) system ( $\square$ )<sup>42</sup> at  $T = 313$  K, (c) methanol (1)–benzene (2) system ( $\square$ )<sup>50</sup> at  $T = 313$  K, (d) 2-propanol (1)–decane (2) system ( $\square$ )<sup>51</sup> at  $T = 363$  K.



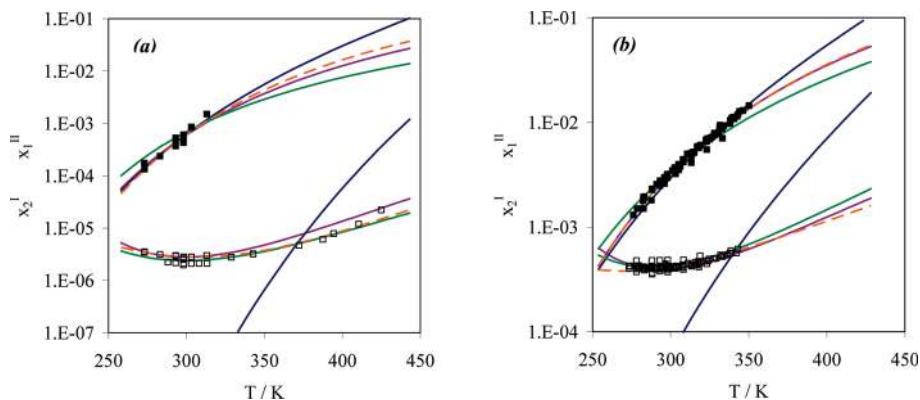
**Figure 5.** Hydrocarbons with polar compounds. Prediction of VLE of the acetone (1)–tetradecane (2) system ( $\square$ )<sup>42</sup> at  $T = 313$  K, using model parameters listed in Table 2 for acetone (1)–pentane\*, with the (a) (blue dashed line) original van Laar, (purple dashed line) original NRTL, and (orange dashed line) HV-NRTL models and the (b) (blue solid line) generalized van Laar, (purple solid line) generalized NRTL, and (green solid line) UNIQUAC models.

of water–hydrocarbon mixtures was performed by focusing on the generalized NRTL and UNIQUAC models. However, because the Huron–Vidal<sup>30</sup> and PPR78<sup>17</sup> equations of state, commonly used in the petroleum industry, are based on the HV-NRTL and generalized van Laar excess Gibbs energies, respectively, these models were also considered for the modeling of the LLE occurring in these systems.

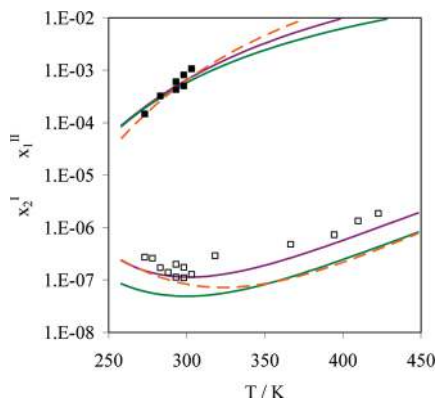
Figure 6 illustrates the LLE of the water–hexane and water–benzene systems. As expected for these strong demixings, the van Laar one-fluid lattice model completely fails in representing both liquid phases; in our example, the hydrocarbon phase was preferentially considered, which

resulted in a rather satisfactory description of this phase, but to the detriment of the aqueous phase. In contrast, the three other models, HV-NRTL, generalized NRTL, and UNIQUAC, which derive from the two-fluid theory, give satisfactory predictions of the solubilities in both phases, once the parameters have been fitted to experimental data. Concerning the UNIQUAC model, the evolution of the solubilities with respect to temperature is slightly less satisfactory for the hydrocarbon phase.

Figure 7 shows the predictions obtained with these last three models for the water–octane system using parameters fitted to water–hexane data (Table 2). It can be observed that the



**Figure 6.** Water–hydrocarbon mixtures. Modeling of LLE at  $P = 1$  atm, using model parameters detailed in Table 2, with the (orange dashed line) HV-NRTL, (blue solid line) generalized van Laar, (purple solid line) generalized NRTL, and (green solid line) UNIQUAC models for ( $\square$ ) aqueous and ( $\blacksquare$ ) hydrocarbon phases. (a) Water (1)–hexane (2) system<sup>52</sup> and (b) water (1)–benzene (2) system.<sup>53</sup>



**Figure 7.** Water–hydrocarbon mixtures. Prediction of LLE of the water (1)–octane (2) system<sup>54</sup> at  $P = 1$  atm, using model parameters listed in Table 2 for water (1)–hexane (2)\*, with the (orange dashed line) HV-NRTL, (purple solid line) generalized NRTL, and (green solid line) UNIQUAC models for the ( $\square$ ) aqueous and ( $\blacksquare$ ) hydrocarbon phases.

generalized NRTL model yields the most reliable solubility predictions, especially in the aqueous phase.

#### 4. Conclusions

The aim of the present work was to study the ability of lattice fluid models to describe nonideal systems in view of their introduction in cubic EoS. For this purpose, a generalized version of the NRTL equation was proposed and compared with other literature models; among them, the original van Laar, NRTL, and modified HV-NRTL equations consider only residual effects, whereas the generalized van Laar, NRTL, and UNIQUAC models also take entropic contributions into account. Mixtures containing size-asymmetric components or polar substances with hydrocarbons were considered, and special attention was paid to the physical meaning of the estimated parameters, which is the condition that must be addressed for the development of further predictive equations of state.

For hydrocarbon mixtures, once parameters have been fitted to experimental data, all models provide exactly the same description of VLE. However, only the generalized versions (van Laar, UNIQUAC, and NRTL), which take the entropic effects into account, allow meaningful estimations of the binary interaction parameters; this explains why the predictive cubic equations of state PPR78, VTPR and UMR-PRU, and NRTL-PR that are based on these  $g^E$  models provide successful descriptions of hydrocarbon mixtures.

The study of systems containing polar and associating components with hydrocarbons shows that, even with fitted

parameters, the generalized van Laar equation based on the one-fluid lattice theory is not suitable for the description of such mixtures. On the contrary, the two-fluid generalized NRTL and UNIQUAC models are able to satisfactorily account for asymmetries due to the size and polarity of substances with meaningful parameter values.

A similar conclusion can be drawn for water–hydrocarbon mixtures, but with a slightly better description of the solubilities in both phases with the generalized NRTL model.

#### List of Symbols

- $A$  = Helmholtz free energy
- $E_{ij}$  = interchange energy
- $g$  = molar Gibbs energy
- $G$  = Gibbs energy
- $G_{ji}$  = molecular repartition coefficient
- LLE = liquid–liquid equilibrium
- $n$  = number of moles
- $N_{ji}$  = number of pair interactions
- $P$  = pressure
- $q$  = surface area factor
- $r$  = volume area factor
- $R$  = ideal gas constant
- $S$  = entropy
- $T$  = temperature
- $U$  = internal energy
- $V$  = volume
- VLE = vapor–liquid equilibria
- $x$  = mole fraction
- $z$  = coordination number

#### Greek Letters

- $\alpha_0$  = nonrandomness factor
- $\Gamma_{ji}$  = configurational energy
- $\theta_i$  = surface fraction of molecule  $i$
- $\theta_{ij}$  = contact probability between molecules  $i$  and  $j$
- $\phi_i$  = volume fraction

#### Subscripts

- combinatorial = combinatorial part of the excess Gibbs energy
- residual = nonathermal part of the excess Gibbs energy

#### Superscripts

- Conf = configurational property
- E = excess property at constant pressure
- EV = excess property at constant volume
- MV = mixing property at constant volume



## Literature Cited

- (1) Wertheim, M. S. Fluids with Highly Directional Attractive Forces. I. Statistical Thermodynamics. *J. Stat. Phys.* **1984**, *35*, 19.
- (2) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New Reference Equation of State for Associating Liquids. *Ind. Eng. Chem. Res.* **1990**, *29*, 1709.
- (3) Huang, S. H.; Radosz, M. Equation of State for Small, Large, Polydisperse, and Associating Molecules: Extension to Fluid Mixtures. *Ind. Eng. Chem. Res.* **1991**, *30* (8), 1994.
- (4) Kontogeorgis, G. M.; Voutsas, E. C.; Yakoumis, I. V.; Tassios, D. P. An Equation of State for Associating Fluids. *Ind. Eng. Chem. Res.* **1996**, *35* (11), 4310.
- (5) Guggenheim, E. A. *Mixtures. The Theory of Equilibrium Properties for Some Simple Classes of Mixtures, Solutions and Alloys*; Clarendon Press: Oxford, U.K., 1952.
- (6) Barker, J. A. *Lattice Theories of the Liquid State*; Pergamon Press: Oxford, U.K., 1963.
- (7) Sanchez, I. C.; Lacombe, R. H. Statistical Thermodynamics of Polymer Solutions. *Macromolecules* **1978**, *11*, 1145.
- (8) Panayiotou, C.; Vera, J. H. An improved lattice-fluid equation of state for pure component polymeric fluids. *Polym. Eng. Sci.* **1982**, *22*, 345.
- (9) Panayiotou, C.; Vera, J. H. Statistical Thermodynamics of r-Mer Fluids and Their Mixtures. *Polym. J.* **1982**, *14*, 681.
- (10) Smirnova, N. A.; Victorov, A. I. Thermodynamic Properties of Pure Fluids and Solutions from the Hole Group-Contribution Model. *Fluid Phase Equilib.* **1987**, *34*, 235.
- (11) Orbey, H.; Sandler, S. On the combination of equation of state and excess free energy models. *Fluid Phase Equilib.* **1995**, *111*, 53.
- (12) Dahl, S.; Michelsen, M. L. High-pressure vapor–liquid equilibrium with a UNIFAC-based equation of state. *AIChE J.* **1990**, *36*, 1829.
- (13) Wong, D. S. H.; Sandler, S. A Theoretically Correct Mixing Rule for Cubic Equations of State. *AIChE J.* **1992**, *38*, 71.
- (14) Boukouvalas, C.; Spiliotis, N.; Coutsikos, P.; Tzouvaras, N.; Tassios, D. Prediction of vapor–liquid equilibrium with the LCVM model: A linear combination of the Vidal and Michelsen mixing rules coupled with the original UNIFAC and the t-mPR equation of state. *Fluid Phase Equilib.* **1994**, *92*, 75.
- (15) Ahlers, J.; Gmehling, J. Development of a Universal Group Contribution Equation of State III. Prediction of Vapor–Liquid Equilibria, Excess Enthalpies and Activity Coefficients at Infinite Dilution with the VTPR Model. *Ind. Eng. Chem. Res.* **2002**, *41* (23), 5890.
- (16) Vouzas, E.; Louli, V.; Boukouvalas, C.; Magoulas, K.; Tassios, D. Thermodynamic property calculations with the universal mixing rule for EoS/ $G^E$  models: Results with the Peng–Robinson EoS and a UNIFAC model. *Fluid Phase Equilib.* **2006**, *241* (2), 216.
- (17) Jaubert, J.-N.; Mutelet, F. VLE Predictions with the Peng–Robinson Equation of State and Temperature Dependent  $k_{ij}$  Calculated Through a Group Contribution Method. *Fluid Phase Equilib.* **2004**, *224* (2), 285.
- (18) Neau, E.; Nicolas, C.; Jaubert, J.-N.; Mutelet, F. The Generalized NRTL Model Associated with the Peng–Robinson Equation of State to Predict Liquid–Liquid Equilibria Between Hydrocarbons, Water and Ethylene Glycol. *Pol. J. Chem.* **2006**, *80*, 27.
- (19) Escandell, J. Mise au point d'une méthode prédictive pour le calcul des équilibres de phases des systèmes eau–hydrocarbures–glycols; Ph.D. Thesis, University of Méditerranée, Marseille, France, 2008.
- (20) Neau, E.; Escandell, J.; Nicolas, C. Modeling of Highly Nonideal Systems: 2. Prediction of High-Pressure Phase Equilibria with the Group Contribution NRTL-PR EoS. *Ind. Eng. Chem. Res.* **2010**, DOI: 10.1021/ie101266x.
- (21) Neau, E.; Escandell, J.; Raspo, I.; Nicolas, C. A new reference state for cubic EoS/ $G^E$  models. Presented at the 12th International Conference on Properties and Phase Equilibria for Product and Process Design, Suzhou, China, May 16–21, 2010.
- (22) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice Hall PTR: Upper Saddle River, NJ, 1999.
- (23) Van Laar, J. J. The Vapor Pressure of Binary Mixtures. *Z. Phys. Chem.* **1910**, *72*, 723.
- (24) Van Laar, J. J. On the theory of vapor pressures of binary mixtures. *Z. Phys. Chem.* **1913**, *83*, 599.
- (25) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, *14*, 135.
- (26) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116.
- (27) Wilson, G. M. Vapor–Liquid Equilibrium XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86* (2), 127.
- (28) Fredenslund, A.; Gmehling, J.; Rasmussen, P. *Vapor–Liquid Equilibria Using UNIFAC, a Group Contribution Method*; Elsevier: Amsterdam, 1977.
- (29) Marina, J. M.; Tassios, D. Prediction of Ternary Liquid–Liquid Equilibrium from Binary Data. *Ind. Eng. Chem. Process. Des. Dev.* **1973**, *12*, 271.
- (30) Huron, M.-J.; Vidal, J. New mixing rules in simple equations of state for representing vapour–liquid equilibria of strongly non-ideal mixtures. *Fluid Phase Equilib.* **1979**, *3* (4), 255.
- (31) Meixner, D.; Lichtenthaler, R. N. Einfluss von Ordnungsstrukturen auf die thermodynamischen Zustandsgrößen. *Ber. Bunsen-Ges. Phys. Chem.* **1979**, *83*, 567.
- (32) Gomez-Ibanez, J. D.; Wang, F. T. The excess Gibbs energy of mixtures of cyclohexane with *n*-eicosane and with two other *n*-alkanes. A relation of congruence. *J. Chem. Thermodyn.* **1971**, *3*, 811.
- (33) Jain, D. V. S.; Gupta, V. K.; Lark, B. S. Thermodynamics of *n*-alkane solutions. I. Vapor pressures and excess free energies of *n*-hexane in benzene and carbon tetrachloride. *Indian J. Chem.* **1970**, *8*, 815.
- (34) Murray, R. S.; Martin, M. L. A continuous-dilution device for the measurement of static vapour pressures of binary liquid mixtures. *J. Chem. Thermodyn.* **1975**, *7*, 839.
- (35) Li, I. P. C.; Wong, Y. W.; Chang, S. D.; Lu, B. C.-Y. Vapor–liquid equilibria in systems *n*-hexane–benzene and *n*-pentane–toluene. *J. Chem. Eng. Data* **1972**, *17*, 492.
- (36) Beyer, W.; Scuberth, H.; Leibnitz, E. The vapor–liquid phase equilibrium study of the *n*-hexane–methylcyclopentane–benzene system at 60 °C using a gas chromatographic analytical method. *J. Prakt. Chem.* **1965**, *27*, 276.
- (37) Saez, C.; Compostizo, A.; Rubio, R. G.; Crespo-Colin, A.; Diaz-Péna, M. *p*, *T*, *x*, *y* data of benzene + *n*-hexane and cyclohexane + *n*-heptane systems. *Fluid Phase Equilib.* **1985**, *24*, 241.
- (38) Jain, D. V. S.; Lark, B. S. Thermodynamics of *n*-alkane mixtures VI. Vapour pressures and excess Gibbs energies of mixtures of *n*-hexadecane + benzene and + carbon tetrachloride. *J. Chem. Thermodyn.* **1973**, *5*, 455.
- (39) Snow, R. L.; Ott, J. B.; Goates, J. R.; Marsh, K. N.; O'Shea, S.; Stokes, R. H. (Solid + liquid) and (vapor + liquid) phase equilibria and excess enthalpies for (benzene + *n*-tetradecane), (benzene + *n*-hexadecane), (cyclohexane + *n*-tetradecane), and (cyclohexane + *n*-hexadecane) at 293.15, 298.15, and 308.15 K. Comparison of GmE calculated from (vapor + liquid) and (solid + liquid) equilibria. *J. Chem. Thermodyn.* **1986**, *18*, 107.
- (40) Messow, U.; Schuetze, D.; Hauthal, W. Thermodynamic studies on *n*-paraffin solvent systems. II. Benzene (1)/*n*-tetradecane (2), benzene (1)/*n*-hexadecane (2) and benzene (1)/*n*-heptadecane (2). *Z. Phys. Chem. (Leipzig)* **1976**, *257*, 218.
- (41) Raal, W.; Schaefer, K. Z. *Elektrochem.* **1959**, *63*, 1019 (in *Vapor–Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series Vol. I, Parts 3 + 4, p 190).
- (42) Messow, U.; Doye, U.; Kuntzsch, S.; Kuchenbecker, D. Thermodynamic studies on solvent/*n*-paraffin systems. V. The acetone/*n*-decane, acetone/*n*-dodecane, acetone/*n*-tetradecane and acetone/*n*-hexadecane systems. *Z. Phys. Chem. (Leipzig)* **1977**, *258*, 90.
- (43) Niini, A. Determination of the vapor pressure isotherms for water–methanol–ethanol mixtures and an estimation of the van der Waals forces in liquids. I. Nonpolar solvents. *Ann. Acad. Sci. Fenn.* **1940**, *A55* (8), 52.
- (44) Schmidt, G. C. Binäre Gemische. *Z. Phys. Chem.* **1926**, *121*, 221.
- (45) Hwang, S. C.; Robinson, R. L. Vapor–liquid equilibria at 25°C for nine alcohol–hydrocarbon binary systems. *J. Chem. Eng. Data* **1977**, *22*, 319.
- (46) Iguchi, A. Vapor–liquid equilibria at 25°C for binary systems between alcohols and hydrocarbons. *Kagaku Sochi* **1978**, *20*, 66.
- (47) Feller, M.; Mc Donald, J. Determination of liquid–vapor equilibrium–dew point–bubble point apparatus. *Anal. Chem.* **1950**, *22*, 338.
- (48) Scatchard, G.; Wood, S. E.; Mochel, J. M. Vapor–Liquid Equilibrium. VI. Benzene–Methanol Mixtures. *J. Am. Chem. Soc.* **1946**, *68*, 1957.
- (49) Morachevskii, A. G.; Komarova, E. G. Investigation of solution–vapor equilibrium in the benzene–cyclohexane–methyl alcohol system. *Vestn. Leningrad. Univ.* **1957**, *12* (4, Ser. Fiz. i Khim. No. 1), 118.
- (50) Lee, S. C. Partial pressure isotherms. II. *J. Phys. Chem.* **1931**, *35*, 3558.
- (51) Ratcliff, G. A.; Chao, K. C. Prediction of thermodynamic properties of polar mixtures by a group solution model. *Can. J. Chem. Eng.* **1969**, *47*, 148.
- (52) Maczynski, A.; Shaw, D. G.; Goral, M.; Wisniewska-Gocłowska, B.; Skrzecz, A.; Owczarek, I.; Blazej, K.; Haulait-Pirson, M. C.; Hefter, G. T.; Kapuku, F.; Maczynska, Z.; Young, C. L. IUPAC–NIST Solubility

Data Series. 81. Hydrocarbons with Water and Seawater—Revised and Updated. Part 4. C<sub>6</sub>H<sub>14</sub> Hydrocarbons with Water. *J. Phys. Chem. Ref. Data* **2005**, *34*, 709.

(53) Maczynski, A.; Shaw, D. G.; Goral, M.; Wisniewska-Gocłowska, B.; Skrzecz, A.; Owczarek, I.; Blazej, K.; Haulait-Pirson, M. C.; Hefter, G. T.; Maczynska, Z.; Szafranski, A.; Tsonopoulos, C.; Young, C. L. IUPAC–NIST Solubility Data Series. 81. Hydrocarbons with Water and Seawater—Revised and Updated. Part 2. Benzene with Water and Heavy Water. *J. Phys. Chem. Ref. Data* **2005**, *34*, 477.

(54) Shaw, D. G.; Maczynski, A.; Goral, M.; Wisniewska-Gocłowska, B.; Skrzecz, A.; Owczarek, I.; Blazej, K.; Haulait-Pirson, M. C.; Hefter,

G. T.; Kapuku, F.; Maczynska, Z.; Szafranski, A. IUPAC–NIST Solubility Data Series. 81. Hydrocarbons with Water and Seawater—Revised and Updated. Part 7. C<sub>8</sub>H<sub>12</sub>–C<sub>8</sub>H<sub>18</sub> Hydrocarbons with Water. *J. Phys. Chem. Ref. Data* **2005**, *34*, 2261.