decane (n-$C_{17}H_{36}$) of Bradley and Shellard (*9*) and Armstrong et al. (*10*) were fitted to the following equations (having the same functional form as reported for the even-numbered n-alkanes)

$$\ln P^s = C + D/T \tag{3}$$

where

$$C = 6.56653 + 1.76232q \tag{4}$$

$$D = -244.831 - 915.569q \tag{5}$$

In eq 3-5, q is the number of carbon atoms in the (odd-numbered) n-alkanes and the units of P and T are MPa and K, respectively. The overall absolute deviation between experimental and calculated sublimation pressures was found to be 0.71% for the two paraffins studied. These equations allow the estimation of the sublimation pressures of other odd-numbered n-alkanes (e.g., n-$C_{29}H_{60}$ and n-$C_{33}H_{68}$) and are similar to those used successfully for the even-numbered n-alkanes in our earlier work.

Empirical Correlation for the Solubility. Because of the need to estimate T_c, P_c, ω, and P_2^s in the equation of state calculations, the solubility was correlated directly with solid-state properties by using the relationship

$$\ln y = A + B(P_t V^s / RT_t) \tag{6}$$

where P_t and T_t are the triple point pressure and temperature, respectively, and V^s is the molar volume of the solid. The triple point temperature T_t can be approximated by the normal melting temperature and, once this is known, the triple point pressure can be estimated from eq 3-5. Thus the solubility of any odd-numbered n-alkane (e.g., n-C_{31} or n-C_{35}) in supercritical ethane near the critical point of ethane can be predicted solely from a knowledge (or estimates) of P_t, T_t, and V^s. Values of P_t, T_t, and V^s used in our calculations are given in Table III.

A similar correlation was developed for even-numbered n-alkanes by Moradinia and Teja (*1*). Because of the ability of the previous correlation for interpolation and (judicious) extrapolation of data, we believe that the correlation presented above can also be used for such purposes, although this obviously cannot be shown from data on two odd-numbered n-alkanes. In addition, it should be emphasized that the correlation is valid only over a limited range of pressures and temperatures.

Registry No. n-$C_{29}H_{60}$, 630-03-5; n-$C_{33}H_{68}$, 630-05-7; ethane, 74-84-0.

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Phase Behavior in the Critical Region of Six Binary Mixtures of 2-Methylalkanes

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The *PTx* diagrams of six binary systems formed from 2-methylpentane, 2-methylhexane, 2-methylheptane, and 2-methyloctane were determined in the critical region. The critical properties and vapor pressures of the pure components were also determined and compared with literature values. A plot of the critical constants of the pure components against the carbon number yielded parallel curves for the *n*-alkane and the 2-methylalkane homologous series. The *PTx* diagrams of the binary systems also closely resemble those of the corresponding *n*-alkane systems. The Peng–Robinson equation was used to model the behavior of these systems with reasonable success. However, there are distinct limitations to the use of this equation in the critical region.

Introduction

The *PVTx* diagrams of mixtures at elevated pressures are of great practical as well as theoretical interest. Of particular interest are systems of close-boiling components since such mixtures are difficult to separate by using conventional distillation techniques. From a theoretical point of view, the study of these mixtures in the critical region yields fundamental information on molecular interactions in fluids and on the critical exponents.

This work was undertaken in an effort to determine the effect of molecular size and shape on the behavior of binary mixtures in the critical region. Six binary systems formed from 2-methylpentane, 2-methylhexane, 2-methylheptane, and 2-methyloctane were studied. The ability of the Peng–Robinson (*1*) equation to correlate and predict the data was also examined.

Experimental Section

The P–T border curves for a series of mixtures of known composition were determined experimentally. The apparatus and experimental techniques were the same as those employed in previous studies (*2*, *3*). Briefly, a sample of known composition (prepared gravimetrically) was confined over mercury in the sealed end of a thick-walled precision-bore glass tube. The tube was secured in one leg of a steel U-tube, with the

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Table I. Critical Temperatures and Pressures of 2-Methylalkanes

substance	ref	crit temp, K	crit press., MPa
2-methylpentane	*4*	497.55	3.035
	5	497.502	3.017
	this work	497.75	3.04
2-methylhexane	*4*	530.30	2.733
	5	530.363	2.733
	this work	530.43	2.75
2-methylheptane	*4*	559.56	2.484
	5	559.639	2.484
	this work	559.70	2.50
2-methyloctane	this work	582.87	2.31

other leg connected to a source of high-pressure nitrogen gas to pressurize the sample. The pressure on the sample was indicated by a precision spring gauge, read to within 1.38 kPa and calibrated by means of a dead-weight gauge. Temperature control was provided by a vacuum reflux column surrounding the experimental tube. The sample temperature was kept constant by maintaining constant pressure on a series of pure organic liquids boiling in a side-arm flask attached to a reflux jacket. The temperature was measured with a precision of ±0.01 K by a calibrated iron–constantan thermocouple projecting into the reflux jacket in close proximity to the sample. The thermocouple was calibrated by comparison with an NBS-certified standard platinum resistance thermometer. Equilibrium between the vapor and liquid phases was attained by rapid movement of a small steel ball in the sample using a magnet held outside the vacuum reflux jacket.

The *PTx* data were obtained by setting the temperature and varying the pressure until dew, bubble, and critical points were observed. A dew point was observed visually when, after vigorous stirring, the first trace of liquid "rain" appeared when a gaseous sample was gradually compressed at a given temperature. A bubble point was observed visually when, after vigorous agitation, a tiny vapor bubble persisted when the pressure on liquid sample was gradually reduced. A critical point was visually observed when the meniscus between the vapor and the liquid disappeared and was replaced by a band of opalescent fog. Further details of the apparatus and procedure are given elsewhere (*3*).

Source and Purity of Materials

The four 2-methylalkanes employed in this study were provided by Phillips Petroleum Co. Their stated purities were as follows: 2-methylpentane (99.95 mol %), 2-methylhexane (99%), 2-methylheptane (99%), 2-methyloctane (99%). They were used without further purification.

Discussion of Experimental Errors

Binary mixtures of known composition were prepared by combining measured amounts of liquid components in the experimental tube. The purest commercially available liquids (purity >99%) were used and weighing was done to ±0.1 mg. The compositions of the mixtures obtained in this manner were estimated to be accurate within 0.1 mol %.

Temperatures were measured with a precision of ±0.01 K with an iron–constantan thermocouple. However, because of temperature gradients in the reflux jacket, radiation to the surroundings and calibration errors, the accuracy was estimated to be ±0.1 K.

The biggest errors encountered were due to dissolved air in the sample since the samples were not degassed. By comparison of the critical pressures of degassed and undegassed samples (Table I), we estimate that this error amounts to an uncertainty in the pressure of ±0.013 MPa. If calibration errors are added, the accuracy of the pressure is estimated to be ±0.02 MPa.

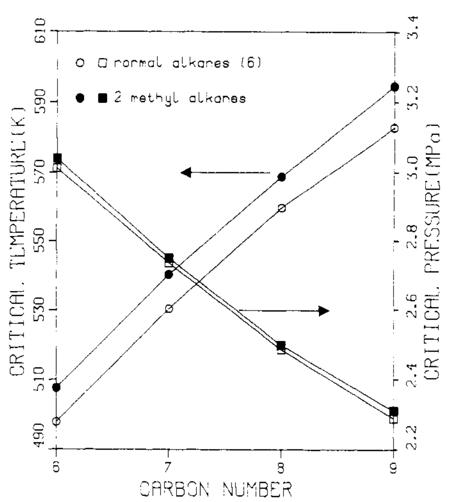

Figure 1. Critical properties of *n*-alkanes and 2-methylalkanes as a function of carbon number.

Table II. Comparison between Experimental and Calculated Vapor Pressures

substance	temp, K	press., MPa exptl	press., MPa calcd
2-methylpentane	491.39	2.771	2.769
	494.39	2.887	2.893
	495.30	2.933	2.932
	496.55	2.983	2.985
2-methylhexane	516.49	2.254	2.248
	520.84	2.389	2.393
	529.37	2.693	2.704
2-methylheptane	547.33	2.484	2.113
	550.22	2.197	2.190
	553.09	2.291	2.279
2-methyloctane	580.04	2.213	
	581.36	2.239	
	581.40	2.256	

Results and Discussion

Pure Component Critical Properties and Vapor Pressures. The critical temperature, critical pressure, and P–T (vapor pressure) behavior were determined for each pure component. The critical properties are given in Table I which also lists values of these properties obtained from the literature (*4*, *5*). In general, our measured critical properties agree extremely well with those of other workers. No literature values were available for 2-methyloctane. A plot of the critical constants of the pure substances against the carbon number (Figure 1) was found to give parallel curves for both the *n*-alkane (*6*) and the 2-methylalkane series. This suggests that structural changes cause a constant change in the critical properties (which is confirmed by the success of group contribution methods for these properties).

The vapor pressures of the four pure components are given in Table II. Also shown are vapor pressures calculated from Wagner equation fits to available literature data (*5*). The experimentally determined critical temperatures and pressures were used in the Wagner equations. Once again, agreement between experimental and "literature" values was found to be excellent. No literature data were available for 2-methyloctane.

Critical States of the Binary System. Table III presents a summary of the experimental critical properties of the six binary systems and therefore defines the critical loci of these systems. When the molecular weights of the pure components are close together, the critical locus approaches a straight line.

Table III. Critical Properties of Binary Systems of 2-Methylalkanes

x_1	T_c, K	P_c, MPa	x_1	T_c, K	P_c, MPa
2-Methylpentane + 2-Methylhexane					
0.1207	527.3	2.81	0.7210	508.7	3.00
0.3326	521.3	2.88	0.9080	501.5	3.04
0.5473	514.3	2.95			
2-Methylpentane + 2-Methylheptane					
0.1375	554.0	2.65	0.7547	517.7	3.07
0.3486	542.4	2.84	0.9206	505.1	3.06
0.5698	529.8	2.99			
2-Methylpentane + 2-Methyloctane					
0.1384	577.4	2.49	0.7854	525.1	3.09
0.3938	560.9	2.79	0.9272	507.3	3.08
0.5976	543.7	2.99			
2-Methylhexane + 2-Methylheptane					
0.1301	557.3	2.55	0.7768	538.8	2.73
0.3236	552.0	2.62	0.9074	534.8	2.75
0.5363	545.9	2.67			
2-Methylhexane + 2-Methyloctane					
0.1270	579.9	2.40	0.7519	548.6	2.72
0.3516	571.2	2.54	0.9199	537.0	2.75
0.5675	559.8	2.64			
2-Methylheptane + 2-Methyloctane					
0.1080	581.1	2.35	0.7265	568.1	2.50
0.3224	576.9	2.41	0.9075	562.9	2.51
0.5235	572.7	2.46			

Table IV. Phase Equilibria in the 2-Methylpentane + 2-Methylhexane System[a]

type	P, MPa	T, K	type	P, MPa	T, K
x_1 = 0.1207					
D	2.71	525.3	D	2.12	508.8
B	2.74	525.3	B	2.21	508.8
D	2.56	521.6	D	1.98	504.0
B	2.62	521.6	B	2.07	504.0
D	2.33	515.1	CT	2.80	527.6
B	2.39	515.1	CB	2.81	527.1
x_1 = 0.3326					
D	2.82	520.4	B	2.71	515.9
B	2.87	520.4	D	2.57	514.7
D	2.75	518.7	B	2.67	514.7
B	2.81	518.7	CT	2.88	521.6
D	2.62	515.9	CB	2.89	521.3
x_1 = 0.5473					
D	2.86	512.8	D	2.58	505.9
B	2.91	512.8	B	2.68	505.9
D	2.76	510.5	D	2.42	501.5
B	2.84	510.5	B	2.54	501.5
D	2.67	508.4	CT	2.93	514.6
B	2.76	508.4	CB	2.96	514.0
x_1 = 0.7210					
D	2.91	507.3	D	2.76	503.8
B	2.95	507.3	B	2.84	503.8
D	2.85	505.9	D	2.68	501.7
B	2.90	505.9	B	2.77	501.7
D	2.80	505.0	CT	3.00	509.0
B	2.87	505.0	CB	3.01	508.7
x_1 = 0.9080					
D	2.97	500.9	D	2.76	495.8
B	3.00	500.9	B	2.83	495.8
D	2.89	499.0	D	2.69	493.8
B	2.93	499.0	B	2.76	501.9
D	2.83	497.4	CT	3.03	501.8
B	2.88	497.4	CB	3.04	497.6

[a] D = dew point, B = bubble point, CT = cricondentherm, CB = cricondenbar.

Table V. Phase Equilibria in the 2-Methylpentane + 2-Methylheptane System

type	P, MPa	T, K	type	P, MPa	T, K
x_1 = 0.1375					
D	2.37	548.4	D	2.13	541.4
B	2.53	548.4	B	2.32	541.4
D	2.25	545.4	CT	2.63	554.2
B	2.44	545.4	CB	2.65	553.3
x_1 = 0.3486					
D	2.54	538.6	B	2.50	531.4
B	2.72	538.6	D	2.06	527.8
D	2.37	535.3	B	2.38	527.8
B	2.61	535.3	CT	2.83	542.8
D	2.20	531.4	CB	2.85	542.3
x_1 = 0.5689					
D	2.78	527.6	B	2.90	524.3
B	2.98	527.6	CT	2.98	530.2
D	2.57	524.3	CB	3.00	529.6
x_1 = 0.7547					
D	2.87	515.9	D	2.55	510.4
B	3.06	515.9	B	2.89	510.4
D	2.78	514.2	D	2.42	508.7
B	3.02	514.2	B	2.83	508.7
D	2.67	512.2	CT	3.06	518.0
B	2.94	512.2	CB	3.07	517.5
x_1 = 0.9206					
D	2.98	504.0	B	2.93	500.8
B	3.06	504.0	D	2.70	498.8
D	2.88	502.4	B	2.86	498.8
B	2.99	502.4	CT	3.06	505.1
D	2.79	500.8	CB	3.06	505.0

Table VI. Phase Equilibria in the 2-Methylpentane + 2-Methyloctane System

type	P, MPa	T, K	type	P, MPa	T, K
x_1 = 0.1384					
D	2.39	576.3	B	2.43	574.2
B	2.48	576.3	D	2.22	572.3
D	2.34	575.1	B	2.38	572.3
B	2.45	575.1	CT	2.48	577.6
D	2.30	574.2	CB	2.50	577.2
x_1 = 0.3938					
D	2.57	560.2	D	2.18	555.2
B	2.79	560.2	B	2.72	555.2
D	2.46	559.0	D	2.31	557.0
B	2.79	559.0	B	2.75	557.0
D	2.27	556.5	CT	2.78	561.2
B	2.74	556.5	CB	2.80	560.8
x_1 = 0.5976					
D	2.58	542.0	B	2.91	537.4
B	2.98	542.0	D	2.26	535.9
D	2.48	539.2	B	2.87	535.9
B	2.95	539.2	CT	2.96	544.0
D	2.35	537.4	CB	2.99	543.2
x_1 = 0.7854					
D	2.80	523.9	B	3.00	520.8
B	3.08	523.9	D	2.02	516.3
D	2.57	522.8	B	2.86	516.3
B	3.06	522.8	CT	3.06	525.6
D	2.38	520.8	CB	3.09	524.7
x_1 = 0.9272					
D	3.00	506.8	D	2.72	502.1
B	3.08	506.8	B	2.93	502.1
D	2.90	505.5	D	2.66	501.3
B	3.05	505.5	B	2.88	501.3
D	2.80	503.6	CT	3.08	507.4
B	2.99	503.6	CB	3.09	507.2

It becomes increasingly nonlinear as the difference in molecular weight increases. In this respect, the critical loci parallel the behavior of the corresponding n-alkane systems. Maximums of pressure were found to occur in the critical loci at approximately 90 mol % of the lighter component.

Dew and Bubble Points. Tables IV–IX present the experimental dew and bubble points for the six binary systems. For

Table VII. Phase Equilibria in the 2-Methylhexane + 2-Methylheptane System

type	*P*, MPa	*T*, K	type	*P*, MPa	*T*, K
		$x_1 = 0.1301$			
D	2.52	566.5	D	2.17	546.9
B	2.54	556.5	B	2.24	546.9
D	2.38	552.9	D	2.07	543.8
B	2.43	552.9	B	2.15	543.8
D	2.26	549.3	CT	2.55	557.4
B	2.31	549.3	CB	2.55	557.3
		$x_1 = 0.3236$			
D	2.40	547.6	B	2.28	541.5
B	2.47	547.6	D	2.07	538.5
D	2.30	544.9	B	2.19	538.5
B	2.39	544.9	CT	2.61	552.2
D	2.17	541.5	CB	2.62	552.0
		$x_1 = 0.5363$			
D	2.59	544.6	B	2.31	534.1
B	2.64	544.6	D	2.11	531.2
D	2.35	538.2	B	2.23	531.2
B	2.44	538.2	CT	2.66	546.1
D	2.21	534.1	CB	2.67	545.7
		$x_1 = 0.7768$			
D	2.48	534.9	B	2.34	528.2
B	2.55	534.9	D	2.14	525.7
D	2.33	531.3	B	2.26	525.7
B	2.43	531.3	CT	2.72	539.2
D	2.23	528.2	CB	2.73	538.8
		$x_1 = 0.9074$			
D	2.65	532.9	D	2.33	523.6
B	2.70	532.9	B	2.40	523.6
D	2.59	531.1	D	2.23	520.7
B	2.63	531.1	B	2.30	520.7
D	2.44	526.8	CT	2.74	534.9
B	2.50	526.8	CB	2.75	534.7

Table VIII. Phase Equilibria in the 2-Methylhexane + 2-Methyloctane System

type	*P*, MPa	*T*, K	type	*P*, MPa	*T*, K
		$x_1 = 0.1270$			
D	2.33	578.6	D	2.19	575.1
B	2.38	578.6	B	2.27	575.1
D	2.27	577.2	D	2.15	573.9
B	2.34	577.2	B	2.24	573.9
D	2.24	576.3	CT	2.40	580.0
B	2.31	576.3	CB	2.40	579.7
		$x_1 = 0.3516$			
D	2.39	569.0	B	2.47	566.4
B	2.50	569.0	D	2.19	564.7
D	2.34	567.6	B	2.42	564.7
B	2.48	567.6	CT	2.53	571.4
D	2.26	566.4	CB	2.54	571.0
		$x_1 = 0.5675$			
D	2.54	557.9	D	2.16	550.5
B	2.64	557.9	B	2.43	550.5
D	2.27	552.2	CT	2.64	559.9
B	2.48	552.2	CB	2.64	559.7
		$x_1 = 0.7519$			
D	2.58	546.2	B	2.65	544.7
B	2.70	546.2	D	2.42	542.3
D	2.51	545.4	B	2.60	542.3
B	2.67	545.4	CT	2.72	548.7
D	2.49	544.7	CB	2.72	548.4
		$x_1 = 0.9199$			
D	2.65	535.1	D	2.42	529.2
B	2.70	535.1	B	2.51	529.2
D	2.57	533.0	D	2.36	527.3
B	2.64	533.0	B	2.45	527.3
D	2.49	531.1	CT	2.75	537.1
B	2.57	531.1	CB	2.75	536.8

Table IX. Phase Equilibria in the 2-Methylheptane + 2-Methyloctane System

type	*P*, MPa	*T*, K	type	*P*, MPa	*T*, K
		$x_1 = 0.1080$			
D	2.26	580.1	B	2.17	576.0
B	2.29	580.1	D	2.08	574.6
D	2.20	578.5	B	2.13	574.6
B	2.24	578.5	CT	2.34	581.2
D	2.12	576.0	CB	2.35	581.1
		$x_1 = 0.3224$			
D	2.32	575.6	D	2.16	571.8
B	2.37	575.6	B	2.25	571.8
D	2.28	574.5	D	2.14	570.7
B	2.33	574.5	B	2.22	570.7
D	2.23	573.0	CT	2.40	577.2
B	2.28	573.0	CB	2.41	576.8
		$x_1 = 0.5235$			
D	2.38	572.0	D	2.28	569.1
B	2.42	572.0	B	2.33	569.1
D	2.35	571.0	D	2.23	568.1
B	2.39	571.0	B	2.30	568.1
D	2.32	570.1	CT	2.45	573.2
B	2.37	570.1	CB	2.46	572.6
		$x_1 = 0.7265$			
D	2.41	565.7	D	2.19	559.6
B	2.47	565.7	B	2.28	559.6
D	2.34	563.8	D	2.13	557.9
B	2.41	563.8	B	2.23	557.9
D	2.24	561.6	CT	2.50	568.4
B	2.34	561.6	CB	2.50	567.7
		$x_1 = 0.9075$			
D	2.45	561.8	D	2.32	558.3
B	2.49	561.8	B	2.37	558.3
D	2.40	560.4	D	2.25	556.4
B	2.45	560.4	B	2.32	556.4
D	2.35	558.8	CT	2.51	563.2
B	2.40	558.8	CB	2.51	562.8

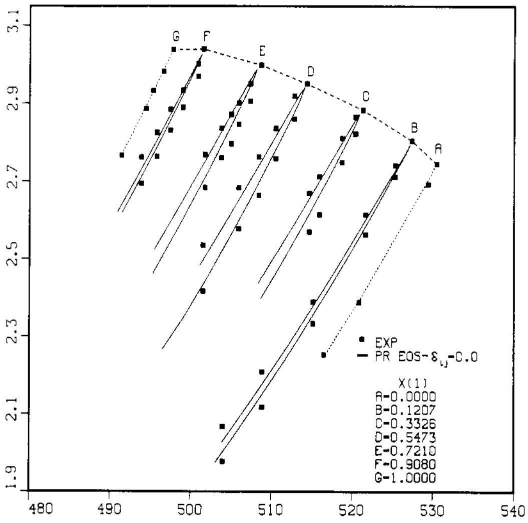

Figure 2. Calculated and experimental phase diagrams of 2-methylpentane + 2-methylhexane mixtures.

each system, experimental data at five compositions (corresponding to approximately 10, 30, 50, 70, and 90 mol %) are presented. Cricondentherms and cricondenbars were also determined and are given in Tables IV–IX. When the two components were similar in size (as in the case of the 2-methylpentane + 2-methylhexane system shown in Figure 2), the phase envelopes were narrow and the dew and bubble point curves were practically linear at all compositions. The envelopes became increasingly broader as the difference in size between the components became appreciable. This is

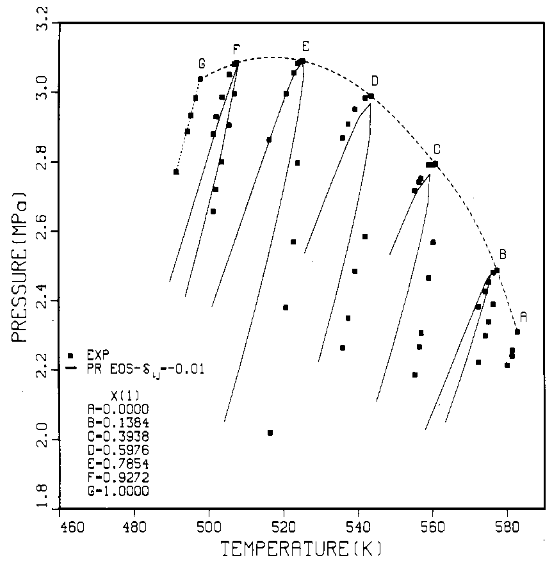

Figure 3. Calculated and experimental phase diagrams of 2-methylpentane + 2-methyloctane mixtures.

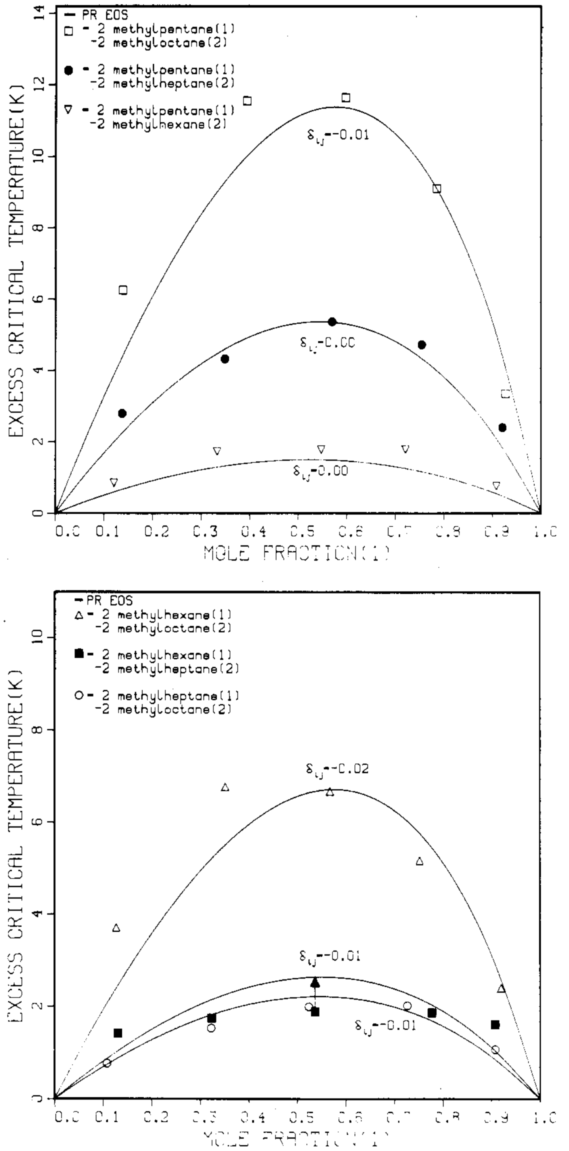

Figure 4. Calculated and experimental excess critical temperatures of six binary systems.

shown for the 2-methylpentane + 2 methyloctane system in Figure 3.

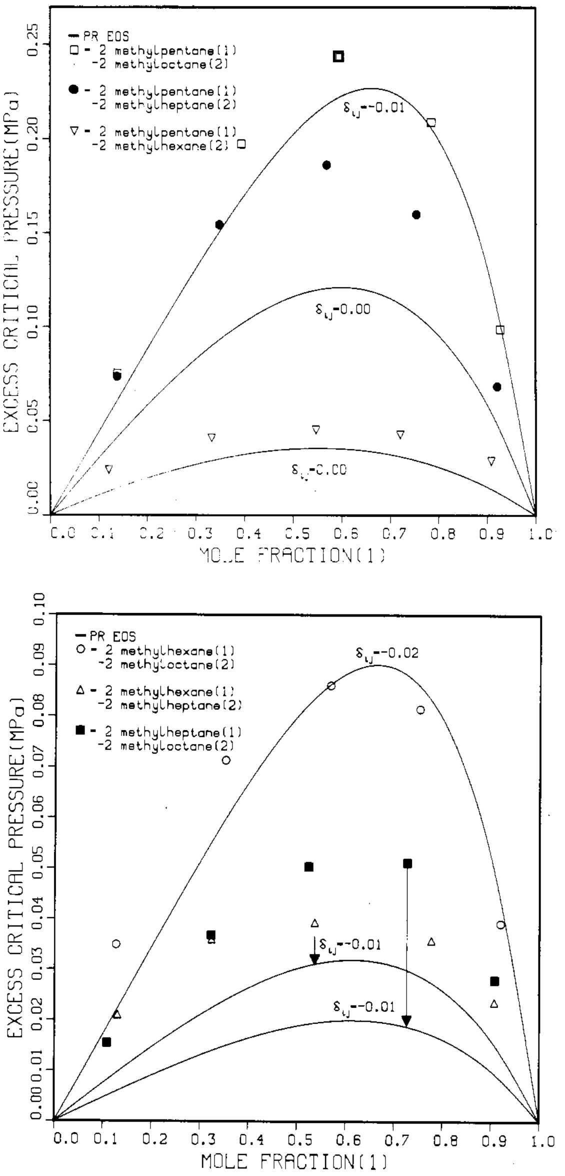

Figure 5. Calculated and experimental excess critical pressures of six binary systems.

Correlation of Data

The accurate description of the phase behavior of mixtures of close-boiling components in the critical region should, in principle, be within the capabilities of simple equations of state. We have therefore examined the abilities of the Peng–Robinson equation for this purpose.

The Peng–Robinson equation is given by

$$P = \frac{RT}{v - b} - \frac{a[T]}{v(v + b) + b(v - b)} \qquad (1)$$

where, for a pure component i, the constants a_i and b_i are given by

$$a_i = 0.45724(R^2 T_{ci}^2/P_{ci})\{1 + k_i(1 - (T/T_{ci})^{1/2})\}^2 \qquad (2)$$

$$b_i = 0.0778RT_{ci}/P_{ci} \qquad (3)$$

$$k_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \qquad (4)$$

For mixtures, the constants a and b are given by the mixing rules

$$a = \sum_i \sum_j (1 - \delta_{ij}) x_i x_j a_i^{1/2} a_j^{1/2} \qquad (5)$$

$$b = \sum_i x_i b_i \qquad (6)$$

where δ_{ij} is a binary interaction parameter characteristic of the binary system $i + j$.

Binary interaction parameters were determined by a fit of the critical locus for each binary system. The objective function used may be expressed as

$$S = \sum_1 \left\{ \left| 1 - \frac{P_{c,n}^{\text{calcd}}}{P_{c,n}^{\text{exptl}}} \right| + \left| 1 - \frac{T_{c,n}^{\text{calcd}}}{T_{c,n}^{\text{exptl}}} \right| \right\} \qquad (7)$$

The fit of the data is shown in terms of excess critical properties (actual critical property minus mole faction average property) in Figures 4 and 5. The optimum values of the parameters are given in the figures. The values are close to zero as would be expected for these simple nonpolar mixtures. The equation of state was then used to predict the phase envelopes of the binary systems (using the binary interaction parameters obtained from a fit of the critical locus). Typical calculated phase envelopes are shown in Figures 2 and 3. In general, the predictions were satisfactory. However, the predicted phase envelopes were, as a rule, too narrow. Deviations from the experimental data increased as the size differences between the components increased. We may therefore conclude that binary interaction parameters calculated from the critical locus should not be used to predict phase equilibria away from the critical region. This is a limitation of simple equations of state, since we did not reach this conclusion when a complex equation of state was used (*7*).

Glossary

a, b	constants in the Peng–Robinson equation
k	constant in the Peng–Robinson equation
P	pressure, MPa
R	gas constant
T	temperature, K
x	mole fraction
δ	binary interaction parameter
ω	acentric factor

Subscripts

1, 2	component 1, 2
c	critical
i, j	component i, j
n	nth data point

Superscripts

calcd	calculated
exptl	experimental

Registry No. 2-Methylpentane, 107-83-5; 2-methylhexane, 591-76-4; 2-methylheptane, 592-27-8; 2-methyloctane, 3221-61-2.

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Isothermal Liquid–Vapor Equilibria of Mixtures Containing Organic Compounds. 2. Excess Gibbs Free Energies of a Hydrocarbon or Tetrachloromethane + a Cyclic Ketone at 298.15 K[†]

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Vapor–liquid equilibrium data for mixtures of heptane, cyclohexane, tetrachloromethane, or benzene with cyclopentanone or with cyclohexanone were determined at 298.15 K by headspace gas chromatographic analysis of the equilibrated vapor phase. Excess molar Gibbs free energies G^E for the examined mixtures were obtained by a least-squares treatment of the equilibrium results. G^E are positive for all systems except for benzene + cyclohexanone and, for each given cosolvent, are in the order cyclopentanone > cyclohexanone and heptane > cyclohexane > tetrachloromethane > benzene. Activity coefficients at infinite dilution as well as free energies of solvation were evaluated for all the solutes in all the solvents investigated here.

Introduction

As a continuation of our study on solute–solute–solvent interactions (*1*–*3*) both in water and nonaqueous solvents, here we report excess molar Gibbs energies G^E at 298.15 K of an apolar component (heptane, cyclohexane, tetrachloromethane, and benzene) + a cyclic ketone (cyclopentanone and cyclohexanone). These results will be used in forthcoming papers either to get the so-called Kirkwood–Buff integrals (*1*) or to test the applicability of a quasi-chemical group contribution model (*4*) to mixtures involving cyclic molecules.

A headspace gas chromatographic technique already used in experiments (*3*), which was proved simpler and faster than conventional static or dynamic methods, was employed for measuring vapor composition, y, as a function of liquid composition, x, over the whole composition range. G^E were obtained from the equilibrium results by a modification of Barker's method (*5*).

[†] Part I, ref *3*.

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