Developing a New Equation of State with Non-Quadratic Mixing Rules for Prediction of the Phase Equilibria of Polar and Associated Fluids

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Abstract

Feyzi-Riazi equation of state (PRFR EOS) which is a modification of Peng-Robinson equation of state is modified in this research. The proposed modification estimates the specific volume of polar and hydrogen-bonded liquids and vapor pressure of pure substances with greater accuracy while maintaining the ability of PRFR EOS in predicting critical compressibility factor of pure compounds. The proposed model is applied to correlate and predict the experimental data of vapor-liquid equilibria (VLE) and liquid densities of various binary nonideal and polar solutions. For this purpose eight mixing rules (van der Waals, HVO, WS, MHV1, MHV2, MHV, LCVM and HVOS) were used. Among the mixing rules considered in this work, only the WS and the MHV are the best predictive tools. In the G^{ex} part of the proposed model the NRTL and the UNIQUAC-type models were used, respectively. NRTL model has weak predictive capabilities due to its temperature-dependent parameters.

Keywords: Equation of state; Non-Quadratic Mixing Rules; Phase equilibria; Vapor-liquid equilibria; Polar solutions

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1. Introduction

Cubic equations of state are frequently used in the chemical and petroleum industries to model complex phase behavior and to design chemical processes. The main difficulty in using conventional EOSs like SRK and PR is that they are not accurate in estimation of liquid densities, especially for polar and hydrogen-bonded fluids. Many modifications have been proposed for these equations that can be classified as follows:

Volume translation methods originally proposed by Peneloux et al.[1] on SRK EOS and then by Javeri and Youngren[2] on PR EOS.

Methods that consider parameter b as a function of reduced temperature like the works of Feyzi et al.[3], Xu and Sandler[4], Wu and Sandler[5], Chadron et al.[6]

Methods that change the temperature-dependency of parameter a, while keeping parameter b a constant for each component like the modification of SRK-EOS by Mathias and Copeman.[7]

Although these modifications improve liquid specific volume predictions of non-polar substances, they are not suitable for polar and substances that form hydrogen bonds.

Recently developed mixing rules have greatly increased the accuracy and range of applicability of such equations. Cubic equations of state with the classical mixing rules [8-11] can be used over wide range of temperature and pressure, although they are recommended only for hydrocarbons and the inorganic gases.

Throughout the chemical manufacturing spectrum, there is the need for vapor-liquid equilibrium (VLE) models of good accuracy. The emphasis is on the use of recently developed mixing rules that combine EOS models with excess free-energy (or liquid activity coefficient) models, that is the new class of EOS- G^{ex} models. The EOS- G^{ex} models offer much greater flexibility, extrapolation capability, and reliability of prediction than the conventional van der Waals mixing rule or than through the direct use of activity coefficient models.

The absence of a valid gas-phase model for polar organic compounds has resulted in difficulties in describing the vapor-liquid equilibrium of polar mixtures at high temperatures and pressures, and for describing supercritical extraction processes. Recently, cubic equations of state have become very powerful in correlating and predicting phase equilibrium behavior for either non-polar or / and polar systems. This capability comes both from the ability to predict pure component vapor pressure accurately for polar and non-polar components (Soave [12]; Mathias [13]; Stryjek and Vera [14]; Twu et al. [15-17]) and the latest development of new mixing rules for cubic equations of state Huran and Vidal [18]; Michelsen [19]; Dahl and Michelsen [20]; Twu et al. [21]; Wong and Sandler [22]).

In this paper, a generalized modification is proposed to improve PRFR EOS [3] predictions for liquid specific volume of polar and hydrogen-bonded substances. The difference between this research and PRFR EOS is that in PRFR model dipole moment was not considered and α and β coefficients are related to acentric factor and reduced dipole moment but the dependency of these parameters to reduced temperature did not change in comparison with previous model. Then, a combination of this generalized EOS with recently developed and van der Waals mixing rules was used to improve the VLE behavior of polar and hydrogen-bonded mixtures. The proposed modification also, is applied to predict liquid specific volumes of polar and associated fluids that are present in binary mixtures.

2. Literature background

To extend pure-fluid equations of state to mixtures of nonpolar (or slightly polar) components, it is customary to use classical one-fluid mixing rules, as proposed by van der Waals [23]. In the one-fluid theory, it is assumed that the properties of a fluid mixture is identical to those of a hypothetical pure fluid, at the same temperature and pressure, whose equation-of-state parameters are functions of mole fraction. In the van der Waals approximation, these functions are quadratic in mole fraction.

For highly nonideal mixtures, however, quadratic mixing rules are inadequate. Several methods have been proposed to modify the original mixing rules. In many cases the modified mixing rules

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include composition-dependent or density-dependent binary interaction parameters. Density-dependent mixing rules are formulated to obtain a correct representation of mixture properties at both high and low density regions; in the limit of low density, they reproduce the correct composition dependence of the mixture second virial coefficient (a quadratic function in mole fraction), whereas in the high-density limit (or infinite pressure), mixing rules are determined to force agreement with some excess-Gibbs-energy model for a liquid mixture [24]. Some authors have suggested mixing rules independent of density, as suggested by excess Gibbs-energy models. Most of these mixing rules however, violate the theoretically-based boundary condition that the second virial coefficient must be quadratic in mole fraction.

3. Proposed method

Reduced dipole moment, which is defined by eq (1), is used as an input parameter in addition to critical temperature (T_c), critical pressure (P_c) and acentric factor (ω), needed to estimate parameters a and b in PRFR EOS.

$$\mu_r = \frac{\mu^2 P_c}{T_c^2}$$

(1)

where μ_r, T_c, P_c are in Debye, K and KPa respectively. The proposed modification which is the modification of the PRFR EOS [3] is presented by eqs 2-10:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+b(v-b)}$$

(2)

$$a = \alpha \left(0.4572355289 \frac{R^2 T_c^2}{P_c} \right)$$

(3)

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$$b = \beta \left(0.0777960739 \frac{RT_c}{P_c} \right) \tag{4}$$

For $T_r \leq 0.97$

$$\alpha = \left[\alpha_1 + \alpha_2 (1 - T_r) + \alpha_3 (1 - T_r)^2 \right]^2 \tag{5}$$

$$\beta = \left[\beta_1 + \beta_2 (1 - T_r) + \beta_3 (1 - T_r)^2 \right]^2 \tag{6}$$

$$\alpha_1 = \sum_{j=0}^{2} a_{1j} (\omega \mu_r)^j \tag{7}$$

$$\beta_1 = \sum_{j=0}^{2} b_{1j} (\omega \mu_r)^j \tag{8}$$

$$\alpha_i = \sum_{j=0}^{2} a_{ij} (\omega)^j \tag{9}$$

i = 2, 3

$$\beta_i = \sum_{j=0}^{2} b_{ij} (\omega)^j \tag{10}$$

i = 2, 3

And for the near critical region $0.97 < T_r < 1.03$[3]:

$$\alpha = \left\{ \begin{array}{l} 1+[-0.03049+(0.61991-0.39384\omega+0.69849\omega^2)(1-T_r) \\ \quad +(-0.44656+1.9584\omega-1.80666\omega^2)(1-T_r)^2] \\ [1-\exp(-100|T_r-1|)] \end{array} \right\}^2 \tag{11}$$

$$\beta = \left\{ \begin{array}{l} (0.999+0.00872\omega-0.02733\omega^2)^{1/2}+[-0.0448609+(0.61013-1.41814\omega+0.94321\omega^2)(1-T_r) \\ \quad +(-0.81945+2.11084\omega-1.75858\omega^2)(1-T_r)^2][1-\exp(-100|T_r-1|)] \end{array} \right\}^2 \tag{12}$$

For $1.03 \leq T_r \leq 1.94$

$$\beta = 1 \tag{13}$$

α is obtained from Eq (11).

where T_c, P_c, ω and μ are critical temperature, critical pressure, acentric factor and dipole moment of the pure component respectively. These parameters are known as input parameters in the model. All of the other constants are presented in the Appendix. According to Eq (12) It is obvious that in the critical region acentric factor should not be greater than 6.22 due to meaningless square root in the first term of this equation. However, the α function in this work and in PRSV [25] equation becomes zero at finite temperatures and then rises again with increasing temperature, which is contrary to the temperature behavior of the attractive force. Therefore, this work could not be applied for $T_r > 1.94$. Moreover, the modification of α in PRSV [25] takes care of inaccuracies in temperature dependence of the *a* term at low temperatures. However, since *a* term is based on vapor pressure in PRSV EOS [25], it is not well defined at temperatures above the critical temperature of a component. Also the value of the α function extrapolated from subcritical conditions tends to increase very rapidly with temperature at supercritical conditions. This is a problem when dealing with a fluid whose critical temperature is very low, such as hydrogen [33]. In these cases the use of other α functions become necessary. Twu et al. [15-17] have made a thorough analysis of this problem and have proposed a new α function that avoids exterma in the supercritical region and smoothly goes to zero at infinite temperature. Readers interested in

applications to mixtures that contain fluids in the highly supercritical state, such as hydrogen-containing mixtures, may wish to consider alternative forms such as those presented by Twu et al. [15-17]

It should be notified that Feyzi et al.[3] did not consider the dependency of parameters to reduced dipole moment. Furtheremore eqs (11) and (12) which represent the critical region are identical to the previous work[3].

The procedure for this modification is explained below:

An objective function has been defined to optimize parameters α and β of eqs (5) and (6), in such a way that the summation of absolute relative errors in calculating vapor pressure, saturated liquid specific volume and saturated vapor specific volume by the FR-EOS and those from experimental data of 27 polar and non-polar substances, using 767 data points with the range of dipole moment from 0 to 2 Debye, and variation of reduced temperature between 0.5 and 0.97, are minimized. Note that 18 parameters in eqs (5) and (6) are regressed from 27 compounds (Tables 1 and 3) as part of the present work. The objective function used is:

$$F = \sum \left| \frac{P_{cal}^{sat} - P_{exp}^{sat}}{P_{exp}^{sat}} \right| + \sum \left| \frac{v_{cal}^{l,sat} - v_{exp}^{l,sat}}{v_{exp}^{l,sat}} \right| + \sum \left| \frac{v_{cal}^{g,sat} - v_{exp}^{g,sat}}{v_{exp}^{g,sat}} \right| \tag{14}$$

The summations are over all data points. The optimization has been performed by the use of a nonlinear regression technique.

The optimum values of α and β obtained for each substance are then generalized in terms of reduced temperature, reduced dipole moment and acentric factor. The generalized equations for α and β are expressed in the eqs (5) and (6).

4. Extension to mixtures

In this section we have compared the performance of all the mixing rules introduced in the previous section and of the PRFR [3] and proposed equations of state discussed earlier. Specially, we have considered the following mixing rules developed in the infinite pressure limit: the one parameter van der Waals model

(vdW) [23], the original Huron-Vidal model (HVO) [18, 26] the Wong-Sandler model (WS) [22] and the approximate model introducing by Orbey and Sandler [27] as a modification of the Huron and Vidal model (HVOS). Among the zero-pressure models, the followings were tested: the MHV1 model of Michelsen (modified Huron-Vidal first-order mixing rule) [19], the MHV2 model of Dahl and Michelsen (modified Huron-Vidal first-order mixing rule) [20], the modified MHV1 by Tochigi et al. [28] (MHV) and the linear combination of HVO and MHV1 models by Boukovalas et al. (LCVM) [29]. In all cases we used the Peng-Robinson EOS as modified by Feyzi et al. [3] and the modification of PRFR that is done in this work which contains regressing new parameters for eqs (5) and (6). These optimized parameters were outlined in the Appendix. [For the MHV2 model the parameters q_1 and q_2 to be used with the PRSV [25] equation were -0.41754 and -0.00461 [30] and with the new EOS were optimized in this work as -0.40676 and -0.00538, respectively]. We have considered binary systems that are azeotropic- forming and nonideal mixtures that have highly polar and hydrogen bonding compounds. The predictive and correlative capabilities of the models are investigated and compared in this work. Consequently we only used two options [31, 32] which are presented below:

In the first option, a simple activity coefficient model (in this case NRTL equation) which its parameters at or near room temperature ($25°C$) were obtained from the $\gamma - \phi$ methods are used to predict VLE behavior at higher temperatures. Since the NRTL parameters are temperature dependent, they are fitted to experimental data to use the model as a correlative tool. The regressed parameters for the NRTL activity coefficient model are presented in the footnotes of Figures 3-6 at each temperature. The non-randomness parameter of the model is obtained from DECHEMA Chemistry Series [44] for the systems for which its value has been reported, otherwise it was assumes to be 0.3 in VLE calculations, as mentioned by Orbey and Sandler [33].

In the second option the UNIQUAC model was used. Its two temperature-independent parameters (Δu_{12} and Δu_{21}) were obtained using infinite dilution activity coefficients predicted from UNIFAC model, as described by Orbey et al. [34]. These parameters were reported only at 298 K in Table 14. In this case the

model is completely predictive. For each of these options the performance of the PRFR [3] EOS is compared with the new EOS.

The parameters of the NRTL and UNIQUAC models have been obtained in two ways which are introduced below.

Method 1- Using $\gamma - \phi$ method in VLE calculations we obtained the best fit of the model parameters at or near room temperature and then used them in the mixing rules at all temperatures. With this method we have examined the predictive capabilities of the Gibbs free energy models.

Method 2- The G^{ex} EOS mixing rules are used in VLE calculations and the best fit of parameters are obtained directly at each temperature. This procedure is used to determine the correlative capabilities of the Gibbs free energy models.

5. Results and Discussion

5.1. Calculation for Pure Polar Compounds

The proposed modified PRFR EOS presented in this work, has been tested for vapor pressure and volumetric data of some pure compounds and mixtures. Original PR EOS, PRFR EOS, a 4-parameter equation of state proposed by Jan-Tsai [35] and PRSV EOS [14] have been used for comparison with the proposed new equation. Data on critical properties, acentric factor and dipole moment are all taken from Polling et al. [23].

In all the tables that follow the percent average absolute deviation (%AAD) is defined as follows:

$$\% AAD = \frac{100}{N} * \sum \left| \frac{\exp erimental - calculated}{\exp erimental} \right| \tag{14}$$

The total average absolute deviation in each table has been calculated and is presented in the last row of each table.

The results of the correlation of saturated vapor and liquid specific volumes are given in Table 1 for training compounds and in Table 2 for validation compounds.

Results show that the error in the prediction and correlation of saturated liquid volume has been reduced especially for liquids that form hydrogen bonds. The influence of introducing dipole moment as an input parameter in the equation of state is more pronounced in the liquid phase specific volume than the vapor phase. This can be attributed to the lower relative distances between molecules in the liquid phase than in the vapor phase. Usually the accuracy in the representation of saturated liquid density leads to a loss of accuracy in the prediction of vapor density. The reason is that the slopes of their curves are different. Nevertheless the proposed modification represents a good compromise. Moreover, one way to improve the poor liquid density predictions of cubic equations of state is to allow the hard core parameter b to be temperature dependent [33].

Results of vapor pressure and enthalpy of vaporization predictions are given in Tables 3 and 4 for training and validation compounds respectively. These results also indicate that the proposed equation predicts vapor pressure and enthalpy of vaporization of hydrogen bonded compounds more accurately than original PR, PRFR and JT equations. Considering polar compounds ($\mu > 0.5$) the average absolute deviation in vapor pressure calculations shows considerable decrease in comparison with PR, PRFR and JT EOSs. The AAD% for these substances predicted with the new modification was 2.33 while the corresponding values for PR, PRFR and JT equations are 5.56, 4.78 and 4.03 for training compounds. For validation components the AAD% is 2.28 for the new EOS and for PR, PRFR and JT EOSs are 4.33, 4.03 and 3.27, respectively.

When our proposed model is compared with a broadly well-known EOS like PRSV [14] it is observed that comparable results are produced for vapor specific volume and enthalpy of vaporization. Liquid specific volume is predicted and correlated better while vapor pressure predictions and correlations are weaker. Note that the PRSV equation includes 1 parameter for each compound, totaling 54 parameters for 54 substances which are used in our training compounds and validation compounds. In the other words PRSV has a free parameter that permits an accurate fit to just about any smooth vapor pressure data and it is really a correlation, not prediction. Stryjek and Vera [15] have introduced ways of adding further species-specific constants to PR EOS to provide accurate vapor pressure correlations, especially at lower temperatures and for nonhydrocarbon fluids that are

needed for a better description of vapor-liquid equilibrium. Also, since the a in PR EOS term is based on vapor pressure, the improvement that was proposed in α term of PRSV has its impact on the accuracy of vapor pressure.

In our work we have used a total of 767 data points of 27 compounds to correlate 18 parameters of the proposed equation which is now generalized for all the compounds especially for hydrogen bonded substances. The new equation does not require fitting a free parameter each time it encounters a new substance.

In comparison with PR, PRFR and JT equations of state the proposed model produces more accurate results for liquid density, enthalpy of vaporization and vapor pressure.

In Table 5, the results of the prediction of specific volume of some alcohols at different temperatures and pressures are presented. These results show the superiority of the proposed equation to the others.

5.2. Modelling of binary solutions

Table 6 presents the liquid specific volume of some binary mixtures. Again more accurate results are observed, especially for the mixtures consisting of at least one polar compound or one compound with hydrogen bond.

The performances of various equations of state in bubble point and dew point calculations are presented in Tables 7 and 8, respectively. In these tables, the binary interaction parameter was assumed to be zero and the conventional van der Waals mixing rules [23] were used for prediction of bubble and dew points of binary solutions.

VLE predictions for two different binary mixtures are presented in Figures 1 and 2. In these calculations ordinary Van der Waals mixing rules with zero interaction coefficient have been used, the slight nonideality of these systems are predicted well.
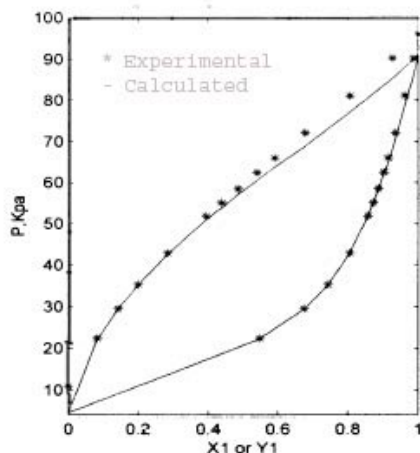
Fig. 1. Comparison of calculated and experimental vapor-liquid equilibria for Hexane (1) + Chlorobenzene (2) system. Data source is ref. [37]
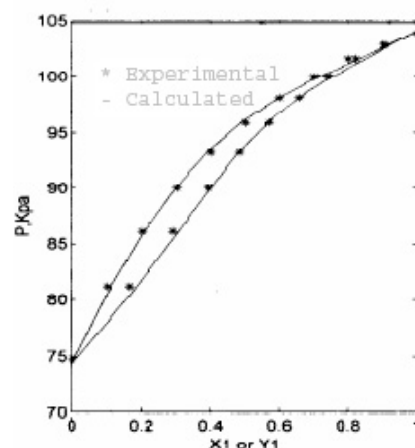
Fig. 2. Comparison of calculated and experimental vapor-liquid equilibria for 2, 2, 4-Trimethylpentane (1) + Toluene (2) system. Data source is ref. [38]

The reliability of the proposed model, the PRSV [14] EOS and the PRFR [3] equation in order to predict phase equilibria of binary solutions, are compared in Tables 9-12.

In Table 9 the correlative capabilities of the NRTL model combined with the two equations of state are compared, and in Table 10 the UNIQUAC model is considered as a predictive option. Table 11 gives number of data points and useful experimental information which was used in Tables 9 and 10. In Table 12, the hydrogen bonding effect is considered via a particular type of UNIQUAC model, named UNIQUAC-HB [55]. According to this table, the results for such systems are clearly improved in comparison with Table 10. Since the binary systems used in Table 12 were selected from Table 9, their experimental conditions and number of data points should not be presented in another table and only Table 11 is suffice. Experimental has shown that the choice of an activity coefficient model coupled with the EOS has some effect on the predictive performance of the WS, HVO, MHV1, MHV2, MHV, LCVM and HVOS models. For example, as the complexity and polarity of the mixture increases, the NRTL and the UNIQUAC-type models, which have temperature dependent parameters, usually produce better results over a range of temperatures in comparison with the simple van Laar or Wilson models [33]. Consequently these two activity coefficient models were selected here.

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Although the binary interaction parameter in WS mixing rule is set equal to zero, very good results are obtained with the proposed EOS. This is attributed to introduction of dipole moment as an extra input parameter to the EOS. The method of using the new mixing rules with the new EOS also improved shortcomings of proposed EOS to predict highly nonideal polar mixtures as reported previously [43] with van der Waals mixing rule.
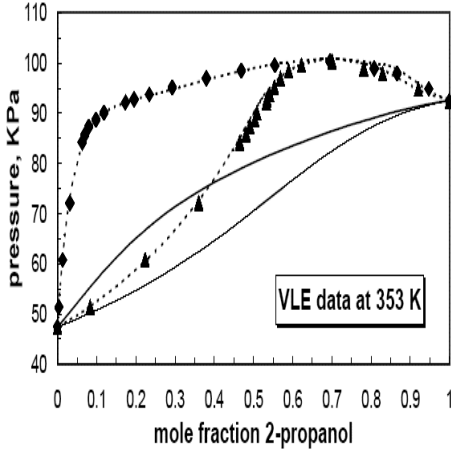
Fig 3. VLE correlation of the 2-propanol and water binary system at 353 K with the Huron-Vidal original (HVO) mixing rule combined with NRTL excess free-energy model and the new equation of state. The dashed lines represents calculated with $\alpha = 0.2893$ and $\tau_{12}/\tau_{21} = 0.7902/3.866$ obtained from fitting the experimental data, and the solid lines denote results calculated with $\alpha = 0.2893$ and $\tau_{12}/\tau_{21} = 0.1519/1.8074$ obtained from $\gamma - \phi$ method. Experimental data are from [47].
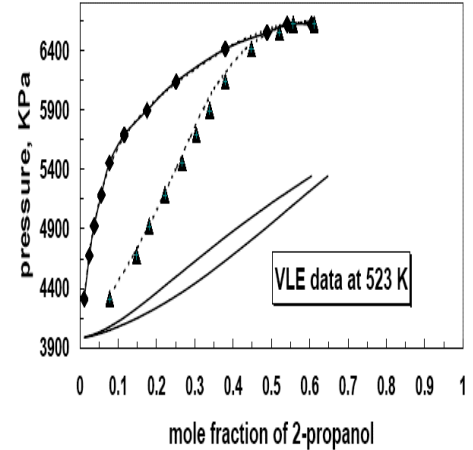
Fig 4. VLE correlation of the 2-propanol and water binary system at 523 K with the Huron-Vidal original (HVO) mixing rule combined with NRTL excess free-energy model and the new equation of state. The dashed lines represents calculated with $\alpha = 0.2893$ and $\tau_{12}/\tau_{21} = 0.4279/3.8138$ obtained from fitting the experimental data, and the solid lines denote results calculated with $\alpha = 0.2893$ and $\tau_{12}/\tau_{21} = 0.1519/1.8074$ obtained $\gamma - \phi$ method. Experimental data are from [47].

It is observed in Table 9 that for highly polar and nonideal mixtures, the HVO model shows good correlative capabilities but Table 10 shows that this is not reliable for extrapolation over a range of a temperature.

The P-x-y diagrams are presented in Figures 3 and 4 for 2-propanol-water binary systems. In these figures, the dashed lines are direct correlation of the isothermal VLE data with the HVO mixing rule and the solid lines are predictions with the model parameters obtained from $\gamma - \phi$ methods at or near room temperature for the excess Gibbs free-energy model.

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The results are not satisfactory, because a fundamental shortcoming of the Huron-Vidal approach is the use of the pressure dependent excess Gibbs free-energy in the EOS rather than excess Helmholtz free-energy, which is much less pressure dependent. This shortcoming was corrected by Wong and Sandler [22]. In Figures 5 and 6, the results for the 2-propanol - water binary system are presented at 353 K and 523 K using WS mixing rules, respectively. In these figures the dashed lines are obtained from the direct fit of the model parameters to the experimental data, whereas the solid lines are prediction with G^{ex} model parameters that have been obtained from the $\gamma - \phi$ correlation for data at 303 K. The results show that the correlations are excellent, but more importantly the predictions at temperatures as much as 200 K above the correlation temperature are almost as accurate as the correlations. Tables 9-12 show the superiority of the new EOS over PRFR [3] and PRSV [14] EOSs for all the binary systems considered in this work which are all highly polar and nonideal, in vapor pressure calculations. It is expected that including mixing rules for the dipole moment would improve VLE predictions and that is why a more substantial improvement over PRSV and PRFR in the mixture predictions (k_{ij}=0) is observed when dipole moment is recognized (Tables 7, 9-12). A reasonable mixing rule on dipole moment should give significant positive deviation in G^{ex} when we mix polar and non-polar in a way that PRSV and PRFR (k_{ij}=0) cannot match, similar to Wertheim's [52-56] hydrogen-bonding theory. A funny thing happens with Wertheim's theory, however. The overall solution actually becomes more stable even though the difference in polarity is driving the instability. In Wertheim's theory, significant pure component energy goes into the hydrogen-bonding, diminishing differences in the disperse interaction energies. The hydrogen-bonding theory accounts for differences in polarity of the compounds (i.e. hydrogen-bonding), but it gives smaller G^{ex} than would be expected from the differences in disperse energies if hydrogen-bonding was ignored. (cf. the methanol + cyclohexane system in Ch.15 of Elliott-Lira [51]). The dipole moment treatment should give similar results.

To demonstrate the differences between the WS and the HVO models, the results of VLE prediction for the 2-propanol - water binary system at 353 K with the parameters obtained from $\gamma - \phi$ procedure at 303 K are shown in Figure 7 in which the solid line is the prediction with the WS mixing rule and the dashed line

describes the results of the HVO model. The significant advantage of the WS model over the HVO model in prediction is clearly visible in this figure.

The results of the approximate methods of combining Gibbs free-energy models and equations of state are presented in Figure 8. Again, two types of calculations were carried out. First, at each temperature the model parameters were separately fitted to the experimental data (dashed lines) with method 1. Second, predictions were made at the higher temperatures with the parameters of the excess Gibbs free-energy model (NRTL in this case) obtained from $\gamma - \phi$ calculations at 303 K as described by method 2. For this system, all four models (MHV1, MHV2, LCVM and HVOS) successfully correlate the data along the 353 K isotherm with parameters optimized in this work. However, the predictive performance of the mixing rules is different. Best results are obtained with the WS model. The MHV1 and the MHV models overpredict the saturation pressure, whereas the HVOS and LCVM models behave very similarly and underpredict the pressure. None of these approximate models, however, was able to predict the phase behavior as accurately as the WS model (Figure 5) at 353 K. At 523 K (Figure 10), the correlations are less accurate than those achieved at 353 K, and the predictions with all models are rather poor, especially when compared with the good predictions from the WS model (Figure 6) at this temperature.

The 2-propanol - water system is considered again using the UNIQUAC model, which is the correlative model closest to the UNIFAC, to examine the effect of activity coefficient model option. The fitted parameters for the 2-propanol - water system are given in the Table 14. The VLE correlation at 298 K and the predictions at 523 K are shown in Figures 9 and 10, respectively. In this case all of the mixing rules are able to provide very accurate correlation of the low-pressure data, as shown in Figure 10. However, when the same parameters are used to predict VLE behavior of this system at 523 K, the performance of various models differs, as shown in Figure 10. The WS model once again gives the best prediction, followed by the HVOS and LCVM models, both of which somewhat underpredict the saturation pressure. The HVO model underpredicts the pressure significantly, and both the MHV1 and MHV2 models overpredict the pressure, the MHV2 model being more seriously in error.
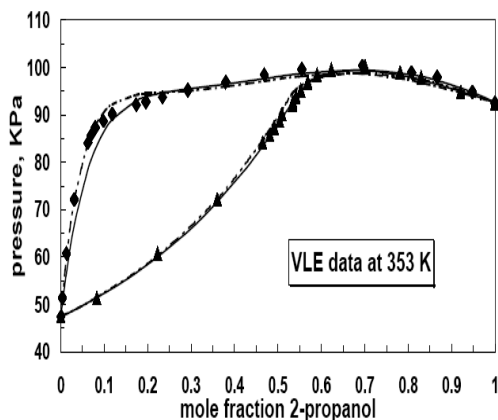
Fig. 5. VLE correlation (solid lines) of the 2-propanol and water binary system at 353 K with the Wong-Sandler (WS) mixing rule combined with the NRTL excess free-energy model and the new equation of state. The dashed lines are calculated with $\alpha = 0.2529, \tau_{12}/\tau_{21} = 0.0755/2.6890$ and with the Wong-Sandler mixing rule parameter $k_{12} = 0.2803$ obtained by fitting the experimental data. The solid lines represent results calculated with $\alpha = 0.2893$ and $\tau_{12}/\tau_{21} = 0.1613/1.8235$ obtained from $\gamma - \phi$ method at 303 K and the Wong-Sandler mixing rule parameter $k_{12} = 0.3762$ obtained by matching the excess Gibbs free-energy from the equation of state and from the NRTL model at 303 K. Experimental data are from [47].
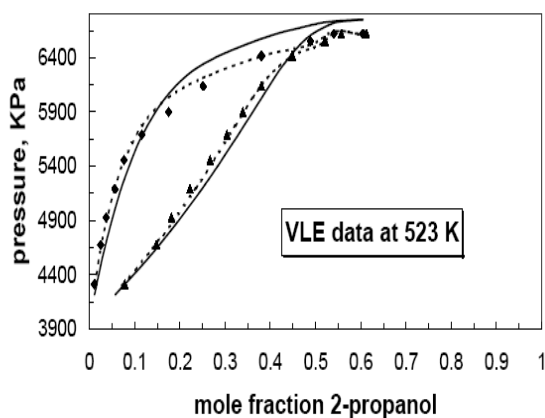
Fig. 6. VLE correlation (solid lines) of the 2-propanol and water binary system at 523 K with the Wong-Sandler (WS) mixing rule combined with the NRTL excess free-energy model and the new equation of state. The dashed lines are calculated with $\alpha = 0.2529, \tau_{12}/\tau_{21} = -0.4400/2.7127$ and with the Wong-Sandler mixing rule parameter $k_{12} = 0.2929$ obtained by fitting the experimental data. The solid lines represent results calculated with $\alpha = 0.2893$ and $\tau_{12}/\tau_{21} = 0.1024/1.3241$ obtained from $\gamma - \phi$ method at 303 K and the Wong-Sandler mixing rule parameter $k_{12} = 0.3931$ obtained by matching the excess Gibbs free-energy from the equation of state and from the NRTL model at 303 K. Experimental data are from [47].
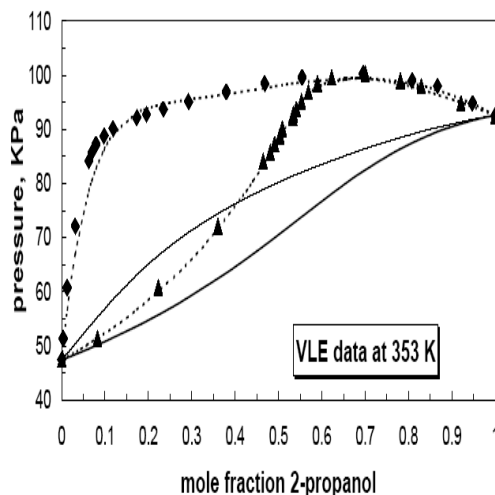
Fig. 7. Comparison of VLE prediction of the 2-propanol and water binary system at 353 K from the Wong-Sandler (dashed lines) and Huron-Vidal original (solid lines) models with both model parameters obtained by fitting the experimental data at 303 K. Points are the experimental data of [47].

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6. Conclusion:

This work demonstrates that the new equation of state is capable of accurate predictions of thermodynamic properties of polar and nonpolar fluids. It can reproduce the liquid and vapor phase densities for pure substances and mixtures with sufficient accuracy. It is also capable of producing good VLE results for slight nonideal systems.

In this paper, a combination of the new mixing rules with the new EOS and compatible G_γ^{ex} models (NRTL, UNIQUAC, and UNIQUAC-HB) was used. This general modification improves previous predictions for VLE behavior and for liquid specific volumes of polar and hydrogen-bonded solutions.

In this research a combination of the new mixing rules and the modification of equation of state which proposed in this research were used to obtain accurate correlation and prediction of VLE of polar mixtures in which the simple equations of state are generally not adequate. Excellent agreement between calculated and experimental data is observed with this method. Also the results obtained from the proposed procedure (using the new EOS) can more accurately correlate the experimental data of VLE for binary polar solutions in comparison with PRFR [3] equation of state. The method of using the new mixing rules with the new EOS also improved its shortcomings to predict the behavior of highly nonideal polar mixtures. Among the mixing rules analyzed here, only the HVO, MHV and WS models are mathematically rigorous, and of the three, only the WS and MHV models have predictive capabilities. All of the approximate methods (MHV1, MHV2, HVOS, and LCVM) demonstrate good correlative and some predictive capabilities, though they are generally less accurate than the WS method for extrapolation. On the other hand the capabilities of the new mixing rules are independent of the type of the EOS and changing the EOS only improves the average absolute deviation for polar mixtures. This is especially obvious when extended ranges of temperature are considered. Although the quality of predictions of the WS and the MHV mixing rules remain about the same over wide temperature ranges, predictions of the approximate methods not satisfactory. Among the approximate models considered in this research, not one is superior to the others. The behavior of the MHV1 and MHV2 models are similar, and the performance of the LCVM and HVOS methods are also comparable in most cases.
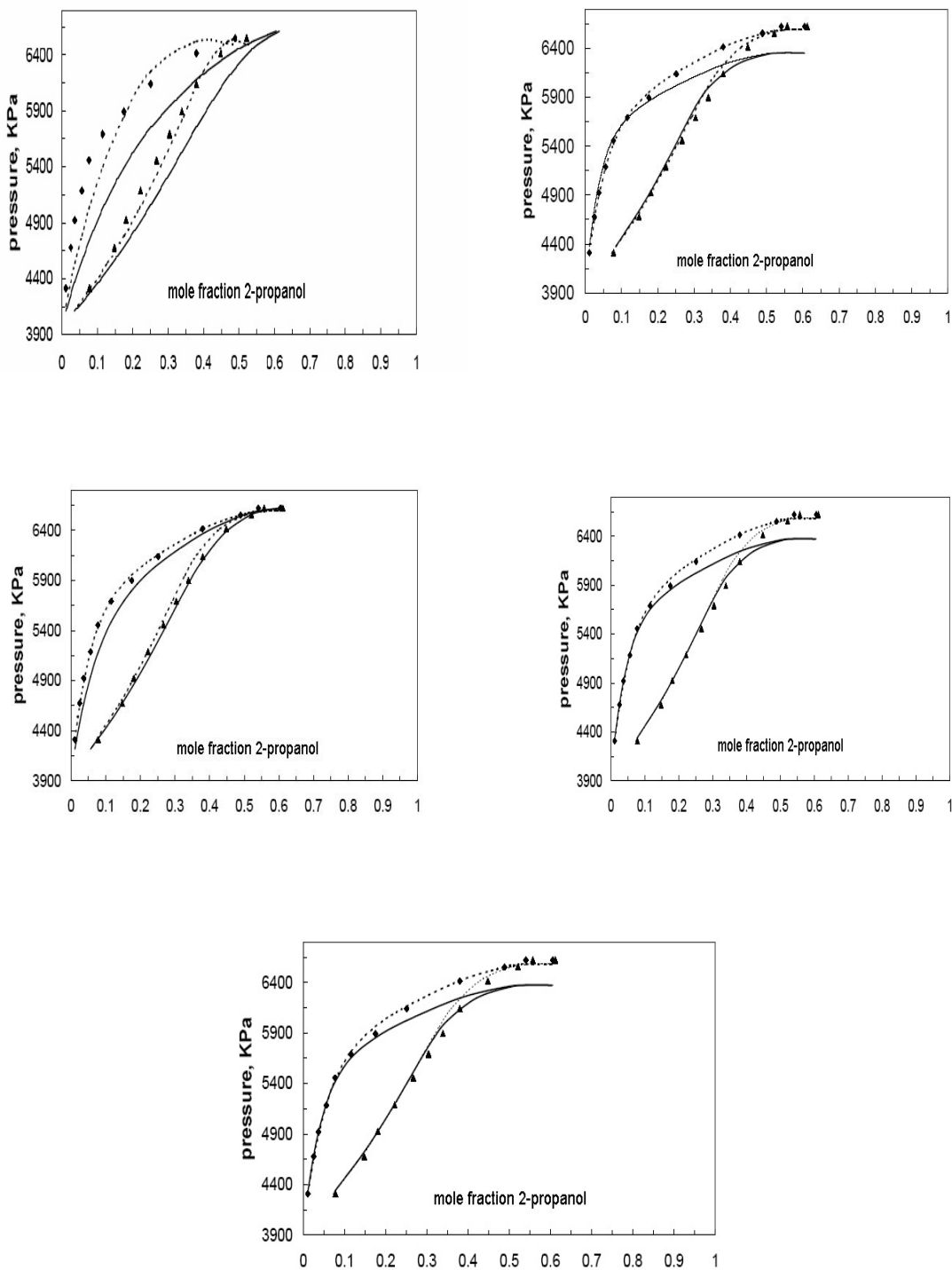
Fig. 8. VLE correlation of the 2-propanol and water binary system at 523 K with various approximate EOS-G^{ex} models. Clockwise from top left: HVOS, MHV2, MHV1, and LCVM mixing rules combined with the NRTL free-energy model and the proposed EOS [17] equation of state. Solid lines represent correlations with NRTL parameters fit to experimental data, the dashed lines represent predictions with the NRTL parameters obtained from the $\gamma - \phi$ correlations for the data at 303 K. Points are VLE data at 523 K from [27]

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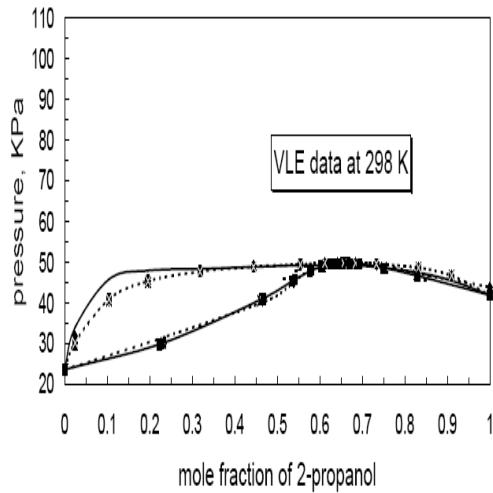
Fig. 9. VLE correlation for the 2-propanol and water binary system at 298 K using UNIQUAC method with the EOS- G^{ex} models. The solid lines reflect the results of WS model. The large, medium, and short dashed lines which almost coincide are from the HVOS, HVO, and MHV1 models; and the dot-dash line denotes the result of the LCVM model. The experimental data are obtained from [47].

Fig. 10. VLE prediction for the 2-propanol and water binary system at 523 K using UNIQUAC method with the EOS- G^{ex} models. The solid lines reflect the results of WS model. The large, medium, and short dashed lines which almost coincide are from the HVOS, HVO, and MHV1 models; and the dot-dash line denotes the result of the LCVM model. The experimental data are obtained from [47].

Acknowledgement

Nomenclature

a, b	= Parameters of equations of state
a_{ij}, b_{ij}	= Correlation factor for parameter a as defined in eqs 7-10.
P	= Pressure
P_c	= Critical pressure
R	= Gas constant

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T	= Temperature
T_c	= Critical temperature
T_r	= Reduced temperature
v	= Specific molar volume
x_i	= Mole fraction of component i in mixture

Greek symbols

α	= Correlation factor for parameter a as defined in eq 2
$\alpha_1, \alpha_2, \alpha_3$	= Correlation factor for parameter a as defined in eqs 7, 9
β	= Correlation factor for parameter b as defined in eq 4
$\beta_1, \beta_2, \beta_3$	= Correlation factor for parameter b as defined in eqs 8,10
ω	= Acentric factor

Superscripts

Sat	= Saturated state
l	= *Liquid phase*
g	= Vapor phase

Subscripts

cal	= Calculated
exp	= *Experimental*

Appendix.

The constants of Equations 7-10 are:

$a_{10} = 0.9749$	$a_{20} = 0.5465$	$a_{30} = -0.2294$
$a_{11} = 1.3827$	$a_{21} = -0.1414$	$a_{31} = 0.7435$
$a_{12} = -134.9547$	$a_{22} = 0.3023$	$a_{32} = 0.0470$
$b_{10} = 0.9646$	$b_{20} = 0.6783$	$b_{30} = -0.8425$
$b_{11} = 0.1949$	$b_{21} = -2.5175$	$b_{31} = 3.0561$
$b_{12} = -44.9857$	$b_{22} = 3.2043$	$b_{32} = -4.1148$

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Table 1
Deviation of saturated liquid and vapor specific volumes from various equations of state for training compounds (Correlations)

Compound	Source Data	No. of Data Points	Dipole Moment (Debye)	%AAD for liquid Specific Volume					%AAD for vapor Specific Volume				
				PR	PRFR	JT	PRSV	NEW EOS	PR	PRFR	JT	PRSV	NEW EOS
1- Heptane	36	30	0.00	2.29	0.41	1.66	0.51	0.56	0.32	0.53	0.34	0.48	0.46
2- 1,3- Butadiene	36	26	0.00	2.96	1.14	1.25	0.98	0.90	1.06	0.88	1.10	0.89	0.89
3- Benzene	36	41	0.00	3.16	1.26	3.02	1.05	0.94	1.28	1.68	1.33	1.54	1.47
4- Hexane	36	32	0.05	2.02	0.47	1.80	0.74	0.87	0.70	0.56	0.72	0.54	0.53
5- 2-Methylbutane	36	28	0.12	4.08	0.97	2.46	1.28	1.43	0.47	0.47	0.47	0.47	0.47
6- Isobutane	36	25	0.13	4.57	0.89	1.30	0.80	0.76	0.64	0.64	0.64	0.61	0.59
7- M-Xylene	36	32	0.33	4.31	2.43	3.88	2.55	2.61	0.33	0.34	0.33	0.33	0.33
8- 1-Butene	36	35	0.33	3.40	0.90	1.19	0.61	0.47	0.58	0.54	0.58	0.55	0.56
9- 1-Octene	36	19	0.34	0.91	0.65	1.69	0.38	0.24	1.87	2.05	1.88	2.04	2.04
10- Propylbenzene	36	19	0.36	1.62	1.48	0.50	1.24	1.12	0.72	0.54	0.76	0.55	0.55
11- Pentane	36	30	0.37	3.01	0.46	2.06	0.61	0.68	0.77	1.13	0.87	0.80	0.63
12- Isopropylbenzene	36	21	0.38	0.68	1.15	0.39	0.73	0.52	0.75	0.82	0.78	0.73	0.69
13- 1-Hexene	36	33	0.40	0.46	1.88	0.91	1.23	0.90	0.75	0.60	0.77	0.61	0.62
14- Toluene	36	27	0.43	2.67	1.21	1.50	1.44	1.55	0.52	1.50	0.70	1.53	1.55
15- Isobutene	36	34	0.50	3.88	0.41	0.52	0.19	0.08	0.74	1.72	0.86	2.25	2.51
16- Dichlorodifluoromethane	36	35	0.54	5.18	1.78	2.31	1.45	1.28	0.23	0.23	0.24	0.20	0.19
17- Propyne	36	37	0.75	3.27	1.00	2.49	0.52	0.28	0.85	1.45	1.05	1.73	1.87
18- Chloroform	36	23	1.10	6.28	2.60	2.92	3.04	3.26	0.55	0.50	0.55	0.51	0.51
19- Chlorodiflouromethane	36	38	1.41	2.88	1.65	4.04	0.76	0.32	0.56	1.27	0.60	1.17	1.12
20- 2-Methyl-1-Propanol	36	27	1.64	3.14	5.06	5.94	1.90	0.32	0.55	0.48	0.55	0.49	0.50
21- 2-Propanol	36	31	1.66	6.25	3.27	5.41	2.38	1.93	0.63	1.38	0.64	1.32	1.29
22- 2-Methyl-2-Propanol	36	35	1.67	1.23	6.27	7.36	2.52	0.64	0.65	0.66	0.65	0.67	0.67
23- 1-Propanol	36	29	1.68	4.65	7.10	5.98	2.96	0.89	0.69	1.03	0.71	1.00	0.98
24- 1,2-Dichloroethane	36	19	1.75	1.13	0.79	0.29	1.40	1.71	1.39	1.78	1.41	1.72	1.69
25- Dichloromethane	36	22	1.80	2.92	8.04	7.73	6.85	6.25	0.92	0.56	0.90	0.57	0.57
26- 1-Butanol	36	30	1.81	2.96	5.17	6.18	2.74	1.53	0.83	1.41	0.84	1.35	1.32
27- Cis-1,2-Dichloroethene	36	9	2.00	5.91	0.70	0.90	1.81	2.37	0.37	0.31	3.44	1.37	0.40
Total		**767**		**3.18**	**2.19**	**2.80**	**1.58**	**1.27**	**0.73**	**0.93**	**0.88**	**0.96**	**0.93**

Table 2
Deviation of saturated liquid and vapor specific volumes from various equations of state for validation compounds (Predictions)

Compound	Source Data	No. of Data Points	Dipole Moment (Debye)	%AAD for liquid Specific Volume					%AAD for vapor Specific Volume				
				PR	PRFR	JT	PRSV	NEW EOS	PR	PRFR	JT	PRSV	NEW EOS
1- 3-Methylheptane	36	36	0.00	3.55	0.59	3.02	0.91	1.07	1.01	1.32	1.00	1.30	1.29
2- Cyclooctane	36	20	0.00	2.95	0.15	0.66	0.63	0.87	0.75	0.39	0.73	0.43	0.45
3- 2,2-Dimethylpropane	36	40	0.02	4.79	2.14	2.69	1.91	1.80	0.83	0.88	0.77	0.90	0.91
4- 2-Methylpentane	36	23	0.03	3.37	1.06	2.92	1.16	1.21	0.60	1.07	0.62	1.02	1.00
5- P-Xylene	36	24	0.10	2.66	2.94	2.48	2.63	2.47	0.45	0.47	0.45	0.46	0.46
6- 1-Pentene	36	32	0.37	2.73	0.94	2.62	0.75	0.65	0.68	0.51	0.66	0.72	0.83
7- Chloropentafluoroethane	36	37	0.52	5.71	4.82	4.26	4.83	4.83	0.81	1.27	0.80	1.18	1.14
8- 1,2-dichloro-1,1,2,2- tetrafluoroethane	36	38	0.52	4.78	3.17	3.32	3.22	3.24	1.33	1.65	0.49	2.02	2.2
9- O-Xylene	36	33	0.52	2.61	0.68	2.58	0.77	0.81	0.33	0.31	0.33	0.32	0.33
10- 3-Methylphenol	36	10	1.65	2.44	1.26	2.60	0.81	0.59	1.27	0.60	1.25	0.65	0.68
11- 1,1,1-Trichloroethane	36	22	1.91	3.12	1.21	11.66	0.62	0.32	0.34	0.35	0.34	0.34	0.34
12- Fluoroethane	36	10	1.95	2.36	7.01	17.27	2.78	0.67	0.3	0.28	1.22	0.29	0.33
13- Methylcyclohexane	36	31	0.00	3.90	0.50	4.66	1.45	0.37	1.13	1.00	0.53	0.71	0.50
14- 2, 3, 4-Trimethyl-pentane	36	33	0.00	3.70	2.20	2.62	1.14	1.07	1.43	1.30	0.96	1.52	0.60
15- Nitrogen Trioxide	48	26	2.12	2.23	1.54	1.97	0.69	0.33	0.71	0.92	0.95	0.82	0.96
16- Formaldehyde	48	23	2.33	1.29	0.31	0.74	0.27	0.13	0.65	0.81	0.52	0.56	0.78
17- Water	48	38	1.85	2.79	1.24	3.23	0.72	0.47	0.52	0.49	0.79	0.51	0.86
18- Carbon Dioxide	33, 48	17	0.00	4.11	3.51	3.75	3.60	3.41	0.23	0.28	0.31	0.40	0.47
19- Hydrogen Sulfide	48	19	0.97	6.91	6.21	6.52	6.41	5.82	0.5	0.51	0.63	0.52	0.57
20- Methyl Acetate	48	34	1.68	6.66	5.82	6.49	5.65	5.36	0.88	1.11	1.16	1.00	1.23
21- Carbon Monoxide	48	7	0.11	1.82	1.66	1.80	1.53	1.41	0.52	0.82	0.88	0.73	0.96
22- Ethanol	48	36	1.69	8.35	6.23	7.11	11.41	5.22	0.6	0.80	0.92	0.76	0.99
23- Sulfur Dioxide	48, 49	33	1.63	2.41	2.35	2.36	2.53	2.29	0.51	0.62	0.60	0.77	0.70
24- Methanol	48	34	1.70	20.56	12.23	18.53	17.52	10.12	1.2	2.06	2.16	1.32	2.32
25- Phenol	48	39	1.45	10.14	9.16	9.65	8.60	8.50	1.01	1.12	1.06	1.13	1.26
26- Acetic Acid	48	31	1.74	29.61	27.43	26.32	32.75	24.39	1.88	2.14	2.19	1.98	2.34
27- Acetone	36, 48	48	2.88	13.49	12.36	13.21	14.72	8.97	6.39	6.73	6.52	6.64	6.97
Total		**774**		**5.89**	**4.40**	**6.11**	**4.82**	**3.57**	**0.99**	**1.10**	**1.07**	**1.07**	**1.16**

Table 3
Deviation of vapor pressure and enthalpy of vaporization from various equations of state for training compounds (Correlations)

Compound	Source of Data	No. of Data Points	Dipole Moment (Debye)	%AAD for vapor pressure					%AAD for enthalpy of vaporization				
				PR	PRFR	JT	PRSV	NEW EOS	PR	PRFR	JT	PRSV	NEW EOS
1- Heptane	36	30	0.00	1.60	0.61	0.57	1.11	1.02	1.40	0.71	0.76	0.75	0.75
2- 1,3- Butadiene	36	26	0.00	0.69	0.84	0.65	0.64	1.03	1.68	1.26	1.55	0.82	0.46
3- Benzene	36	41	0.00	1.64	1.38	1.27	0.65	1.55	1.63	1.13	1.05	0.76	0.62
4- Hexane	36	32	0.05	1.12	0.49	0.55	0.94	1.10	1.68	1.42	1.42	1.21	1.11
5- 2-Methylbutane	36	28	0.12	0.33	0.63	0.49	0.38	0.75	1.10	0.98	0.99	0.98	0.97
6- Isobutane	36	25	0.13	1.32	1.01	1.16	0.72	0.74	1.48	1.46	1.10	1.17	1.20
7- M-Xylene	36	32	0.33	0.42	0.84	0.79	0.41	0.76	1.15	1.55	1.45	1.30	1.22
8- 1-Butene	36	35	0.33	0.47	0.58	0.70	0.30	0.75	0.94	0.85	1.16	1.07	1.03
9- 1-Octene	36	19	0.34	0.78	2.11	1.63	0.52	2.33	1.78	2.08	1.96	2.15	2.25
10- Propylbenzene	36	19	0.36	1.97	0.59	0.46	0.30	0.46	1.45	0.10	0.23	0.23	0.17
11- Pentane	36	30	0.37	0.77	0.42	0.25	0.51	0.93	1.08	0.47	0.69	0.39	0.17
12- Isopropylbenzene	36	21	0.38	3.13	1.19	1.17	1.46	2.13	2.36	0.87	0.91	1.14	1.25
13- 1-Hexene	36	33	0.40	1.59	1.42	0.86	0.07	2.22	0.93	0.18	0.12	0.23	0.28
14- Toluene	36	27	0.43	0.75	0.62	0.40	0.65	0.97	1.09	0.97	0.92	0.86	0.69
15- Isobutene	36	34	0.50	0.72	0.63	1.20	0.57	0.88	1.37	0.83	1.09	1.05	1.03
16- Dichlorodifluoromethane	36	35	0.54	0.77	0.63	0.49	0.42	0.47	1.05	1.44	0.77	0.76	0.76
17- Propyne	36	37	0.75	0.90	0.75	0.68	0.63	0.43	1.72	0.71	1.22	0.75	0.51
18- Chloroform	36	23	1.10	0.86	0.73	0.52	0.13	0.49	0.67	0.70	0.56	0.83	0.61
19- Chlorodiflouromethane	36	38	1.41	0.61	0.80	0.68	0.20	0.51	1.10	0.76	0.60	3.15	0.95
20- 2-Methyl-1-Propanol	36	27	1.64	8.26	7.46	7.54	0.61	3.01	5.14	4.89	4.55	3.78	2.45
21- 2-Propanol	36	31	1.66	7.43	5.80	5.86	1.07	5.13	3.01	4.05	2.18	3.15	4.58
22- 2-Methyl-2-Propanol	36	35	1.67	8.26	7.46	7.54	0.23	3.01	5.14	4.89	4.55	3.78	2.45
23- 1-Propanol	36	29	1.68	19.63	15.64	5.72	1.20	4.64	7.01	6.55	2.14	2.92	4.61
24- 1,2-Dichloroethane	36	19	1.75	3.16	5.11	5.34	0.52	5.66	1.05	3.03	2.80	2.00	2.98
25- Dichloromethane	36	22	1.80	4.71	4.12	4.04	0.39	2.79	2.94	2.63	2.46	3.59	1.77
26- 1-Butanol	36	30	1.81	12.29	10.11	10.27	0.45	2.77	5.70	6.04	4.93	1.08	2.92
27- Cis-1,2-Dichloroethene	36	9	2.00	4.71	2.90	2.51	0.07	0.57	1.86	0.65	0.41	1.00	1.42
Total		**767**		**3.29**	**2.77**	**2.34**	**0.56**	**1.74**	**2.13**	**1.90**	**1.58**	**1.51**	**1.45**

Table 4
Deviation of vapor pressure and enthalpy of vaporization from various equations of state for validation compounds (Predictions)

Compound	Source of Data	No. of Data Points	Dipole Moment (Debye)	%AAD for vapor pressure					%AAD for enthalpy of vaporization				
				PR	PRFR	JT	PRSV	NEW EOS	PR	PRFR	JT	PRSV	NEW EOS
1- 3-Methylheptane	36	36	0.00	1.25	0.17	0.20	0.58	0.30	1.39	1.30	0.99	0.96	1.
2- Cyclooctane	36	20	0.00	3.43	2.78	2.27	0.19	3.70	1.96	0.91	1.06	1.17	1.
3- 2,2-Dimethylpropane	36	40	0.02	0.43	0.65	0.61	0.37	0.72	1.59	0.29	1.21	0.41	0.
4- 2-Methylpentane	36	23	0.03	0.38	0.32	0.22	0.41	0.80	1.25	1.37	1.02	0.73	0.
5- P-Xylene	36	24	0.10	0.49	0.99	0.84	0.27	0.79	0.81	1.32	1.27	0.96	1.
6- 1-Pentene	36	32	0.37	0.99	0.68	0.66	0.38	0.84	1.42	0.98	0.85	0.70	0.
7- Chloropentafluoroethane	36	37	0.52	0.70	0.56	0.61	0.43	0.64	1.85	1.85	1.62	1.40	1.
8- 1,2-dichloro-1,1,2,2-tetrafluoroethane	36	38	0.52	1.98	1.68	1.31	1.12	2.11	2.06	1.04	1.59	1.39	1.
9- O-Xylene	36	33	0.52	0.70	0.71	0.77	0.57	0.60	1.47	1.72	1.59	1.17	1.
10- 3-Methylphenol	36	10	1.65	17.41	11.35	12.25	0.67	4.67	6.24	4.62	3.99	2.14	2.
11- 1,1,1-Trichloroethane	36	22	1.91	4.34	2.90	0.62	0.10	1.76	2.16	0.40	2.22	0.30	0.
12- Fluoroethane	36	10	1.95	0.61	1.89	1.58	0.27	2.71	0.86	2.84	4.19	3.66	4.
13- Methylcyclohexane	36	31	0.00	1.20	0.70	1.36	0.25	0.71	1.95	2.13	3.33	0.93	0.
14- 2, 3, 4-Trimethyl pentane	36	33	0.00	0.60	0.10	0.37	0.04	0.37	2.07	2.11	2.01	1.26	1.
15- Nitrogen Trioxide	48	26	2.12	3.54	2.96	3.13	0.73	2.60	4.42	3.96	3.86	2.44	1.
16- Formaldehyde	48	23	2.33	5.49	4.32	2.46	0.80	3.87	4.69	4.47	4.49	2.25	1.
17- Water	48	38	1.85	3.57	2.70	3.24	0.25	1.93	3.84	3.39	3.43	3.36	3.
18- Carbon Dioxide	33, 48	17	0.00	0.83	0.65	0.71	0.86	0.62	1.61	1.41	1.25	1.21	1.
19- Hydrogen Sulfide	48	19	0.97	3.44	1.83	1.86	0.57	1.72	3.63	1.92	3.65	3.44	3.
20- Methyl Acetate	48	34	1.68	3.58	3.41	3.32	1.22	2.93	3.14	3.05	2.26	3.08	2.
21- Carbon Monoxide	48	7	0.11	1.62	1.51	2.12	1.22	1.69	2.17	2.12	2.05	1.86	1.
22- Ethanol	48	36	1.69	2.40	2.16	2.35	1.81	1.91	4.45	4.32	4.21	4.12	3.
23- Sulfur Dioxide	48, 49	33	1.63	4.90	4.70	3.37	1.91	1.99	7.51	5.33	4.26	4.22	3.
24- Methanol	48	34	1.70	6.26	1.89	4.97	0.53	1.66	6.85	5.41	5.88	4.71	4.
25- Phenol	48	39	1.45	5.53	4.26	4.41	3.94	3.99	2.02	0.97	0.98	0.93	0.
26- Acetic Acid	48	31	1.74	7.28	2.41	6.13	1.54	1.89	3.46	3.39	3.21	2.54	2.
27- Acetone	33, 48	48	2.88	1.83	1.37	1.52	1.25	1.77	3.03	2.90	2.96	2.79	2.
Total		**774**		**3.14**	**2.21**	**2.34**	**0.86**	**1.83**	**2.89**	**2.43**	**2.57**	**2.00**	**1.**

Table 5
Prediction of liquid specific volumes of alcohols

Compound	Source of Data	No. of Data	Dipole Moment (Debye)	Range of P bar	Range of T K	AAD %			
						PR	PRFR	JT	NEW EOS
1- Methanol	38	10	1.70	1.01-338.1	298	21.12	11.76	12.56	5.22
2- Ethanol	38	10	1.73	1.01-338.1	298	10.41	2.26	5.78	0.96
3- 1-Propanol	38	10	1.68	1.01-338.1	298	3.62	8.16	11.14	0.51
4- 1-Butanol	50	6	1.70	1.01	298-318	1.09	6.51	8.26	1.56
5- 1-Pentanol	40	16	1.64	0.001-0.1	323-375	0.35	7.10	8.89	1.08
6- 1-Hexanol	40	16	1.65	0.001-0.1	323-375	0.82	6.77	8.36	1.02
7- 1-Heptanol	40	16	1.70	0.001-0.1	323-375	3.78	3.16	4.89	2.98
8- 1-Octanol	40	16	2.00	0.001-0.1	323-375	0.90	6.77	8.39	0.31
9- 1-Nonanol	40	16	1.61	0.001-0.1	323-375	2.53	4.53	5.87	2.76
Total		**116**				**4.96**	**6.33**	**8.24**	**1.82**

Table 6
Prediction of liquid specific volume of binary mixtures with van der Waals mixing rule and $k_{ij} = 0$.

System	Data Source	No. of data	Dipole moment 1 (Debye)	Dipole moment 2 (Debye)	T-Range K	P-Range bar	PR AAD	JT AAD	PRFR AAD	NEW EOS AAD
1- Benzene(1) + Octane(2)	40	11	0.00	0.00	298.15	1.01	1.68	1.71	1.13	1.00
2- Ethyl benzene(1) + Octane(2)	40	11	0.40	0.00	298.15	1.01	1.89	1.48	1.29	0.85
3- M-xylene(1) + Octane(2)	40	11	0.33	0.00	298.15	1.01	1.76	1.48	1.43	0.99
4- P-xylene(1) + Hexane(2)	40	11	0.32	0.05	298.15	1.01	1.95	1.94	1.73	1.22
5- P-xylene(1) + Heptane(2)	40	10	0.32	0.00	298.15	1.01	1.97	1.70	1.74	1.12
6- Ethyl benzene(1) + 2-Propanone(2)	41	15	0.40	2.86	298.15	1.01	8.87	9.05	9.76	1.95
7- Hexane(1) + 1-Propanol(2)	38	20	0.05	1.68	298.15	1.01-338.1	2.86	2.08	1.13	2.07
8- Hexane(1) + Ethanol(2)	38	20	0.05	1.73	298.15	1.01-338.1	4.77	1.98	2.03	2.27
9- 2-Butanone(1) + Dibutyl ether(2)	42	11	2.76	1.17	303.15	1.01	8.45	6.16	6.66	4.08
10- 2-Picoline(1) + Dibutyl ether(2)	42	11	1.97	1.17	303.15	1.01	11.09	8.26	8.77	8.94
11- Isopropyl acetate(1) + Cyclohexane(2)	50	13	1.75	0.00	298.15	1.01	4.28	2.63	2.11	2.67
12- 1,2- Ethandiol(1) + 2-Methoxyethanol(2)	50	11	2.30	2.04	353.00	1.01	7.30	9.32	6.91	4.03
Total		**155**					**4.74**	**3.98**	**3.72**	**2.60**

Table 7
Prediction of bubble point pressure for binary systems with van der Waals mixing rule and $k_{ij} = 0$.

System	Data Source	No. of data	Dipole moment 1 (Debye)	Dipole moment 2 (Debye)	T-Range °C	P-Range bar	PR		PRFR		PRSV		NEW EOS	
							AAD P	Δy [1]	AAD P	Δy	AAD P	Δy	AAD P	Δy
1- 1,1-Dichloroethane(1) + Chloroform(2)	50	9	0.24	1.10	57-70	1.01	0.71	0.0347	1.49	0.0347	0.57	0.0375	0.33	0.0366
2- Chloroform(1) + Benzene(2)	50	6	1.10	0.00	25.05	0.14-0.25	6.41	0.0227	4.76	0.0222	5.67	0.0242	4.97	0.0227
3- Carbon tetrachloride(1) + Benzene(2)	50	11	0.00	0.00	40	0.24-0.28	3.59	0.0063	2.76	0.0061	3.94	0.0089	3.08	0.0062
4- 1,2-Dichloroethane(1) + Toluene(2)	50	13	1.80	0.40	85-110	1.01	4.30	0.0163	3.24	0.0160	5.24	0.0201	4.68	0.0190
5- Ethyl bromide(1) + Heptane(2)	50	9	2.00	0.00	30	0.16-0.73	5.15	0.0092	2.08	0.0087	3.12	0.0099	2.66	0.0080
6- 1-Chlorobutane(1) + Heptane(2)	50	13	2.00	0.00	50	0.20-0.37	2.49	0.0168	3.21	0.0187	4.87	0.0176	3.28	0.0173
7- Toluene(1) + Phenol(2)	45	11	0.40	1.60	110-170	1.01	4.59	0.0555	3.07	0.0580	3.76	0.0605	3.35	0.0599
8- Hexane(1) + Chlorobenzene(2)	50	12	0.05	1.60	65	0.22-0.85	2.11	0.0045	2.32	0.0044	2.81	0.0077	2.56	0.0044
9- Benzene(1) + Aniline(2)	46	10	0.00	1.60	119.3	0.81-2.64	7.92	0.0093	5.22	0.0050	5.32	0.0059	5.17	0.0040
10- 2,2,4-Trimethylpentane(1) + Toluene(2)	37	9	0.00	0.40	100	0.80-1.03	0.26	0.0035	0.35	0.0040	0.55	0.0062	0.33	0.0042
Total							3.75	0.0179	2.92	0.0178	3.58	0.0198	3.04	0.0182

[1] - $\Delta y = \dfrac{1}{N} \sum_1^N \left| y_{exp} - y_{cal} \right|$

Table 8
Prediction of dew point pressure for binary systems with van der Waals mixing rule and $k_{ij} = 0$.

System	Data Source	No. of data	Dipole moment 1 (Debye)	Dipole moment 2 (Debye)	T-Range °C	P-Range bar	PR		PRFR		NEW EOS	
							AAD P	Δx^2	AAD P	Δx	AAD P	Δx
1- 1,1-Dichloroethane(1) + Chloroform(2)	50	9	0.24	1.10	57-70	1.01	1.09	0.0329	1.88	0.0329	0.47	0.0348
2- Chloroform(1) + Benzene(2)	50	6	1.10	0.00	25.05	0.14-0.25	7.70	0.0301	5.64	0.0291	5.46	0.0302
3- Carbon tetrachloride(1) + Benzene(2)	50	11	0.00	0.00	40	0.24-0.28	3.63	0.0062	2.80	0.0061	2.69	0.0061
4- 1,2-Dichloroethane(1) + Toluene(2)	50	13	1.80	0.40	85-110	1.01	3.93	0.0146	3.48	0.0156	3.82	0.0190
5- Ethyl bromide(1) + Heptane(2)	50	9	2.00	0.00	30	0.16-0.73	2.29	0.0142	1.66	0.0172	1.51	0.0132
6- 1-Chlorobutane(1) + Heptane(2)	50	13	2.00	0.00	50	0.20-0.37	9.70	0.0197	3.13	0.0233	3.18	0.0207
7- Toluene(1) + Phenol(2)	45	11	0.40	1.60	110-170	1.01	4.53	0.0214	4.05	0.0166	4.12	0.0229
8- Hexane(1) + Chlorobenzene(2)	50	12	0.05	1.60	65	0.22-0.85	1.85	0.0099	1.15	0.0164	1.20	0.0164
9- Benzene(1) + Aniline(2)	46	10	0.00	1.60	119.3	0.81-2.64	4.16	0.0345	3.44	0.0255	3.75	0.0252
10- 2,2,4-Trimethylpentane(1) + Toluene(2)	37	9	0.00	0.40	100	0.80-1.03	0.25	0.0037	0.35	0.0039	0.37	0.0042
Total		**103**					**3.91**	**0.0187**	**2.70**	**0.0187**	**2.66**	**0.0193**

^{2} - $\Delta x = \dfrac{1}{N}\sum_1^N \left| x_{exp} - x_{cal} \right|$

Table 9

AAD in pressure calculation with optimum binary parameters reported in the text with NRTL G^{ex} model as a correlative tool

System	Data Source	AAD Mixing rule HVO			AAD MHV1			AAD MHV2			AAD MHV			AAD HVOS			AAD LCVM			AAD WS		
		PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS
1- 2-Propanol(1) + Water(2)	33	7.54	2.6	5.36	2.68	1.62	0.55	7.65	3.61	2.28	5.45	5.04	3.42	2.56	1.51	0.46	9.06	1.37	0.47	2.68 (7.90)[3]	1.93 (2.25)	0.83 (1.10)
2- Acetone(1) + Benzene(2)	33	3.18	1.26	1.23	1.51	1.33	0.12	1.30	1.13	0.13	1.21	1.11	0.11	1.31	1.14	0.17	1.39	1.13	0.23	1.47 (1.69)	1.29 (1.57)	0.31 (0.51)
3- Acetone(1) + Methanol(2)	33	3.33	1.82	0.96	4.74	2.41	1.05	2.98	2.29	1.20	5.19	3.86	3.29	2.83	1.80	0.83	2.74	1.75	0.96	2.64 (3.21)	2.06 (2.42)	0.90 (1.28)
4- Acetone(1) + Water(2)	33	6.19	4.55	3.94	5.45	4.80	3.36	5.62	4.11	3.41	5.14	3.94	3.25	4.79	4.32	2.77	4.96	4.24	2.73	5.10 (6.50)	3.94 (4.81)	2.98 (4.25)
5- Methane(1) + n-Pentane(2)	33	2.73	1.55	0.61	3.03	2.68	1.32	2.65	2.72	1.42	2.76	2.39	1.27	2.69	2.54	1.29	2.91	2.60	1.44	2.58 (2.87)	2.45 (2.68)	1.23 (1.47)
6- Methane(1) + n-Heptane(2)	33	3.46	2.5	1.52	3.18	2.75	1.33	2.76	2.47	1.26	2.97	2.68	1.42	2.82	2.70	1.45	2.94	2.86	1.74	4.46 (4.76)	3.52 (3.79)	2.12 (2.63)
7- Methane(1) + n-Decane(2)	33	4.78	2.31	3.65	4.19	3.57	2.36	3.45	2.92	1.97	3.76	3.55	2.12	3.26	2.95	1.77	4.21	3.33	2.49	3.50 (4.45)	1.98 (2.99)	1.74 (2.10)
8- Carbon dioxide(1) + Benzene(2)	33	5.39	3.13	2.08	5.37	3.63	2.03	5.11	3.32	1.97	5.21	4.92	3.33	5.02	3.07	1.84	5.21	3.41	2.01	4.61 (5.09)	2.95 (3.22)	1.69 (1.95)
9- Carbon dioxide(1) + Propane(2)	33	2.69	1.47	0.56	2.12	1.88	0.69	1.88	1.80	0.65	1.63	1.46	0.39	1.64	1.39	0.37	1.82	1.74	0.59	1.37 (2.13)	1.33 (1.75)	0.31 (0.85)
10- Carbon dioxide(1) + Methanol(2)	33	6.23	3.22	2.62	6.28	3.81	2.47	6.02	3.76	2.34	5.99	3.48	2.24	5.86	3.52	2.19	6.25	3.67	2.30	4.87 (5.96)	3.04 (4.93)	1.65 (3.13)
11- Ethanol(1) + n-Heptane(2)	33	3.29	2.16	1.39	2.17	2.12	0.54	2.01	1.47	0.41	1.87	1.53	0.48	1.80	1.36	0.33	1.89	1.47	0.40	1.34 (1.42)	1.13 (1.34)	0.12 (0.29)
12- Methyl acetate(1) + Cyclohexane(2)	33	4.21	3.19	2.23	3.75	3.39	1.86	1.49	1.28	0.27	3.45	2.71	1.59	1.46	1.24	0.21	1.47	1.27	0.23	1.45 (2.07)	1.21 (1.88)	0.19 (0.76)
13- Methanol(1) + ...	33	4.17	2.35	2.14	2.96	2.73	0.97	2.53	2.18	1.01	4.06	3.73	2.31	2.62	2.25	1.11	2.54	2.29	1.13	2.22 (2.58)	3.00 (3.58)	2.31 (2.62)

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[3] - ( ) = The results obtained with zero binary interaction parameter

33

Benzene(2)

System																						
14- Methanol(1) + Water(2)	33	5.81	2.07	3.67	5.07	3.99	2.57	3.10	2.72	1.60	4.74	4.12	2.89	1.93	1.55	0.54	1.88	1.52	0.51	2.29 (2.53)	1.86 (2.19)	0.96 (1.19)
15- Pentane(1) + Ethanol(2)	33	4.2	3.28	2.41	1.81	1.62	0.36	1.68	1.48	0.44	1.66	1.42	0.40	1.48	1.23	0.22	1.71	1.39	0.44	1.43 (1.49)	1.31 (1.48)	0.30 (0.16)
16- Propane(1) + Methanol(2)	33	6.02	5.22	4.24	7.02	7.09	4.99	6.43	6.62	4.87	6.81	5.70	4.01	6.22	6.33	4.44	6.66	6.07	4.21	3.67 (6.02)	3.51 (5.40)	2.13 (3.93)
17- Benzene(1) + Chloroform(2)	50	3.77	2.81	1.90	3.52	3.37	1.86	3.33	3.13	1.85	3.32	3.20	1.86	3.21	3.10	1.81	3.36	3.20	1.89	3.16 (3.33)	3.05 (3.26)	1.75 (1.91)
18- Benzene(1) + Toluene(2)	50	2.89	1.81	1.33	2.47	2.15	1.30	2.21	1.90	1.26	2.16	1.87	1.22	2.17	1.87	1.24	2.18	1.86	1.23	2.13 (2.19)	2.45 (2.50)	0.70 (0.78)
19- Carbon tetrachloride(1) + 1,2-Dichloroethane(2)	50	4.6	3.66	2.71	4.49	4.38	2.66	4.29	4.17	2.65	4.26	4.12	2.64	4.20	4.06	2.61	4.23	4.09	2.69	4.21 (4.28)	4.05 (4.24)	2.61 (2.69)
20- Chloroform(1) + Triethylamine(2)	50	10.81	9.86	8.89	10.72	10.47	7.77	10.55	10.23	7.72	10.44	10.17	7.71	10.53	10.30	7.76	9.95	9.68	7.33	9.93 (16.96)	9.71 (16.66)	7.31 (13.11)
21- Acetone(1) + Chloroform(2)	50	2.28	1.45	0.46	1.77	1.72	0.45	1.58	1.51	0.46	1.62	1.48	0.49	1.64	1.54	0.50	1.57	1.51	0.44	1.54 (1.83)	1.49 (1.76)	0.43 (0.66)
22- Ethane(1) + Heptane(2)	50	6.34	5.36	4.41	4.56	3.79	2.41	6.26	5.72	4.00	3.70	3.68	2.17	4.05	4.02	2.50	4.61	4.45	2.89	4.00 (5.66)	3.46 (4.97)	2.26 (3.77)
23- Water(1)+ Ethylenglycole(2)	50	5.33	4.21	3.26	8.60	8.06	5.74	8.21	7.77	5.69	7.56	7.33	5.33	5.60	5.11	3.53	5.54	5.09	3.49	4.41 (5.11)	4.06 (4.75)	2.61 (3.29)
24- Toluene(1) + n-Octane(2)	50	2.99	1.98	1.06	2.76	2.39	1.08	2.53	2.18	1.06	2.52	2.18	1.03	2.47	2.18	1.02	2.53	2.18	1.14	2.51 (2.60)	2.21 (2.18)	1.04 (1.16)
25- Methylcyclohexane (1) + Toluene(2)	50	3.14	2.12	1.19	2.24	2.07	0.82	2.01	1.84	0.79	1.96	1.83	0.77	1.87	1.80	0.70	1.99	1.86	0.76	2.06 (2.36)	1.87 (2.16)	0.79 (1.06)
26- Methanol(1) + Acetone(2)	50	2.44	1.46	0.49	1.93	1.89	0.59	1.69	1.70	0.55	1.66	1.66	0.56	1.60	1.66	0.58	1.81	1.77	0.65	1.74 (1.71)	1.55 (1.54)	0.59 (0.57)
27- Acetone(1) + Cyclohexane(2)	50	6.9	5.8	4.86	7.24	6.86	4.77	7.01	6.66	4.76	6.95	6.66	4.74	6.84	6.78	4.80	6.99	6.71	4.79	7.26 (7.42)	7.10 (7.26)	5.07 (5.26)
28- Chloroform(1) + Acetone(2)	50	2.98	1.92	0.99	2.44	2.29	0.93	2.22	2.06	0.90	2.17	2.04	0.83	2.09	2.00	0.85	2.23	2.05	0.92	2.15 (2.31)	2.04 (2.19)	0.92 (1.04)
29-n-Pentane(1) + n-Propionaldehyde	50	3.06	1.96	1.05	2.56	2.45	1.09	2.31	2.29	1.06	2.25	2.23	1.00	2.22	2.19	1.03	2.28	2.21	1.04	2.83 (2.56)	2.58 (2.12)	1.37 (0.97)
Total		**4.51**	**3.00**	**2.46**	**4.02**	**3.49**	**2.00**	**3.82**	**3.28**	**2.00**	**3.88**	**3.45**	**2.17**	**3.34**	**2.95**	**1.69**	**3.69**	**2.99**	**1.76**	**3.23 (4.10)**	**2.83 (3.51)**	**1.63 (2.22)**

Table 10

AAD in pressure calculation with optimum binary parameters reported in the text with UNIQUAC G^{ex} model as a predictive tool

System	Data Source	AAD Mixing rule HVO			AAD MHV1			AAD MHV2			AAD MHV			AAD HVOS			AAD LCVM			AAD WS		
		PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS
1- 2-Propanol(1) + Water(2)	33	5.54	3.89	2.44	4.87	3.99	2.80	9.47	2.40	1.61	4.91	4.03	2.82	5.62	3.73	2.40	5.32	3.36	2.17	5.87 (8.83)[4]	2.82 (3.33)	1.59 (2.01)
2- Acetone(1) + Benzene(2)	33	2.95	2.76	1.53	3.73	2.94	1.94	2.76	2.22	1.14	3.57	3.23	2.01	1.77	1.75	0.61	3.00	2.75	1.53	2.99 (3.18)	2.46 (2.71)	1.30 (1.69)
3- Acetone(1) + Methanol(2)	33	2.41	3.05	1.77	3.01	2.46	1.25	2.07	1.51	0.47	2.64	2.23	1.13	2.25	2.89	1.61	3.10	2.54	1.51	2.00 (2.34)	2.68 (2.89)	1.42 (1.60)
4- Acetone(1) + Water(2)	33	5.28	4.00	2.96	11.14	7.04	5.24	7.79	7.18	5.31	10.20	6.28	4.65	5.34	3.80	2.58	5.33	4.65	3.15	3.88 (7.83)	3.39 (7.15)	2.18 (5.22)
5- Methane(1) + n-Pentane(2)	33	2.34	1.98	0.91	3.35	3.32	1.97	2.92	2.27	1.24	2.80	2.58	1.32	2.74	2.40	1.22	3.06	2.77	1.52	2.64 (3.39)	2.57 (3.27)	1.33 (1.91)
6- Methane(1) + n-Heptane(2)	33	4.23	3.58	2.32	2.23	1.78	0.77	3.12	2.38	1.21	2.11	1.81	0.63	1.59	1.33	0.29	2.51	2.31	1.12	5.80 (6.58)	5.49 (6.30)	3.81 (4.47)
7- Methane(1) + n-Decane(2)	33	4.39	3.86	2.51	3.80	3.33	2.25	3.69	3.42	2.17	3.58	3.57	2.15	3.06	2.72	1.57	3.91	3.71	2.33	3.30 (3.88)	3.15 (3.67)	1.80 (2.27)
8- Carbon dioxide(1) + Benzene(2)	33	5.38	5.25	3.64	5.31	5.23	3.55	5.22	5.15	3.41	5.29	5.09	3.41	5.37	5.00	3.41	5.73	5.33	3.62	4.24 (4.78)	4.10 (4.81)	2.56 (3.09)
9- Carbon dioxide(1) + Propane(2)	33	1.72	1.74	0.71	1.62	1.63	0.42	1.45	1.22	0.22	1.57	1.42	0.41	1.37	1.28	0.21	1.75	1.52	0.41	1.29 (1.72)	1.28 (1.71)	0.21 (0.51)
10- Carbon dioxide(1) + Methanol(2)	33	6.69	6.13	4.32	6.42	5.97	4.28	6.05	5.87	4.16	6.26	5.60	4.05	3.62	3.41	2.04	6.26	5.98	4.17	5.85 (6.66)	5.35 (6.19)	3.65 (4.32)
11- Ethanol(1) + n-Heptane(2)	33	6.61	5.74	4.11	3.24	2.89	1.65	2.44	2.34	1.21	3.28	2.92	1.66	5.79	5.34	3.62	5.99	5.45	3.82	4.69 (5.05)	4.64 (4.88)	3.13 (3.43)
12- Methyl acetate(1) + Cyclohexane(2)	33	3.92	3.56	2.23	3.99	3.65	2.23	4.06	3.61	2.18	3.80	3.55	2.14	4.43	4.05	2.81	4.02	3.81	2.41	4.62 (5.35)	4.47 (5.17)	2.91 (3.54)
13- Methanol(1) + Benzene(2)	33	5.00	4.74	3.09	2.51	2.17	1.01	3.68	2.09	0.93	2.46	2.39	1.20	2.57	2.28	1.12	2.92	2.82	1.50	2.33 (2.56)	2.15 (2.28)	0.95 (1.11)
14- Methanol(1) + Water(2)	33	4.63	3.71	2.88	2.40	1.75	0.66	2.27	1.49	0.58	2.42	2.21	1.07	2.53	2.09	1.11	2.57	2.10	1.11	2.27 (2.83)	2.34 (2.41)	1.18 (1.30)

[4] - ( ) = The results obtained with zero binary interaction parameter

System	N																				
15- Pentane(1) + Ethanol(2)	33	4.09	3.83	2.41	1.84	1.51	0.52	1.99	1.72	0.79	1.72	1.74	0.63	1.70	1.58	0.51	1.80	1.60	0.63	1.59 (1.86)	1.45 (1.66)	0.41 (0.64)
18- Benzene(1) + Toluene(2)	50	2.42	2.19	1.53	2.39	2.17	1.48	2.38	2.16	1.48	2.34	2.10	1.41	2.29	2.06	1.37	2.31	2.09	1.40	2.28 (2.36)	2.07 (2.12)	1.34 (1.38)
19- Carbon tetrachloride(1) + 1,2-Dichloroethane(2)	50	4.76	4.64	3.08	4.57	4.39	2.85	4.55	4.40	2.83	4.41	4.29	2.67	4.38	4.24	2.66	4.61	4.43	2.79	4.39 (4.64)	4.33 (4.59)	2.79 (3.00)
20- Chloroform(1) + Triethylamine(2)	50	13.06	12.68	9.72	11.45	11.13	8.49	11.40	11.08	8.44	11.48	11.14	8.60	11.52	11.05	8.51	12.18	11.75	9.15	11.43 (17.17)	10.78 (15.91)	8.39 (13.00)
21- Acetone(1) + Chloroform(2)	50	1.57	1.54	0.46	1.71	1.62	0.57	1.75	1.65	0.61	1.99	1.59	0.76	1.87	1.54	0.64	1.55	1.62	0.49	1.57 (2.65)	1.39 (2.39)	0.42 (1.31)
22- Ethane(1) + Heptane(2)	50	2.57	2.13	1.16	7.26	6.57	4.81	4.62	3.67	2.28	4.39	3.64	2.23	4.51	4.27	2.83	7.53	6.97	5.10	2.46 (2.79)	2.31 (2.60)	1.14 (1.36)
23- Water(1)+ Ethylenglycole(2)	50	3.92	3.75	2.31	8.10	7.42	5.46	7.31	6.42	4.66	7.21	6.61	4.72	6.38	5.99	4.20	5.96	5.54	3.89	4.22 (4.49)	3.88 (3.94)	2.45 (2.56)
24- Toluene(1) + n-Octane(2)	50	2.35	2.12	1.07	2.34	2.12	1.02	2.33	2.12	1.00	2.30	2.12	0.97	2.28	2.12	0.95	2.40	2.12	1.04	2.10 (2.48)	2.05 (2.44)	0.89 (1.19)
25- Methylcyclohexane (1) + Toluene(2)	50	2.92	2.62	1.40	2.50	2.34	1.16	2.47	2.31	1.12	2.45	2.25	1.11	2.36	2.22	1.07	2.45	2.36	1.16	2.40 (2.70)	2.33 (2.52)	1.13 (1.32)
26- Methanol(1) + Acetone(2)	50	1.74	1.68	0.58	2.01	1.81	0.72	1.98	1.82	0.70	1.98	1.81	0.68	1.87	1.76	0.68	2.12	1.98	0.84	1.57 (1.47)	1.46 (1.42)	0.41 (0.37)
27- Acetone(1) + Cyclohexane(2)	50	8.48	8.13	6.03	8.37	8.07	5.92	8.25	8.02	5.87	8.23	8.02	5.83	8.14	7.65	5.54	8.23	7.71	5.61	6.68 (7.38)	6.61 (7.22)	4.69 (5.22)
28- Chloroform(1) + Acetone(2)	50	2.47	2.36	1.09	2.42	2.28	1.09	2.39	2.25	1.06	2.35	2.22	1.02	2.30	2.23	1.05	2.52	2.33	1.16	2.41 (2.58)	2.31 (2.40)	1.13 (1.23)
29-n-Pentane(1) + n-Propionaldehyde	50	2.54	2.15	1.17	2.16	1.99	0.88	2.12	1.96	0.87	2.09	1.92	0.85	2.01	1.89	0.77	2.13	2.04	0.91	2.13 (2.40)	2.01 (2.17)	0.89 (1.06)
Total		**4.30**	**3.94**	**2.57**	**4.38**	**3.91**	**2.53**	**4.05**	**3.43**	**2.12**	**4.13**	**3.73**	**2.35**	**3.80**	**3.47**	**2.14**	**4.24**	**3.90**	**2.50**	**3.93 (4.53)**	**3.46 (5.17)**	**2.11 (2.69)**

Table 21
Experimental condition and number of data points for binary systems used in Tables 9 and 10

System	No. of Data points	Data type			
		Isothermal		Isobaric	
		Temperatures (°C)	Pressure ranges (bar)	Pressures (bar)	Temperature ranges (°C)
1	47	25, 80, 250	0.03-0.06, 0.47-0.92, 43.10-66.2		
2	21	25	0.13-0.3		
3	24	25, 200	0.17-0.31, 28.92-39.86		
4	84	25, 100, 200, 250, 523	0.03-0.31, 1.11, 3.69, 16-27.93, 40.41-65.79, 40.41-65.79		
5	39	37, 104, 171	1.08-169.27, 6.54-143.48, 22.70-70.67		
6	36	4, 104, 204	0.02-229.46, 1.21-227.39, 55.16-131.41		
7	34	104, 150, 269	1.38-327.5, 30.40-70.93, 30.5-151.43		
8	31	0, 40, 120	8.26-32, 7.4-77.2, 3.05-132.95		
9	42	4, 37, 71	5.45-37.92, 13.01-68.95, 26.46-67.29		
10	29	0, 121, 204	6.9-34.47, 6.65-165, 44.1-127.5		
11	15	60	0.28-0.47		
12	9	40	0.3-0.57		
13	21	20, 180	0.1-0.13, 131.19-27.34		
14	28	250	46.96-68.55		
15	34	100, 125, 150	2.2-5.91, 4.83-10.03, 9.48-15.95		
16	12	40	3.5-13.6		
17	101	50	0.39-0.67	1.01, 2.05, 3.03, 1.01	61-80, 84-105, 99-120, 62-78
18	32	52, 100, 137	0.13-0.44, 0.76-1.86, 2.02-4.48	0.99, 0.99	80-111, 89-111
19	62	25, 30, 40	0.11-0.15, 0.13-0.19, 0.22-0.29	1.01	76-81
20	16	25, 10	0.09-0.12, 0.04-0.13		
21	6	35	0.35-0.43		
22	32	66, 93, 121, 149, 177	31.38-66.76, 36.14-77.72, 39.8-83.79, 40.69-85.17, 40.41-79.72		
23	60	98, 110, 122	0.04-0.93, 0.05-1.18, 0.07-1.5	0.99	110-184
24	29	40, 60	0.04-0.08, 0.11-0.18		
25	68	40, 60, 80	0.03-0.12, 0.07-0.27, 0.17-0.54	0.27, 0.53	60-69, 80-89
26	182	100, 125, 150, 20, 150, 55	3.5-4.05, 6.67-7.83, 11.21-13.99, 0.13-0.25, 0.22-0.38, 0.73-1.01	1.01, 1.01, 1.01, 0.99	56-65, 55-65, 55-64, 56-61
27	109	20, 30, 50, 25	0.1-0.28, 0.16-0.43, 0.36-0.91, 0.31-0.35	1.01	57-65
28	44	30	0.27-0.37		
29	26	40	0.76-1.36		
Total	**1273**				

Table 12

AAD in pressure calculation with optimum binary parameters reported in the text with UNIQUAC-HB model as a correlative tool

System	Data Source	Mixing rule T-Range °C	AAD HVO			AAD MHV1			AAD MHV2			AAD MHV			AAD HVOS			AAD LCVM			AAD WS		
			PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS	PRFR	PRSV	NEW EOS
1- 2-Propanol(1) + Water(2)	33	25-250	5.20	3.42	2.02	4.14	4.14	2.66	9.46	2.47	1.25	4.17	3.51	2.11	4.50	3.42	2.04	4.53	2.83	1.67	5.54 (6.90)[5]	2.64 (3.13)	1.57 (1.82)
2- Acetone(1) + Methanol(2)	33	25-200	2.21	2.80	1.56	2.53	2.27	1.11	1.93	1.40	0.36	2.27	2.25	1.05	2.09	2.53	1.39	2.57	2.60	1.35	1.98 (2.05)	2.19 (2.46)	1.07 (1.24)
3- Acetone(1) + Water(2)	33	25-523	4.75	4.45	2.93	9.83	7.03	5.04	7.77	6.80	4.82	9.67	6.10	4.31	5.13	3.71	2.28	5.06	3.83	2.50	3.47 (7.28)	3.40 (6.17)	2.10 (4.87)
4- Carbon dioxide(1) + Methanol(2)	33	0-204	6.16	5.09	3.58	5.55	6.08	4.26	5.74	5.85	4.04	5.47	5.49	3.75	3.17	3.24	1.92	6.14	5.34	3.62	5.73 (6.60)	4.39 (5.06)	2.90 (3.49)
5- Ethanol(1) + n-Heptane(2)	33	60	5.64	5.58	3.82	3.13	2.89	1.60	2.36	2.38	1.17	2.85	2.59	1.43	4.72	4.84	3.27	5.43	5.33	3.63	4.23 (4.63)	4.49 (4.62)	2.92 (3.02)
6- Methanol(1) + Benzene(2)	33	20-180	3.98	4.29	2.85	2.16	2.11	0.93	3.35	1.86	0.70	2.31	2.16	0.93	2.42	2.13	0.96	2.77	2.42	1.21	2.33 (2.53)	2.06 (2.29)	0.85 (1.10)
7- Methanol(1) + Water(2)	33	25-250	4.61	4.22	2.77	2.38	1.74	0.64	1.95	1.47	0.45	2.38	1.90	0.90	2.27	1.83	0.96	2.27	2.19	1.10	1.99 (2.44)	2.21 (2.39)	1.01 (1.19)
8- Pentane(1) + Ethanol(2)	33	100-150	3.86	3.57	2.28	1.69	1.42	0.41	1.84	1.63	0.59	1.71	1.64	0.51	1.58	1.54	0.45	1.75	1.59	0.51	1.47 (1.66)	1.43 (1.87)	0.34 (0.61)
9- Propane(1) + Methanol(2)	33	40	6.60	6.80	4.84	7.36	7.38	5.38	3.17	2.77	1.72	8.13	6.84	4.99	6.08	6.57	4.76	6.99	7.53	5.54	6.72 (6.83)	6.67 (7.10)	4.89 (5.21)
Total			**4.78**	**4.47**	**2.96**	**4.30**	**3.89**	**2.45**	**4.17**	**2.95**	**1.68**	**4.33**	**3.61**	**2.22**	**3.55**	**3.32**	**2.00**	**4.17**	**3.74**	**2.35**	**3.71 (2.94)**	**3.28 (2.40)**	**1.96 (2.51)**

[5] - ( ) = The results obtained with zero binary interaction parameter

Table 13
Some structural parameters for UNIQUAC-HB equation [55]

Component	q	Component	q
Water	1.00	C_4-alcohols	0.88
CH_3OH	0.96	C_5-alcohols	1.15
C_2H_5OH	0.92	C_6-alcohols	1.78
C_3-alcohols	0.89	C_7-alcohols	2.71

Table 14
UNIQUAC model parameters (cal/mol) for the 2-propanol-water system at 298 K for various new mixing rules

Model parameters	HVO	MHV1	MHV2	MHV	HVOS	LCVM	WS[6]
Δu_{12}	651.35	746.02	704.48	748.62	724.70	720.37	838.18
Δu_{21}	208.98	-240.90	-128.36	-242.36	-190.60	-122.62	-28.40

[6] - $k_{ij} = 0.15$