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Bubble Point Measurements of the System Butane + Octylbenzene in the Temperature Range 290–450 K

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Bubble points of butane + octylbenzene at eight different mole fractions have been determined at 290–440 K using the synthetic method. The raw experimental data have been fitted using the Peng–Robinson and the Soave–Redlich–Kwong equations of state in combination with a number of different mixing rules.

Introduction

As a part of research on nitrogen displacement in light-oil reservoirs, the phase behavior of mixtures of a model oil and nitrogen is studied. The model oil consists of methane, butane, and tetradecane or octylbenzene. For reliable phase behavior calculations in the multicomponent system at reservoir conditions—about 370 K and 50 MPa in the North Sea—measurements are needed of at least the binary subsystems in the temperature and pressure range of interest, in order to determine binary interaction coefficients.

The phase behavior of the binary systems nitrogen + methane and methane + butane is known from the literature (*1*). Vapor–liquid equilibrium (VLE) of the binary systems nitrogen + tetradecane, methane + tetradecane, and butane + tetradecane have been presented elsewhere by de Leeuw et al. (*2*).

In this paper experimental bubble point results for the binary system butane + octylbenzene are presented. The Peng–Robinson and the Soave–Redlich–Kwong equations of state with different mixing rules have been used to represent the data.

Experimental Section

Method. The so-called Cailletet apparatus has been used that was described by de Loos et al. (*3*). The equipment has been designed for the synthetic method, i.e., the visual determination of bubble or dew point pressures as a function of temperature for mixtures of known overall composition. Pressures have been measured to an accuracy within 5 kPa. Temperatures have been measured within ±0.02 K.

The sample preparation has been exactly the same as for the system butane + tetradecane, as described by de Leeuw et al. (*2*). The accuracy of the mole fractions is estimated to be between 5×10^{-4} and 1×10^{-3}.

The chemicals used and their purities can be found in Table 1. Octylbenzene was obtained from Fluka with a minimum purity of >98 mass %. It has been further purified according to a procedure described elsewhere (*4, 5*).

To check the purity of butane, its vapor pressure was measured between 330 K and the critical temperature, 425 K, at intervals of 10 K. The results are given in Table 2. The experiments, as well as literature values in the same temperature range (*6*), have been fitted with the Wagner equation (*7*, cf. eq 14). The deviations of the experimental versus calculated values show random distribution; therefore, comparison of the fits shows the systematic deviations only. The root mean square (rms) deviations between the experiments and the fits are 0.6 kPa and 5×10^{-4} K, which is at least a factor of 10 smaller than the total experimental error. In the temperature range from 330 to 380 K the difference between the calculated vapor pressures according to the two fits (at the same temperature) is within 0.6 kPa and is therefore insignificant. Between 380 and 415 K, the deviations are smaller than the experimental error of 5 kPa, and only the critical point deviates 15 kPa. The experimental critical temperature and pressure are T_c = 425.12 K and p_c = 3.775 MPa; the literature values are T_c = 425.16 K and p_c = 3.796 MPa.

Table 1. Suppliers and Purities of the Chemicals Used

compound	supplier	purity
butane	Air Products	99.95 mol %
octylbenzene	Fluka	99.0 mass %

Table 2. Vapor Pressure of Butane as a Function of Temperature

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
334.11	0.655	375.14	1.585	414.71	3.190
343.71	0.820	385.32	1.920	424.86	3.760
353.22	1.015	395.36	2.300	425.12	3.775
365.41	1.310	405.23	2.725		

Results. In Table 3, the experimental series of (p, T) bubble point data or isopleths are given. From these curves isothermal (p, x) cross-sections can be obtained by interpolation. The interpolated points are indicated by the open circles in Figure 1. The experimental bubble point data form at constant temperatures nearly straight lines between the pure component vapor pressures. Dew point measurements have not been made.

Calculations

Introduction. For the purpose of a study on mixing rules for equations of state, the experimental data have been fitted with different equations of state (Peng–Robinson (*8*), Soave–Redlich–Kwong (*9*), the modified van der Waals equation of state, according to Adachi and Lu (*10*) (ALvdW) and Soave (*11*) (SvdW)) and different mixing rules including Huron–Vidal mixing rules (*12*) and density-dependent mixing rules according to Mohamed and Holder (*13*) and de Leeuw et al. (*2*). The combinations of equations of state and mixing rules have been described in detail by de Leeuw et al. (*2*). A relatively ideal system as such butane + octylbenzene can be described very well with the Peng–Robinson or Soave–Redlich–Kwong equation of state with a simple mixing rule. When applying Huron–Vidal or density-dependent mixing rules, no additional improvement of the fit in terms of the

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Table 3. Liquid + Vapor Equilibria for (1 − x) C_4H_{10} + x $C_{14}H_{22}$: Bubble Point Pressures as a Function of Temperature at a Given Mole Fraction x

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
x = 0.1011		x = 0.2959		x = 0.5068	
326.83	0.510	332.27	0.470	343.20	0.440
332.20	0.585	342.26	0.590	352.92	0.535
343.00	0.750	352.99	0.735	362.95	0.645
353.52	0.940	362.96	0.895	373.18	0.770
363.21	1.140	372.84	1.075	382.90	0.900
373.33	1.385	382.86	1.280	392.19	1.040
383.41	1.660	393.12	1.510	402.14	1.205
393.29	1.960	403.02	1.755	412.97	1.395
403.20	2.300	412.94	2.025	422.89	1.580
413.14	2.675	422.79	2.315	433.01	1.775
423.05	3.085	432.66	2.625	442.91	1.985
432.89	3.525	442.54	2.945	452.78	2.195
442.77	3.985	452.34	3.285		
452.52	4.460				
x = 0.2017		x = 0.4006		x = 0.6022	
334.58	0.550	333.15	0.415	355.06	0.455
345.54	0.700	341.64	0.505	364.01	0.530
355.79	0.870	352.76	0.635	375.58	0.645
365.79	1.055	363.02	0.770	384.38	0.745
376.16	1.280	373.22	0.930	394.26	0.860
385.98	1.520	383.27	1.100	403.97	0.985
395.76	1.785	393.25	1.285	413.76	1.120
405.81	2.085	403.18	1.490	423.75	1.265
415.37	2.400	413.02	1.710	433.46	1.410
425.10	2.740	422.91	1.945	443.32	1.570
434.78	3.105	432.79	2.195	453.61	1.740
444.51	3.490	442.62	2.455		
454.17	3.995	455.24	2.810		
x = 0.7018		x = 0.8015			
368.48	0.415	395.07	0.425		
378.64	0.490	405.00	0.485		
388.49	0.575	414.83	0.550		
398.58	0.660	424.62	0.615		
408.28	0.755	434.40	0.685		
418.34	0.855	444.18	0.755		
428.24	0.960	454.21	0.835		
438.11	1.070				
447.97	1.190				

sum of the average absolute relative (aar) deviations can be obtained with the same number of binary interaction parameters (*14*). So only the results using the Peng–Robinson or Soave–Redlich–Kwong equation of state with simple mixing rules as described below will be reported here.

Pure Components. Standard correlations have been used for the calculation of the pure component fugacities (*8, 9, 15*). The parameters of the correlations, the critical temperature, the critical pressure, and the acentric factor which have been used in the calculations are given in Table 4.

Mixtures. The classical mixing rules for equations of state are quadratic for a and linear in b, with a binary interaction coefficient for the a parameter:

$$a = \sum\nolimits_i \sum\nolimits_j x_i x_j a_{ij} \tag{1}$$

$$b = \sum\nolimits_i \sum\nolimits_j x_i x_j b_{ij} \tag{2}$$

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2} \tag{3}$$

$$b_{ij} = (b_i + b_j)/2 \quad \text{(with (2), } b = \sum\nolimits_i x_i b_i) \tag{4}$$

A secondary binary parameter can be used for high-pressure equilibria, or in the case where the two components differ strongly in shape and size as shown by Deiters and Schneider (*17*), Mathias (*18*), and de Loos et al. (*19*)):

$$b_{ij} = (1 - l_{ij})(b_i + b_j)/2 \tag{4a}$$

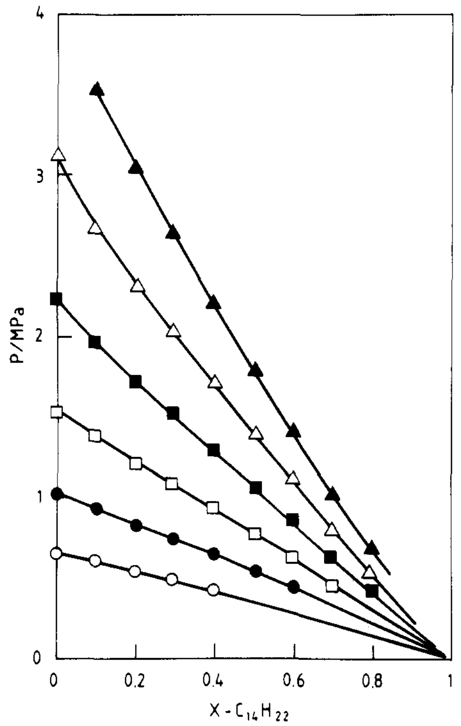

Figure 1. Vapor–liquid equilibria in the system butane + octylbenzene. Isothermal (p, x) sections: (○) 333.15 K; (●) 353.15 K; (□) 373.15 K; (■) 393.15 K; (△) 413.15 K; (▲) 433.15 K; (—) calculated using the Redlich–Kwong–Soave equation of state with *klmn* mixing rule (see text).

Table 4. Critical Temperature, Critical Pressure, and Acentric Factor of Butane and Octylbenzene

	C_4H_{10}	$C_{14}H_{22}$
ref	*a*	*b*
p_c/bar	37.9969	19.5
T_c/K	425.2	728.4
ω	0.193	0.582

[a] Reid et al. (*16*). [b] Private communication, Koninklijke/Shell Laboratory Amsterdam.

To both k_{ij} and l_{ij} a temperature-dependent term can be added (*18*):

$$k_{ij} = k^{\circ}_{ij} + m_{ij}T \tag{5}$$

$$l_{ij} = l^{\circ}_{ij} + n_{ij}T \tag{6}$$

With both the Peng–Robinson and the Soave–Redlich–Kwong equations of state, the following combinations of parameters of the generalized classical mixing rules (eqs 5 and 6) have been used: *k*, the classical mixing rule, as reference (m_{ij} = 0, l_{ij} = 0); *km*, temperature-dependent classical (l_{ij} = 0); *kl*, extended classical (m_{ij} = 0, n_{ij} = 0); *klmn*, temperature-dependent extended classical.

Interaction parameters have been fitted to the experimental phase behavior by using the Data Regression System (DRS) of the ASPEN PLUS process simulator, version 8.5 (*20*). Fugacity equations that correspond to the methods described above were derived before and are described in detail by de Leeuw et al. (*2*). The equations were programmed and interfaced to the ASPEN PLUS simulator (*21*). In all regression runs, the Britt–Luecke algorithm which searches the maximum likelihood state has been used for all iterations (*20, 22*). All the experimental points (the original isopleths) have been used in the data regression. The standard deviations used in the maximum likelihood method are 0.1 in T, 0.5% in p, and 0.001 in x_t.

Table 5. Regressed Binary Interaction Parameters, Their Standard Deviations, Average rms (arms) Deviations as Well as Average Absolute Relative (aar) Deviations in T, p, and x_t (ΔT, Δp, Δx) of the Data Set (cf. Table 3), and 100 Times the Sum of the Deviations (Σ) for the Mixture Butane + Octylbenzene

mixing rule	parameters	ΔT	Δp	Δx	Σ
Peng–Robinson Equation of State					
k	$k = (1.9401 \pm 0.0058) \times 10^{-2}$	arms = 7.20×10^{-5}	0.013 9	0.000 87	1.5
		aar = 5.18×10^{-5}	0.011 5	0.000 66	1.2
kl	$k = (2.0364 \pm 0.1659) \times 10^{-2}$	arms = 7.06×10^{-5}	0.013 9	0.000 86	1.5
	$l = (1.1642 \pm 1.8769) \times 10^{-3}$	aar = 5.13×10^{-5}	0.011 5	0.000 66	1.2
km	$k = (5.5904 \pm 0.5940) \times 10^{-2}$	arms = 4.67×10^{-5}	0.009 4	0.000 69	1.0
	$m = -(9.1852 \pm 1.4907) \times 10^{-5}$	aar = 2.98×10^{-5}	0.007 3	0.000 47	0.8
klmn	$k = (8.5792 \pm 1.6454) \times 10^{-2}$	arms = 4.432×10^{-5}	0.008 74	0.000 62	0.9
	$l = (4.0050 \pm 2.0878) \times 10^{-2}$	aar = 2.932×10^{-5}	0.006 84	0.000 42	0.7
	$m = -(1.6722 \pm 0.4095) \times 10^{-4}$				
	$n = -(1.0036 \pm 5.1157) \times 10^{-4}$				
Soave–Redlich–Kwong Equation of State					
k	$k = (1.6111 \pm 0.0585) \times 10^{-2}$	arms = 6.57×10^{-5}	0.0135	0.000 79	1.4
		aar = 4.84×10^{-5}	0.0112	0.000 64	1.2
kl	$k = (1.4727 \pm 0.1598) \times 10^{-2}$	arms = 6.70×10^{-5}	0.0134	0.000 77	1.4
	$l = -(1.6743 \pm 1.7986) \times 10^{-3}$	aar = 4.84×10^{-5}	0.0110	0.000 62	1.2
km	$k = (4.9849 \pm 6.1734) \times 10^{-2}$	arms = 4.27×10^{-5}	0.0099	0.000 65	1.1
	$m = -(8.5007 \pm 1.5513) \times 10^{-5}$	aar = 3.32×10^{-5}	0.0085	0.000 53	0.9
klmn	$k = (6.8171 \pm 1.5205) \times 10^{-2}$	arms = 4.03×10^{-5}	0.0090	0.000 56	1.0
	$l = (2.1636 \pm 1.9310) \times 10^{-2}$	aar = 2.97×10^{-5}	0.0074	0.000 44	0.8
	$m = -(1.3765 \pm 0.3792) \times 10^{-5}$				
	$n = -(6.1932 \pm 4.7349) \times 10^{-5}$				

Results. Table 5 contains parameter values with their standard deviations and the average root mean square (arms) deviations as well as the aar deviations in temperature, pressure, and composition. The aar and arms deviations were added for the three variables temperature, pressure, and composition and multiplied by 100. These sums, given by Σ in Table 5, can be considered as a measure of the accuracy of the fit.

Bubble points calculated with the Redlich–Kwong–Soave equation of state using the *klmn* mixing rule have been plotted in Figure 1.

Discussion and Conclusions

New bubble point measurements in the binary system butane + octylbenzene show little deviation from ideality (see Figure 1). Older preliminary measurements (*4*) show systematically positive deviations with respect to the data presented here. The latter phase behavior would indicate nonideality in the liquid phase, which is improbable for this binary system, so the preliminary measurements must be regarded as inaccurate. The reason for the errors could be contamination of the samples with air and/or impurities in the octylbenzene (*2*).

With the Soave–Redlich–Kwong and the Peng–Robinson equations of state, good fits of the experiments can be obtained using simple mixing rules. A temperature-dependent binary interaction coefficient in the mixing rule of the attraction parameter a is clearly the most effective (cf. Table 5). At the cost of a second temperature-dependent binary interaction parameter in the mixing rule for the covolume b, a slightly better description can be obtained. Further improvement in the description of the binary equilibria cannot be obtained without fitting the pure component vapor pressure curves before regression of the binary data.

List of Symbols

a	mixture attraction parameter in equations of state
a_i	attraction parameter in equations of state for pure component i
a_{ij}	parameter in equations of state for attraction between components i and j
b	mixture covolume parameter in equations of state
b_i	covolume parameter in equations of state for pure component i
b_{ij}	parameter in equations of state for the covolume of components i and j
k°_{ij}	constant in the expression for k_{ij}
k_{ij}	binary interaction parameter for components i and j
l°_{ij}	constant in the expression for l_{ij}
l_{ij}	binary interaction parameter for components i and j
m_{ij}	temperature coefficient in the expression for k_{ij}
n_{ij}	temperature coefficient in the expression for l_{ij}
p	absolute pressure
p_c	absolute critical pressure
T	absolute temperature
T_c	absolute critical temperature
x_i	mole fraction of component i
x_t	mole fraction of tetradecane
ω	Pitzer acentric factor

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