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Isothermal Vapor–Liquid Equilibria of 1-Pentanol with 2-Methyl-1-butanol, 2-Methyl-2-butanol, and 3-Methyl-2-butanol

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Vapor–liquid equilibria were measured for binary systems of 1-pentanol + 2-methyl-1-butanol, + 2-methyl-2-butanol, and + 3-methyl-2-butanol at 373.15 K. The results are thermodynamically consistent according to the point-to-point consistency test, and deviation from ideal behavior is small in all cases.

Introduction

The separation of liquid mixtures through distillation is one of the most common operations in chemical industry, and the efficient design of distillation equipment requires a quantitative knowledge of vapor–liquid equilibria (VLE).

The group contribution approach has been widely used to predict the VLE of binary and multicomponent mixtures. The UNIFAC method (*1*) has been used to predict activity coefficients in the liquid phase in the absence of experimental information, because the obtained values are good, even for systems with large deviations from ideality.

Moreover, the generation of reliable interaction parameters for the functional groups requires experimental VLE data. The main aim of this study is to provide VLE results of binary systems in which both components are alcohols, in order to improve the VLE data bank. Furthermore these results can be used to generate interaction parameters of the OH functional group in different positions (primary, secondary, and tertiary OH).

Experimental Section

Chemicals. All components used in this study were purchased from Aldrich Chemie Co. The purity of all chemicals was checked by gas chromatography (GC): 1-pentanol (99.30 mass %), 2-methyl-1-butanol (99.05 mass %), 2-methyl-2-butanol (99.88 mass %), and 3-methyl-2-butanol (99.18 mass %). They were used without further purification. The water content was small in all chemicals (<0.1 mass %, checked by GC). The experimental densities, refractive indexes, and vapor pressures given in Table 1 are compared with literature values (*2, 3*). The concordance between experimental data and those found in the literature is good.

Apparatus and Procedure. The equilibrium vessel used in this work was an all-glass, dynamic recirculating still described by Walas (*4*), 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 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. The manometer was calibrated against high-purity (>99.9 mass %) hexane vapor pressures. VLE measurements were obtained at 373.15 K for all systems.

Table 1. Densities d, Refractive Indexes n, and Vapor Pressure P° of the Chemicals

	$d/(\mathrm{g\ cm^{-3}})$		n(D, 293.15 K)		P°(373.15 K)/kPa	
component	exptl	lit. (2)	exptl	lit. (2)	exptl	lit.[a]
1-pentanol	0.814 68[b]	0.8144[b]	1.4099	1.4101	24.48	25.13
2-methyl-1-butanol	0.815 09[c]	0.8152[c]	1.4100	1.4092	34.35	34.49
2-methyl-2-butanol	0.805 38[c]	0.8059[c]	1.4046	1.4052	95.18	94.54
3-methyl-2-butanol	0.817 87[b]	0.8180[b]	1.4090	1.4089	68.93	na

[a] Calculated using the Antoine coefficients from ref 3. [b] Measured at 293.15 K. [c] Measured at 298.15 K.

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, samples of liquid and condensate were taken for analysis. The extractions were carried out with special syringes which allowed us to take small volume samples in a system under partial vacuum.

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. 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

The vapor pressures of the pure components P_i° were measured with the same recirculating still. These values were fitted to the Antoine equation. The parameters of this equation, together with the mean absolute deviation between experimental and calculated vapor pressures, $\delta(P_i^\circ)$, are given in Table 2.

The VLE measurements were made at 373.15 K and are presented in Tables 3–5. The P–x–y diagram for the three systems is shown in Figure 1.

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Table 2. Vapor Pressure $P_i°$, Antoine Coefficients A, B, and C, and Mean Average Deviations $\delta(P_i°)$, of Pure Components

component	temp range/K	Antoine coefficients[a] A	B	C	$\delta(P_i°)$[b]
1-pentanol	335–410	15.8163	3708.62	−79.441	0.15
2-methyl-1-butanol	330–405	14.8958	3107.20	−99.883	0.11
2-methyl-2-butanol	308–375	14.5382	2739.80	−98.888	0.22
3-methyl-2-butanol	325–385	14.4293	2754.37	−103.139	0.14

[a] $\ln(P_i°/\mathrm{kPa}) = A - B((T/\mathrm{K}) + C)$. [b] $\delta(P_i°) = \sum|P°_{\mathrm{exptl}} - P°_{\mathrm{calc.}}|/N$ (N = no. data points).

Table 3. Vapor–Liquid Equilibrium Data: Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Pressure P, and Activity Coefficients γ_i for 2-Methyl-1-butanol (1) + 1-Pentanol (2) at 373.15 K

x_1	y_1	P/kPa	γ_1	γ_2
0.000	0.000	24.48		
0.039	0.055	24.82	1.0057	0.9844
0.089	0.124	25.32	1.0134	0.9818
0.137	0.189	25.82	1.0230	0.9782
0.194	0.255	26.36	0.9948	0.9820
0.247	0.322	26.85	1.0047	0.9741
0.318	0.405	27.52	1.0057	0.9671
0.381	0.470	28.12	0.9951	0.9695
0.447	0.539	28.81	0.9962	0.9667
0.525	0.616	29.57	0.9945	0.9618
0.602	0.685	30.35	0.9895	0.9661
0.668	0.744	31.06	0.9909	0.9629
0.732	0.797	31.72	0.9889	0.9656
0.786	0.840	32.23	0.9860	0.9682
0.846	0.889	32.85	0.9878	0.9510
0.902	0.930	33.47	0.9872	0.9599
0.956	0.968	33.95	0.9832	0.9911
1.000	1.000	34.35		

Table 4. Vapor–Liquid Equilibrium Data: Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Pressure P, and Activity Coefficients γ_i for 2-Methyl-2-butanol (1) + 1-Pentanol (2) at 373.15 K

x_1	y_1	P/kPa	γ_1	γ_2
0.000	0.000	24.48		
0.035	0.114	26.44	0.8956	0.9783
0.079	0.236	29.28	0.9086	0.9775
0.129	0.353	32.75	0.9297	0.9773
0.183	0.455	36.60	0.9426	0.9789
0.238	0.552	40.31	0.9670	0.9484
0.313	0.652	45.69	0.9823	0.9237
0.375	0.708	50.11	0.9748	0.9322
0.434	0.766	54.61	0.9913	0.8970
0.510	0.821	60.10	0.9930	0.8698
0.594	0.870	65.78	0.9866	0.8321
0.655	0.894	70.55	0.9843	0.8542
0.724	0.924	75.86	0.9876	0.8210
0.784	0.941	80.30	0.9814	0.8601
0.841	0.959	84.35	0.9779	0.8512
0.887	0.972	87.82	0.9771	0.8501
0.912	0.978	89.50	0.9738	0.8733
0.957	0.990	93.26	0.9774	0.8449
0.979	0.995	94.43	0.9719	0.8754
1.000	1.000	95.18		

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

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

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.

Table 5. Vapor–Liquid Equilibrium Data: Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Pressure P, and Activity Coefficients γ_i for 3-Methyl-2-butanol (1) + 1-Pentanol (2) at 373.15 K

x_1	y_1	P/kPa	γ_1	γ_2
0.000	0.000	24.48		
0.028	0.074	25.72	0.9735	0.9881
0.078	0.181	27.94	0.9315	0.9992
0.128	0.282	30.24	0.9526	1.0016
0.188	0.402	32.56	0.9957	0.9634
0.236	0.486	35.76	1.0547	0.9642
0.296	0.546	37.78	0.9957	0.9763
0.388	0.647	42.29	1.0059	0.9756
0.419	0.669	42.86	0.9745	0.9776
0.502	0.746	46.99	0.9932	0.9577
0.561	0.785	49.42	0.9827	0.9662
0.624	0.833	52.32	0.9921	0.9248
0.696	0.870	55.67	0.9880	0.9415
0.735	0.896	57.06	0.9860	0.8887
0.786	0.920	59.74	0.9901	0.8851
0.843	0.942	61.60	0.9741	0.9012
0.899	0.964	64.82	0.9822	0.9133
0.954	0.984	67.21	0.9786	0.9230
1.000	1.000	68.93		

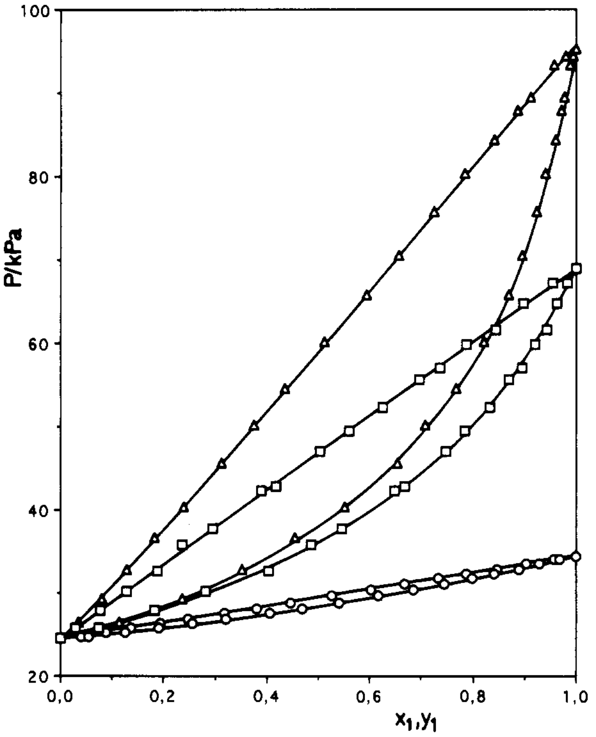

Figure 1. Vapor–liquid equilibrium of the systems 1-pentanol (2) + 2-methyl-1-butanol (1) (○), + 2-methyl-2-butanol (1) (△), and + 3-methyl-2-butanol (1) (□) at 373.15 K as a function of the mole fraction of component 1.

The exponential term (Poynting factor) was taken as 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 (*5*) and the Tsonopoulos correlation correction (*6*) for polar compounds. The γ_i values calculated with eq 1 are listed in Tables 3–5.

For the system 2-methyl-2-butanol + 1-pentanol a slight negative deviation from ideality is observed. For the other two systems the activity coefficients mantain a rare variation quite close to unity. In these conditions, small experimental errors can give rise to the small deviations observed.

The results were tested for thermodynamic consistency using the point-to-point method of Van Ness et al. (*7*), modified by Fredenslund et al. (*1*). A four-parameter Legendre polynomial was used for the excess Gibbs free energy. According to Fredenslund et al., the P–T–x–y data

Table 6. Results of the Thermodynamic Consistency Test for the Three Systems at 373.15 K

system	$\delta(y)^a$ (T = 373.15 K)
2-methyl-1-butanol + 1-pentanol	0.0046
2-methyl-2-butanol + 1-pentanol	0.0064
3-methyl-2-butanol + 1-pentanol	0.0060

[a] $\delta(y) = \sum|y_{\mathrm{exptl}} - y_{\mathrm{calc}}|/N$ (N = no. data points).

are 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. The results of this test for the binary systems in consideration given in Table 6 indicate that the experimental data for the three systems are thermodynamically consistent.

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