J. Chem. Eng. Data **2004,** *49,* 1535−1538

Isobaric Vapor−Liquid Equilibria for the Ternary System of 2-Methyl-1-butanol, 3-Methyl-1-butanol, and Ethylene Glycol at 101.3 kPa

Hang Song,* Liangming Liu, Yongkui Zhang, and Chao Fu

School of Chemical Engineering, Sichuan University, 610065 Chengdu, China

---

Isobaric vapor−liquid equilibrium data for the ternary system 2- methyl-1-butanol (1) + 3- methyl-1-butanol (2) + ethylene glycol (3) were measured in a modified Rose recirculation still at 101.3 kPa. The experimental data were satisfactorily correlated with the Wilson equation. They were also compared with the predictions by Weidlich's modified UNIFAC group contribution method, and the deviations were also small. The both models are satisfied with the accuracy demanded of process development, design, and simulation.

Introduction

2-Methyl-1-butanol and 3-methyl-1-butanol are useful solvents and important fine chemicals. They coexist in mixed isoamyl alcohols (a mixture of 2-methyl-1-butanol and 3-methyl-1-butanol), which are routinely obtained as a byproduct during ethyl alcohol production after wine and similar raw material distillation.[1] Separation of them with usual distillation is very difficult because they are isomeric compounds and the difference of their boiling points is only 2.8 °C.[2]

Adding a third component ethylene glycol as an extractive solvent in the distillation could improve the separation and be a preferable way.[3] To simulate and design this separation process, the determination of vapor−liquid equilibrium (VLE) data for the ternary system and the study of its correlating models are essential. In a previous work, we investigated the VLE data for the binary systems 2-methyl-1-butanol (1) + ethylene glycol (3)[4] and 3-methyl-1-butanol (2) + ethylene glycol (3).[5] The VLE data for the binary system 2-methyl-1-butanol (1) + 3-methyl-1-butanol (2) was reported by other authors.[6] However, the VLE data for the ternary system 2-methyl-1-butanol (1) + 3-methyl-1-butanol (2) + ethylene glycol (3) is not available in open literature.

This work has been carried out as part of a project to simulate the separation of 2-methyl-1-butanol from 3-methyl-1-butanol by extractive distillation using ethylene glycol as extractant. The isobaric VLE data for the ternary system were measured in this work. In addition, the correlation of the VLE data for the binary and ternary systems by the Wilson[7] equation as well as the prediction of the VLE by a modified UNIFAC[8] model was studied as well. The correlation and the prediction were discussed.

Experimental Section

Chemicals. Ethylene glycol (analytical reagent grade, 98% mass) was from the Chengdu Kelong Chemicals Factory. After further purification by rectification to eliminate some impurities, it was 99.9% mass of purity. 2-Methyl-1-butanol and 3-methyl-1-butanol were the same as in the previous work[3,4] made from their mixture by rectification with about 100 theoretical plates in our laboratory.[2] Their purities are up to 99.9% mass. The properties of pure reagents and their Antoine coefficients are shown in Tables 1 and 2, respectively.

Apparatus and Procedures. An all-glass dynamically recirculating still with a liquid volume of 150 mL shown in Figure 1 was used for the measurement of the VLE. The still is a Rose-type modified to adapt to the experiment under atmospheric pressure.[11] It has some advantages over the conventional type. For example, with mixing of liquid and vapor in the mixing chamber instead of in recirculating tube, it can easily mix recirculating flows of quite different boiling points and speed up to reach the VLE; without dead space in its structure, the whole solution can be mixed more uniformly; a midified outlet can drain completely the remains from a previous measurement.

Auxiliary equipment includes two precision mercury thermometers with an accuracy of ±0.1 °C, a pressure adjuster with an accuracy of ±1 mm Hg, and a heater stirrer. Figure 2 shows the apparatus system for the measurement of isobaric VLE at 101.3 kPa.

The experiments were done under a dried inert air atmosphere at a constant pressure of 101.3 kPa. The pressure was automatically adjusted to the desired value by the pressure adjuster. The liquid phase was kept to boil for 40 min to ensure complete VLE. Equilibrium conditions were assumed when constant temperature and pressure were kept for 15 min or longer.

After equilibrium, about 1.5 mL of the vapor and liquid samples were taken from the liquid outlet and the condensate outlet with syringes at almost the same time, and the temperature was recorded simultaneously. The apparatus and procedure were checked by binary system ethanol−water with satisfactory results.

Analytical Methods. The equilibrium compositions of the liquid and vapor phases were analyzed with a gas chromatograph with a flame ionization detector (FID) and a thermal conductivity conductor (TCD) (SQ-206, Beijing Analysis Instrument Factory) and a chromatographic workstation (FJ2000-NEW, Shanghai Jinghua Science & Technology Ltd.). An external standard *n*-propanol[12] was used for peak-area quantification.

---

* To whom correspondence may be addressed. E-mail: hangsong@vip.sina.com.

10.1021/je030216r CCC: $27.50

Table 1. Physical Properties of Pure Reagents

components	T_b(100.0 kPa)/K		n_D(293.15 K)		ρ(293.15 K)/g·cm^{-3}	
	exp	lit[10]	exp	lit[9]	exp	lit[9]
2-methyl-1-butanol(dl)	401.55	401.48	1.4095	1.4102	0.8178	0.8152
3-methyl-1-butanol	404.45	403.97	1.4054	1.4098	0.8081	0.8092
Ethylene glycol	470.63	470.45	1.4328	1.4318	1.1136	1.1088

Table 2. Antoine Coefficients *A*, *B*, and *C*[10]

components	*T* range/K	Antoine coefficients[a]		
		A	*B*	*C*
2-methyl-1-butanol(1)	307−402	16.2708	2752.19	−116.3
3-methyl-1-butanol(2)	298−426	16.7127	3026.43	−104.1
Ethylene glycol(3)	364−494	20.2501	6022.18	−28.25

[a] $\ln(P_i^0/\text{mm Hg}) = A - B/((T/\text{K}) + C)$.

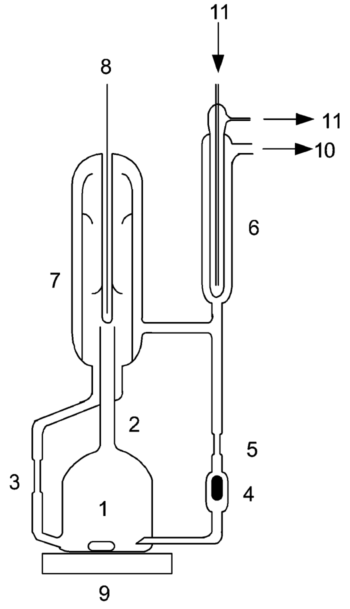

Figure 1. Modified Rose still: 1, reboiler; 2, vapor−liquid lift tube; 3, silicone rubber hose (liquid-phase sample extracted from here); 4, check bobber; 5, silicone rubber hose (condensed vapor-phase sample extracted from here); 6, condenser; 7, vapor−liquid segregator; 8, thermometer; 9, heater-stirrer; 10, to isobaric equipment; 11, cooling water.

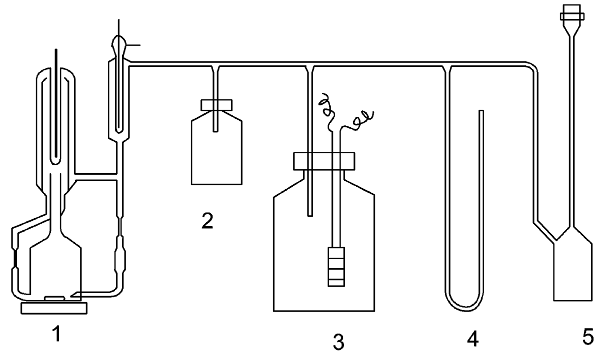

Figure 2. System for the determination of isobaric VLE: 1, the modified Rose still; 2, drying vessel; 3, isobaric bottle; 4, water manometer; 5, mercury manometer.

The properties of ethylene glycol are quite different from those of the others; it is difficult to find perfect chromatographic stationary phase and operation conditions to separate completely the three compounds with one injection of sample. So, two stainless columns (2m by 3 mm i.d.) with different stationary phases were used in analysis. One column filled with 6201 red spherical carriers (Shanghai Chemicals Ltd,) coated by 15% *meso*-erythritol was used for analyzing the components of 2-methyl-1-butanol and 3-methyl-1-butanol. Another one filled with GDX-103, a little macromolecule ball (Tianjing Chemicals Ltd.), was used for the component of ethylene glycol. Chromatographic conditions for analyzing the alcohols: FID detector; injector and detector temperatures, 190 °C; column temperature, 96 °C; carrier gas, nitrogen. The flow rates of gases were: V_{N_2}, 32 mL·min^{-1}; V_{H_2}, 37 mL·min^{-1}; V_{air}, 320 mL·min^{-1}. Chromatographic conditions for ethylene glycol: TCD; injector and detector temperatures, 230 °C; column temperature, 172 °C; carrier gas, hydrogen; flow rate, 32 mL·min^{-1}.

Quantitative determination of the three components: A series of component-known solutions, which were made up of solvent (*n*-propanol) and solute 2-methyl-1-butanol (1), 3-methyl-1-butanol (2), or ethylene glycol (3), were analyzed respectively by gas chromatogrpahy. The curve equations, which correlate the mass fractions of the component *i* (x_i/mg·kg^{-1}) with the chromatographic peak area of the components *i* (S_i), were given in Table 3.

The reproducibility of concentration measurements was better than ±0.003 mass fraction for the liquid phase and ±0.004 for the vapor phase. The maximum uncertainty for the measurements was ±0.005.

Results and Discussion

The thermodynamic criterion of VLE implies that the fugacity of the component *i* in the liquid phase must be equal to that in the vapor phase. At low pressure, it can be considered that Raoult's law is fulfilled and the exponential term (Poynting correction) of the VLE equation can be neglected. Therefore, the equilibrium equation is given as

$$Py_i = \gamma_i x_i P_i^0 \qquad \text{(a)}$$

where x_i and y_i are the mole fractions of the liquid and vapor phases in equilibrium, respectively, P is the total pressure of the system, 101.3 kPa in this study, and γ_i is the activity coefficient. The subscript *i* is the component *i*. P_i° values are the vapor pressures for the pure components that were calculated by the Antoine equation. The Antoine equations and their constants (A_i, B_i, and C_i) are listed in Table 2. In this work, the liquid-phase activity coefficients can be calculated by eq a. Liquid and vapor compositions, temperature determined experimentally, and liquid-phase

Table 3. Fitting Results of the Linear Determination of Components

components	fitting equations	relating coefficients
2-methyl-1-butanol (1)	$x_1 = -0.00106 + 4.43868 \times 10^{-6} S_1$	0.9957
3-methyl-1-butanol (2)	$x_2 = -0.00126 + 4.55462 \times 10^{-6} S_2$	0.9879
ethylene glycol (3)	$x_3 = 0.00571 + 6.75858 \times 10^{-7} S_3$	0.9765

Table 4. Isobaric Experimental Vapor−Liquid Equilibrium Data: Temperature *T*, Liquid-Phase Mole Fraction x_i, Vapor-Phase Mole Fraction y_i, and Activity Coefficients γ_i for the 2-Methyl-1-butanol(1) + 3-Methyl-1-butanol(2) + Ethylene Glycol(3) System at 101.3 kPa

T/K	x_1	x_2	y_1	y_2	γ_1	γ_2	γ_3
402.34	0.9365	0.0206	0.9547	0.0204	1.0035	1.0602	6.9409
404.16	0.4331	0.4857	0.4835	0.4864	1.034	1.0082	4.1005
405.46	0.6851	0.0523	0.8827	0.0577	1.1432	1.0634	2.3757
407.44	0.0515	0.7654	0.0672	0.883	1.0852	1.0414	2.6193
408.95	0.2812	0.3309	0.4483	0.4661	1.2627	1.2102	1.9954
409.36	0.3737	0.0922	0.7565	0.1632	1.5825	1.5007	1.3365
410.76	0.102	0.4681	0.1922	0.7327	1.4087	1.2683	1.4657
411.36	0.1862	0.2768	0.3672	0.5145	1.4465	1.4774	1.8033
412.98	0.0478	0.3999	0.1079	0.7822	1.5735	1.4764	1.5246
414.89	0.0431	0.2997	0.0997	0.7563	1.5196	1.7934	1.5538
417.13	0.0435	0.2115	0.1658	0.7161	2.3378	2.2443	1.0277
419.81	0.0482	0.1405	0.2088	0.6309	2.4508	2.7419	1.1521
430.47	0.0431	0.0412	0.3844	0.3865	3.7094	4.1884	0.9705
444.83	0.0188	0.0168	0.2828	0.2932	4.266	5.2714	1.0178

Table 5. Fitting Interaction Energy Parameters (Δg_{ij}) by Wilson Equation and the Average Composition Deviations in *y* (Δy_1) for Three Binary Systems at 101.3 kPa

binary systems	*i*, *j*	Δg_{ij}[a]	Δg_{ji}	Δy_1[b]
2-methyl-1-butanol(1) + 3-methyl-1-butanol(2)	1, 2	479.95	−479.88	0.0107
2-methyl-1-butanol(1) + ethylene glycol(3)	1, 3	5469.38	1974.39	0.0082
3-methyl-1-butanol(2) + ethylene glycol(3)	2, 3	7356.94	−175.18	0.0084

[a] $\Delta g_{ij} = (g_{ij} - g_{ii})/(\mathrm{J{\cdot}mol^{-1}})$. [b] $\Delta y_1 = \sum |y_{\mathrm{exp}} - y_{cal}|/N$ (N = number of data points).

Table 6. Correlation by the Wilson Equation and Prediction by the Modified UNIFAC Method for the Ternary System 2-Methyl-1-butanol (1) + 3-Methyl-1-butanol (2) + Ethylene Glycol (3): Average Deviations in *T* (Δ*T*) and Average Deviations in *y* (Δ*y*) at 101.3 kPa[a]

model	ΔT/K	Δy	Δy_1	Δy_2	Δy_3
Wilson Equation	0.58	0.0104	0.0098	0.0031	0.0183
Modified UNIFAC	0.31	0.0155	0.0166	0.0081	0.0218

[a] $\Delta y = (\Delta y_1 + \Delta y_2 + \Delta y_3)/3$; $\Delta T/\mathrm{K} = \sum |T_{\mathrm{exp}} - T_{\mathrm{cal}}|/N$; $\Delta y_i = \sum |y_{\mathrm{exp}} - y_{\mathrm{cal}}|/N$ (N = number of data points)).

activity coefficients calculated from these data of the ternary system are given in Table 4.

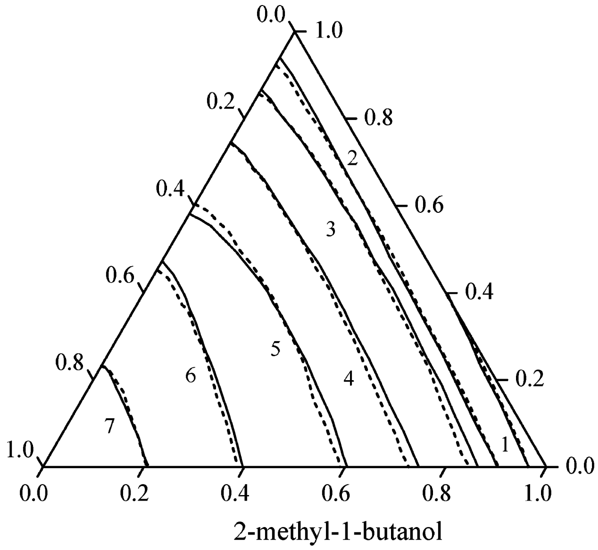

Figure 3. Isobaric VLE of the ternary system 2-methyl-1-butanol + 3-methyl-1-butanol + ethylene at 101.3 kPa: solid line, correlated by Wilson; dashed line, predicted by the modified UNIFAC model. 1, 2, 3, 4, 5, 6, and 7 represent the temperatures of 403.15 K, 413.15 K, 423.15 K, 433.15 K, 443.15 K, 453.15 K, and 463.15 K, respectively.

Correlation. In this study, the activity coefficients of three binary systems and a ternary system were correlated by the Wilson model.[7] The binary interaction energy parameters of the Wilson equation (Δg_{ij}) were obtained by correlating several sets of experimental VLE data.[4−6] Table 5 gives the binary interaction energy parameters (Δg_{ij}) and the average deviations (Δy_1) for the three binary systems between the experiments and the correlations.

Ternary system data were calculated with binary interaction energy parameters and compared with experimental data, which are listed in Tables 6 and 7. It can be seen that the Wilson equation gives very small deviations for the ternary system.

Prediction. Weidlich and Gmehling[9] modified the original UNIFAC activity coefficient model mainly in the aspects of van der Waals characters and interaction parameters of the group from 1987. Compared with the original model, the accuracy and applying field of the modified UNIFAC model were improved.[8,13] In this study, this modified UNIFAC model was also employed to predict the VLE of the ternary system. The deviations of the

Table 7. Calculated Results by Wilson, Predicted Results by UNIFAC for the Ternary System 2-Methyl-1-butanol (1) + 3-Methyl-1-butanol (2) + Ethylene Glycol (3) and Difference between the Results, Respectively, and the Experimental Values

	calculated by Wilson						predicted by UNIFAC					
$T_{i,\mathrm{exp}}$/K	$\|\Delta T_i\|$[a]/*K*	y_1	y_2	$\|\Delta y_1\|$[b]	$\|\Delta y_2\|$	$\|\Delta y_3\|$	$\|\Delta T_i\|$[a]/*K*	y_1	y_2	$\|\Delta y_1\|$[b]	$\|\Delta y_2\|$	$\|\Delta y_3\|$
402.34	1.97	0.9668	0.0203	0.0121	0.0001	0.0163	0.67	0.9716	0.0233	0.0169	0.0029	0.0164
404.16	0.96	0.4914	0.4854	0.0079	0.0010	0.0194	0.26	0.4902	0.4756	0.0067	0.0108	0.0214
405.46	0.10	0.8849	0.0567	0.0022	0.0010	0.0129	0.33	0.8949	0.0498	0.0122	0.0079	0.0219
407.44	1.53	0.0665	0.8731	0.0007	0.0099	0.0165	0.24	0.0713	0.8931	0.0041	0.0101	0.0103
408.95	0.31	0.4561	0.4650	0.0078	0.0011	0.0196	0.09	0.4686	0.4545	0.0203	.0116	0.0188
409.36	0.21	0.7536	0.1600	0.0029	0.0032	0.0138	1.08	0.7336	0.1589	0.0229	0.0043	0.0138
410.76	0.24	0.1801	0.7325	0.0121	0.0002	0.0135	0.17	0.1601	0.7425	0.0321	0.0098	0.0203
411.36	0.34	0.3896	0.5133	0.0224	0.0012	0.0252	0.16	0.3996	0.5183	0.0324	0.0038	0.0352
412.98	0.15	0.1043	0.7923	0.0036	0.0101	0.0183	0.34	0.1143	0.7945	0.0064	0.0123	0.0183
414.89	1.19	0.1176	0.7642	0.0179	0.0079	0.0285	0.14	0.1076	0.7542	0.0079	0.0021	0.0172
417.13	0.22	0.1517	0.7135	0.0141	0.0026	0.0232	0.09	0.1317	0.7035	0.0341	0.0126	0.0473
419.81	0.24	0.2160	0.6293	0.0072	0.0016	0.0199	0.21	0.1863	0.6223	0.0225	0.0086	0.0313
430.47	0.19	0.3713	0.3835	0.0131	0.0030	0.0129	0.18	0.3913	0.3735	0.0069	0.0130	0.0156
444.83	0.49	0.2859	0.2941	0.0031	0.0009	0.0162	0.36	0.2899	0.2894	0.0071	0.0038	0.0146

[a] $|\Delta T_i| = |T_{i,\mathrm{exp}} - T_{i,\mathrm{cal}}|$. [b] $|\Delta y_i| = |y_{i,\,\mathrm{exp}} - y_{i,\mathrm{cal}}|$.

temperature (ΔT), the vapor compositions predicted (y_i), and the composition deviations (Δy_i) are given in Tables 5 and 6. The predicted curves of the vapor compositions at different temperatures are also shown in Figure 3 and compared with those by the Wilson. It indicates that Weidlich's modified UNIFAC, as to the temperature average deviation, is better than Wilson's, while for vapor-component average deviations, it is contrary. Both methods can give good results for this ternary system.

Conclusions

Experimental isobaric VLE data for the ternary system were measured in a modified Rose recirculation still. The data can correlate or predict satisfactorily with the two theoretical models, the Wilson model and Weidlich's modified UNIFAC model. Both models can be used satisfactorily for the simulation and design of this extractive separation process.

Literature Cited

(1) Perez, L. High Alcohols and Other Components Generation and Evolution in Sherry Wines. Doctoral Thesis, University of Câdiz: Câdiz, 1979.

(2) Zhou, Q. Study on Separation Technology of 2-Methyl-1-butanol and 3-Methyl-1-butanol from Fusel Oil. Master Thesis, Sichuan University: Chengdu, China, 2000.

(3) Li, X.; Ji, J.; Zhu, F. Selection of Extractant for the Separation of Active Amyl Alcohol and Isomayl Alcohol. *J. Zhejiang Univ. Technol.* **1998**, *26* (2), 104−107.

(4) Hu, K.; Fu, C.; Song, H. The Vapor-Liquid Equilibrium of the Binary System of Active Amyl Alcohol and Ethylene Glycol. *J. Sichuan Univ.* **2002**, *34* (2), 121−123.

(5) Jiang, L.-k.; Song, H.; Fu, C. Study on Isobaric VLE Data for the System of Isopentanol and Ethylene Gylcol. *J. Chin. Chem. Eng.* **2002**, *30* (2), 68−69.

(6) Zu, F.-y.; Zhou, S.; Feng, X. Study of Separating 2-Methyl-1-butanol from 3-Methyl-1-butanol. *J. Chin. Chem. Eng.* **2001**, *18* (3), 183−185.

(7) Wilson, G. M. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127−130.

(8) Weidlich, U.; Gmehling, J. A Modified UNIFAC Model 1 Prediction of VLE, h^E, γ^∞. *Ind. Eng. Chem. Res.* **1987**, *26*, 1372−1381.

(9) *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boca Raton, FL, 1990.

(10) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.

(11) Hu, W.; Chen, J.; Liu, Q.; Xiao, Z. Study on Vapor Liquid Equilibria for Three Binary Systems, Methyl Iodide-Methyl Acetate, Methyl Iodide-Methanol, Methyl Iodide-Acetic Acid at Normal Pressure. *J. Chem. Ind. Eng.* **1980**, *4*, 353−363.

(12) Yuan, S.; Wang, J.; Cai, S. Isothermal Analysis of Alcohols. *J. Anal. Chem.* **1988**, *16* (6), 573.

(13) Gmehling, J.; Li, J.; Schiller, M. A Modified UNIFAC Model 2 Present Parameter Matrix and Results for Different Thermodynamic Properties. *J. Ind. Eng. Chem. Res.* **1993**, *32* (1), 178−193.

Received for review August 15, 2003. Accepted June 8, 2004.

JE030216R