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Vapor-liquid equilibria of the aqueous and organic mixtures composed of dipropylene glycol methyl ether, dipropylene glycol n-butyl ether and propylene glycol n-butyl ether. Part II: Modeling based on the NRTL-PR model

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Abstract

Further to the Part I¹ of the present paper, the second Part is concentrated around the VLE modeling of binary mixtures involving the three glycol ethers previously studied experimentally. The authors propose to use the NRTL-PR model for the representation of these non-ideal mixtures. The main difficulties of modelling related to very low vapor pressures and the way of dealing with them are highlighted. The unknown critical parameters for DPM, DPnB and PnB were determined using robust group contribution methods. However, the experimental values of these parameters have never been published before. The main goal of the authors was to obtain the most satisfactory representation of the experimental data provided in the Part I.¹ Some issues that mostly occurred in mixtures involving the PnB as well as in mixtures having very low vapor pressures, were encountered. Nevertheless, we have obtained in general a satisfactory representation of measured points regardless of those issues.

1 Introduction

The Part II of this paper represents a continuation of our previous work where the VLE involving three glycol ethers, namely Dipropylene Glycol Methyl Ether (DPM), Dipropylene Glycol n-Butyl Ether (DPnB) and Propylene Glycol n-Butyl Ether (PnB) were studied experimentally. Within the present Part, our effort is concentrated around the VLE modelling of all the mixtures studied in the Part I.¹ We have considered aqueous and organic solutions of DPM, DPnB and PnB, forming in total 6 binary mixtures. These mixtures can be characterized as highly non-ideal size asymmetric. Some of them are partially miscible.

In literature, the application of different models to the VLE of such systems was studied. Among them, the CPA EoS model of Kontogeorgis *et al.*² was applied by Garrido *et al.*³ to 2-methoxyethanol, 2-ethoxyethanol and 2-butoxyethanol mixtures for which a lot of experimental data were available. It was shown that this model was able to satisfactorily represent mixtures of glycol ethers with alkanes as well as their aqueous mixtures. In other work, Tochigi *et al.*⁴ used an empirical NRTL equation for the VLE modelling of water+Propylene Glycol Methyl Ether mixture that was satisfactorily represented at 53 kPa. The same model was also used by Ramsauer *et al.*⁵ for the VLE of 1-propoxy-2-propanol+water system at 20 kPa where it was compared with the modified UNIQUAC model and yielded to better representation. More complex models, such as COSMO-SAC, were used by Lin *et al.*⁶ to represent the liquid-liquid equilibrium of Dipropylene Glycol Dimethyl Ether+water systems.

The PC-SAFT model was applied to the modelling of binary mixtures containing glycol ethers in the work made by Avlund *et al.*⁷ and NguyenHuynh *et al.*⁸ The authors studied namely the mixtures of 2-methoxyethanol, 2-ethoxyethanol, 2-butoxyethanol, 2-alkoxyethanol with hydrocarbons. Along with this, Zarei *et al.*⁹ used the sPC-SAFT to obtain thermophysical properties of 2-ethoxyethanol, 2-propoxyethanol and 2-butoxyethanol.

In the frame of our work, we have chosen the NRTL-PR model due to its robust capability to represent complex size asymmetric and non-miscible systems of different nature. This model was proposed by Neau *et al.*¹⁰ and is based on the G^E/EoS approach, namely the

coupling of the Peng-Robinson EoS with the generalized excess Gibbs energy model, so as to provide a totally predictive equation of state.

Section 2 of this paper presents the NRTL-PR model and its main expressions. The estimated critical properties for glycol ethers as well as the modelling of their vapor pressures can be found in this Section as well. In the end, the VLE modelling of binary mixtures is covered altogether with the values of the NRTL-PR interaction parameters for each functional group.

The results are detailed in Section 3. The discussion includes, as an example, the graphical overview of the modelling results for three main types of mixtures: fully miscible aqueous solutions, partially miscible aqueous solutions and fully miscible organic solutions. Additional results covering the rest of mixtures are given in the Appendix.

2 Thermodynamic modelling

2.1 Pure compounds parameters estimation

2.1.1 Definition of the equation of state parameters

The physical properties of pure components were estimated using the Peng-Robinson equation of state¹¹:

$$p = \frac{RT}{v - b} - \frac{a}{v^2 + 2bv - b^2} \quad (1)$$

for which, in case of pure components, the attractive term a and the covolume b are obtained from the critical temperature and pressure of the compound of interest, T_c and p_c , as:

$$a = 0.45724 \frac{R^2 T_c^2}{p_c^2} \alpha(T_r) \quad \text{and} \quad b = 0.0778 \frac{RT_c}{p_c} \quad (2)$$

with $T_r = T/T_c$, a reduced temperature and $\alpha(T_r)$, a function depending on temperature. It is extremely important to choose the appropriate $\alpha(T_r)$ function for representing the pro-

properties of pure compounds in vapor and liquid phases. An exhaustive theoretical analysis of different alpha functions was done by Neau *et al.*^{12,13} in a wide range of temperatures and pressures. It was proven in the above mentioned study, that the generalized Soave function¹⁴ (Equation 3) provides the most satisfactory vapor pressure representation together with Peng-Robinson EoS in the range of temperatures and pressures generally used in chemical engineering applications. That was the first reason of considering namely this function in the present work:

$$\alpha(T_r) = [1 + m(1 - T_r^\gamma)]^2 \quad (3)$$

In the above Equation, it is necessary to know the critical temperature T_c as well as the parameters γ and m . When calculating the $\alpha(T)$ function for any compound, a value of $\gamma = 0.5$ ¹⁵ corresponding to the classical Soave function can be considered. For the m parameter, a piecewise expression was proposed by Robinson and Peng¹⁴. The m parameter is expressed by the 2nd or 3rd order polynomial correlation to the acentric factor ω . One should choose the appropriate correlation for substances whose acentric factor is lower than or greater than that of n-decane:

$$\begin{aligned} m &= 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad \text{if } \omega < 0.49 \\ m &= 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.16666\omega^3 \quad \text{if } \omega \geq 0.49 \end{aligned} \quad (4)$$

Nevertheless, in case of bad estimations, the γ and m parameters can be modified in a reasonable range ($0 < \gamma < 1$)¹³ in order to improve the vapor pressure representation.

To summarize, at this point, in order to calculate the Peng-Robinson EoS pure compound parameters a (attractive term) and b (covolume), one needs to know the critical temperature and pressure of a compound, T_c , p_c , the parameters of the Soave function, γ , m , and the acentric factor ω .

2.1.2 Application of the Peng-Robinson EoS to glycol ethers

Critical properties To the best of our knowledge, the experimental critical properties of DPM, DPnB and PnB are not available in the literature. Therefore, they were estimated using the predictive Wilson & Jasperson method¹⁶. This method includes the atomic and the group contributions as the First and Second Order estimations, respectively. Both of the Orders use the following equation:

$$T_c = T_b / \left[0.048271 - 0.019846N_r + \sum_k N_k(\Delta tck) + \sum_j M_j(\Delta tcj) \right]^{0.2} \quad (5)$$

$$p_c = 0.0186233T_c / [-0.96601 + e^Y] \quad (6)$$

$$Y = -0.00922295 - 0.0290403N_r + 0.041 \left[\sum_k N_k(\Delta pck) + \sum_j M_j(\Delta pcj) \right] \quad (7)$$

where N_r is the number of rings in the compound, N_k is the number of atoms for type k with First Order atomic contributions Δtck and Δpck while M_j is the number of groups of type j with Second Order group contributions Δtcj and Δpcj . T_b is the normal boiling point temperature of the compound (at 760 mmHg).

Pitzer acentric factor As for DPM, DPnB and PnB, along with the critical parameters T_c, p_c , the experimental value for the acentric factor is not available and should also be estimated. In this work, the Ambrose-Walton¹⁷ corresponding states method was used to estimate the acentric factor. It uses the Pitzer expansion:

$$\omega = - \frac{\ln(p_c/1.01325) + f^{(0)}(T_{br})}{f^{(1)}(T_{br})} \quad (8)$$

where $T_{br} = T_b/T_c$ and $f^{(0)}$ and $f^{(1)}$ are the analytical expressions proposed by Ambrose and Walton:

$$f^{(0)} = \frac{-5.97616\tau + 1.29874\tau^{1.5} - 0.60394\tau^{2.5} - 1.06841\tau^5}{T_{br}} \quad (9)$$

$$f^{(1)} = \frac{-5.03365\tau + 1.11505\tau^{1.5} - 5.41217\tau^{2.5} - 7.46628\tau^5}{T_{br}} \quad (10)$$

with $\tau = 1 - T_{br}$. Here, p_c is in bar while T_b and T_c are both absolute temperatures.

2.1.3 Estimation and fitting of pure compounds properties

The critical properties for the DPM, DPnB and PnB were firstly estimated using the Eqs. 5 to 7 for the T_c and p_c as well as the Eq. 8 for the ω . Then, using the obtained properties, the pure compounds vapor pressures were calculated using the Eq. 1. The blue color lines in Figure 1 demonstrate the results of this calculation. As for DPM, the calculation yielded to satisfactory results for vapor pressure in the whole temperature range, so, for this reason, its vapor pressure is represented by the red line meaning the final results (this aspect is described further in the paper). The results were less encouraging for the other compounds and especially for PnB, leading to significant errors for higher temperatures. As for DPnB, its high errors for lower temperatures are explained by the extremely low vapor pressures, where a slight difference of several Pa between the experiment and estimation yields to a high error.

In order to improve the results, we have adjusted the values of ω and p_c in order to minimize the error in vapor pressures. If needed, the values of T_c were adjusted as well. All the properties were, of course, adjusted to be physically adequate. The results obtained by this approach have considerably improved the representation of vapor pressures of all the three ethers and not only of PnB. Only for DPM the adjusted values were almost identical to those estimated using the W&J method. These new obtained values are presented in Table 1 and will be further used for the VLE predictions in the NRTL-PR model and the results will be presented in the following sections.

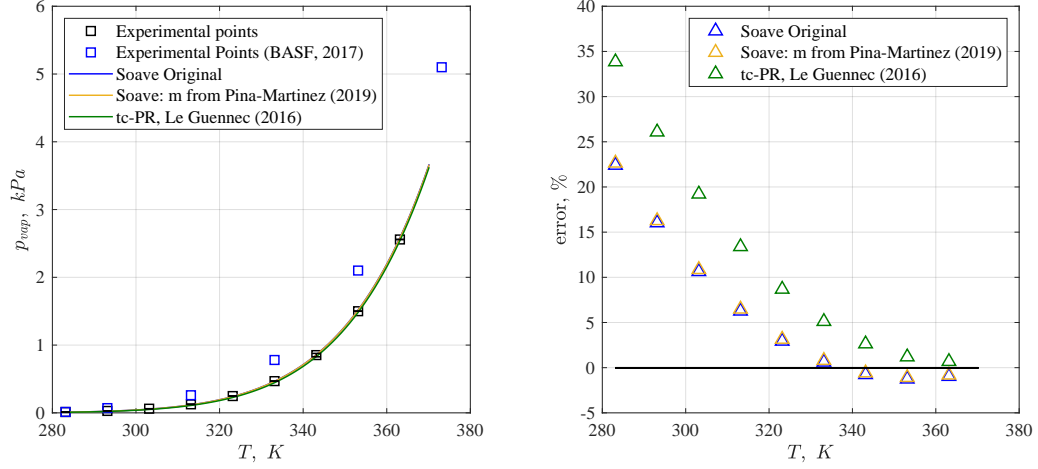
Table 1: Estimated and adjusted critical properties of DPM, DPnB and PnB providing the minimal error in vapor pressures

Compound	T_b [K]	T_c [K]	p_c [kPa]	ω
DPM	461.15	626.88	2780	0.7022
DPnB	503.15	655.90	2450	0.7996
PnB	444.15	619.50	3830	0.5800

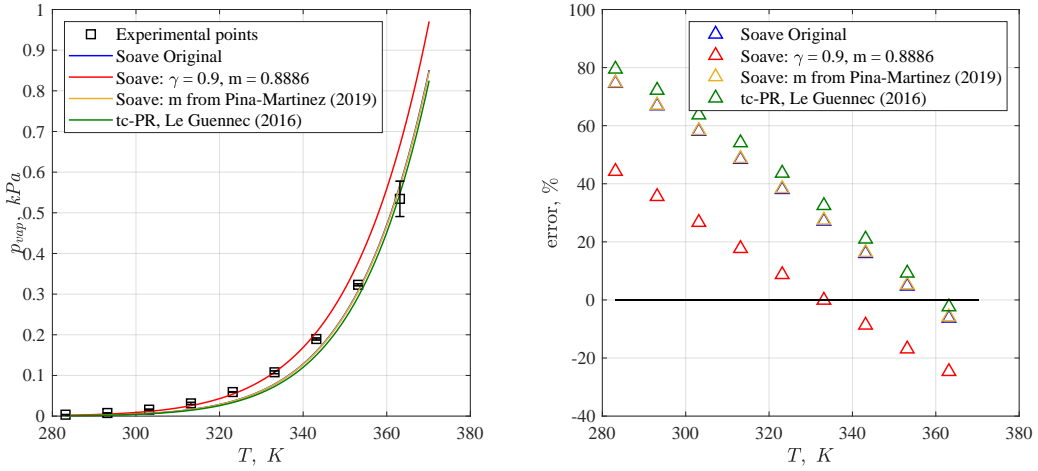
Although the fitting of estimated critical properties allows in general to improve the result, at the same time, some of the p_{vap} representation problems still persist in case of DPnB and PnB, and namely the simultaneous representation of their vapor pressures in both low and high temperature ranges. In fact, if we try to correctly represent the vapor pressures in the low temperature range, the high temperature range will have higher error and vice versa. This phenomenon can occur for some compounds (for example, the monoethylene glycol). The reason for that is actually hidden in the $\alpha(T)$ function of the equation of state as this function represents the temperature influence.

In their work, Neau et al.¹³ have illustrated, using multiple examples, the influence of different $\alpha(T)$ functions on the vapor pressure representation. It was also proven there, that, for the PR EoS, the original Soave (Eq. 3) function with $\gamma = 0.5$ yields to the best results. When it is not possible to satisfactorily represent the vapor pressures in both low and high temperature ranges simultaneously, the γ parameter becomes adjustable and its value can be estimated by fitting to the experimental data. In this case, we talk about the *generalized* Soave function. Moreover, in some cases, not only γ parameter can be fitted, but also the m parameter (Eq. 4).

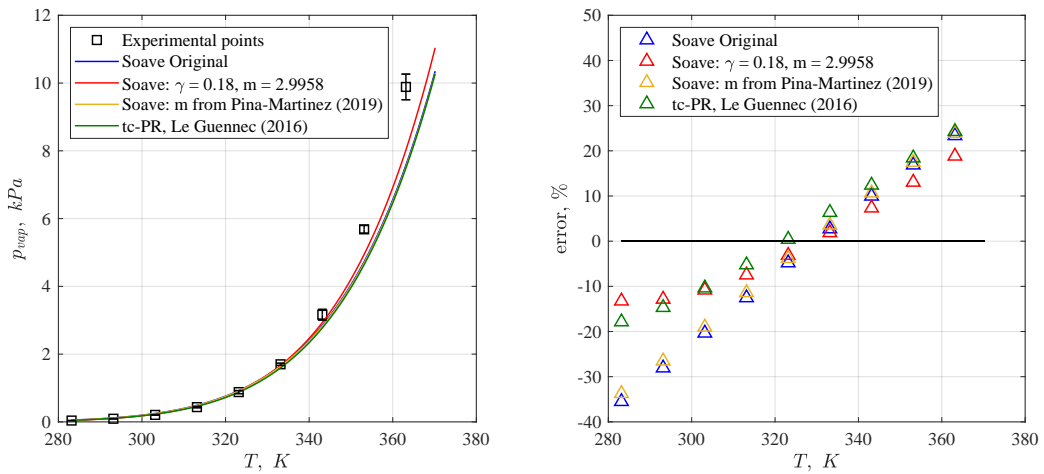
These parameters were fitted for DPnB and PnB respecting the condition $0 < \gamma < 1$. Using this method, the errors for these compounds were reduced more and the vapor pressure representation became more homogeneous in the whole temperature range. Thus, the errors



(a)



(b)



(c)

Figure 1: Vapor pressures calculated using the PR EoS and T_c , p_c and ω from Table 1 and final γ , m parameters compared to other approaches: a) DPM: $error = 6.88\%$; b) DPnB: $error = 20.36\%$; c) PnB: $error = 9.85\%$

obtained at this point are mostly due to very low vapor pressures. It is well known that the cubic equations of state were initially designed for high vapor pressure systems, such as hydrocarbons, and it is sometimes very hard to obtain a perfect representation of systems having very low pressures. Having taken all the previous hypotheses into account, our main intention was to obtain such γ and m values that yield to the lowest and the most homogeneous errors for the given temperature range. The final results are presented as red color lines in Figure 1 and compared with the results obtained using the original γ and m parameters (i.e. $\gamma = 0.5$ and m from Eq. 4).

A comparison was also made with some improvements recently proposed in literature for the PR EoS. More precisely, we considered:

- the update correlation of the m parameter of the Soave function proposed by Pina-Martinez et al.¹⁸ in order to improve the representation of vapor pressures;
- and the translated-consistent PR EoS (tc-PR), based on a modified Twu $\alpha(T)$ function, developed by Le Guennec et al.¹⁹

The results obtained with these two modifications of the PR EoS are also reported in Figure 1. First, it can be noted that the update correlation of the m parameter (orange lines and symbols) does not really improve the representation of the vapor pressure for the three glycol ethers compared to the original Soave function (blue lines and symbols). Then, the error curves in Figure 1 show that the tc-PR EoS (green symbols) is unable to bring a real improvement compared to the Soave function with fitted (γ, m) parameters (red symbols) in the whole temperature range. Therefore, we can conclude that the PR-EoS with fitted (γ, m) parameters of the Soave function is the best EoS for the modeling of the glycol ethers considered in this work.

The final values of the Soave parameters, that will be used for further calculations, are as follows:

- DPM: $\gamma = 0.5$, $m = 1.3471$;

- DPnB: $\gamma = 0.9$, $m = 0.8886$;
- PnB: $\gamma = 0.18$, $m = 2.9958$;

2.2 The NRTL-PR model

The NRTL-PR model¹⁰ represents a combination of the Peng-Robinson EoS (Eq. 1) and the Gibbs excess energy expressed with the generalized NRTL model. In case of mixtures, the EoS attractive term a is written according to the generalized reference state²⁰ as:

$$\alpha = \frac{a}{bRT} = \sum_i \alpha_i x_i - \frac{1}{C} \left[\frac{g^E}{RT} - \sum_i x_i \ln \frac{r_i}{r} \right] \quad (11)$$

The covolume b is found as $b = \sum_i x_i b_i$, and b_i , the covolume of a pure compound, is obtained using the Eq. 2. The r_i is a volume area factor and $r = \sum x_i r_i$. The reference state constant, C , is equal to $C = 0.56$.¹⁰ The g^E term is the excess Gibbs energy, represented using the generalized NRTL model:²¹

$$g^E = RT \sum_i x_i \ln \frac{r_i}{r} + \sum_i x_i q_i \frac{\sum_j x_j q_j G_{ji} \Gamma_{ji}}{\sum_l x_l q_l G_{li}} \quad (12)$$

In the above equations (Eq. 11 and 12), r_i and q_i are the volume and surface area factors, respectively:

$$r_i = \sum_k \nu_{ik} R_k \quad \text{and} \quad q_i = \sum_k \nu_{ik} Q_k \quad (13)$$

with R_k and Q_k , the UNIFAC subgroup parameters, and ν_{ik} , the number of subgroups k in a molecule i .

The term G_{ji} is the molecular repartition coefficient expressed as:

$$G_{ji} = \exp(-\alpha_0 \Gamma_{ji}/RT) \quad (14)$$

where α_0 is the non-randomness factor, taken as $\alpha_0 = -1$ ²².

If one substitutes the Eq. 12 into the Eq. 11, the following expression can be obtained for the attractive term:

$$\alpha = \sum_i \alpha_i x_i - \frac{1}{C} \left[\frac{g_{eos}^E}{RT} \right] \quad (15)$$

where g_{eos}^E is the residual part of the generalized NRTL equation:

$$g_{eos}^E = \sum_i x_i q_i \frac{\sum_j x_j q_j G_{ji} \Gamma_{ji}}{\sum_l x_l q_l G_{li}} \quad (16)$$

For computing the Γ_{ji} binary interaction parameter of Eq. 12 a group contribution method was used¹⁰:

$$\Gamma_{ji} = \sum_K \theta_{iK} \sum_L (\theta_{jL} - \theta_{iL}) \Gamma_{LK}, \quad \theta_{iK} = \sum_k \nu_{ik(K)} \frac{Q_k}{q_i} \quad (17)$$

with $\Gamma_{KK} = 0$, $\Gamma_{KL} \neq \Gamma_{LK}$. θ_{iK} is a probability that a contact from a molecule i involves a main group K and $\nu_{ik(K)}$ is the number of subgroup k that belongs to the main group K in the molecule i . For the group interaction parameter Γ_{LK} the following expression was considered with respect to temperature²³:

$$\Gamma_{LK} = \Gamma_{LK}^{(0)} + \Gamma_{LK}^{(1)} \left(\frac{T_0}{T} - 1 \right) + \Gamma_{LK}^{(2)} \left(\frac{T}{T_0} - 1 \right) \quad \text{with} \quad T_0 = 298.15 \text{ K} \quad (18)$$

It is important to take into account that the parameters Γ_{LK} and Γ_{KL} should be different for highly non-ideal mixtures according to the two-fluid theory.

The molecules of DPM, DPnB and PnB were decomposed into functional groups, listed in Table 2 together with the respective ν_{ik} values and the UNIFAC subgroup parameters R_k and Q_k . The molecule of H₂O represents a single functional group by itself and thus does not need a decomposition.

Table 2: Groups decomposition of DPM, DPnB and PnB and the corresponding UNIFAC subgroups parameters. OH₍₁₎ and OH₍₂₎ correspond to the primary and secondary alcohol group, respectively

Group	ν_{ik} (DPM)	ν_{ik} (DPnB)	ν_{ik} (PnB)	ν_{ik} (H ₂ O)	R_k	Q_k
CH₃	3	3	2	—	0.9011	0.848
CH₂	2	5	4	—	0.6744	0.540
CH	2	2	1	—	0.4469	0.228
H₂O	—	—	—	1	0.9200	1.400
OH₍₁₎	1	—	—	—	1.2700	1.152
OH₍₂₎	—	1	1	—	1.2700	1.152
-O-	2	2	1	—	0.2439	0.240

The parameters for paraffin (CH_n), water (H₂O) and alcohol (OH_n) groups were taken from Neau et al.²³, while the ether (-O-) group was added by us to the NRTL-PR parameter matrix.

The parameters $\Gamma_{LK}^{(0)}$, $\Gamma_{LK}^{(1)}$ and $\Gamma_{LK}^{(2)}$ for the "-O-" group were estimated by a fitting to a data set made up of different ether, glycol ether, alcohol and water systems. Usually, a group contribution method requires a large database for parameters fitting made up of hundreds of systems. However, as previously stated, one of the main problems of our research was a very limited amount (or even a complete absence) of experimental VLE data for such systems, especially at such low total pressures. Assuming that fact, our main target was to collect as much data as possible to be able to satisfactorily represent our binary systems of interest and not to develop a real group contribution method. For that reason, we have chosen the systems containing paraffin (CH₃, CH₂, CH), alcohol (OH₍₁₎, OH₍₂₎), water (H₂O) and, of course, "-O-" group. Our data set used for fitting contains 15 VLE systems listed in Table 3 below. All the binary mixtures used for fitting were previously tested in order to confirm their good prediction by the NRTL-PR model. As an example, we took one paraffin mixture (Diisopropyl ether + 2,2,4-Trimethylpentane published by Ku and Tu²⁴) and one aqueous glycol ether mixture (water + Propylene glycol methyl ether published by Chiavone-Filho *et al.*²⁵). Figures 2(a) and Figure 2(b) represent our modelling results for these systems. Very

good agreement between experiment and modelling was obtained for these mixtures.

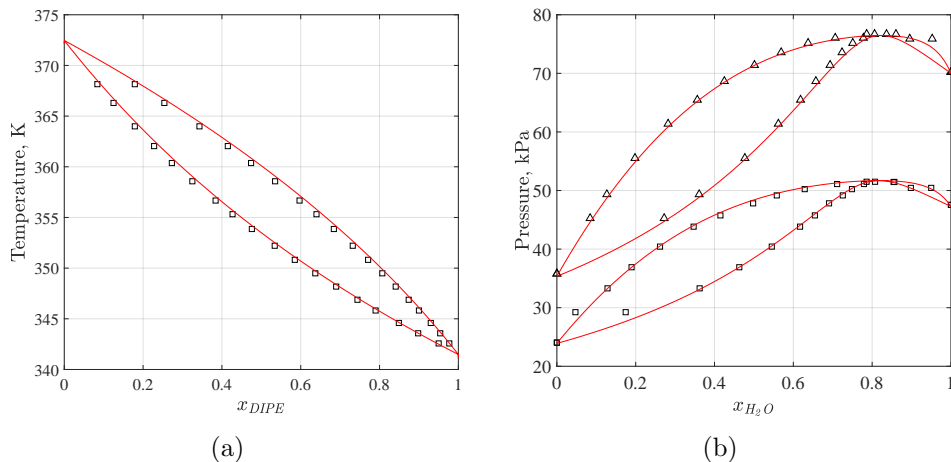


Figure 2: Examples of VLE used for the group parameters fitting and calculated by NRTL-PR model:

- a) Diisopropyl ether (DIPE)+2,2,4-Trimethylpentane at 101.3 kPa;
- b) H₂O+Propylene glycol methyl ether, (\square) - 353.15 K and (\triangle) - 363.15 K

Table 3: Data set of different VLE systems containing ethers, glycol ethers, alcohols and water used for fitting of group contribution parameters for the ”-O-” group

System	Source
Diisopropyl Ether (DIPE) + n-Heptane	Vijayaraghavan et al. ²⁶
Diethyl Ether + n-Hexane	Goloborodkina et al. ²⁷
Diisopropyl Ether (DIPE) + 2,2,4-Trimethylpentane	Ku and Tu ²⁴
Di-n-propyl Ether (DNPE) + n-Heptane	Cripwell et al. ²⁸
Dimethyl Ether (DME) + 1-Propanol	Park et al. ²⁹
Dimethyl Ether (DME) + 1-Butanol	Park et al. ²⁹
Diisopropyl Ether (DIPE) + 1-Propanol	Vijayaraghavan et al. ³⁰
Diisopropyl Ether (DIPE) + 2-Propanol	Shawaqfeh ³¹ , Verhoeve ³²
Methyl tert-butyl Ether (MTBE) + 2-Propanol	Segura et al. ³³
Dimethyl Ether (DME) + 2-propanol	Elbaccouch and Elliott ³⁴
Diethyl Ether + Water	Signer et al. ³⁵
Water + Propylene glycol methyl ether (PM)	Chiavone-Filho et al. ²⁵
Water + Ethylene glycol methyl ether (EM)	Chiavone-Filho et al. ²⁵
Water + Ethylene glycol ethyl ether (EE)	Chiavone-Filho et al. ²⁵
Water + Ethylene glycol isopropyl ether (EISOP)	Chiavone-Filho et al. ²⁵

This data set had one significant drawback. In fact, the VLE of all the systems included in

the data set were measured at pressures much higher than the pressures of DPM, DPnB, PnB and water mixtures. This led to group contribution parameters that yield in overestimated bubble pressures for our systems, especially H₂O + DPM. In order to fix this issue, we found mandatory to include the H₂O + DPM system into the data set. Of course, in this case we cannot talk about the full prediction of the VLE and VLLE anymore.

The corresponding values for $\Gamma_{LK}^{(0)}$, $\Gamma_{LK}^{(1)}$, $\Gamma_{LK}^{(2)}$ are reported in Tables 4 to 6 respectively.

Table 4: Values (in J/mol) of the NRTL-PR group interaction parameters $\Gamma_{LK}^{(0)}$ used for compounds in this work

L/K	CH ₃	CH ₂	CH	C	H ₂ O	OH ₍₁₎	OH ₍₂₎	-O-
CH ₃	0.00	0.00	0.00	0.00	2398.94	4413.01	4413.01	-751.36
CH ₂	0.00	0.00	0.00	0.00	2398.94	4413.01	4413.01	-131.61
CH	0.00	0.00	0.00	0.00	2398.94	4413.01	4413.01	-530.42
C	0.00	0.00	0.00	0.00	2398.94	4413.01	4413.01	-530.42
H ₂ O	3245.43	3245.43	3245.43	3245.43	0.00	2818.87	2843.36	-8058.60
OH ₍₁₎	3460.73	3460.73	3460.73	3460.73	-969.98	0.00	0.00	-13414.40
OH ₍₂₎	3460.73	3460.73	3460.73	3460.73	-1075.32	0.00	0.00	-17451.93
-O-	-209.18	165.93	-1533.82	-1533.82	-9157.88	644.45	735.12	0.00

Table 5: Values (in J/mol) of the NRTL-PR group interaction parameters $\Gamma_{LK}^{(1)}$ used for compounds in this work

L/K	CH ₃	CH ₂	CH	C	H ₂ O	OH ₍₁₎	OH ₍₂₎	-O-
CH ₃	0.00	0.00	0.00	0.00	-3417.62	-6467.13	-6467.13	472.34
CH ₂	0.00	0.00	0.00	0.00	-3417.62	-6467.13	-6467.13	-3505.06
CH	0.00	0.00	0.00	0.00	-3417.62	-6467.13	-6467.13	567.81
C	0.00	0.00	0.00	0.00	-3417.62	-6467.13	-6467.13	567.81
H ₂ O	-294.87	-294.87	-294.87	-294.87	0.00	-6350.58	-5370.02	-447.12
OH ₍₁₎	-470.23	-470.23	-470.23	-470.23	-1115.52	0.00	0.00	5989.73
OH ₍₂₎	-470.23	-470.23	-470.23	-470.23	-2112.07	0.00	0.00	7812.21
-O-	331.80	407.42	887.82	887.82	1746.05	1812.40	2429.93	0.00

Table 6: Values (in J/mol) of the NRTL-PR group interaction parameters $\Gamma_{LK}^{(2)}$ used for compounds in this work

L/K	CH ₃	CH ₂	CH	C	H ₂ O	OH ₍₁₎	OH ₍₂₎	-O-
CH ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH ₂	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
C	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ O	0.00	0.00	0.00	0.00	0.00	-1037.78	-527.76	0.00
OH ₍₁₎	0.00	0.00	0.00	0.00	-518.21	0.00	0.00	0.00
OH ₍₂₎	0.00	0.00	0.00	0.00	-326.80	0.00	0.00	0.00
-O-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Finally, in order to solve the equilibrium condition, one need to calculate the fugacity coefficients ϕ_i for each phase. For the NRTL-PR model, the fugacity coefficient of a component i is following:

$$\ln \phi_i = -\ln Z(1 - \eta) + (Z - 1)\frac{1}{b} \left(\frac{\partial nb}{\partial n_i} \right)_{n_j} - \frac{1}{2\sqrt{2}} \ln \left(\frac{1 + (1 + \sqrt{2})\eta}{1 + (1 - \sqrt{2})\eta} \right) \left(\frac{\partial n\alpha}{\partial n_i} \right)_{T, n_j} \quad (19)$$

where $Z = pv/RT$ is the compressibility factor, $\eta = b/v$, and:

$$\left(\frac{\partial n\alpha}{\partial n_i} \right)_{T, n_j} = \frac{a_i}{b_i RT} - \frac{1}{C} \left(\frac{\partial ng_{eos}^E/RT}{\partial n_i} \right)_{T, n_j} \quad (20)$$

3 Results and discussion

The isothermal VLE of 6 binary mixtures (3 aqueous and 3 organic) were calculated using the NRTL-PR model for temperatures ranging from 283.15 to 363.15 K. The modeling has shown no azeotrope in these mixtures. The water critical properties and acentric factor used in our calculations were taken from Poling et al.³⁶ and are: $T_c = 647.14$ K, $p_c = 220.64$ bar and $\omega = 0.344$.

The modeling results were compared with the respective experimental data measured

by us and published in the Part I¹ of this paper. Table 7 contains pressure deviations for all the calculated mixtures and temperatures. The deviations in pressure, $\delta p/p$, for each temperature were calculated as follows:

$$\delta p/p[\%] = \left| \frac{100}{N} \sum \left(\frac{p_{exp} - p_{calc}}{p_{exp}} \right) \right| \quad (21)$$

Table 7: Deviations in pressure, $\delta p/p[\%]$, between experimental data (Part I¹ of this paper) and results calculated using the NRTL-PR model for aqueous and organic binary mixtures of DPM, DPnB and PnB. Temperature range: 283.15 to 363.15 K

Temperature, K	Aqueous mixtures			Organic mixtures		
	H2O+DPM	H2O+DPnB	H2O+PnB	PnB+DPM	PnB+DPnB	DPM+DPnB
283.15	5.05	11.86	9.32	21.76	31.12	29.22
293.15	4.09	9.85	7.99	14.77	23.28	22.20
303.15	4.24	7.79	8.68	8.43	15.67	15.79
313.15	4.72	6.73	8.32	6.05	8.52	10.06
323.15	5.87	5.77	7.49	4.52	6.90	5.40
333.15	7.36	5.08	6.78	5.57	8.44	2.26
343.15	9.44	7.1	6.76	8.36	12.92	3.29
353.15	11.50	8.97	6.83	10.33	16.89	5.38
363.15	13.80	13.96	7.95	11.50	20.36	7.44

In general, all obtained VLE curves can be represented as three main types depending on their shape. The first type concerns the fully miscible aqueous system, namely the H₂O+DPM, presented in Figure 3. It can be seen from this Figure that the representation of the H₂O+DPM system is very good, though the deviation in pressure increases for higher temperatures. The same VLE was then also calculated using the PSRK model of Holderbaum and Gmehling³⁷ in order to check if the same behavior would be observed. In this example, for the PSRK model we have used its original functional groups (that best fit our molecules structure) and their parameters. Figure 3(d)) illustrates this comparison.

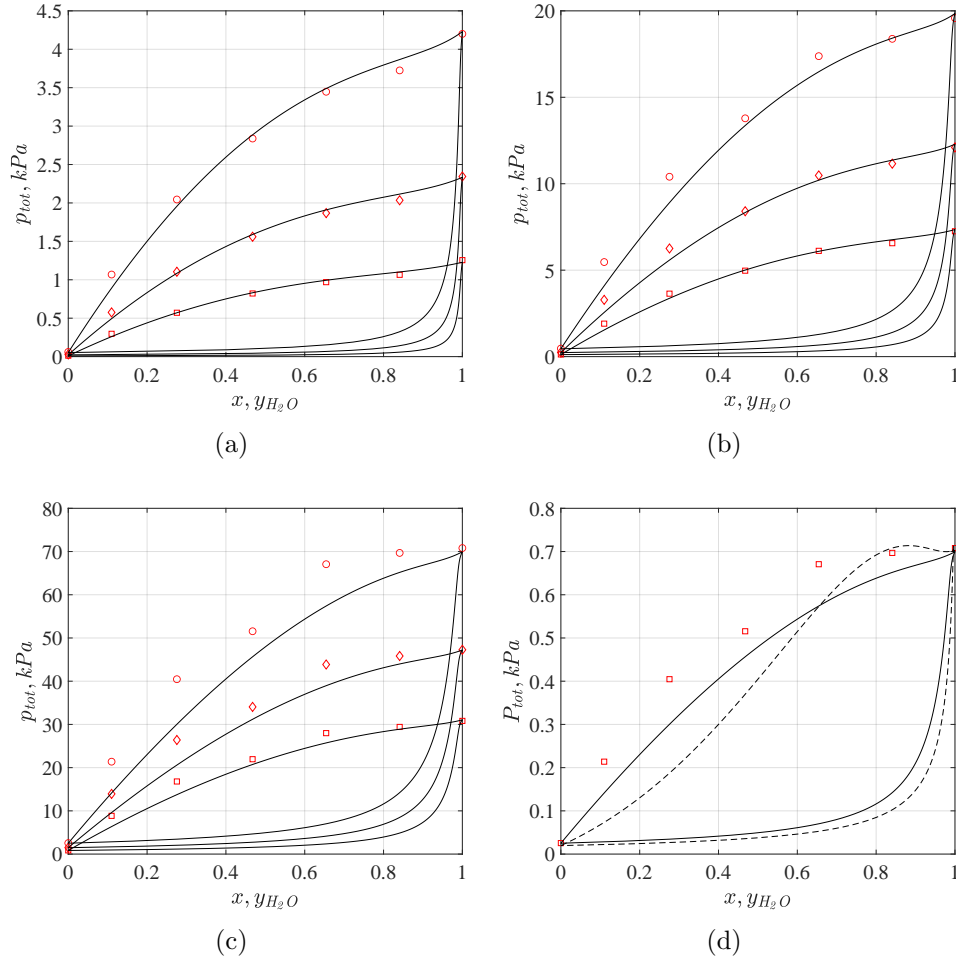


Figure 3: Vapor-liquid equilibria of water+DPM mixture calculated using the NRTL-PR model: a) (\square) - 283.15 K; (\diamond) - 293.15 K; (\circ) - 303.15 K; b) (\square) - 313.15 K; (\diamond) - 323.15 K; (\circ) - 333.15 K; c) (\square) - 343.15 K; (\diamond) - 353.15 K; (\circ) - 363.15 K; d) comparison of the NRTL-PR model (solid line) with the PSRK model (dashed line) at 363.15 K

The second type concerns aqueous mixtures, such as $\text{H}_2\text{O}+\text{DPnB}$ and $\text{H}_2\text{O}+\text{PnB}$, which are partially miscible by nature. An example of the mixture $\text{H}_2\text{O}+\text{PnB}$ is presented in Figure 4.

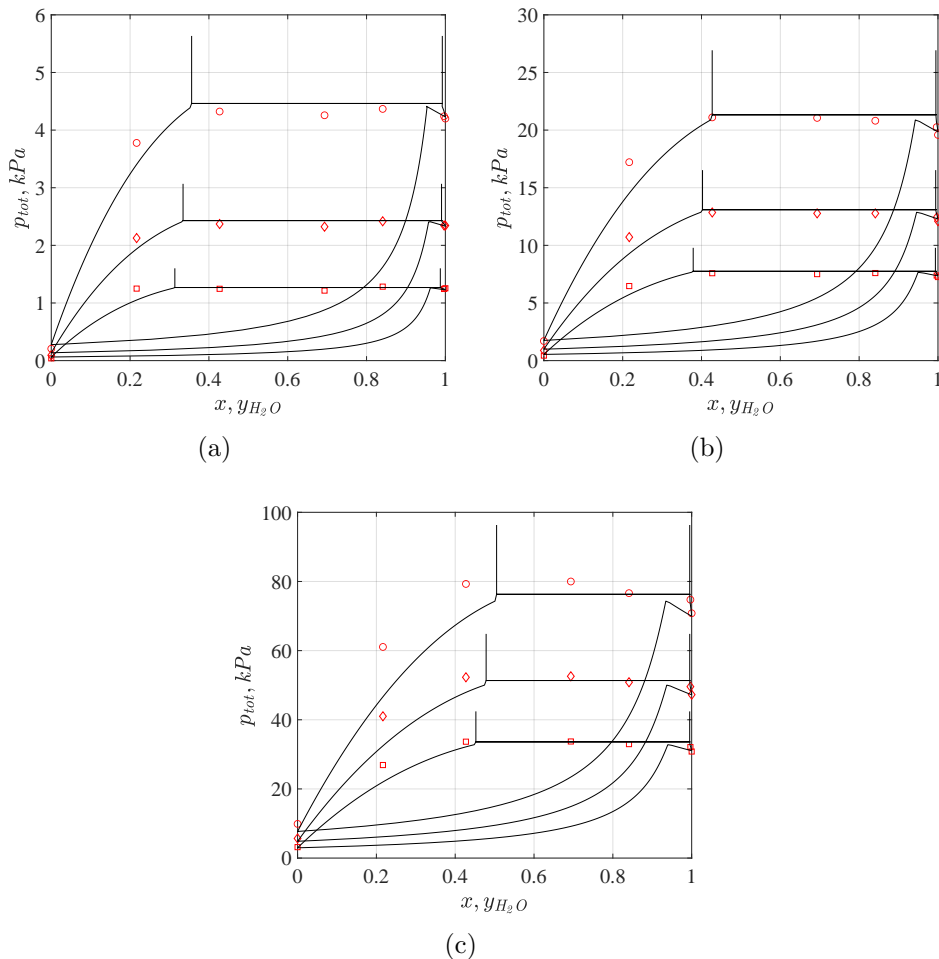


Figure 4: Vapor-liquid-liquid equilibria of water+PnB mixture calculated using the NRTL-PR model: a) (\square) - 283.15 K; (\diamond) - 293.15 K; (\circ) - 303.15 K; b) (\square) - 313.15 K; (\diamond) - 323.15 K; (\circ) - 333.15 K; c) (\square) - 343.15 K; (\diamond) - 353.15 K; (\circ) - 363.15 K

The NRTL-PR is in good agreement with the experimental points. The liquid-liquid zone is also correctly represented by the model. As in the previous case, the model yields to a slight underestimation of total pressures at higher temperatures.

The third group of curves corresponds to all the organic mixtures: PnB+DPM, PnB+DPnB and DPM+DPnB. Their curves have a classic shape of fully miscible organic systems. As an example, the mixture DPM+DPnB is illustrated in Figure 5.

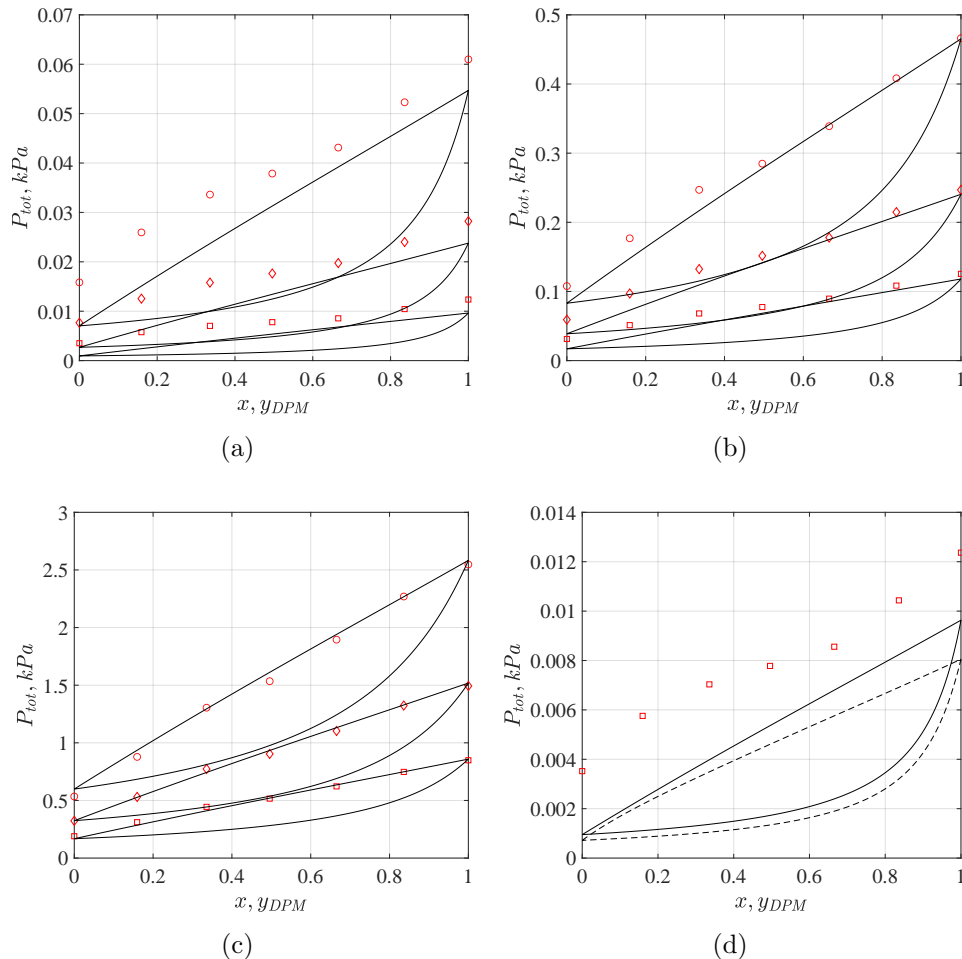


Figure 5: Vapor-liquid equilibria of DPM+DPnB mixture calculated using the NRTL-PR model: a) (\square) - 283.15 K; (\diamond) - 293.15 K; (\circ) - 303.15 K; b) (\square) - 313.15 K; (\diamond) - 323.15 K; (\circ) - 333.15 K; c) (\square) - 343.15 K; (\diamond) - 353.15 K; (\circ) - 363.15 K; d) comparison with the PSRK model at 283.15 K (solid line) - NRTL-PR model; (dashed line) - PSRK model

The DPM+DPnB mixture is a perfect example of systems having extremely low vapor pressures (order of 10^{-4} bar at lower temperatures). It can be very difficult to represent the pressures of such an order using a cubic equation of state with available $\alpha(T)$ functions. Moreover, the influence of critical parameters on the final calculated result is becomes more important compared to middle and high pressure systems. The fact, that in our case, the critical parameters for glycol ethers were estimated and not experimentally obtained, also influences the modeling results. However, if we analyze the lowest measured temperature (where the deviations in pressure are the highest), the actual pressure difference between

measured and calculated points is around $0.28 \cdot 10^{-4}$ bar, which remains a very low value, even though this pressure difference is visible in the plot (due to its scale). Again, if compared, for example, with the PSRK model (that uses the Soave-Redlich-Kwong EoS with Boston-Mathias alpha function), the NRTL-PR model shows better representation.

The issue of very low vapor pressures persists in case of all measured organic mixtures. For mixtures involving PnB, the deviations in pressure increase for higher temperatures as well. The reason for that is in the representation of PnB vapor pressures as a pure compound.

4 Conclusions

In this work, the VLE of aqueous and organic mixtures of DPM, DPnB and PnB were calculated with the NRTL-PR model and validated using VLE data, previously measured in the Part I¹ of this paper.

In order to adapt the NRTL-PR model to our systems, a new group "-O-" (ethers) was added to the matrix of interaction parameters. These parameters were obtained by fitting to an experimental VLE data set composed of 15 systems containing "-O-", "H₂O", "-OH_(1,2)" and paraffins groups. In order to solve the very low pressure issue, the system H₂O+DPM was also included in the data set. This led to the fact that the binary systems were not fully predicted, but rather represented.

The modeling has shown a good overall representation of the isothermal VLE and VLLE of all systems. The estimation quality of the pure compounds vapor pressures strongly depends on their critical parameters. The critical parameters, also absent in the literature, were not experimentally determined in this work. The representation of pure compounds was improved by adjusting the γ and m parameters of the Soave function. For the mixtures, the problem of low vapor pressures still persists and is visible on the phase equilibria curves. The solution presents several difficulties related to the model limits in representation of very low pressures. For the mixtures (and temperatures) exhibiting the highest deviations

in pressure, the calculated results were compared with those from the PSRK model. This comparison revealed that the NRTL-PR model leads to a better representation than that provided by the PSRK equation.

Some additional work can be done in order to improve the obtained modelling results. For example, more experimental points could be obtained for binary mixtures, describing their vapor pressures as a function of composition more precisely, especially at the end regions of the equilibrium curves. Also, it is highly preferable to obtain the measured critical parameters for pure compounds and improve their representation by the Peng-Robinson EoS.

Finally, the representation of mixtures could be more improved by enriching the experimental data set used to estimate the interaction parameters for the group "-O-" and including the data for mixtures of very low pressures that were difficult to find before. These perspectives are included in our future research plan.

Appendix

The VLE modelling results for (H₂O+DPM, H₂O+PnB, DPM+DPnB) were presented earlier in the paper in order to illustrate three main types of equilibrium curves. Additional results for three other binary mixtures (H₂O+DPnB, PnB+DPM and PnB+DPnB) are reported in this appendix.

Figure 6 shows that some of the experimental points (especially for PnB+DPnB) are deviated from the overall equilibrium curve flow. This unexpected behavior occurred due to the influence of several factors, related to measurements, such as the difficulty of obtaining precise measurement at very low pressures, the instability of the sample during the experiment, the degassing *etc.* These points were discussed in the Part I¹ of this paper that was devoted to experimental measurements. However, apart from these particular data points, the NRTL-PR model provides a satisfactory representation of the VLE.

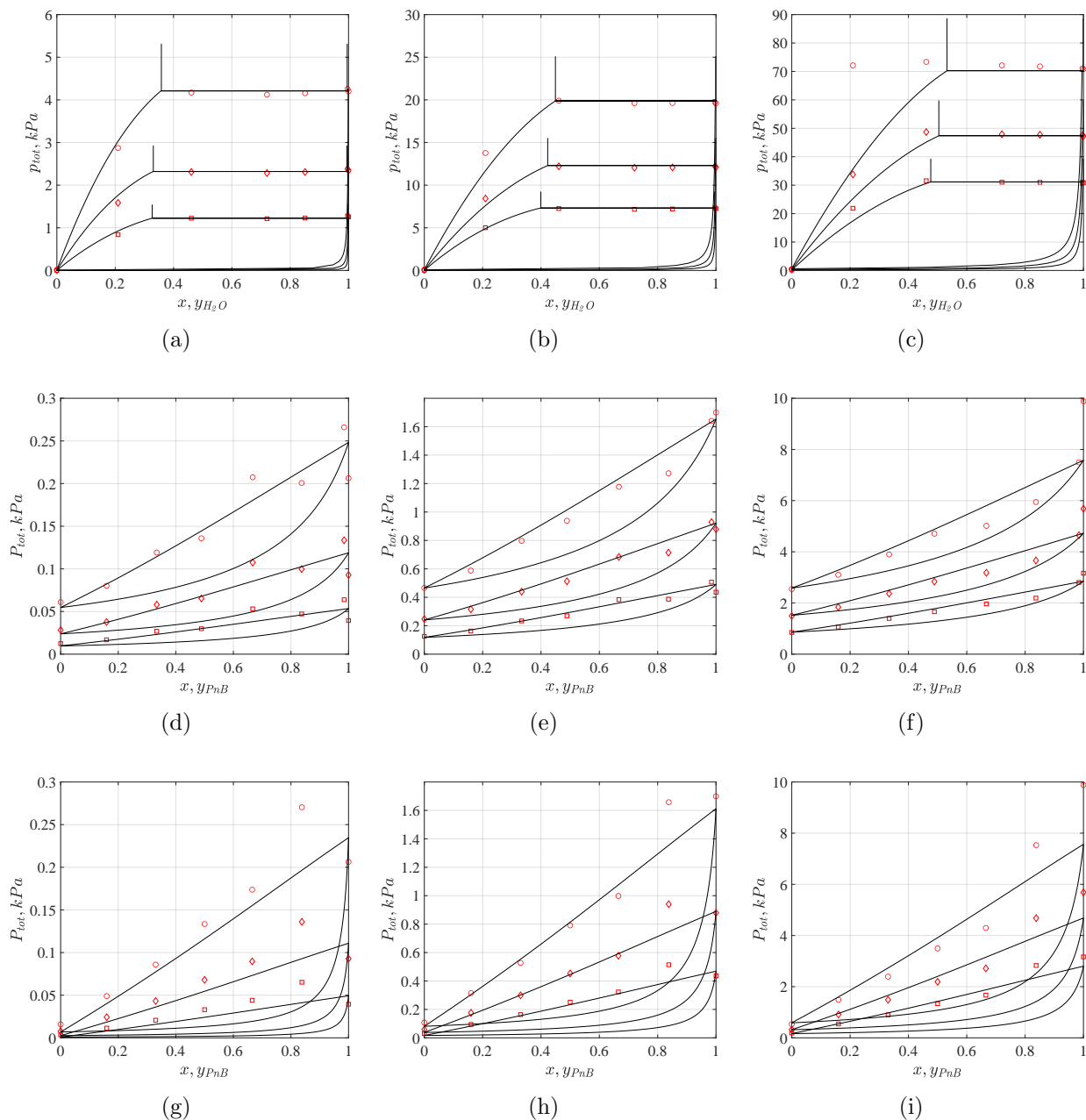


Figure 6: Vapor-liquid equilibria of additional glycol ether mixtures studied experimentally in Part I¹ and calculated with the NRTL-PR model (solid line): a) H₂O+DPnB at (□) 283.15 K, (◇) 293.15 K, (○) 303.15 K; b) H₂O+DPnB at (□) 313.15 K, (◇) 323.15 K, (○) 333.15 K; c) H₂O+DPnB at (□) 343.15 K, (◇) 353.15 K, (○) 363.15 K; d) PnB+DPM at (□) 283.15 K, (◇) 293.15 K, (○) 303.15 K; e) PnB+DPM at (□) 313.15 K, (◇) 323.15 K, (○) 333.15 K; f) PnB+DPM at (□) 343.15 K, (◇) 353.15 K, (○) 363.15 K; g) PnB+DPnB at (□) 283.15 K, (◇) 293.15 K, (○) 303.15 K; h) PnB+DPnB at (□) 313.15 K, (◇) 323.15 K, (○) 333.15 K; i) PnB+DPnB at (□) 343.15 K, (◇) 353.15 K, (○) 363.15 K.

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Graphical TOC Entry

