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.

Literature Cited

(1) Prasad, N.; Prakash, S. *J. Chem. Eng. Data* **1977**, *22*, 49.
(2) Kumar, A.; Prakash, O.; Prakash, S. *J. Chem. Eng. Data* **1981**, *26*, 64.
(3) Singh, S.; Sivanarayana, K.; Kushman, R.; Prakash, S. *J. Chem. Eng. Data* **1979**, *24*, 279.
(4) Bertrand, G. L.; Smith, L. E. *J. Phys. Chem.* **1970**, *74*, 4171.
(5) Benson, G. C.; Kiyohara, O. *J. Chem. Thermodyn.* **1979**, *11*, 1061.
(6) Kiyohara, O.; Benson, G. C. *J. Chem. Thermodyn.* **1979**, *11*, 861.
(7) Weast, R. C. "Handbook of Chemistry and Physics", 52nd ed.; Chemical Rubber Publishing Co.: Cleveland, OH, 1971.
(8) Timmermans, J. "Physico-chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1959.

Received for review December 3, 1981. Revised manuscript received November 3, 1982. Accepted November 18, 1982.

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

Hwayong Kim, Wenchuan Wang, Ho-mu Lin, and Kwang-Chu Chao*

School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907

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

0021-9568/83/1728-0216$01.50/0

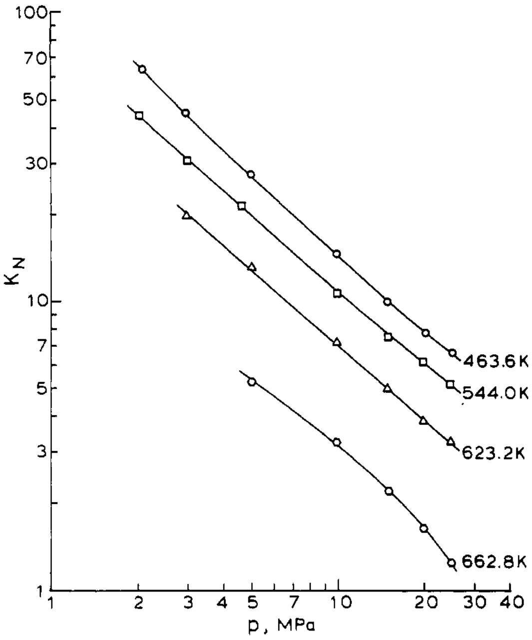

Figure 1. *K* value of nitrogen in nitrogen + Tetralin.

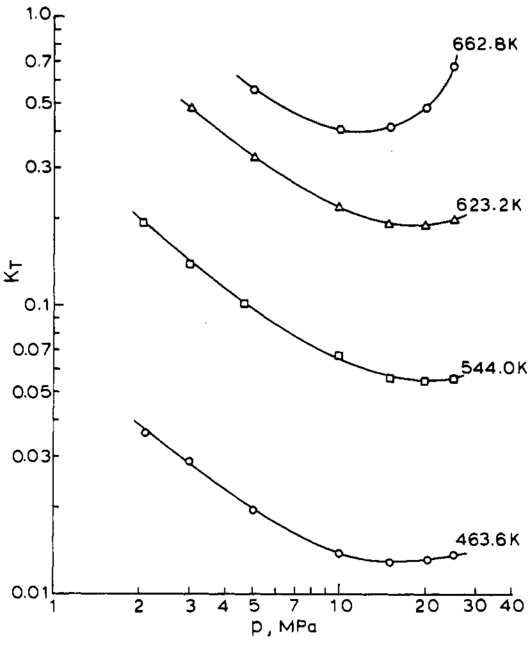

Figure 2. *K* value of Tetralin.

Table I. Nitrogen + Tetralin Vapor-Liquid Equilibrium Data

p/MPa	x_N	y_N	K_N	K_T
		$T = 463.6$ K		
2.132	0.0152	0.9646	63.38	0.036
3.034	0.0215	0.9720	45.13	0.029
5.05	0.0356	0.9810	27.53	0.020
10.15	0.0675	0.9871	14.63	0.014
15.25	0.0991	0.9883	9.975	0.013
20.58	0.1286	0.9886	7.685	0.013
25.56	0.1495	0.9884	6.612	0.014
		$T = 544.0$ K		
2.074	0.0183	0.8112	44.25	0.192
3.068	0.0276	0.8641	31.30	0.140
4.70	0.0424	0.9033	21.31	0.101
10.06	0.0885	0.9380	10.60	0.068
15.34	0.1282	0.9513	7.422	0.056
20.23	0.1560	0.9541	6.118	0.054
25.20	0.1875	0.9548	5.091	0.056
		$T = 623.2$ K		
3.069	0.0274	0.5413	19.78	0.472
5.12	0.0529	0.6891	13.04	0.328
10.05	0.1127	0.8056	7.151	0.219
15.16	0.1687	0.8415	4.990	0.191
20.25	0.2228	0.8528	3.828	0.189
25.42	0.2633	0.8530	3.240	0.200
		$T = 662.8$ K		
5.07	0.0948	0.4937	5.206	0.559
10.09	0.2057	0.6754	3.283	0.409
15.44	0.3267	0.7190	2.201	0.417
20.37	0.4460	0.7289	1.634	0.489
25.37	0.5734	0.7112	1.240	0.677

Table II. Nitrogen + *m*-Cresol Vapor-Liquid Equilibrium Data

p/MPa	x_N	y_N	K_N	K_{Cr}
		$T = 462.2$ K		
2.047	0.0086	0.9575	112.0	0.043
3.028	0.0127	0.9707	76.32	0.030
5.08	0.0211	0.9800	46.49	0.021
10.06	0.0405	0.9869	24.35	0.014
15.16	0.0592	0.9888	16.70	0.012
20.20	0.0758	0.9894	13.05	0.011
25.27	0.0928	0.9899	10.67	0.011
		$T = 542.7$ K		
2.042	0.0106	0.7463	70.73	0.257
3.108	0.0174	0.8242	47.42	0.179
5.08	0.0318	0.8832	27.78	0.121
10.08	0.0604	0.9311	15.42	0.073
15.30	0.0929	0.9420	10.14	0.064
20.34	0.1144	0.9459	8.267	0.061
25.42	0.1401	0.9494	6.779	0.059
		$T = 624.3$ K		
3.092	0.0157	0.3934	24.99	0.616
5.08	0.0341	0.5748	16.85	0.440
10.21	0.0835	0.7286	8.723	0.296
15.22	0.1289	0.7787	6.040	0.254
20.04	0.1751	0.7969	4.551	0.246
25.37	0.2188	0.8065	3.686	0.248
		$T = 663.6$ K		
5.19	0.0337	0.3214	9.539	0.702
10.10	0.0999	0.5361	5.368	0.515
15.31	0.1651	0.6068	3.675	0.471
20.34	0.2373	0.6167	2.599	0.503
22.89	0.2856	0.6102	2.137	0.546
25.24	0.3497	0.5728	1.638	0.657

compositions reported in the tables are the mean values of at least two duplicate samples. The temperature of the equilibrium cell fluctuated no more than 0.2 K during a complete isothermal run.

Figures 1 and 2 show the *K* values of nitrogen and Tetralin, respectively, as a function of system pressure for the mixtures of nitrogen + Tetralin, while Figures 3 and 4 represent similar results for nitrogen + *m*-cresol. For both mixtures close approach to the critical state is indicated at the highest observed temperature by a rapid change of the *K* values with pressure.

Glossary

K	vaporization equilibrium ratio
p	system pressure, MPa
T	temperature, K
x	mole fraction in liquid phase
y	mole fraction in vapor phase

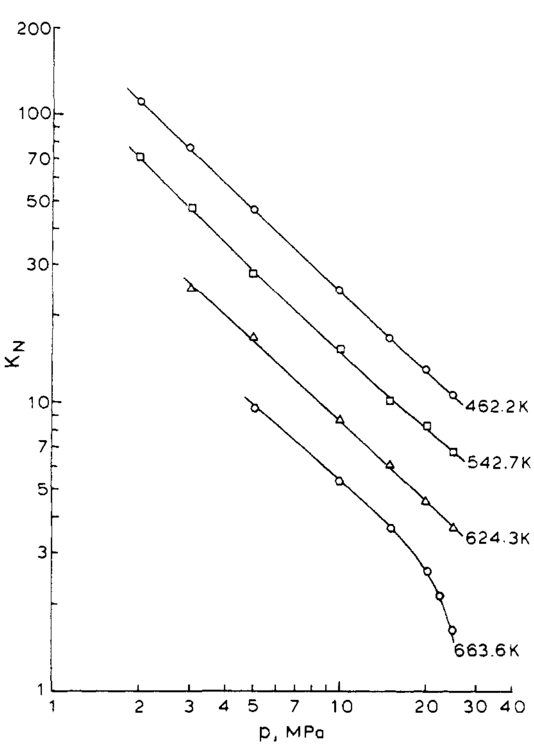

Figure 3. *K* value of nitrogen in nitrogen + *m*-cresol.

Subscripts

Cr	*m*-cresol
N	nitrogen
T	Tetralin

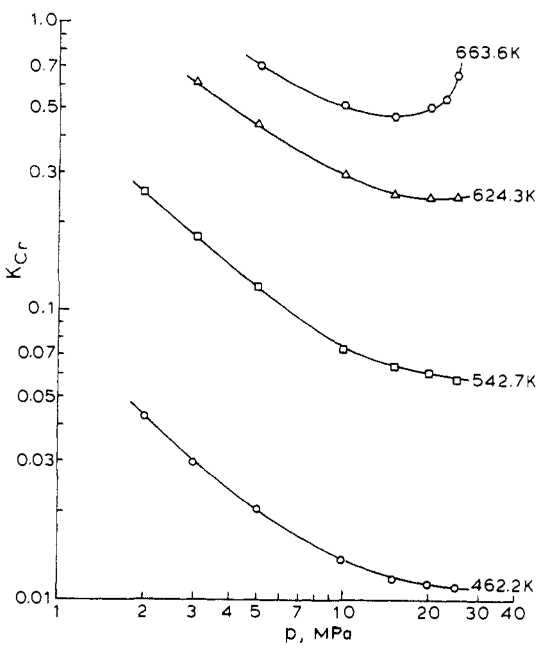

Figure 4. *K* value of *m*-cresol.

Registry No. Nitrogen, 7727-37-9; Tetralin, 119-64-2; *m*-cresol, 108-39-4.

Literature Cited

(1) Simnick, J. J.; Lawson, C. C.; Lin, H. M.; Chao, K. C. *AIChE J.* **1977**, *23*, 469-76.

Received for review June 7, 1982. Accepted November 29, 1982. Funds for this research were provided by Electric Power Research Institute through research project RP-367.

Equation of State and Thermodynamic Properties of Liquid Methanol from 298 to 489 K and Pressures to 1040 bar

Jose R. S. Machado† **and William B. Streett***

School of Chemical Engineering, Cornell University, Ithaca, New York 14853

The *PVT* properties of liquid methanol have been measured with a direct-weighing *PVT* apparatus, from 298 to 489 K and pressures to 1040 bar. The apparatus and the method are described. The results have been fitted to a 16-constant equation of state that has been used, together with published data for vapor pressure and saturated-vapor densities, to calculate the following properties of saturated and compressed liquid methanol over the experimental range: specific volume, isothermal compressibility, thermal expansion coefficient, thermal pressure coefficient, enthalpy, entropy, and constant-pressure heat capacity. The calculated properties are presented in tabular form, at round values of *P* and *T*.

Introduction

World demand for methanol, at about 12 × 10^6 t in 1980, is expected to soar to 48 × 10^6 t by the end of the century. New markets will account for most of the increase, with the Mobil Corp.'s methanol-to-gasoline conversion process the largest potential consumer.

Existing sources of thermodynamic properties of methanol are few and scattered (*1*–*10*). Figure 1 shows the pressure–temperature regions covered by previous *PVT* experiments, as well as that covered by this work. A preliminary analysis of the earlier *PVT* measurements suggests that only those of Zubarev and Bagdonas (*7*) and Ta'ani (*3*) are of suitable accuracy for constructing an equation of state (*11*). In this work (*12*) we have measured the *PVT* properties of liquid methanol at 167 points, including seven isotherms from 298 to 489 K (25–216 °C) and pressures from saturation to about 1000 bar; this covers a wide region that has not previously been studied, and overlaps with the two most accurate recent studies (*3*, *7*) so that comparisons can be made.

Our *PVT* data have been fitted to a 16-constant equation of state which has been used to calculate, at regular intervals of pressure and temperature, the following properties of compressed liquid methanol: specific volume, isothermal compressibility, thermal expansion coefficient, thermal pressure

---

† Present address: Air Products and Chemicals, Allentown, PA 18105.

0021-9568/83/1728-0218$01.50/0 © 1983 American Chemical Society