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Vapor−Liquid Equilibrium Measurements for Tetraethyl Orthosilicate + Ethanol at 24.00 kPa and 53.32 kPa

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The isobaric vapor−liquid equilibrium data of the tetraethyl orthosilicate and ethanol binary mixture were collected using a modified Othmer still at pressures of 24.00 kPa and 53.32 kPa. The experimental data showed that this mixture could be separated by a distillation process at lower temperatures under pressures of 24.00 kPa and 53.32 kPa than under atmospheric pressure. The experimental data were examined with the Herington thermodynamic consistency test and the χ^2 distribution of statistics. They are fairly well correlated with the UNIQUAC model. Also, the optimum interaction parameters of the UNIQUAC model were determined by the maximum likelihood principle.

Introduction

Vapor−liquid equilibrium (VLE) data are essential to the design and operation of a separation process such as distillation, absorption, and extraction and the optimization of a process design or a flowsheet construction. Moreover, accurate VLE data are indispensable for developing and evaluating an activity coefficient model that will be used for prediction where there is a lack of experimental data. Tetraethyl orthosilicate (boiling point, 168.5 °C) is used as an adhesive for precision casting, a binder for ceramics, a gelling agent for alcohol fuels, a source of finely divided amorphous silica, and in the preparation of glass adherent lacquers. The preparation of tetraethyl orthosilicate is by the direct reaction between anhydrous ethyl alcohol and silicon tetrachloride, with hydrogen chloride being formed as a byproduct. The ester is then distilled at low pressure to avoid a high distillation temperature that could cause decomposition. Because of its extensive use in the refractory and foundry industries, it is economical to recover it from the mixtures for reuse. Unfortunately, a literature survey revealed that VLE data are scarce for systems involving tetraethyl orthosilicate with ethanol. Therefore, the VLE of tetraethyl orthosilicate and ethanol at the pressures of 24.00 kPa and 53.32 kPa were measured in this study. The experimental data were obtained using a modified Othmer still and examined by the consistency tests of thermodynamics and statistics. The experimental data were then correlated with the UNIQUAC model by means of the maximum-likelihood principle, and the binary interaction parameters of this model were determined.

Experimental Section

Materials. The chemicals, tetraethyl orthosilicate and ethanol with purities of 99+ mass % and 99.8+ mass %, respectively, were purchased from Merck Chemical. Both chemicals were used without further purification.

Apparatus and Procedures. The equilibrium apparatus is shown schematically in Figure 1. The main part of this apparatus is the recirculation still. The apparatus is designed to avoid the rectifying effect due to heat loss of the vapor phase by the double-insulating jackets and the inner jacket evacuated to 1 mPa. Baffles were placed on the chamber wall in the vapor path to prevent liquid entrainment. The evaporating vapor mixture was condensed in a condenser and recirculated back to mix with the liquid phase in the still until equilibrium was reached. The liquid phase was stirred to guarantee the uniformity of mixture in the still.

The temperatures of vapor and liquid were measured with thermocouples with an uncertainty of ±0.1 K, and the still pressure was controlled at the desired value by a pressure controller with an uncertainty of ±0.1333 kPa. The pressure indicator and thermometers were calibrated before experimental measurements. The pressure calibration was done at the saturated vapor pressure of the deionized distilled water. Before performing the experiments below atmospheric pressure, the apparatus was carefully examined any leakage from any connection.

For each experiment, about 140 mL of liquid mixture was fed into the still. Heat was supplied from an electrical heater to evaporate the liquid steadily and keep both liquid and vapor phases at the same temperature for more than 1 h to ensure phase equilibrium. The equilibrium temperature and pressure were recorded. The vapor and liquid samples were then taken separately from different positions of the still for gas chromatogrpahy (GC) analysis. The analysis of compositions is given in the following section.

A test experiment was run for ethanol + water at 66.65 kPa, and the results were compared to the literature data of Kirschbaub and Gerstner[1] to guarantee the reliabilities of the apparatus and experimental skill. We found that the data of the present run and that of the literature[1] were not carried out at the same compositions, thus, these two data sets were plotted in Figure 2 for comparison. It is clear that two data sets agree with each other very well and we could have confidence in the experimental method.

Method of Analysis. The compositions of vapor- and liquid-phase samples were analyzed by a gas chromatograph (China Chromatography Co. Model 8900) with a TCD detector. The column used was 10% SE30, 80/100 supelcoport, and 20 ft by $^1/_8$ in. The optimum operation conditions of GC are: injector temperature, 180 °C; oven

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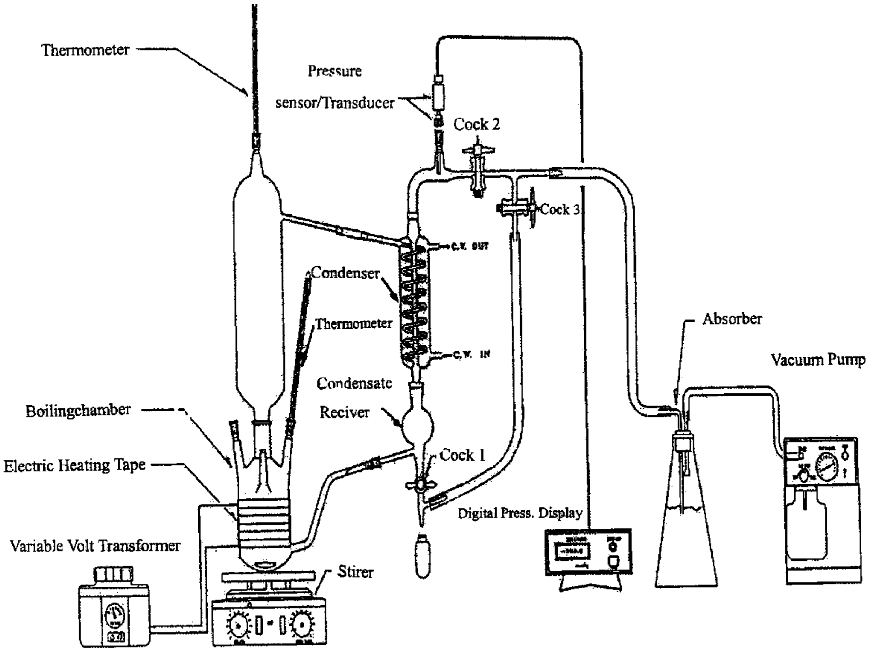

Figure 1. The experimental apparatus for present study.

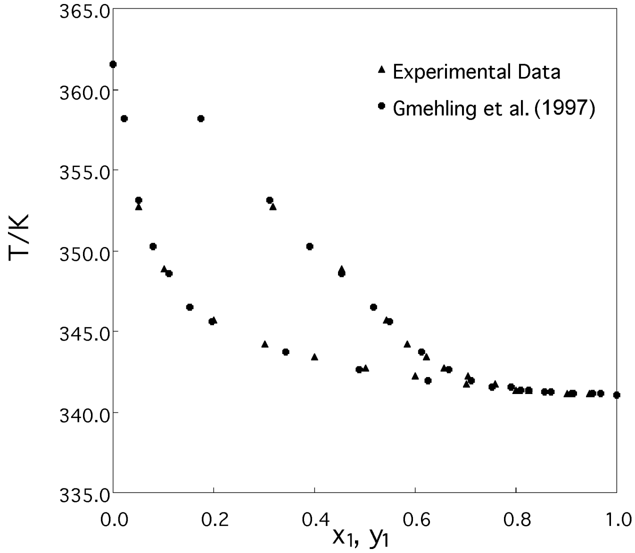

Figure 2. $T-x-y$ diagram of the ethanol (1) + water (2) binary mixture at 66.65 kPa.

temperature, 170 °C; TCD detector temperature, 170 °C; carrier gas, pure helium gas with a flow rate of 28 $\text{mL}\cdot\text{min}^{-1}$; sample volume, 1 μL. A calibration curve was constructed prior to the experiment by the mole fraction and the peak area ratios of a set of standard solutions of known compositions. The regressed calibration curve of this system has the form

$$m = c_1A + c_2A^2 + c_3A^3 + c_4A^4 \tag{1}$$

where m is the mole fraction of tetraethyl orthosilicate and A is the peak area ratios of tetraethyl orthosilicate to ethanol, the coefficients were determined by fitting the standard solutions and the values are 0.1931, 1.4389, −2.4467, and 1.8075, respectively. The R^2 value of this fit is 0.9996.

Experimental Results

The VLE data at the pressures of 24.00 kPa and 53.32 kPa were given in Tables 1 and 2 and were also plotted as Figures 3 and 4, respectively. It is clear that the saturated liquid and vapor lines are far away from each other, and this implies that a separation of this mixture at these pressures is not a difficult task. It can also be observed from these figures that the operation temperature of distillation column can be reduced from approximate 441.7 K (the boiling temperature of tetraethyl orthosilicate) to 419.2 K (boling point (bp) at 53.32 kPa) or 393.4 K (bp at 24.00 kPa). Both VLE diagrams at these two different pressures are very similar except for the fact that the bubble temperatures are different.

Table 1. Experimental VLE Data of the Tetraethyl Orthosilicate (1) + Ethanol (2) Binary Mixture at 24.00 kPa

no.	T/K	x_1	y_1	γ_1	γ_2
1	319.5	0.0000	0.0000		1.0000
2	319.8	0.0430	0.0101	5.9456	1.0239
3	320.2	0.0661	0.0106	3.9699	1.0280
4	321.0	0.1080	0.0118	2.5875	1.0333
5	321.8	0.1623	0.0168	2.3458	1.0525
6	323.1	0.2224	0.0199	1.8888	1.0607
7	323.9	0.3402	0.0260	1.5448	1.1949
8	325.6	0.4322	0.0323	1.3788	1.2712
9	327.0	0.5064	0.0395	1.3360	1.3577
10	329.0	0.5931	0.0511	1.3287	1.4806
11	333.1	0.7131	0.0753	1.3196	1.6928
12	338.5	0.7875	0.1080	1.3113	1.7300
13	342.0	0.8227	0.1311	1.2878	1.7333
14	350.5	0.8875	0.1973	1.2140	1.7640
15	355.8	0.9163	0.2494	1.1772	1.7894
16	358.5	0.9281	0.2745	1.1395	1.8098
17	366.0	0.9534	0.3713	1.0995	1.8150
18	371.7	0.9681	0.4670	1.0859	1.8210
19	375.0	0.9749	0.5202	1.0575	1.8499
20	376.6	0.9782	0.5541	1.0563	1.8701
21	382.0	0.9872	0.6830	1.0553	1.8758
22	384.9	0.9911	0.7533	1.0436	1.9020
23	387.5	0.9942	0.8214	1.0339	1.9363
24	390.7	0.9987	0.9121	1.0215	3.8249
25	393.4	1.0000	1.0000	1.0000	

Consistency Tests of Experimental Data

It is possible that a set of experimental data might exhibit systematic or random errors and fail to represent the true phase behavior of a mixture regardless of the effort and time that was invested in experiments. Thus, an

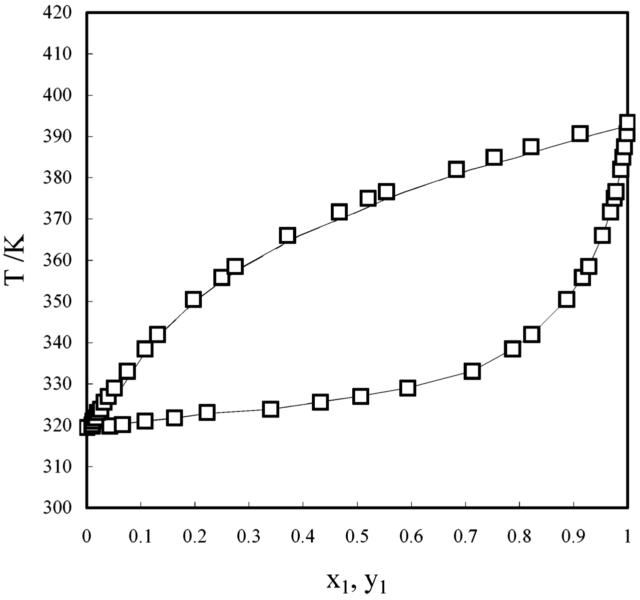

Figure 3. $T-x-y$ diagram of the tetraethyl orthosilicate (1) + ethanol (2) binary mixture at 24.00 kPa: □, experimental values; dashed line, UNIQUAC model.

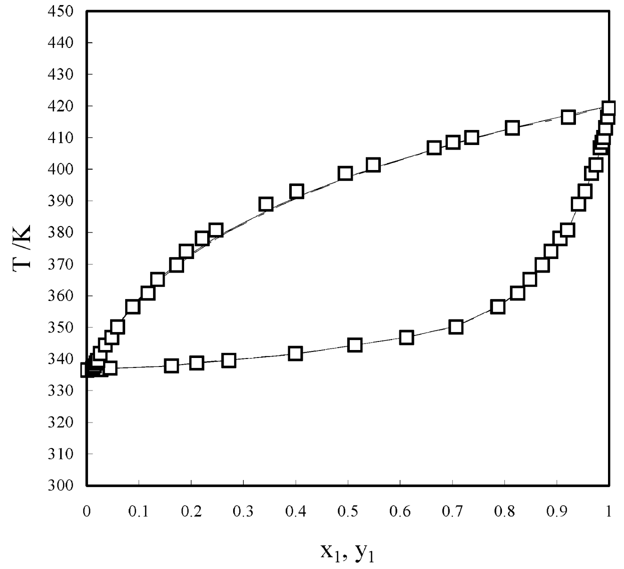

Figure 4. $T-x-y$ diagram of the tetraethyl orthosilicate (1) + ethanol (2) binary mixture at 53.32 kPa: □, experimental values; dashed line, UNIQUAC model.

experimental data set has to be carefully examined before it can be further implemented to design a separation column. The thermodynamic consistency, usually considered as a criterion of a reliable experimental data set, must be satisfied. The Herington consistency test,[2] based on the principle of the Gibbs−Duhem theorem and is a necessary rather than a sufficient condition, was employed to verify our experimental data. The formula for thermodynamic consistency at constant pressure proposed by Herington[2] is

$$D = \frac{|U - V|}{|U + V|} \times 100 \tag{2}$$

$$J = 150 \times \frac{T_{\max} - T_{\min}}{T_{\min}} \tag{3}$$

Table 2. Experimental VLE Data of the Tetraethyl Orthosilicate (1) + Ethanol (2) Binary Mixture at 53.32 kPa

no.	T/K	x_1	y_1	γ_1	γ_2
1	336.5	0.0000	0.0000		1.0000
2	336.7	0.0271	0.0105	8.9908	1.0090
3	337.1	0.0442	0.0115	5.9198	1.0078
4	337.9.	0.1622	0.0144	1.9423	1.1064
5	338.7	0.2103	0.0175	1.7510	1.1294
6	339.5	0.2721	0.0205	1.5251	1.1793
7	341.7	0.3990	0.0257	1.1733	1.2908
8	344.4	0.5132	0.0352	1.1002	1.4053
9	346.8	0.6123	0.0477	1.1181	1.5736
10	350.2	0.7070	0.0590	1.0264	1.7863
11	356.5	0.7871	0.0880	1.0426	1.8474
12	360.8	0.8252	0.1170	1.1017	1.8410
13	365.1	0.8482	0.1352	1.0372	1.7618
14	369.7	0.8721	0.1721	1.0679	1.6866
15	374.0	0.8890	0.1910	0.9832	1.6245
16	378.2	0.9061	0.2211	0.9521	1.5930
17	380.8	0.9204	0.2474	0.9522	1.6586
18	389.0	0.9413	0.3430	0.9611	1.4880
19	393.0	0.9545	0.4018	0.9665	1.5334
20	398.7	0.9668	0.4953	0.9707	1.4782
21	401.4	0.9748	0.5482	0.9750	1.6025
22	406.7	0.9832	0.6650	0.9889	1.5157
23	408.5	0.9870	0.7011	0.9814	1.6558
24	410.0	0.9892	0.7370	0.9823	1.6771
25	413.1	0.9931	0.8152	0.9836	1.6836
26	416.5	0.9975	0.9222	0.9995	1.7729
27	419.2	1.0000	1.0000	1.0000	

where U is the upper part of the area confined by the curve $\ln(\gamma_1/\gamma_2)$ and the x_1 axis and V is the lower part of the area confined by the curve $\ln(\gamma_1/\gamma_2)$ and the x_1 axis on the diagram, $T_{\max}$ and $T_{\min}$ are the maximum and minimum temperatures in the range $0 \leq x_1 \leq 1$, respectively. The constant 150 is an empirical value estimated by Herington. The original criterion of consistency of a set of experimental data concluded by Herington[2] is

$$|D - J| < 10 \tag{4}$$

In this study, the values of $|D - J|$ are 1.3 and 9.8 for experimental data at 24.00 kPa and 53.32 kPa, respectively, and indicate that the experimental data of the present study satisfy the Herington test.

It is recognized that the reliability of an experimental data set is still not guaranteed even if it satisfies the Herington test. Thus, the statistical analysis of the χ^2 test proposed by Neau and Peneloux[3] was also considered to examine the consistency of our experimental data. Neau and Peneloux[3] proposed that an experimental data set is consistent if the minimum objective function, $S_{\min}$, given in eq 7, was confined in the χ^2 region with degrees of freedom $2n-p$ and a significant level α. This criterion is expressed as

$$S_{\min} < {\chi_{1-\alpha}}^2(2n - p) \tag{5}$$

where S is the minimum objective function value defined in eq 7, n is the number of experimental points, and p is the number of parameters.

In this study, the significant value α is 0.05 and the degrees of freedom, $2n-p$, are 48 and 52 for experiments at 24.00 kPa and 53.32 kPa, respectively. Then the χ^2 distribution values obtained from the table of a statistics textbook are $\chi^2_{0.95}(48) = 65.14$ and $\chi^2_{0.95}(52) = 68.92$. After comparison of these two values with the minimum objective function values $S_{\min}$ in Table 4, we concluded that this consistency test was also satisfied.

Data Reduction

For the correlation of the experimental binary VLE data, the vapor phase was treated as an ideal gas since the

Table 3. Molecular-Structure[a] and Antoine Parameters Used in Present Work

	tetraethyl orthosilicate(1)	ethanol(2)
r	0.71	2.11
q	0.52	1.97
q'	0.52	0.92
Antoine coefficients[b]	$\ln P_i^{sat}\,(\text{mmHg}) = A_i - (B_i/T(°\text{C}) + C_i)$	
A_i	16.784	20.421
B_i	3942.79	4657.84
C_i	219.353	259.428

[a] The molecular-structure parameters for tetraethyl orthosilicate and ethanol were estimated by method of Bondi[6] and taken from Prausnitz et al.,[7] respectively. [b] Parameters were taken from Reid et al.[8]

Table 4. Regression Results of the UNIQUAC Model

		24.00 kPa	53.32 kPa
model parameters	$\Delta u_{12}/R^{(K)}$	-367.91 ± 41.79	-295.72 ± 44.75
	$\Delta u_{21}/R^{(K)}$	95.42 ± 18.31	66.43 ± 24.57
sum square of residual	$S_{\min}$	19.22	16.00
estimated variance of fit	$\sigma_{\text{fit}}^{2,\text{est}}$	0.1057585	0.0979230

pressure is so low that the pressure effect on the phase equilibrium was neglected. The vapor liquid equilibrium equation for binary mixture is expressed as

$$y_i P = x_i \gamma_i P_i^s \quad i = 1,2 \tag{6}$$

In this study, the activity coefficient model of UNIQUAC[4] was used to estimate the component activity coefficients, γ_i, and the Antoine equation was used to calculate the vapor pressures of the pure components. All the pure-component molecular-structure parameters used in the UNIQUAC model and the Antoine parameters used in present work of tetraethyl orthosilicate and ethanol were given in Table 3.

After all the methods and formulations for the evaluations of thermodynamic properties were determined, the experimental data were reduced by the maximum-likelihood principle of Kemeny and Manczinger,[5] which assumed that the experimental errors were random and independent and had the advantage of accounting for each concerned variable. The objective function for the maximum likelihood principle is formulated as

$$S_{\min} = \sum_i \left\{ \left(\frac{P_i^{\exp} - P_i^{\text{cal}}}{\sigma_{P_i}^{\text{est}}} \right)^2 + \left(\frac{T_i^{\exp} - T_i^{\text{cal}}}{\sigma_{T_i}^{\text{est}}} \right)^2 + \left(\frac{x_{1i}^{\exp} - x_{1i}^{\text{cal}}}{\sigma_{x_{1i}}^{\text{est}}} \right)^2 + \left(\frac{y_{1i}^{\exp} - y_{1i}^{\text{cal}}}{\sigma_{y_{1i}}^{\text{est}}} \right)^2 \right\} \tag{7}$$

where the pressure and temperature variances, σ_P^2 and σ_T^2, were estimated by the uncertainty of the measurement and the experimenter's reading error, while liquid and vapor composition variances were determined by the inaccuracy of the calibration curve. All the standard deviations used for our calculations were $\sigma_P = 1$ mmHg, $\sigma_T = 0.1$ K, $\sigma_x = 0.01$, and $\sigma_y = 0.01$. The regression results of different models at 24.00 and 53.32 kPa were shown in Table 4. This table gives the optimum binary interaction parameters of the UNIQUAC model, the minimum objective function value, and the estimated variance of fit. The correlation results were also plotted in Figures 3 and 4, showing two curves overlap on each other. These two figures showed the model of UNIQUAC[4] represents the VLE of this binary mixture very well.

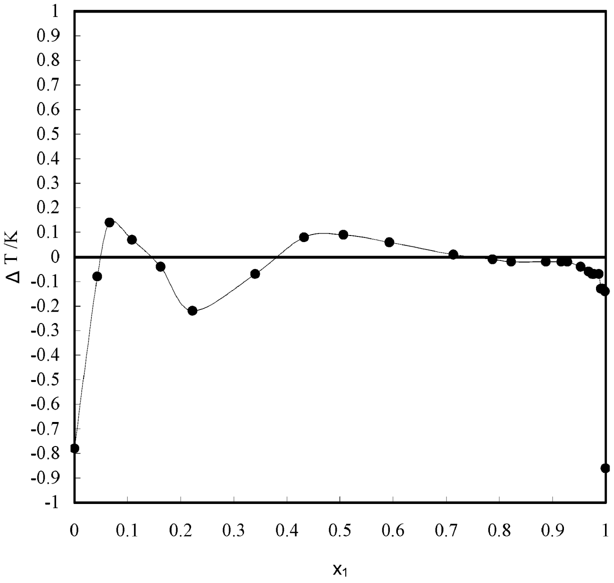

Figure 5. Deviations between calculated and measured bubble temperatures vs liquid mole fractions of tetraethyl orthosilicate (1) + ethanol (2) at 24.00 kPa.

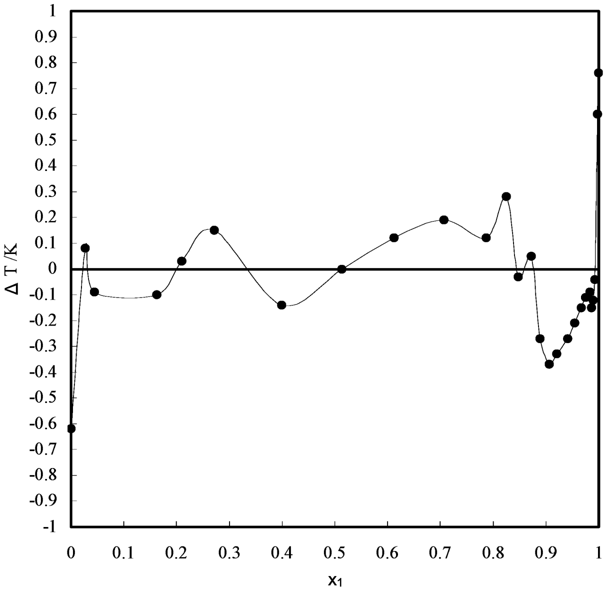

Figure 6. Deviations between calculated and measured bubble temperatures vs liquid mole fractions of tetraethyl orthosilicate (1) + ethanol (2) at 53.32 kPa.

The optimum parameters of the UNIQUAC model were then used to estimate the bubble temperatures. The average absolute deviations (AAD) of bubble temperatures and vapor-phase compositions were $\Delta T = 0.13$ and $\Delta y = 0.0.0159$ at 24.00 kPa and $\Delta T = 0.19$ and $\Delta y = 0.0068$ at 53.32 kPa, respectively. Also, the ΔT values of two pressures were plotted against x_1 in Figures 5 and 6. These two figures give the deviations at different compositions of mixture and show the reasonable estimations by the UNIQUAC model.

Conclusion

In this study, isobaric VLE data for tetraethyl orthosilicate + ethanol were collected separately at 24.00 kPa and 53.32 kPa. The experimental data satisfied both the

Herington thermodynamic consistency test and the statistical χ^2 test. Correlations of experimental data with the UNIQUAC[4] equation show that this model is suitable to represent this binary mixture. The VLE data of this binary mixture are useful for process design to separate this mixture.

Appendix

The UNIQUAC Model.

$$\ln \gamma_i = \ln \gamma_i(\text{combinatorial}) + \ln \gamma_i(\text{residual})$$

$$\ln \gamma_1(\text{combinatorial}) = \ln \frac{\Phi_1}{x_1} + \frac{z}{2} q_1 \ln \frac{\theta_1}{\Phi_1} + \Phi_2\left(l_1 - \frac{r_1}{r_2} l_2\right)$$

$$\ln \gamma_1(\text{residual}) = -q_1 \ln(\theta_1 + \theta_2\tau_{21}) + \theta_2 q_1\left(\frac{\tau_{21}}{\theta_1 + \theta_2\tau_{21}} - \frac{\tau_{12}}{\theta_1\tau_{12} + \theta_2}\right)$$

$$\ln \gamma_2(\text{combinatorial}) = \ln \frac{\Phi_2}{x_2} + \frac{z}{2} q_2 \ln \frac{\theta_2}{\Phi_2} + \Phi_1\left(l_2 - \frac{r_2}{r_1} l_1\right)$$

$$\ln \gamma_2(\text{residual}) = -q_2 \ln (\theta_2 + \theta_1\tau_{12}) + \theta_1 q_2\left(\frac{\tau_{12}}{\theta_2 + \theta_1\tau_{12}} - \frac{\tau_{21}}{\theta_2\tau_{21} + \theta_1}\right)$$

where

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \qquad z = 10$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j}$$

is the area fraction of component i

$$\Phi_i = \frac{x_i r_i}{\sum_j x_j r_j}$$

is the volume fraction of component i

$$\tau_{12} = \exp\left(-\frac{A_{12}}{T}\right)$$

$$\tau_{21} = \exp\left(-\frac{A_{21}}{T}\right)$$

Literature Cited

(1) Kirschbaub, E.; Gerstner, H.; Vdi Beth, Z. *Verfahrenstechnik* **1939**, *1*, 10.
(2) Herington, E. F. G. Tests for The Consistency of Experimental Isobaric Vapor-Liquid Equilibrium Data. *J. Inst. Petrol.* **1965**, *37*, 457−470.
(3) Neau, E.; Peneloux, A. Estimation of Model Parameters. Comparison of Methods Based on The Maximum Likelihood Principle. *Fluid Phase Equilib.* **1981**, *6*, 1−19.
(4) Abrams, D. S.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixture: A New Expression for The Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, *21*, 116−128.
(5) Kemeny, S.; Manczinger, J. Reduction of Thermodynamic Data by Means of the Multiresponse Maximum Likelihood Principle. *AIChE J.* **1982**, *28*, 20−30.
(6) Bondi, A. *Physical Properties of Molecular Liquids, Crystals and Glases*; Wiley: New York, 1968.
(7) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*; Prentice Hall: Englewood Cliffs, 1980.
(8) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

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