J. Chem. Eng. Data **2001,** *46,* 1231−1234 **1231**

Vapor−Liquid Equilibria for the Binary Mixtures Dehydrolinalool + 1-Propanol and Dehydrolinalool + 1-Butanol

Longhua Zhu, Haoran Li, Congmin Wang, and Shijun Han*

Department of Chemistry, Zhejiang University, Hangzhou, 310027, People's Republic of China

Vapor−liquid (VLE) equilibria for the binary mixtures dehydrolinalool + 1-propanol and dehydrolinalool + 1-butanol were measured using an inclined ebulliometer. The results were correlated by the modified UNIQUAC equation with satisfactory results. Experimental vapor pressures of dehydrolinalool are also included.

Introduction

Dehydrolinalool (CA Registry No. 29171-20-8), 3,7-dimethyl-6-octen-l-yn-3-ol ($C_{10}H_{16}O$), one of the intermediates of vitamin synthesis, is a transparent liquid with a strong odor. The open literature includes a shortage of physical and thermodynamic properties of this material.[1] During the process of vitamin production, such information is indispensable for the separation of dehydrolinalool and other alcohols, but vapor−liquid equilibria (VLE) for these binary mixtures have not been measured. To further understand the nature of dehydrolinalool and to design separation processes, VLE data are indispensable.

In this paper, VLE data for mixtures of dehydrolinalool + 1-propanol and dehydrolinalool + 1-butanol are reported. VLE data are correlated using the UNIQUAC equation with temperature-dependent binary parameters. The vapor pressures of dehydrolinalool are also reported.

Experimental Section

Dehydrolinalool was maintained under special conditions before its use. It was distilled in a 150-cm-high column under reduced pressure. 1-Propanol and 1-butanol (analytical reagent grade, Shanghai Chemical Co.) were refluxed over freshly activated CaO for at least 2 h and then fractionally distilled. The pure materials were dried with 0.3- and 0.4-nm molecular sieves. The purities of these materials were determined by gas chromatography to be dehydrolinalool, 99.80 mass %; 1-propanol, 99.90 mass %; and 1-butanol, 99.94 mass %. The physical properties of these materials are listed in Table 1, along with literature values.

VLE measurements were carried out using an inclined ebulliometer with a pump-like stirrer as described previously.[3] The temperature was measured with a standard platinum resistance thermometer connected to a digital multimeter (Keithley 195A) with a finial accuracy of 0.01 K. The pressure was indirectly measured by the boiling temperature of pure water in a separate ebulliometer.

Table 1. Physical Properties of the Materials

	ρ (293.15 K) (g cm^{-3})		n_D (293.15 K)		T_b (101.325 kPa) (K)	
material	expt.	lit.	expt.	lit.	expt.	lit.
dehydrolinalool	0.87854	0.87860[a]	1.4650	1.4652[a]	471.47	469.61[a]
1-propanol	0.80370	0.80350[b]	1.3855	1.3850[b]	370.30	370.35[b]
1-butanol	0.80952	0.80980[b]	1.3991	1.3993[b]	390.40	390.15[b]

[a] Baglay et al.[1] [b] CRC Handbook of Chemistry and Physics, 1999−2000.[2]

Table 2. Experimental Vapor Pressure P_i^S and Antoine Constants of Dehydrolinalool, Equation 2

T (K)	P_i^S (kPa)	T (K)	P_i^S (kPa)	T (K)	P_i^S (kPa)
408.46	13.51	437.83	37.84	457.60	68.95
416.57	18.26	441.95	42.99	461.49	76.83
422.62	22.66	445.57	48.04	464.89	84.91
427.34	26.89	449.10	53.71	467.88	91.76
432.48	31.76	453.78	61.42	470.86	99.99

	A	B	C
dehydrolinalool	6.5167	1750.30	−83.47

Results and Discussion

At vapor−liquid equilibrium

$$Py_i\phi_i = P_i^S\phi_i^S x_i\gamma_i \exp[V_i^L(P_i - P_i^S)/RT] \tag{1}$$

where P is the total pressure and x_i and y_i are the liquid- and vapor-phase mole fractions of component i, respectively. ϕ_i is the vapor-phase fugacity coefficient of component i, and γ_i is the liquid-phase activity coefficient. V_i^L is the pure-liquid molar volume, which was calculated from the modified Rackett equation.[4] P_i^S is the saturated vapor pressure, calculated from the Antoine equation

$$\log(P_i^S/\mathrm{kPa}) = A - B/(C + T/\mathrm{K}) \tag{2}$$

For 1-propanol and 1-butanol, the constants given in DECHEMA Chemistry Data Series[5] were used. The experimental vapor pressure data for pure dehydrolinalool are listed in Table 2. The constants in eq 2 were fitted by a nonlinear optimization method to minimize the mean

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* To whom correspondence should be addressed. E-mail: lihr@cm163.net.

10.1021/je010041q CCC: $20.00

Table 3. Physical Properties of the Pure Materials

material	P_c (kPa)	T_c (K)	V_c (cm^3 mol^{-1})	RD (Å)	DM (D)	R	Q
dehydrolinalool	2476.4[a]	663.95[a]	554.4[a]	4.353[c]	1.70[d]	6.75[e]	5.99[e]
1-propanol[b]	5238.5	536.71	218.2	2.736	1.68	2.78	2.51
1-butanol[b]	4471.5	562.93	274.6	3.225	1.66	3.45	3.05

[a] Data from Reid et al.[8] [b] Data from Prausnitz et al.[7] [c] Data from Fredenslund et al.[9] [d] Data from Smyth.[10] [e] Data from Walas.[11]

Table 4. Experimental Data for xDehydrolinalool (1) + (1 − x)1-Propanol (2)

T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
$x = 0.0497$		$x = 0.1010$		$x = 0.2005$		$x = 0.2960$	
325.79	13.25	326.28	12.78	328.20	12.78	330.49	12.59
332.61	18.74	333.53	18.62	340.55	23.62	338.09	18.29
337.90	24.25	338.22	23.62	345.33	29.46	343.86	23.86
342.40	29.86	343.12	29.46	348.81	34.50	347.97	28.92
345.44	35.02	346.65	34.50	354.95	44.95	351.97	34.64
348.49	40.19	352.36	44.95	362.27	61.16	355.54	40.39
351.36	45.42	356.54	53.60	365.33	68.92	359.67	47.67
358.47	61.54	359.69	61.16	372.04	89.90	363.58	55.67
363.81	76.56	362.53	68.92	374.87	99.81	369.96	71.40
$x = 0.5052$		$x = 0.7011$		$x = 0.7987$		$x = 0.9010$	
337.73	12.59	348.06	12.59	353.72	10.81	367.34	10.47
345.26	18.29	363.65	23.86	369.73	20.93	386.29	21.37
368.08	47.67	368.35	28.92	375.95	26.80	397.97	32.13
372.31	55.67	372.95	34.64	380.55	31.67	402.75	38.05
376.01	64.20	377.02	40.39	385.41	37.63	406.13	43.04
379.19	71.40	386.04	55.67	394.63	50.90	412.71	51.30
382.14	78.97	393.27	71.40	398.53	59.29	416.02	58.72
385.98	89.87	400.47	89.87	402.80	67.09	425.08	74.68
389.06	99.55	403.87	99.55	406.45	74.53	435.41	100.40

Table 5. Experimental Data for xDehydrolinalool (1) + (1 − x)1-Butanol (2)

T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)	T (K)	P (kPa)
$x = 0.0502$		$x = 0.0990$		$x = 0.3017$		$x = 0.4943$	
340.38	11.26	341.29	11.26	370.11	32.71	355.96	13.46
348.31	16.69	349.50	16.69	373.79	38.05	363.74	18.78
354.01	21.78	355.33	21.78	376.94	43.24	370.45	25.15
359.15	27.50	360.54	27.50	379.83	48.34	374.38	29.40
363.12	32.71	364.47	32.71	382.58	53.62	378.93	34.91
366.64	38.05	368.04	38.05	386.25	61.69	382.86	40.75
369.78	43.24	370.76	43.23	389.64	69.33	390.75	54.34
372.00	48.34	373.34	48.34	392.93	77.81	398.09	69.81
374.61	53.62	376.04	53.62	395.37	84.75	401.22	77.66
378.15	61.69	379.60	61.69	400.49	100.77	406.63	92.52
$x = 0.0990$		$x = 0.0990$		$x = 0.0990$		$x = 0.0990$	
366.57	13.46	388.42	22.66	387.08	13.51	388.60	10.97
374.79	18.78	393.15	26.89	395.09	18.26	402.64	18.19
382.24	25.15	397.55	31.77	400.94	22.66	407.60	22.03
386.86	29.40	402.77	37.84	406.01	26.89	419.72	32.92
404.78	54.34	406.65	42.99	416.46	37.84	424.20	37.90
408.79	62.31	410.05	48.04	420.47	42.99	427.72	43.06
412.44	69.81	413.4	53.71	427.10	53.71	733.17	50.76
415.94	77.66	417.73	61.42	432.03	61.42	438.60	59.24
418.78	84.88	421.60	68.95	436.26	68.95	442.59	67.33
424.87	100.62	434.90	99.99	440.04	76.83	456.74	99.45

Table 6. Correlation Results for Binary Systems and Root-Mean-Square Deviations for $\delta P/P$ and δT

system	a_{12} (K)	a_{21} (K)	$10^2\delta P/P$	δT (K)
dehydrolinalool (1) + 1-propanol (2)	$385.49 - 17.82T_k + 9.03T_k^2$	$-130.63 - 63.81T_k - 5.52T_k^2$	0.862	0.23
dehydrolinalool (1) + 1-butanol (2)	$173.52 + 229.10\ T_k - 6.73\ T_k^2$	$162.20 - 329.970\ T_k - 19.98\ T_k^2$	0.939	0.26

relative deviation in P_i^S. The mean relative deviation was 0.27%.

ϕ_i and ϕ_i^S were calculated from the virial equation

$$\ln\phi_i = (2\sum_j y_j B_{ij} - \sum_i \sum_j y_i y_j B_{ij})P/RT \qquad (3)$$

where the second virial coefficients of pure materials B_{ii} and mixtures B_{ij} were calculated according to the method of Hayden and O'Connell.[6]

The physical properties of the pure materials are given in Table 3. For 1-propanol and 1-butanol, the physical properties were obtained from Prausnitz et al.[7] For dehydrolinalool, the critical properties P_c, T_c, and V_c were obtained using the Lydersen group contribution method from Reid et al.[8] The mean radius of gyration, RD, was calculated using the method of Fredenslund et al.[9] The dipole moment, DM, was estimated according to the method provided by Smyth.[10] The UNIQUAC volume parameter R and area parameter Q were calculated from Walas.[11]

The experimental temperature measurement magnitude is about 100 K. To correlate the experimental VLE data more satisfactorily, the modified UNIQUAC equation[12] with temperature-dependent binary parameters α_{ij} was

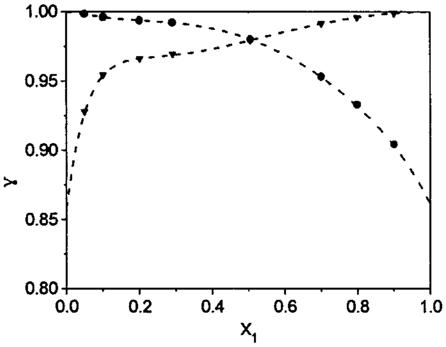

Figure 1. Activity coefficients for dehydrolinalool (1) + 1-propanol (2) at 50.00 kPa: ▼, γ_1; ●, γ_2 experimental data; - - -, UNIQUAC correlation.

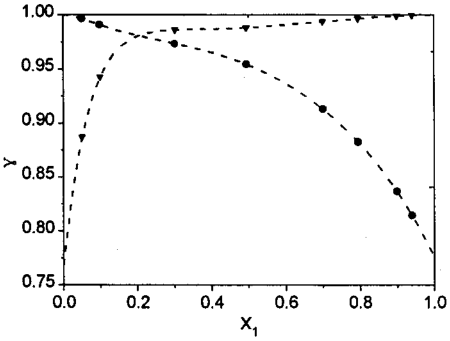

Figure 2. Activity coefficients for dehydrolinalool (1) + 1-butanol (2) at 50.00 kPa: ▼, γ_1; ●, γ_2 experimental data; - - -, UNIQUAC correlation.

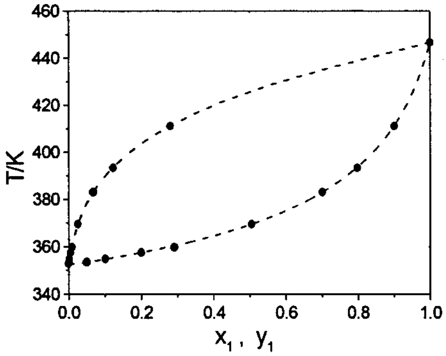

Figure 3. $T-x_1-y_1$ diagram for dehydrolinalool (1) + 1-propanol (2) at 50.00 kPa: ●, experimental data; - - -, UNIQUAC correlation.

Table 7. Infinite Dilution Activity Coefficients for Dehydrolinalool + 1-Propanol and Dehydrolinalool + 1-Butanol at 50.00 kPa

system	T (K)	γ_1^{∞}
dehydrolinalool (1) + 1-propanol (2)	338.15	0.8587
	348.15	0.8583
	353.15	0.8575
	363.15	0.8547
dehydrolinalool (1) + 1-butanol (2)	353.15	0.9435
	363.15	0.8420
	368.15	0.7968
	373.15	0.7553

used to calculate the liquid-phase activity coefficient γ_i. The temperature dependence of α_{ij} is as follows

$$\alpha_{ij} = \alpha_{ij}^{(0)} + \alpha_{ij}^{(1)}T_k + \alpha_{ij}^{(2)}T_k^{2} \qquad (4)$$

with $T_k = T/T_0$, where T_0 is an arbitrarily chosen reference temperature, in this case 315.00 K.

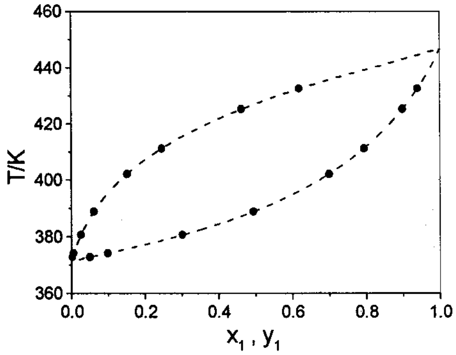

Figure 4. $T-x_1-y_1$ diagram for dehydrolinalool (1) + 1-butanol (2) at 50.00 kPa: ●, experimental data; - - -, UNIQUAC correlation.

The optimum binary parameters were obtained by minimizing the objective function J, using a modified Powell optimization technique.[13]The objective function is defined as

$$J = \sum_j [(P - P_{\mathrm{exp}})/P_{\mathrm{exp}}]_j^{2} \qquad (5)$$

The measured binary VLE data are listed in Tables 4 and 5. The optimal parameters and the root-mean-square deviations (RMSDs) between the experimental and calculated values of the measured variables are collected in Table 6. The results show that the RMSDs in pressure and temperature for the binary systems are less than 1.0% and 0.3 K, respectively.

Figures 1 and 2 show the activity coefficients for the systems dehydrolinalool + 1-propanol and dehydrolinalool + 1-butanol, respectively, at 50.00 kPa, where the experimental data are calculated from the isopletic VLE data. The results show only minor deviations from ideal solution behavior. This is attributed to dehydrolinalool being a kind of alcohol. Infinite dilution activity coefficients are listed in Table 7.

Figures 3 and 4 show isobaric vapor−liquid equilibria for the two systems at 50.00 kPa, where the experimental data are calculated from the isopletic VLE data. The systems show negative deviations from ideality, as can be seen from the activity coefficients at infinite dilution.

Acknowledgment

This work was financed by the National Natural Science Foundation of China (No. 29976035).

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Received for review February 12, 2001. Accepted May 30, 2001.

JE010041Q