Predictions of the vapor-liquid equilibrium data for low-GWP Hydrofluorocarbons + polyethylene-glycol dimethylether solvents by modified UNIFAC model

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Abstract. The working fluids are crucial for developing the absorption refrigeration system. Our previous work has proposed three novel working pairs, which uses the low-GWP HFCs (R32, R152a and R161) as the refrigerants and the polyethylene-glycol dimethylether solvent DMEDEG as the absorbent. To explore the VLE behaviors of HFCs in other longer chain structures of polyethylene-glycol dimethylether solvents, the modified UNIFAC (Dortmund) model was applied for prediction. The previous binary parameters showed large deviations from the experimental data. Then the new binary parameters were obtained by regression. For R32+DMEDEG and R152a/R161+DMETrEG, the prediction ARAD results were reduced from 17.13%, 24.06% and 12.48% to 3.71%, 2.61% and 6.86%, respectively. Finally, the VLE data of R161 + PGDE at the temperatures of 293.15-343.15K were predicted.

1 Introduction

The absorption refrigeration system is of great significance for the energy utilization, especially the waste heat source. It can greatly promote my country's process of achieving carbon peaking or carbon neutrality. The working pairs of the absorption system is crucial as they greatly influence the performances of the system. Thus, a lot of researchers have recently explored the novel binary working pairs using the low-GWP Hydrofluorocarbons (HFCs, i.e., R32, R152a, and R161) as the refrigerant and the organic solvents as the absorbent.

Deng et al. [1] developed the three binary working fluids, R161+DMF/DMEDEG and R134a+DMF. their vapor-liquid equilibrium (VLE) data were measured by the static-analytical method. The results showed that the R161+DMEDEG is more favorable for the hybrid refrigeration system. Also three new binary mixtures were compared by Li et al. [2] based on the five-parameter nonrandom two-liquid (NRTL) activity coefficient model. From low to high, the solubilities are arranged into R152a+DMEDEG < R32+DMAC < R32+DMEDEG. The VLE data of R161 + DMAC/NMP at a temperature of 293.15-353.15K were also measured and correlated by Jing et al[3]. Besides, because of the atmospheric lifetime of only 11 days and the 100-year GWP about 4 [4], the extremely environmentally friendly R1234yf was explored by Fang et al. [5] for its solubility in NMP and DMETrEG by using a dual-cycle experimental device.

Our previous work [6] has proved the strong affinity of polyethylene-glycol dimethylether solvents for the low GWP HFCs, it's vital to explore the influences of longer chain structures of ether solvents on the VLE behaviors of

the HFCs refrigerants. However, it's unrealistic to perform each VLE measurement. The group contribution method, modified UNIFAC (Dortmund) model, is a good theory to predict the VLE behaviors of the solutions. So, in this work, the new interaction parameters of the modified UNIFAC model are obtained for the VLE predictions of the low GWP HFCs+ polyethylene-glycol dimethylether mixtures.

2 Methodology

The eight different reported VLE data [1, 2, 6-8] were used for reaches. For any binary system, its inner equilibrium states can be expressed as:

$$p = p_1^s x_1 \gamma_1 \exp\left(\frac{(V_1^{sl} - B_1)(p - p_1^s)}{RT}\right) \quad (1)$$

Where p , T are the system pressure and temperature, respectively; x_1 is the refrigerant mole fraction; p_1^s , V_1^{sl} and B_1 are the saturated vapor pressure, saturated mole volume of liquid refrigerants and second virial coefficient at the temperature T , respectively, which can be obtained from REFPROP 9.1; γ_1 is the refrigerant activity coefficient and is calculated by the modified UNIFAC (Dortmund) model.

The modified UNIFAC model is developed based on the original UNIFAC model. The activity coefficient of the species i is the function of temperature and composition of the solution, and can be expressed as the sum of a combinatorial and a residual part:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (2)$$

The combinatorial part $\ln \gamma_i^C$ reflects the repulsive interactions caused by the different molecular groups' size

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and shape, and is treated by the empirical way:

$$\ln \gamma_i^C = 1 - V_i' + \ln V_i' - \frac{Z}{2} q_i \left(1 - \frac{V_i}{F_i} + \ln \left(\frac{V_i}{F_i} \right) \right) \quad (3)$$

$$V_i' = \frac{r_i^{3/4}}{\sum_j x_j r_j^{3/4}}; F_i = \frac{q_i}{\sum_j x_j q_j}; V_i = \frac{r_i}{\sum_j x_j r_j} \quad (4)$$

Where Z is commonly equal to 10; r_i and q_i are the relative van der Waals volumes and surface area, respectively. r_i and q_i can be calculated from:

$$r_i = \sum_k v_k^{(i)} R_k; q_i = \sum_k v_k^{(i)} Q_k \quad (5)$$

Where $v_k^{(i)}$ stands for the number of molecular group k of specie i ; R_k and Q_k are the volume parameter and surface area parameter of group k , respectively.

The residual activity coefficient, $\ln \gamma_i^R$, reflects the intermolecular interactions attributed to the different molecular groups. It is the sum of group activity coefficients deviations between the solution and pure component, as expressed by:

$$\ln \gamma_i^R = \sum_k v_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}) \quad (6)$$

Where Γ_k and $\Gamma_k^{(i)}$ stand for the activity coefficient of group k in solution and pure component i , respectively. They can be obtained as follows:

$$\ln \Gamma_k = Q_k [1 - \ln \left(\sum_m \theta_m \Psi_{mk} \right) - \sum_m (\theta_m \Psi_{km} / \sum_n \theta_n \Psi_{nm})] \quad (7)$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}; X_m = \frac{\sum_i v_m^{(i)} x_i}{\sum_i \sum_k v_k^{(i)} x_i} \quad (8)$$

Where θ_m and X_m denote the surface area fraction and the mole fraction of group m in solution; Ψ_{mn} denotes the time-dependent group interaction parameter between groups m and n , as expressed by:

$$\Psi_{mn} = \exp \left(- \frac{a_{mn} + b_{mn} T + c_{mn} T^2}{T} \right) \quad (9)$$

Where a_{mn} (K), b_{mn} and c_{mn} (K⁻¹) are the adjustable interaction parameters regressed from the corresponding experimental data. It's noted that for the calculation of $\Gamma_k^{(i)}$, θ_m and X_m , they are treated in pure component i .

Because of the strong electronegativity effects caused by the strongly polarizing atoms (i.e. F, Cl or O) in HFCs, Kleiber and Axmann proposed the new group assignments and extended ten additional structure groups to the modified UNIFAC models to reduce the vapor-liquid prediction deviations of the mixtures containing the common fluorinated refrigerants. The corresponding volume parameters (R_k), surface area parameters (Q_k) and temperature-dependent interaction parameters of the new structure groups were determined through regressing the VLE experimental database. Thus, the calculation results of their previously correlated group interaction parameters are used for comparison.

According to the new group assignments proposed by Kleiber and Axmann [9, 10], for the halogenated methane derivatives, i.e. CH_mF_n ($m+n=4$), the different main groups were defined based on its number of F atoms, i.e. CHF, CHF₂ and CHF₃; while for the halogenated ethane derivatives with a CH₃ segment, i.e. CH₃CH_mF_n ($m+n=3$), the CH₃ segment can be replaced by an H atom and the ethane derivative yields the aforementioned corresponding methane derivatives, so the halogenated ethane derivatives can be divided into a CHF_n group and a CH₃ group. Then the HFCs refrigerants, R32, R152a and R161, are segmented into the corresponding groups as listed in 0. Because of the same structure formula, H₃C[OCH₂CH₂]_nOCH₃, the polyethylene-glycol dimethylether chemical solvents have four different molecular groups (CH₃, CH₂, CH₂O, CH₃O). Several different functional-group assignment configurations were proposed. And the configuration consists of 2 CH₃ groups, $n-1$ CH₂ groups and $n+1$ CH₂O groups were found the lowest deviations when used for the regressions among all the configurations. Therefore, this configuration is adopted in this work and the group assignments are also listed in 0. The relevant volume parameters and the surface area parameters of the subgroups are obtained from Kleiber and Axmann and Gmehling et al. [11]. The group interaction parameters between main groups taken from Kleiber, Axmann and Gmehling et al. [11] are used as the previous parameters for the result comparisons.

Table 1. Modified UNIFAC Group assignments for the HFCs refrigerants and the chemical solvents

Substances	Subgroups	Main groups	No.	R_k	Q_k
R32	CH ₂ F ₂	CHF ₂	1	1.7529	1.8147
R152a	CHF ₂	CHF ₂	1	1.1396	1.439
	CH ₃	CH ₂	1	0.6325	1.0608
R161	CH ₂ F	CHF	1	1.0685	1.0007
	CH ₃	CH ₂	1	0.6325	1.0608
DMEDEG	CH ₃	CH ₂	2	0.6325	1.0608
	CH ₂	CH ₂	1	0.6325	0.7081
	CH ₂ O	CH ₂ O	3	1.1434	1.2495
DMETREG	CH ₃	CH ₂	2	0.6325	1.0608
	CH ₂	CH ₂	2	0.6325	0.7081
	CH ₂ O	CH ₂ O	4	1.1434	1.2495
DMETEG	CH ₃	CH ₂	2	0.6325	1.0608
	CH ₂	CH ₂	3	0.6325	0.7081
	CH ₂ O	CH ₂ O	5	1.1434	1.2495

3 Results and discussion

Figure 1. Experimental and calculated vapor pressures of R32/R152a/R161 in several polyethylene-glycol dimethylether solvents at different temperatures; symbols: the experimental data; solid line: modified UNIFAC with new parameters; dashed line: modified UNIFAC with previous parameters

Table 2. New group interaction parameters of modified UNIFAC (Dortmund)

Main group m	Main group n	a_{mn}/K	a_{nm}/K	b_{mn}	b_{nm}	c_{mn}/K^{-1}	c_{nm}/K^{-1}
CHF ₂	CH ₂	-0.0539	-0.2103	2.96044	-2.4577	-0.0083	0.00721
CHF ₂	CH ₂ O	0.69702	0.9682	2.59157	-2.3053	-0.006	0.00608
CHF	CH ₂	0.00111	-0.0161	-0.2944	13.7253	-0.00036	-0.0514
CHF	CH ₂ O	0.10316	0.19416	-5.7566	14.5816	0.02258	-0.0543

In this study, the new group interaction parameters of the modified UNIFAC (Dortmund) model are obtained by regressing the experimental VLE data. Considering the group assignments of the HFCs, the five binary mixtures, R32+DMEDEG, R152a+DMEDEG/DMEDEG and R161+DMEDEG/DMEDEG, are selected for the regression. And the other measured VLE data of R32+DMEDEG, R152a/R161+DMETrEG are used for verification. This regression is carried out by the least-squares method using the MATLAB software. Eq. (1) is applied to describe the non-ideality VLE behavior of the binary mixtures and the maximum-likelihood principle is used as the objection function for minimization. 0 shows the regressed new group interaction parameters of the modified UNIFAC model. 0 illustrates the experimental and calculated vapor pressures by the previous and new interaction parameters of the studied 8 HFCs+ polyethylene-glycol dimethylether binary mixtures at the temperatures of 293.15, 313.15 and 343.15 K, respectively.

For the five binary mixtures used for regression, the average relative absolute deviation (ARAD) between the experimental and calculated pressures using the new parameters is about 4.37%, while the modified UNIFAC (Dortmund) model using the previous parameters shows an ARAD of 18.69% from the experimental data. The regressed results are found in better agreement with the experimental data as depicted in 0. Also, for the remaining three mixtures, R32+DMEDEG and R152a/R161+DMETrEG, the prediction ARAD calculated by the regressed new parameters are 3.71%, 2.61% and 6.86%; while the prediction ARAD calculated by the previous parameters shows 17.13%, 24.06% and 12.48%, respectively. All the results prove that the new regressed parameters of the modified UNIFAC model have lower prediction deviations than that obtained from literature, and they can be used to predict the isothermal solubilities of HFCs + polyethylene-glycol dimethylether binary mixtures. Finally, the predicted VLE data of R161 + PGDE (Pentaethyleneglycol dimethyl ether, CAS:1191-87-3, $H_3C[OCH_2CH_2]_5OCH_3$) at the temperatures of 293.15-343.15 K are illustrated in 0.

Figure 2. p - T - x diagram for the predicted VLE results of R161(1) + PGDE (2) by modified UNIFAC model with new parameters

4 Conclusions

An advanced group contribution model based on the molecular structure, the modified UNIFAC (Dortmund) model, was introduced to predict the VLE behaviors of HFCs+ polyethylene-glycol dimethylether chemical solvents when lacking of experimental data.

The VLE data of all reported eight working fluids were studied, of which five binary mixtures were adopted for regression and the other three were used for prediction verification. The results showed that our regressed model had an average regression deviation of 4.37% while the modified UNIFAC model using the previous parameters showed a deviation of 18.69%. As for their prediction, our model also showed the lower deviations than that of the reference.

Finally, the VLE data of R161 + PGDE (Pentaethyleneglycol dimethyl ether, CAS:1191-87-3, $H_3C[OCH_2CH_2]_5OCH_3$) at the temperatures of 293.15-343.15 K were predicted by our regressed model.

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