Isothermal Vapor–Liquid Equilibria for 2-Methyl-2-butanol + 2-Methyl-1-butanol + 1-Pentanol

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Vapor–liquid equilibria (VLE) for 2-methyl-2-butanol + 2-methyl-1-butanol and 2-methyl-2-butanol + 2-methyl-1-butanol + 1-pentanol have been measured at 373.15 K. The binary VLE results have been correlated by different liquid-phase activity coefficient models. The binary interaction parameters obtained from Wilson, NRTL, and UNIQUAC models in this and a previous study are used to predict the VLE data for the ternary system.

Introduction

Vapor–liquid equilibrium (VLE) data are necessary for the design of distillation processes. The usual technique for obtaining VLE data is by direct measurements. The amount of experimental work required to make all the measurements necessary for a complete description of a multicomponent system rises very shapely as the number of components in the mixture increases. However, a useful assumption of models for the excess Gibbs energy is that only experimental binary data are needed to estimate multicomponent activity coefficients, because interactions in multicomponent systems are considered to be the sum of all possible binary interactions. The quality of ternary correlation is directly related to the quality of the binary data used to determine the model parameters.

This work is a part of a program to provide consistent VLE data to determine UNIFAC parameters for alcohols. In a previous work (*1*) we have reported VLE data for the 2-methyl-2-butanol + 1-pentanol and 2-methyl-1-butanol + 1-pentanol binary systems which were thermodynamically consistent. In this work, we report VLE measurements for 2-methyl-2-butanol + 2-methyl-1-butanol and 2-methyl-2-butanol + 2-methyl-1-butanol + 1-pentanol. Wilson, NRTL, and UNIQUAC parameters obtained for the binary systems have been used to predict the VLE data for the ternary mixture.

Experimental Section

Chemicals. All components used in this study were purchased from Aldrich Chemical Co. with the following purities, checked by gas–liquid chromatography (GLC): 1-pentanol (99.30 mass %), 2-methyl-1-butanol (99.05 mass %), and 2-methyl-2-butanol (99.88 mass %). They were used without further purification. The water content was small (< 0.1 mass %, checked by GLC). The physical properties of these components are listed in a previous work (*1*).

Apparatus and Procedure. The equilibrium vessel used in this work was an all-glass, dynamic recirculating still described by Walas (2), equipped with a Cottrell pump. The still (Labodest model) manufactured by Fischer Labor und Verfahrenstechnik (Germany) is capable of handling pressures P from 0.25 to 400 kPa and temperatures T up to 523.15 K. The Cottrell pump ensures that both liquid and vapor phases are in intimate contact and also in contact with the temperature-sensing element. The important components of this still include the Cottrell pump, a silver-plated vacuum jacket, and magnetic sampling valves. The vacuum jacket surrounds the equilibrium chamber and eliminates partial condensation of the vapor separating from the liquid at the exit of the Cottrell pump. The equilibrium temperature was measured with a digital Fisher thermometer with an accuracy of ±0.1 K and the pressure with a digital manometer with an accuracy of ±0.01 kPa. The temperature probe was calibrated against the ice and steam points of distilled water. Then the manometer was calibrated against high-purity (>99.9 mass %) hexane vapor pressures. Measurements were made at 373.15 K for all systems.

In each experiment the temperature was fixed and the heating and shaking system of the liquid mixture was connected. The still was operated until equilibrium was reached. Equilibrium conditions were assumed when constant temperature and pressure were obtained for 15 min or longer. At this time, a sample of liquid and condensate was taken for analysis. The extractions were carried out with special syringes which allowed us to take small volume samples (0.1 cm^3) in a system under partial vacuum, without disruption of operation of the still.

Analysis. Compositions of the sampled liquid and condensed vapor phases were analyzed with a Hewlett-Packard 5890 S-II gas chromatograph (GC), after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a 60-m, 0.2-mm-i.d. fused silica capillary column, SUPELCOWAX 10, with a modified polyethylene glycol as the stationary phase. The oven temperature was 373.15 K. The GC response peaks were integrated by using a Hewlett-Packard 3396 integrator. A single analysis of the vapor or liquid composition by gas chromatography is frequently imprecise. However, with repeated measurements, the standard deviation of a composition analysis was usually less than 0.001 mole fraction. At least two analyses were made of each liquid and each vapor composition.

Results and Discussion

Vapor pressures of pure components used in this study have already been measured and reported in a previous work (*1*).

Analysis of Data for the Binary Mixture. Table 1 presents the binary VLE data for 2-methyl-2-butanol + 2-methyl-1-butanol at 373.15 K. Figure 1 shows the P–x–y diagram for this system.

The liquid-phase activity coefficients of the components in a nonideal mixture are given by the equation

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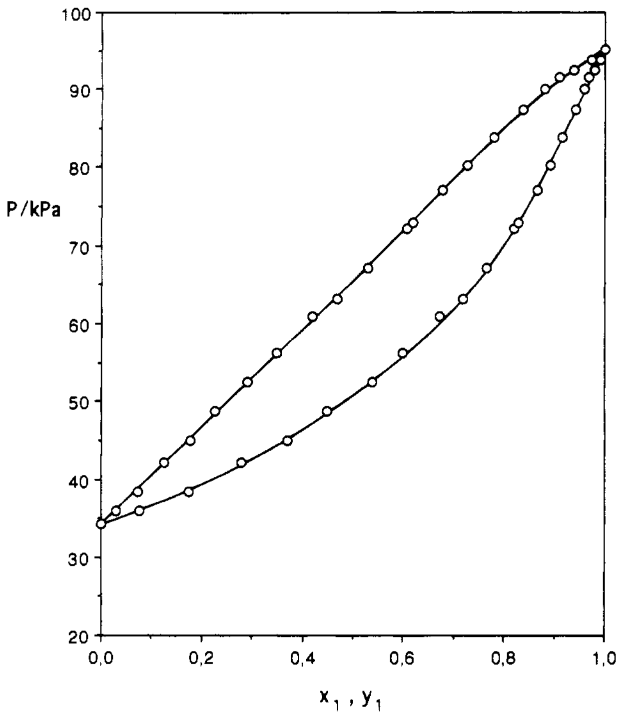

Figure 1. Vapor–liquid equilibrium data for 2-methyl-2-butanol (1) + 2-methyl-1-butanol (2) at 373.15 K.

Table 1. Vapor–Liquid Equilibrium Data for the 2-Methyl-2-butanol (1) + 2-Methyl-1-butanol (2) at 373.15 K

x_1	y_1	P/kPa	γ_1	γ_2
0.000	0.000	34.35		
0.030	0.075	35.93	0.931	0.979
0.074	0.173	38.36	0.929	0.978
0.126	0.279	42.10	0.951	0.976
0.177	0.369	45.00	0.969	0.981
0.226	0.447	48.77	0.995	0.989
0.291	0.538	52.54	1.000	0.970
0.349	0.599	56.26	0.993	0.980
0.418	0.670	60.87	1.001	0.974
0.467	0.717	63.10	0.993	0.944
0.530	0.765	67.09	0.991	0.943
0.606	0.820	72.15	0.997	0.925
0.618	0.827	72.97	0.997	0.927
0.676	0.865	77.00	1.005	0.898
0.727	0.893	80.35	1.005	0.880
0.778	0.915	83.80	1.002	0.895
0.838	0.942	87.50	0.999	0.872
0.881	0.959	90.00	0.994	0.862
0.911	0.969	91.50	0.987	0.885
0.940	0.980	92.50	0.977	0.856
0.973	0.991	93.85	0.998	0.867
1.000	1.000	95.18		

$$y_i\phi_i P = x_i\gamma_i\phi_i^{s}P_i^{\circ}\exp[v_i(P - P_i^{\circ})/RT] \qquad (1)$$

where x_i and y_i are the liquid and vapor mole fractions in equilibrium, ϕ_i is the fugacity coefficient, P is the total pressure, γ_i is the activity coefficient, ϕ_i^s is the pure component fugacity coefficient at saturation, P_i° is the pure component vapor pressure, v_i is the liquid molar volume, R is the universal gas constant, and T is the absolute temperature.

The exponential term (Poynting factor) was proved to be unity for the experimental conditions of this work. Fugacity coefficients ϕ_i and ϕ_i^s were calculated by means of the virial equation of state, and the second virial coefficients were calculated from the Pitzer and Curl equations (*3*) and the Tsonopoulos correlation correction (*4*) for polar compounds. The γ_i values calculated with eq 1 are listed in Table 1. This system showed small deviation from ideality.

Table 2. Ternary Vapor–Liquid Equilibrium Data for 2-Methyl-2-butanol (1) + 2-Methyl-butanol (2) + Pentanol (3) at 373.15 K

x_1	x_2	y_1	y_2	P/kPa	γ_1	γ_2	γ_3
0.792	0.103	0.931	0.041	80.90	1.006	0.948	0.889
0.688	0.205	0.884	0.086	74.85	1.018	0.925	0.864
0.583	0.310	0.820	0.147	68.24	1.016	0.953	0.867
0.466	0.424	0.720	0.237	60.50	0.989	0.996	0.974
0.397	0.500	0.668	0.292	56.42	1.005	0.970	0.903
0.295	0.602	0.543	0.409	50.47	0.983	1.010	0.969
0.199	0.697	0.409	0.536	45.59	0.992	1.032	0.993
0.104	0.793	0.241	0.697	40.05	0.982	1.037	0.993
0.102	0.695	0.243	0.631	38.74	0.977	1.036	0.991
0.195	0.600	0.425	0.467	44.00	1.015	1.008	0.955
0.289	0.505	0.548	0.354	48.89	0.981	1.009	0.958
0.384	0.408	0.663	0.250	54.84	1.002	0.989	0.945
0.504	0.296	0.775	0.155	62.41	1.016	0.962	0.900
0.571	0.209	0.828	0.101	66.44	1.020	0.945	0.883
0.689	0.099	0.890	0.045	73.33	1.002	0.981	0.926
0.542	0.106	0.817	0.056	62.44	0.996	0.971	0.928
0.553	0.104	0.818	0.056	63.40	0.993	1.005	0.959
0.525	0.202	0.797	0.106	62.72	1.008	0.969	0.918
0.405	0.311	0.688	0.191	55.18	0.992	0.998	0.968
0.309	0.409	0.581	0.284	48.93	0.974	1.000	0.965
0.179	0.520	0.397	0.445	41.26	0.968	1.040	0.892
0.115	0.593	0.273	0.543	38.15	0.958	1.029	0.990
0.107	0.492	0.265	0.470	36.60	0.959	1.030	0.996
0.192	0.398	0.426	0.335	40.91	0.961	1.014	0.982
0.298	0.295	0.583	0.214	47.02	0.974	1.004	0.966
0.398	0.197	0.704	0.123	53.25	0.997	0.979	0.937
0.496	0.098	0.794	0.055	59.46	1.007	0.983	0.911
0.377	0.101	0.696	0.067	50.67	0.990	0.990	0.948
0.288	0.204	0.587	0.153	45.64	0.984	1.008	0.962
0.201	0.298	0.447	0.256	40.62	0.956	1.028	0.992
0.100	0.401	0.259	0.399	35.36	0.969	1.036	0.998
0.107	0.296	0.279	0.299	34.52	0.953	1.027	1.005
0.198	0.197	0.462	0.172	39.30	0.970	1.010	0.979
0.286	0.098	0.594	0.075	44.08	0.969	0.993	0.976
0.196	0.099	0.468	0.089	38.36	0.969	1.015	0.993
0.097	0.203	0.263	0.217	32.97	0.946	1.038	1.009
0.095	0.104	0.265	0.115	31.94	0.943	1.040	1.018

The binary data were first tested for thermodynamic consistency using the point-to-point method of Van Ness et al. (*5*), modified by Fredenslund et al. (*6*). A four-parameter Legendre polynomial was used for the excess Gibbs free energy. According to this test, the data are considered consistent if the mean absolute deviation between calculated and measured mole fractions of component 1 in the vapor phase, $\delta(y)$, is less than 0.01. For 2-methyl-2-butanol + 2-methyl-1-butanol the $\delta(y)$ was 0.0082; therefore the data are thermodynamically consistent.

The activity coefficients were correlated with the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations (*7*). For fitting the binary parameters, the Rosenbrok method (*8*) was used, taking as the objective function the sum of the squares of relative deviations in pressure and vapor composition:

$$F = \sum_{i=1}^{n}\left(\frac{y_{\text{exp}} - y_{\text{calc}}}{y_{\text{exp}}}\right)_i^2 + \sum_{i=1}^{n}\left(\frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}}\right)_i^2 \qquad (2)$$

where n is the number of data points. Each model gives a good fit of the binary results.

Analysis of Data for the Ternary Mixture. Table 2 presents ternary VLE data for 2-methyl-2-butanol + 2-methyl-1-butanol + 1-pentanol at 373.15 K. The ternary results were found to be thermodynamically consistent, as tested by the McDermont–Ellis method (*9*) modified by Wisniak and Tamir (*10*). According to this test, two experimental points (a and b) are considered thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\text{max}} \qquad (3)$$

Table 3. Comparison of Ternary Experimental Data with Those Calculated Using Binary Data Parameters for Activity Coefficients

model	$\delta(y_1)^a$	$\delta(y_2)^a$	$\delta(P)$/kPa^b
Wilson	0.0076	0.0075	0.50
NRTL	0.0046	0.0025	0.65
UNIQUAC	0.0052	0.0023	0.64

[a] $\delta(y_i) = \sum|y_{i,\mathrm{exp}} - y_{i,\mathrm{calc}}|/N$ (N = no. data points). [b] $\delta(P) = \sum|P_{\mathrm{exp}} - P_{\mathrm{calc}}|/N$ (N = no. data points).

where D is the local deviation given by

$$D = \sum_{i=1}^{m} (x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \qquad (4)$$

where m is the number of components in the mixture and $D_{\max}$ is the local maximum deviation given by

$$D_{\max} = \sum_{i=1}^{m} (x_{ia} + x_{ib})\left[\frac{1}{x_{ib}} + \frac{1}{y_{ib}} + \frac{1}{x_{ia}} + \frac{1}{y_{ia}}\right]\Delta x + 2\sum_{i=1}^{m} |(\ln \gamma_{ib} - \ln \gamma_{ia})|\Delta x + \sum_{i=1}^{m} (x_{ia} + x_{ib})\frac{\Delta P}{P} \qquad (5)$$

The errors in the measurements are $\Delta x = \pm 0.001$ and $\Delta P = \pm 0.01$ kPa.

Multicomponent VLE can be predicted by means of suitable models for the activity coefficients using the binary interaction parameters obtained from the regression of binary data. To test this, we used the binary parameters obtained in this study and a previous work (*1*) to predict the bubble pressures and vapor-phase mole fractions of the ternary system. The equations used to determine the activity coefficients (Wilson, NRTL, and UNIQUAC) were taken from ref 7.

Table 3 lists the mean absolute deviation between experimental and calculated pressures and the vapor-phase mole fraction for each model. The experimental and calculated data were found to be very close to each other for the bubble pressures and vapor-phase compositions, suggesting that ternary data can really be predicted directly from the binary systems. The isobars for this system are presented in Figure 2.

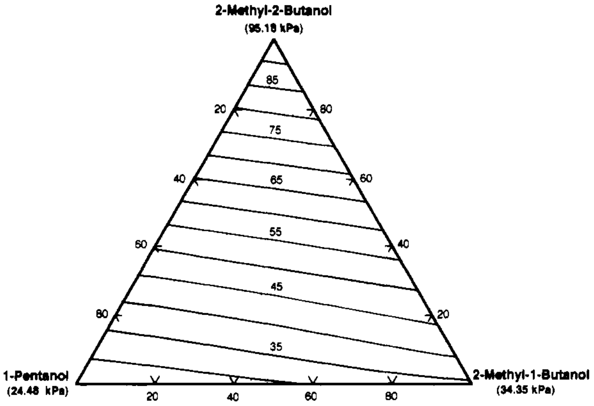

Figure 2. Isobars for the ternary system 2-methyl-2-butanol (1) + 2-methyl-1-butanol (2) + 1-pentanol (3) at 373.15 K calculated from the Wilson equation.

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