Table VII. Experimental Data for the Methane + *n*-Hexane Binary[a]

		mole fraction of *n*-hexane		molar vol, mL/(g-mol)	
temp, K	press., atm	L_1	L_2	L_1	L_2
		K (L_1-L_2 = V)			
195.72	51.33	0.2323	0.0117	57.82	153.86
		L_1-L_2-V			
194.00	48.67	0.2525	0.0179	63.89	67.36
192.00	45.81	0.2458	0.0286	64.09	63.65
190.00	43.08	0.2302	0.0353	62.56	60.24
188.00	40.51	0.2145	0.0434	60.91	58.84
186.00	37.98	0.1982	0.0566	59.99	61.10
184.00	35.61	0.1841	NA	61.13	NA
		LCST (L_1 = L_2-V)			
182.73	34.05	0.1479	0.1479	57.97	57.97

[a] Each point given is average of several actual data points. NA = Not measured.

S	solid phase
T	temperature
V	vapor phase

Registry No. Methane, 74-82-8; pentane, 109-66-0; octane, 111-65-9; hexane, 110-54-3; carbon dioxide, 124-38-9.

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Isentropic Compressibility of an Ideal Ternary Solution

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An equation is given for the isentropic compressibility of an ideal ternary solution and is used to calculate excess isentropic compressibilities of *o*-xylene + acetone + benzene, *o*-xylene + acetone + cyclohexane, and *o*-xylene + acetone + carbon tetrachloride mixtures. The results of these calculations indicate that the three ternary mixtures do not exhibit the large deviations from ideality as had been suggested by the earlier calculations of Prasad and Prakash.

In several recent publications appearing in this journal (*1–3*), the excess isentropic compressibility K_s^{ex} of a liquid mixture was defined as the difference between the observed isentropic compressibility and that of an ideal solution K_s^{ideal} as in eq 1.

$$K_s^{ex} = K_s - K_s^{ideal} \qquad (1)$$

The isentropic compressibility of the ideal solution was represented as the mole fraction average of the isentropic compressibilities of the pure liquids $K_s{}^\circ{}_i$ (eq 2). While many

$$K_s^{ideal} = \sum_{i=1}^{N} X_i K_s{}^\circ{}_i \qquad (2)$$

thermodynamic and physical properties of an ideal solution are correctly described by mole fraction averages, the isentropic compressibility is not one of these properties.

Table I. Excess Isentropic Compressibilities of Several Ternary Mixtures

X_2	X_3	$10^{12}K_s$, cm² dyn⁻¹	K_s^{ex}	
			eq 1 and 2	eq 1 and 9
		o-Xylene + Acetone + Benzene		
0.00	0.60	64.22	−0.59	−0.76
0.10	0.50	65.24	−1.73	−1.02
0.20	0.40	66.33	−2.80	−1.55
0.30	0.30	67.66	−3.63	−1.90
0.40	0.20	69.44	−4.01	−1.84
0.50	0.10	71.15	−4.46	−1.91
0.60	0.00	73.55	−4.22	−1.35
0.50	0.50	74.92	−2.61	−1.60
		o-Xylene + Acetone + Cyclohexane		
0.00	0.60	72.04	−1.86	−1.72
0.10	0.50	72.69	−1.85	−1.22
0.20	0.40	73.02	−2.17	−1.09
0.30	0.30	73.30	−2.54	−0.98
0.40	0.20	73.45	−3.03	−1.44
0.50	0.10	73.53	−3.60	−1.14
0.60	0.00	73.55	−4.22	−1.35
0.50	0.50	86.68	+1.58	+2.26
		o-Xylene + Acetone + Carbon Tetrachloride		
0.00	0.60	67.11	−1.65	−1.59
0.10	0.50	67.59	−2.67	−2.01
0.20	0.40	68.19	−3.57	−2.41
0.30	0.30	69.24	−4.03	−2.36
0.40	0.20	70.68	−4.09	−1.92
0.50	0.10	72.07	−4.20	−1.80
0.60	0.00	73.55	−4.22	−1.35
0.50	0.50	78.30	−2.52	−1.50

The isentropic compressibility of any solution is related to the isothermal compressibility K_t by

$$K_s = K_t(C_v/C_p) \qquad (3)$$

$$K_s = -(\partial \ln V/\partial P)_S \qquad (4)$$

$$K_t = -(\partial \ln V/\partial P)_T \qquad (5)$$

the ratio of heat capacities at constant volume and pressure, which are themselves related through

$$C_p - C_v = \alpha^2 VT/K_t \qquad (6)$$

the coefficient of thermal expansion ($\alpha = (\partial \ln V/\partial T)_P$). The isothermal compressibility of an ideal solution can easily be

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shown to equal the volume fraction (ϕ_i) average of the isothermal compressibilities of the pure liquids

$$K_t^{\text{ideal}} = \sum_{i=1}^{N} \phi_i K_t{}^\circ{}_i \tag{7}$$

and the isobaric heat capacity to equal the mole fraction average of the heat capacities of the pure liquids

$$C_p{}^{\text{ideal}} = \sum_{i=1}^{N} X_i C_p{}^\circ{}_i \tag{8}$$

Combination of eq 3-8 gives the following expression for the isentropic compressibility of an ideal ternary solution

$$K_s{}^{\text{ideal}} = \sum_{i=1}^{3} \phi_i \{K_s{}^\circ{}_i + TV^\circ{}_i(\alpha^\circ{}_i)^2/C_p{}^\circ{}_i\} - T[\sum_{i=1}^{3} X_i V^\circ{}_i][\sum_{i=1}^{3} \phi_i \alpha^\circ{}_i]^2/[\sum_{i=1}^{3} X_i C_p{}^\circ{}_i] \tag{9}$$

which in no way resembles a mole fraction average of the individual $K_s{}^\circ{}_i$, except in the very special case when the molar volumes, isobaric heat capacities, and isobaric thermal expansivities of all three components are identical. It should be noted that eq 9 is identical with equations derived by Bertrand and Smith (*4*) and Benson and Kiyohara (*5*, *6*) for binary mixtures.

In Table I, I compare the excess isentropic compressibilities as calculated by Prasad and Prakash (*1*), using eq 1 and 2, to those values calculated from eq 1 and 9 for the ternary systems *o*-xylene + acetone + benzene, *o*-xylene + acetone + cyclohexane, and *o*-xylene + acetone + carbon tetrachloride. The isobaric heat capacities of the pure components were taken directly from the literature (*7*) and the numerical values of the thermal expansivities were calculated from the density data of the pure liquids at several different temperatures (*8*). Most noticeable in this comparison is the fact that the three ternary mixtures do not exhibit the large deviations from ideality as had been suggested by the earlier calculations of Prasad and Prakash.

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Vapor-Liquid Equilibria in Binary Mixtures of Nitrogen + Tetralin and Nitrogen + *m*-Cresol

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Vapor-liquid equilibria were experimentally determined for binary mixtures of nitrogen with Tetralin and with *m*-cresol at temperatures between 463 and 663 K. At each temperature, measurements were made at pressures from 2 to 25 MPa.

Introduction

Vapor-liquid equilibrium data for nitrogen mixtures are scarce at high temperature and high pressure but are basic to design of heavy fossil fuel refining processes. In this work, we report compositions of saturated vapor and liquid phases at equilibrium for two binary systems, nitrogen + Tetralin and nitrogen + *m*-cresol, at temperatures from 463 to 663 K and pressures to 25 MPa.

Data on these two systems are not found in the literature at temperatures and pressures comparable to the present work.

Experimental Section

Measurements were made in a flow-type apparatus to minimize thermal degradation at high temperatures. The experimental apparatus and procedure have been described by Simnick et al. (*1*).

Nitrogen gas was purchased from Airco with a purity of 99.995+%. Both Tetralin and *m*-cresol were supplied by Aldrich Chemical Co. with a minimum purity of 99%.

Gas-chromatographic analysis of the condensate from the equilibrium cell effluents showed no appreciable degradation for *m*-cresol at all conditions studied. For Tetralin impurities up to 2% were detected at the higher temperatures. Liquid Tetralin from cell bottom effluent also turned light yellow in color. The impure Tetralin was purified by distillation under a reduced nitrogen atmosphere prior to being reused.

The attainment of equilibrium in the flow process used in the present work has been verified by various methods (*1*). In this study, additional tests were made by reducing the liquid feed rate from the usual 20-25 cm^3/min to about 10 cm^3/min at 544 K and 15 MPa for nitrogen + Tetralin and at 462 K and 3 MPa for nitrogen + *m*-cresol. No appreciable effect of flow rate on the phase compositions was found.

Results

Experimental results are summarized in Table I for nitrogen + Tetralin and Table II for nitrogen + *m*-cresol. The saturated

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