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Isobaric Vapor−Liquid Equilibria for Binary Systems Composed of Octane, Decane, and Dodecane at 20 kPa

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Vapor−liquid equilibria were measured for binary systems of octane + decane, decane + dodecane, and octane + dodecane at 20.00 kPa using a recirculating still. The results are thermodynamically consistent according to the point-to-point consistency test, and deviation from ideal behavior is small for all systems.

Introduction

The most common operation in the chemical industry is the separation of liquid mixtures through distillation. Efficient design of distillation equipment requires quantitative knowledge of vapor−liquid equilibria (VLE) in binary or multicomponent mixtures. VLE data for *n*-alkane mixtures are of interest to industry. These aliphatic hydrocarbons constitute basic species in the composition of crude oil as well as in many fractions obtained in the oil-refining process.

No literature data have been found for octane + decane. Dunyushkin et al. (1978) studied a multicomponent mixture of *n*-alkanes including octane and dodecane. Pak and Kay (1972) determined critical properties of binary hydrocarbon systems including decane and dodecane. On the other hand, there are many studies on the VLE of binary mixtures of *n*-alkanes different from those studied here (Gmehling et al. 1980; Wichterle et al., 1993). In this work, the results have been treated thermodynamically considering the nonideality of both phases and verifying their thermodynamic consistency.

Experimental Section

Chemicals and Physical Properties. All components used in this study were purchased from Aldrich Chemie Co. The purities of all chemicals, checked by gas chromatography (GC), were for octane 99.8 mass %, for decane 99.5 mass %, and for dodecane 99.7 mass %. They were used without further purification. The physical properties of the compounds are listed in Table 1 along with literature values. The density (ρ) was measured in a digital precision densimeter, Anton Paar DMA 55, and the refractive index (n_D) in an Abbe refractometer, Atago 3T. The accuracies in density and refractive index measurements are ±0.000 01 $g \cdot cm^{-3}$ and ±0.0002, respectively. The boiling points of the compounds were determined using the recirculating still apparatus described below.

Apparatus and Procedure. The apparatus and procedure used in this work were described in detail in a previous paper (Dejoz et al., 1995).

Analysis. Compositions of the sampled liquid and condensed vapor phases were analyzed by using a Varian 3400 gas chromatograph, after calibration with gravimetrically prepared standard solutions. A flame ionization detector (FID) was used together with a 100 m, 0.25 mm i.d. fused silica capillary column, PETROCOL DH from Supelco. Chromatographic analyses were carried out at

Table 1. Densities ρ, Refractive Indexes n_D, and Boiling Points T_b of the Compounds

	ρ(293.15 K)/(g cm^{-3})		n_D(293.15 K)		T_b(20 kPa)/K	
compound	exptl	lit.[a]	exptl	lit.[a]	exptl	lit.[a]
octane	0.702 56	0.702 56	1.3978	1.397 50	349.05	349.081
decane	0.729 99	0.730 12	1.4121	1.411 89	392.95	392.909
dodecane	0.749 41	0.748 75	1.4222	1.421 60	431.25	431.284

[a] TRC (1995).

Table 2. Vapor Pressure P_i° Data as a Function of Temperature

T/K	P_i°/kPa	T/K	P_i°/kPa	T/K	P_i°/kPa
		Octane			
291.25	1.25	334.55	11.13	378.15	54.98
293.85	1.45	337.15	12.41	381.95	61.88
297.75	1.82	339.85	13.89	386.15	70.21
300.55	2.13	341.45	14.82	388.25	74.89
302.75	2.41	344.95	17.05	390.65	80.42
304.35	2.63	348.05	19.24	392.85	85.62
306.95	3.02	350.75	21.33	396.55	95.15
309.95	3.52	353.85	23.90	400.25	105.42
315.55	4.67	358.45	28.33	402.55	112.40
321.75	6.29	363.65	34.03	404.65	118.85
324.55	7.15	369.25	41.18	405.45	121.40
328.85	8.69	373.65	47.68	407.95	129.72
332.05	10.00	375.35	50.30	409.05	133.52
		Decane			
314.75	0.52	381.45	13.18	424.35	54.38
318.35	0.65	383.55	14.25	426.55	57.92
322.65	0.84	386.45	15.87	429.65	63.22
328.35	1.17	390.25	18.20	432.95	69.33
333.25	1.52	394.95	21.47	435.45	74.19
342.25	2.41	399.75	25.28	438.65	80.89
348.95	3.33	402.55	27.75	441.55	87.35
357.35	4.90	406.55	31.60	447.75	102.46
366.25	7.20	410.35	35.66	452.05	114.16
371.05	8.76	415.05	41.25	455.85	125.37
373.85	9.82	417.25	44.09	458.45	133.47
376.65	10.97	419.85	47.64		
379.05	12.02	422.45	51.42		
		Dodecane			
344.35	0.44	408.35	8.96	470.75	63.48
348.75	0.57	416.15	11.93	473.15	67.57
354.75	0.80	422.65	14.98	478.05	76.60
359.85	1.04	427.95	17.93	480.25	80.95
364.25	1.31	433.95	21.81	484.05	88.92
371.35	1.86	439.25	25.80	486.55	94.50
375.15	2.23	444.15	29.99	488.75	99.67
379.95	2.78	448.85	34.53	491.25	105.77
384.35	3.38	453.95	40.06	495.05	115.60
390.65	4.43	456.45	42.99	497.35	121.84
396.05	5.54	459.15	46.39	499.25	127.21
399.55	6.38	462.95	51.53	501.55	134.02
403.75	7.52	466.35	56.51		

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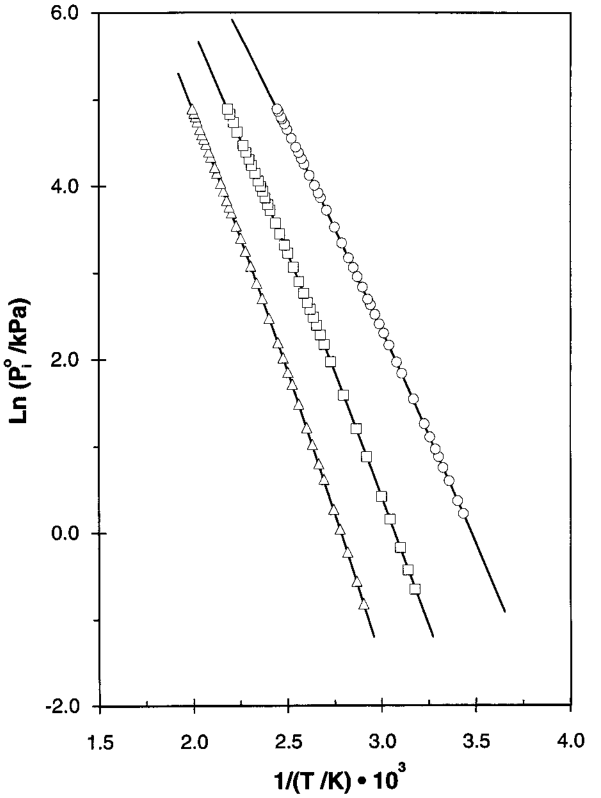

Figure 1. Vapor pressures P_i° of the pure components as a function of temperature: experimental data obtained in this work for (○) octane, (□) decane, and (△) dodecane and obtained from the literature (—) (TRC, 1995).

Table 3. Vapor Pressure P_i°, Antoine Coefficients *A*, *B*, and *C*, and Mean Absolute Deviations $\delta(P_i^\circ)$ of the Pure Components

		Antoine coefficients			$\delta(P_i^\circ)$/
component	*T*/K	*A*	*B*	*C*	kPa
octane	291.25−409.05	13.9183	3114.43	−63.925	0.0064
decane	314.75−458.45	13.9735	3441.40	−79.434	0.0107
dodecane	344.35−501.55	14.1090	3781.84	−90.975	0.0082

200 °C. The GC response peaks were integrated by using a Varian 4400 integrator. A single analysis of a vapor or liquid sample 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 sample.

Results and Discussion

The vapor pressures P_i° of the three pure components octane, decane, and dodecane are presented in Table 2 and Figure 1. This figure shows that these P_i° values are in close agreement with those reported in the literature (TRC, 1995). Table 3 gives parameters of the Antoine equation

$$\ln(P_i^\circ/\mathrm{kPa}) = A_i - \frac{B_i}{(T/\mathrm{K}) + C_i} \tag{1}$$

together with the temperature range of application and the mean absolute deviations $\delta(P_i^\circ)$ between experimental and calculated vapor pressures from the equation

$$\delta(P_i^\circ/\mathrm{kPa}) = \sum |P^\circ_{\mathrm{exptl}} - P^\circ_{\mathrm{calcd}}|/N \tag{2}$$

where N is the number of data points.

Table 4. Vapor−Liquid Equilibrium Data, Liquid-Phase Mole Fraction x_1, Vapor-Phase Mole Fraction y_1, Temperature *T*, and Activity Coefficients γ_i at 20 kPa

x_1	y_1	*T*/K	γ_1	γ_2	x_1	y_1	*T*/K	γ_1	γ_2
Octane (1) + Decane (2)									
0.000	0.000	392.95			0.439	0.803	366.65	0.967	0.945
0.008	0.032	392.25	1.022	0.991	0.495	0.845	364.05	0.987	0.919
0.016	0.065	391.75	1.012	0.982	0.557	0.874	361.85	0.978	0.938
0.023	0.097	391.05	1.046	0.979	0.608	0.895	359.75	0.988	0.967
0.036	0.141	390.05	1.008	0.978	0.675	0.924	357.65	0.992	0.919
0.053	0.194	388.65	0.978	0.981	0.728	0.940	356.05	0.989	0.938
0.074	0.259	387.25	0.969	0.970	0.784	0.956	354.45	0.992	0.922
0.099	0.327	385.55	0.962	0.963	0.832	0.967	353.05	0.994	0.953
0.125	0.383	383.85	0.940	0.968	0.919	0.985	350.65	1.003	0.986
0.151	0.443	381.65	0.957	0.977	0.942	0.989	350.15	1.001	1.018
0.200	0.540	378.95	0.960	0.949	0.960	0.994	349.65	1.005	0.916
0.241	0.604	376.15	0.973	0.958	0.979	0.996	349.25	1.004	1.004
0.284	0.669	373.65	0.989	0.938	0.989	0.998	349.15	0.999	0.989
0.333	0.713	371.35	0.968	0.958	1.000	1.000	349.05		
0.388	0.771	368.35	0.992	0.940					
Decane (1) + Dodecane (2)									
0.000	0.000	431.25			0.436	0.750	408.75	1.010	0.962
0.010	0.031	430.55	1.005	0.993	0.503	0.806	406.45	1.014	0.920
0.016	0.056	430.05	1.063	0.990	0.570	0.845	404.25	1.007	0.924
0.026	0.082	429.55	1.006	0.988	0.631	0.880	402.15	1.015	0.902
0.037	0.121	428.85	1.055	0.980	0.698	0.908	400.45	1.000	0.905
0.052	0.152	427.95	0.969	0.989	0.749	0.926	398.85	1.003	0.931
0.069	0.202	426.85	0.997	0.983	0.801	0.945	397.35	1.006	0.931
0.093	0.256	425.55	0.977	0.983	0.859	0.961	396.05	0.997	0.977
0.121	0.311	423.95	0.962	0.989	0.898	0.975	395.05	1.001	0.910
0.150	0.380	422.05	0.997	0.983	0.938	0.985	394.25	0.995	0.902
0.188	0.442	420.05	0.982	0.991	0.964	0.991	393.65	0.995	0.947
0.235	0.519	417.75	0.987	0.983	0.981	0.996	393.25	0.995	0.923
0.284	0.587	415.55	0.987	0.974	0.992	0.998	393.05	0.994	1.005
0.338	0.658	413.15	0.997	0.954	1.000	1.000	392.95		
0.382	0.701	410.95	1.007	0.967					
Octane (1) + Dodecane (2)									
0.000	0.000	431.25			0.451	0.948	371.15	0.958	1.008
0.005	0.056	429.85	0.950	0.985	0.514	0.959	367.25	0.968	1.077
0.011	0.103	427.95	0.933	1.002	0.577	0.970	363.85	0.979	1.071
0.023	0.203	425.25	0.911	0.986	0.635	0.979	360.55	1.006	1.028
0.036	0.302	422.05	0.915	0.976	0.705	0.985	357.95	1.000	1.038
0.050	0.381	418.35	0.907	0.998	0.765	0.989	355.85	0.998	1.093
0.068	0.486	414.25	0.948	0.978	0.811	0.993	353.95	1.013	0.997
0.097	0.587	409.15	0.912	0.977	0.856	0.995	352.65	1.010	0.982
0.131	0.682	403.45	0.913	0.970	0.899	0.997	351.45	1.007	0.888
0.179	0.777	396.75	0.911	0.938	0.930	0.998	350.65	1.004	0.978
0.231	0.839	390.55	0.909	0.930	0.955	0.999	350.05	1.001	1.048
0.296	0.892	384.05	0.915	0.902	0.975	0.999	349.65	0.996	1.023
0.348	0.918	379.55	0.921	0.902	0.988	0.999	349.35	0.994	1.091
0.395	0.937	375.35	0.944	0.903	1.000	1.000	349.05		

In order to fit the Antoine constants, a nonlinear optimization method was used to minimize the mean relative deviations in P_i°:

$$\lambda(P_i^\circ/\mathrm{kPa}) = \sum \left|\frac{P^\circ_{\mathrm{exptl}} - P^\circ_{\mathrm{calcd}}}{P^\circ_{\mathrm{exptl}}}\right|/N \tag{3}$$

The VLE measurements were made at 20 kPa and are presented in Table 4. The *T*−*x*−*y* diagrams for the three systems are shown in Figures 2−4.

The liquid-phase activity coefficients of the components were calculated by the equation

$$y_i\phi_i P = x_i\gamma_i\phi_i^{\mathrm{s}}P_i^\circ \exp[v_i(P - P_i^\circ)/RT] \tag{4}$$

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.

Fugacity coefficients ϕ_i and ϕ_i^{s} were calculated by means of the virial equation of state. The liquid molar volumes

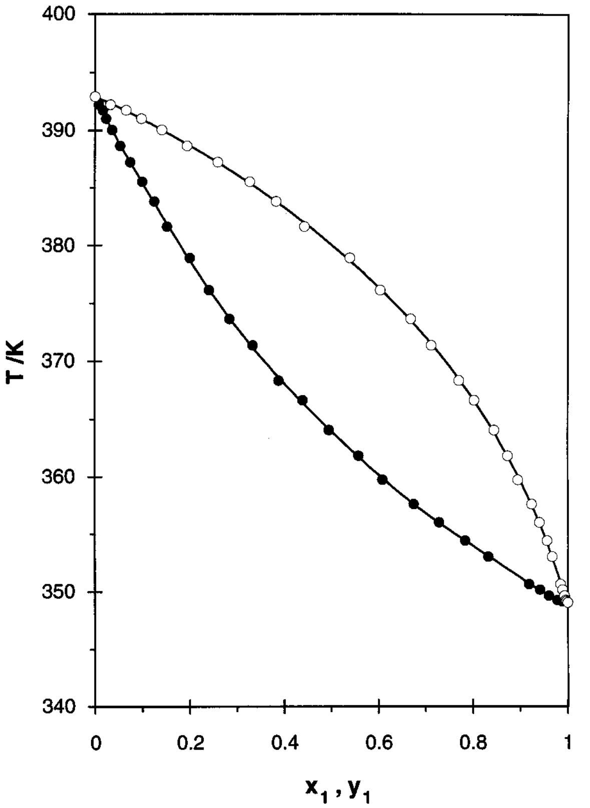

Figure 2. Vapor–liquid equilibrium of the system octane (1) + decane (2) at 20.00 kPa as a function of the mole fraction of component 1: experimental points of the liquid phase (●) and the vapor phase (○), splined curves (—).

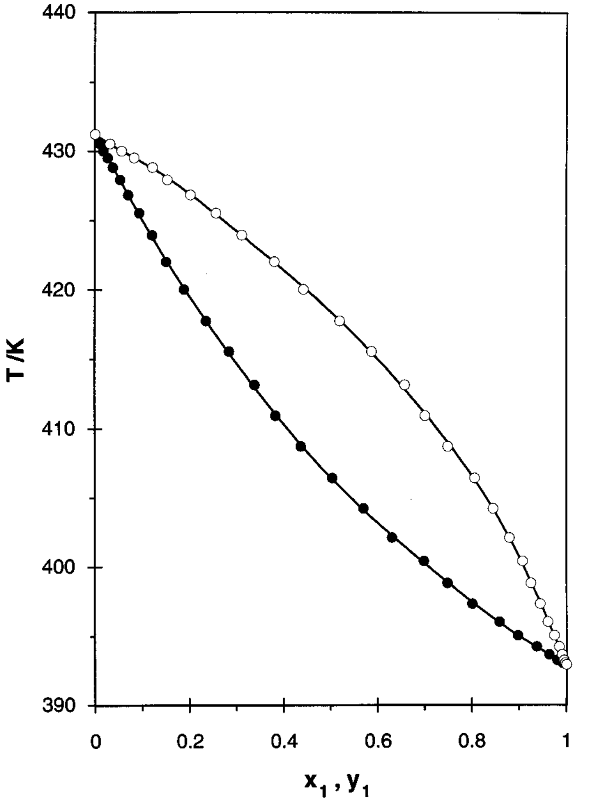

Figure 3. Vapor–liquid equilibrium of the system decane (1) + dodecane (2) at 20.00 kPa as a function of the mole fraction of component 1: experimental points of the liquid phase (●) and the vapor phase (○), splined curves (—).

as well as the equation and the parameters to calculate the second virial coefficients were taken from the literature (Daubert and Danner, 1994). The values of the activity coefficients calculated using eq 4 are listed in Table 4. It can be observed that for these systems the activity coefficients show a rare variation quite close to unity. In these conditions, small experimental errors can give rise to the small deviations observed.

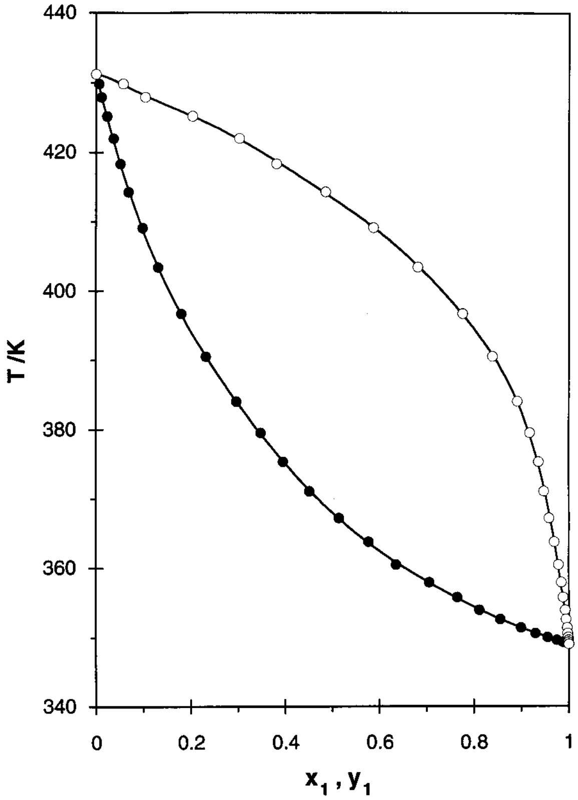

Figure 4. Vapor–liquid equilibrium of the system octane (1) + dodecane (2) at 20.00 kPa as a function of the mole fraction of component 1: experimental points of the liquid phase (●) and the vapor phase (○), splined curves (—).

The results were tested for thermodynamic consistency using the point-to-point method of Van Ness et al. (1973), modified by Fredenslund et al. (1977). A four-parameter Legendre polynomial was used for the excess Gibbs free energy. The selected objective function to minimize was the sum of the squared relative deviations in total pressure, SSRD(P):

$$\mathrm{SSRD}(P) = \sum\left(\frac{P_{\mathrm{exptl}} - P_{\mathrm{calcd}}}{P_{\mathrm{exptl}}}\right)^2 \tag{5}$$

According to Fredenslund et al., the $P-T-x-y$ data 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:

$$\delta(y) = \sum|y_{\mathrm{exptl}} - y_{\mathrm{calcd}}|/N \tag{6}$$

The results of this test for the binary systems in consideration are $\delta(y) = 0.0062$ for octane + decane, $\delta(y) = 0.0037$ for decane + dodecane, and $\delta(y) = 0.0036$ for octane + dodecane. These results indicate that the experimental data for the three systems are thermodynamically consistent.

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