interstitial accommodation of alkanes with increase in the size of molecules. Finally, the results point out that there is no regular trend between excess volume and temperature in the four mixtures.

Registry No. 1,1,2,2-Tetrachloroethane, 79-34-5; *n*-hexane, 110-54-3; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-nonane, 111-84-2.

Literature Cited

(1) Krishnaiah, A.; Rao, D. N.; Naidu, P. R. *Aust. J. Chem.* **1980**, *33*, 2543.
(2) Krishnaiah, A.; Rao, D. N.; Naidu, P. R. *Indian J. Pure Appl. Phys.* **1981**, *19*, 590.
(3) Krishnaiah, A.; Naidu, P. R. *J. Chem. Eng. Data* **1980**, *25*, 135.
(4) Choudary, N. V.; Naidu, P. R. *Can. J. Chem.* **1981**, *59*, 2210.
(5) Choudary, N. V.; Naidu, P. R. *Chem. Scr.* **1981**, *19*, 89.
(6) Choudary, N. V.; Mouli, J. C.; Naidu, P. R. *Acoust. Lett.* **1982**, *6*, 56.
(7) Choudary, N. V.; Krishnaiah, A.; Naidu, P. R. *J. Chem. Eng. Data* **1982**, *27*, 412.
(8) Mouli, J. C.; Choudary, N. V.; Krishnaiah, A.; Naidu, P. R. *Fluid Phase Equilib.* **1982**, *8*, 87.
(9) Mouli, J. C.; Choudary, N. V.; Naidu, P. R. *Indian J. Pure Appl. Phys.* **1982**, *20*, 755.
(10) Rao, M. V. P.; Naidu, P. R. *Can. J. Chem.* **1974**, *52*, 788.
(11) Reddick, J. A.; Bunger, W. S. "Techniques of Chemistry", 3rd ed.; Wiley-Interscience: New York, 1970; Vol. II.
(12) Timmermans, J. "Physico-chemical Constants of Pure Organic Compounds"; Elsevier: Amsterdam, 1950.
(13) McClellan, A. L.; Nicksic, S. W. *J. Phys. Chem.* **1965**, *69*, 446.

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Vapor–Liquid Equilibria for the Ternary System 2-Propanol–Chloroform–Benzene at 50 °C

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Isothermal $P-x-y$ data for the binary system 2-propanol–chloroform and the ternary system 2-propanol–chloroform–benzene at 50 °C are reported. Experimental data are reduced with the UNIQUAC associated solution theory with good accuracy.

Vapor–liquid equilibrium (VLE) measurements were made for the 2-propanol–chloroform and 2-propanol–chloroform–benzene systems at 50 °C. VLE data for the two constituent binaries at 50 °C have been reported: 2-propanol–benzene (*1*); chloroform–benzene (*2*). The apparatus for experimental work is a Boublik vapor-recirculating still described by Ohta et al. (*3*).

All first-grade chemicals supplied were purified for VLE measurements. 2-Propanol was distilled in a 1-m glass column packed with McMahon packing after being dried over anhydrous copper sulfate. Chloroform was washed with concentrated sulfuric acid, dilute sodium hydroxide, and distilled water. It was dried over calcined sodium carbonate and fractionally distilled in an atmosphere of nitrogen. Benzene was recrystallized 3 times. Vapor and liquid sample compositions were analyzed by a Shimadzu (GC-7A) gas chromatograph combined with a Shimadzu (ITG-2A) digital integrator. Measured variables have the following errors: composition, 0.002 mole fraction; pressure, 13.3 Pa; temperature, 0.05 K.

Results and Data Analysis

Table I shows pure-component vapor pressures obtained in this work, pure liquid molar volumes calculated from the modified Rackett equation (*4*), second virial coefficients estimated from the generalized method of Hayden and O'Connell (*5*), and pure-component structure constants calculated by the method of Vera et al. (*6*). These values were used in calculating the liquid-phase activity coefficients from experimental VLE data and data analysis. Tables II and III give experimental VLE data for binary and ternary mixtures.

Table I. Properties Used in Data Analysis

	2-propanol (1)–chloroform (2)	2-propanol (1)–benzene (3)	chloroform (2)–benzene (3)
P_i^s, kPa	23.931	23.931	69.181
P_j^s, kPa	69.181	36.210	36.210
v_i^L, cm^3/mol	81	81	83
v_j^L, cm^3/mol	83	92	92
B_{ii}, cm^3/mol	-1619	-1619	-958
B_{jj}, cm^3/mol	-958	-1205	-1205
B_{ij}, cm^3/mol	-815	-808	-1126
r_i	2.23	2.23	2.30
r_j	2.30	2.56	2.56
q_i	1.98	1.98	2.04
q_j	2.04	2.05	2.05

Table II. Vapor–Liquid Equilibrium Data for the System 2-Propanol (1)–Chloroform (2) at 50 °C

x_1	y_1	P, kPa	γ_1	γ_2	ϕ_1	ϕ_2
0.047	0.043	69.088	2.625	1.003	0.981	0.976
0.061	0.053	68.874	2.484	1.004	0.981	0.976
0.164	0.105	67.861	1.800	1.051	0.979	0.976
0.230	0.135	66.288	1.611	1.078	0.978	0.977
0.377	0.188	62.395	1.288	1.180	0.977	0.979
0.411	0.199	61.248	1.227	1.209	0.977	0.979
0.511	0.243	57.889	1.139	1.303	0.977	0.981
0.620	0.306	52.756	1.078	1.404	0.977	0.983
0.713	0.383	47.263	1.052	1.485	0.978	0.986
0.824	0.508	39.757	1.017	1.631	0.980	0.990
0.901	0.658	33.077	1.005	1.684	0.982	0.993

The liquid-phase activity coefficients were derived from eq 1

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

where the fugacity coefficients, ϕ_i and ϕ_i^s, were calculated from the volume-explicit virial equation truncated after the second term.

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Table III. Ternary Vapor-Liquid Equilibrium Data for the System 2-Propanol (1)-Chloroform (2)-Benzene (3) at 50 °C

x_1	x_2	x_3	y_1	y_2	y_3	P, kPa	γ_1	γ_2	γ_3	ϕ_1	ϕ_2	ϕ_3
0.710	0.043	0.247	0.452	0.082	0.466	41.330	1.093	1.153	2.156	0.981	0.987	0.986
0.306	0.049	0.645	0.297	0.062	0.641	46.023	1.859	0.849	1.260	0.983	0.983	0.981
0.051	0.051	0.898	0.130	0.065	0.805	40.850	4.364	0.760	1.009	0.989	0.984	0.982
0.573	0.083	0.344	0.378	0.133	0.489	44.063	1.206	1.031	1.728	0.981	0.985	0.983
0.471	0.093	0.436	0.341	0.134	0.525	45.316	1.364	0.953	1.504	0.981	0.984	0.982
0.141	0.097	0.762	0.225	0.119	0.656	45.023	2.998	0.805	1.067	0.985	0.983	0.981
0.317	0.133	0.550	0.287	0.174	0.539	46.636	1.757	0.890	1.258	0.982	0.984	0.981
0.491	0.223	0.286	0.316	0.343	0.341	48.423	1.294	1.086	1.589	0.980	0.984	0.981
0.049	0.235	0.716	0.119	0.296	0.585	45.063	4.580	0.828	1.013	0.988	0.983	0.980
0.269	0.282	0.449	0.239	0.363	0.398	50.209	1.855	0.941	1.223	0.982	0.982	0.979
0.138	0.379	0.483	0.169	0.466	0.365	51.889	2.647	0.928	1.075	0.983	0.982	0.978
0.156	0.531	0.313	0.151	0.635	0.214	56.369	2.269	0.979	1.054	0.982	0.980	0.975
0.252	0.656	0.092	0.156	0.784	0.060	62.315	1.599	1.080	1.108	0.979	0.979	0.972
0.108	0.715	0.177	0.101	0.800	0.099	62.343	2.422	1.011	0.950	0.981	0.978	0.972
0.268	0.432	0.300	0.205	0.553	0.242	54.542	1.733	1.015	1.205	0.981	0.981	0.977
0.366	0.459	0.175	0.223	0.628	0.149	56.502	1.427	1.124	1.317	0.979	0.981	0.976

Table IV. Binary Parameters and Root-Mean-Square Deviations at 50 °C

	no. of data points	root-mean-square deviations				parameters, K		
		ΔP, kPa	ΔT, K	Δx	Δy	a_{AB}	a_{BA}	K_{AB}(50 °C)
2-propanol (A)-chloroform (B)	11	0.1613	0.00	0.0005	0.0023	134.44	-50.14	4
2-propanol (A)-benzene (B)	15	0.1040	0.02	0.0006	0.0041	129.75	12.72	2.5
chloroform (A)-benzene (B)	19	0.1227	0.03	0.0004	0.0032	9.97	-53.91	

The UNIQUAC associated solution theory (*7*) provides the activity coefficients of 2-propanol (A), chloroform (B), and benzene (C) as follows:

$$\ln \gamma_A = \ln\left(\frac{\Phi_{A_1}}{\Phi^\circ_{A_1} x_A}\right) + \frac{r_A}{V^\circ} - \frac{r_A}{V} - (Z/2)q_A\left(\ln\frac{\Phi_A}{\theta_A} + 1 - \frac{\Phi_A}{\theta_A}\right) + q_A\left[1 - \ln\left(\sum_J \theta_J\tau_{JA}\right) - \sum_J \frac{\theta_J\tau_{AJ}}{\sum_K \theta_K\tau_{KJ}}\right] \quad (2)$$

$$\ln \gamma_B = \ln\frac{\Phi_{OB}}{x_B} + 1 - \frac{r_B}{V} - (Z/2)q_B\left(\ln\frac{\Phi_B}{\theta_B} + 1 - \frac{\Phi_B}{\theta_B}\right) + q_B\left[1 - \ln\left(\sum_J \theta_J\tau_{JB}\right) - \sum_J \frac{\theta_J\tau_{BJ}}{\sum_K \theta_K\tau_{KJ}}\right] \quad (3)$$

where Z is the coordination number set as 10 and

$$\Phi_I = x_I r_I / \sum_J x_J r_J \quad (4)$$

$$\theta_I = x_I q_I / \sum_J x_J q_J \quad (5)$$

$$\tau_{IJ} = \exp(-a_{IJ}/T) \quad (6)$$

$\ln \gamma_C$ is obtained by changing the subscript B to C in eq 3.

The monomer segment fractions, Φ_{A_1}, Φ_{OB}, and Φ_{OC}, are analytically solved from eq 7-9.

$$\Phi_A = [\Phi_{A_1}/(1 - K_A\Phi_{A_1})^2][1 + r_A(K_{AB}\Phi_{OB} + K_{AC}\Phi_{OC})] \quad (7)$$

$$\Phi_B = \Phi_{OB}[1 + r_B K_{AB}\Phi_{A_1}/(1 - K_A\Phi_{A_1})] \quad (8)$$

$$\Phi_C = \Phi_{OC}[1 + r_C K_{AC}\Phi_{A_1}/(1 - K_A\Phi_{A_1})] \quad (9)$$

The value of $\Phi^\circ_{A_1}$ in pure alcohol is calculated by

$$\Phi^\circ_{A_1} = [(2K_A + 1) - (1 + 4K_A)^{1/2}]/2K_A^2 \quad (10)$$

Table V. Ternary Calculated Results for the System 2-Propanol (1)-Chloroform (2)-Benzene (3) at 50 °C

	Δy_1	Δy_2	Δy_3	ΔP, kPa	$\Delta P/P$, %
mean deviation	0.0039	0.0019	0.0042	0.4968	0.98
root-mean-square deviation	0.0052	0.0030	0.0053	0.5903	1.15

Then, the true molar volume of the ternary mixture and that in pure alcohol are given by

$$\frac{1}{V} = \frac{\Phi_{A_1}}{r_A(1 - K_A\Phi_{A_1})} + \frac{\Phi_{OB}}{r_B}\left[1 + \frac{K_{AB}r_B\Phi_{A_1}}{(1 - K_A\Phi_{A_1})}\right] + \frac{\Phi_{OC}}{r_C}\left[1 + \frac{K_{AC}r_C\Phi_{A_1}}{(1 - K_A\Phi_{A_1})}\right] \quad (11)$$

$$1/V^\circ = (1 - K_A\Phi^\circ_{A_1})/r_A \quad (12)$$

At 50 °C, the value of K_A for 2-propanol is 49.1 (*8*). Binary parameter estimation was performed by using a computer program similar to that described by Prausnitz et al. (*9*). Standard deviations in the measured variables were the same as suggested by Prausnitz et al.: pressure, σ_P = 133.3 Pa; temperature, σ_T = 0.05 K; liquid mole fraction, σ_x = 0.001; vapor mole fraction, σ_y = 0.003. Table IV summarizes results of correlation for the three binary systems. The values of K_{AB} were selected which reproduce best the experimental VLE data. As shown in Table V, the ternary VLE data are well predicted with parameters for the binary systems in Table IV.

Glossary

A, B, C	alcohol, chloroform, and benzene
a_{IJ}	binary interaction parameter
B_{11}, B_{22}, B_{12}	second virial coefficients
K_A	association equilibrium constant, $(\Phi_{A_{i+1}}/\Phi_{A_i}\Phi_{A_1})[i/(i + 1)]$
K_{AB}	solvation equilibrium constant, $(\Phi_{A_iB}/\Phi_{A_i}\Phi_{OB})[i/(ir_A + r_B)]$
K_{AC}	solvation equilibrium constant, $(\Phi_{A_iC}/\Phi_{A_i}\Phi_{OC})[i/(ir_A + r_C)]$
P	total pressure

P_i^s	vapor pressure of pure component i
q	pure-component area parameter
R	universal gas constant
r	pure-component volume parameter
T	absolute temperature
V	true molar volume of alcohol mixture
V°	true molar volume of pure alcohol solution
v_i^L	molar volume of pure liquid i
x	liquid mole fraction
y	vapor mole fraction
Z	coordination number equal to 10

Greek Letters

γ_i	liquid-phase coefficient
θ	area fraction
σ_P, σ_T	standard deviations in pressure and temperature
σ_x, σ_y	standard deviations in liquid and vapor mole fractions
τ_{IJ}	$\exp(-a_{IJ}/T)$
ϕ_i	fugacity coefficient of component i
ϕ_i^s	fugacity coefficient of pure component i at its saturation pressure
Φ_A, Φ_B, Φ_C	segment fractions of components A, B, and C
Φ_{A_1}	segment fraction of alcohol monomer
$\Phi^\circ{}_{A_1}$	segment fraction of alcohol monomer in pure alcohol solution
Φ_{OB}	segment fraction of chloroform monomer in mixture
Φ_{OC}	segment fraction of benzene monomer in mixture

Registry No. 2-Propanol, 67-63-0; chloroform, 67-66-3; benzene, 71-43-2.

Literature Cited

(1) Nagata, I.; Ohta, T.; Uchiyama, Y. *J. Chem. Eng. Data* **1973**, *18*, 54-9.
(2) Nagata, I.; Hayashida, H. *J. Chem. Eng. Jpn.* **1970**, *3*, 161-6.
(3) Ohta, T.; Koyabu, J.; Nagata, I. *Fluid Phase Equilib.* **1981**, *7*, 65-73.
(4) Spencer, C. F.; Danner, R. P. *J. Chem. Eng. Data* **1972**, *17*, 236-41.
(5) Hayden, J. G.; O'Connell, J. P. *Ind. Eng. Chem. Process Des. Dev.* **1975**, *14*, 209-16.
(6) Vera, J. H.; Sayegh, C. G.; Ratcliff, G. A. *Fluid Phase Equilib.* **1977**, *1*, 113-35.
(7) Nagata, I.; Kawamura, Y. *Chem. Eng. Sci.* **1979**, *34*, 601-11.
(8) Brandani, V. *Fluid Phase Equilib.* **1983**, *12*, 87-104.
(9) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. "Computer Calculations for Multicomponent Vapor–Liquid and Liquid–Liquid Equilibria"; Prentice-Hall: Englewood Cliffs, NJ, 1980; Chapters 3 and 4, Appendix D.

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Liquid–Liquid–Vapor Immiscibility Limits in Carbon Dioxide + *n*-Paraffin Mixtures

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Liquid–liquid–vapor equilibria for the binary systems CO_2 + *n*-nonadecane and CO_2 + *n*-heneicosane were studied. Liquid–liquid–vapor data on the binary mixture CO + *n*-eicosane were also taken and compared with an earlier study in the literature. For the homologous series of *n*-paraffins it appears that the extent of the liquid–liquid–vapor immiscibility decreases from a maximum at carbon number 14 to carbon number 21. The liquid–liquid–vapor locus has a length of about 3.0 K for CO_2 + *n*-heneicosane and is nonexistent for carbon number 22 and higher. Also studied were solid–liquid–vapor equilibria for CO_2 + *n*-nonadecane and CO_2 + *n*-heneicosane and liquid–vapor isotherms for CO_2 + *n*-nonadecane at 40 and 60 °C and CO_2 + *n*-heneicosane at 45 and 65 °C.

Introduction

In this paper we report on the occurrence of liquid–liquid–vapor (LLV) equilibria in the homologous series of binary CO_2 + *n*-paraffin mixtures. Specifically, phase equilibria data are presented that identify the limit of LLV immiscibility in this series of mixtures. In addition to the LLV data on the binary systems, liquid–vapor (LV) and solid–liquid–vapor (SLV) data are also presented. These data are helpful in understanding the occurrence of LLV behavior in complex mixtures such as CO_2 + oil systems that are encountered in CO_2-enhanced recovery processes. A quantitative description of these binary systems is useful in supporting the development of equations-of-state purporting to be applicable to these multicomponent systems.

LLV immiscibility has been observed in CO_2 + *n*-paraffin binary systems ranging from *n*-heptane (*1*) to *n*-eicosane (*2*). Schneider et al. (*3–5*) performed early studies showing LLV immiscibility in the CO_2 + *n*-paraffin binary systems with *n*-octane, *n*-undecane, *n*-tridecane, and *n*-hexadecane. Hottovy et al. (*6*) detailed the LLV behavior of the binary systems containing *n*-dodecane to *n*-pentadecane, while Kulkarni et al. (*7*) studied the CO_2 + *n*-decane system along its multiphase loci, including LLV. It was learned from the Hottovy and Schneider studies that there is a transition in the nature of the LLV loci between the *n*-tridecane and *n*-tetradecane species and that the greatest extent of LLV locus occurs with *n*-tetradecane, which had an LLV locus extending from an upper critical end point, or K point (L–L=V), at 311.15 K to a quadruple point, or Q point (SLLV), at 269.10 K.

Obviously, the occurrence of LLV behavior in the CO_2 + *n*-paraffin binary system homologous series must eventually disappear as the molecular nature of the CO_2 and the *n*-paraffin become too diverse to support the existence of an LLV locus. In particular, if the triple point of the *n*-paraffin occurs at a temperature too far above the critical point of CO_2, then the binary SLV locus that evolves from the triple point of the *n*-paraffin will be located too high in temperature to form a lower terminus (SLLV) to an LLV locus.

In this paper, data will be presented for the binary systems CO_2 + *n*-nonadecane and CO_2 + *n*-heneicosane along their LLV loci and compared with earlier studies on the binary systems CO_2 + *n*-eicosane and CO_2 + *n*-docosane. Also presented will be the data along the SLV loci of these binary systems and along two nearby LV isotherms for each of the systems. A discussion will follow focusing on the relative location

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