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Viscosity of Associated Liquids. 2. Methylamine

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The viscosity of methylamine is represented by the expression $\log \eta = 1.635 + 203.2(T - 69.87)$ in cP, with a relative uncertainty of 0.18% from −70 to 30 °C. (T is the temperature in K.)

In a previous paper (*1*) we reported an apparent inconsistency between the data for the viscosity of methylamine and that of certain other hydrogen-bonded liquids; specifically, we noted that when out data were fitted by the Fulcher equation (*2*)

$$\log \eta = A + B/(T - T_0)$$

(where A, B, and T_0 are empirical constants, T_0 being related to the glass transition temperation) the value of T_0 obtained for methylamine, 102.0 K, seemed too large when compared to those obtained for the related liquids ammonia (50.7 K) and methanol (48.6 K).

We have now carried out further measurements of the viscosity of methylamine over a wider temperature range, −70 to +30 °C. The original range was −70 to −10 °C only. The new measurements were done in part with the same and other similar viscometer, and in part with sealed Ostwald viscometers. The experimental details are as described (*1*).

The results are listed in Table I. The new set of constants to fit the Fulcher equation to all our data are $A = 1.635$, $B = 203.2$, and $T_0 = 69.87$ K and the relative standard error of estimate for viscosity over the range −70 to +30°C is 0.18%.

Table I. Viscosity of Methylamine at Various Temperatures[a]

t, °C	η, cP	t, °C	η, cP	t, °C	η, cP
29.3	0.173	−14.8	0.283	−45.2	0.445
27.2	0.176	−15.2	0.281	−50.1	0.486
24.8	0.179	−18.1	0.295	−50.6	0.495
22.1	0.184	−20.1	0.301	−50.7	0.494
18.5	0.190	−24.6	0.381	−55.3	0.541
15.5	0.196	−25.2	0.319	−58.4	0.582
12.5	0.202	−27.4	0.337	−60.2	0.605
10.1	0.206	−30.2	0.350	−60.7	0.614
9.9	0.206	−32.0	0.358	−65.2	0.681
7.7	0.212	−35.2	0.375	−66.8	0.713
5.4	0.217	−37.4	0.385	−68.0	0.740
0.1	0.231	−40.1	0.405	−68.8	0.755
−9.6	0.256	−42.7	0.425	−70.7	0.805
−10.1	0.266	−44.1	0.437		

[a] Pressure is 1 atm in hydrogen for all the data at temperatures below −15 °C, and the vapor pressure of methylamine at the higher temperatures.

Literature Cited

(1) R. C. Makhija and R. A. Stairs, *Can. J. Chem.*, **48**, 1214 (1970). (N.B.: p 1217, column 2, line 7; the two negative signs should be deleted.)
(2) G. S. Fulcher, *J. Am. Ceram. Soc.*, **8**, 339 (1925).

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Gas–Liquid Equilibrium in Mixtures of Methane plus 9,10-Dihydrophenanthrene at Elevated Temperatures and Pressures

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Gas–liquid equilibrium in mixtures of methane and 9,10-dihydrophenanthrene was studied at four temperatures from 190 to 430 °C in a flow apparatus. The pressures of the measurements were from 20 to 250 atm at each of the three lower temperatures and to 150 atm at the highest temperature.

Introduction

Gas–liquid equilibrium data on mixtures of light gases and heavy hydrocarbon solvents are of industrial and technological interest. Information on the solubility of the gases in the saturated liquid and the concentration of oil vapor in the saturated gas is needed for process design and analysis. The needed information in some form of correlation must be developed from experimental data.

Experimental information is extremely scarce on mixtures of heavy aromatic hydrocarbons containing more than two rings. Sebastian et al. (*1*) reported gas–liquid equilibrium data on hydrogen plus 9,10-dihydrophenanthrene. Lee-Bechtold et al. (*2*) studied thermodynamic properties of 9,10-dihydrophenanthrene (abbreviated as NTDP from here on) at temperatures up to 145 °C. No previous study for the present mixture system has been reported in the literature.

Experimental Section

The experimental apparatus and procedure of this study were described by Simnick and co-workers (*3*). A minor change has been made in the apparatus with the addition of a Heise gauge (Model CMM) which reads pressures below 34 atm to an increased accuracy of ±0.03 atm.

Methane gas was supplied by Matheson with a minimum purity of 99%. NTDP was purchased from Aldrich Chemical Co. and from Columbia Co. with a reported purity of 97%. It was further purified before use by zone refining to a purity of 99+% as determined from gas-chromatographic analysis.

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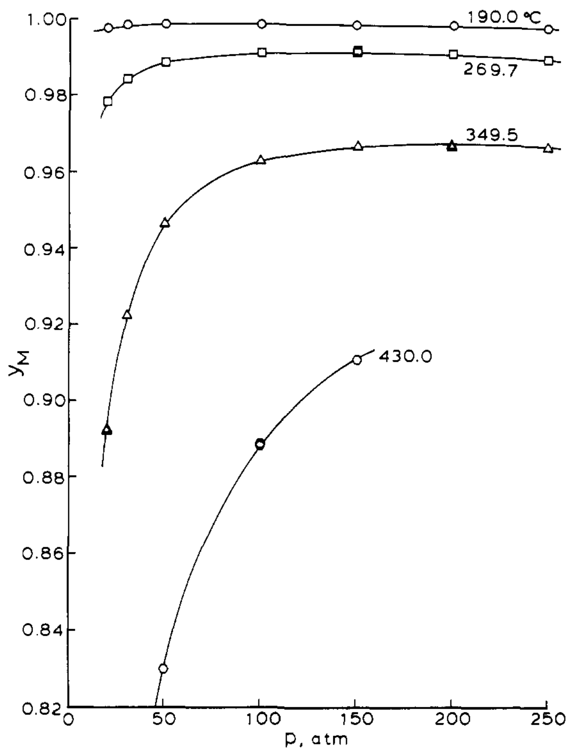

Figure 1. Mole fraction of methane in the saturated vapor of methane plus 9,10-dihydrophenanthrene mixtures.

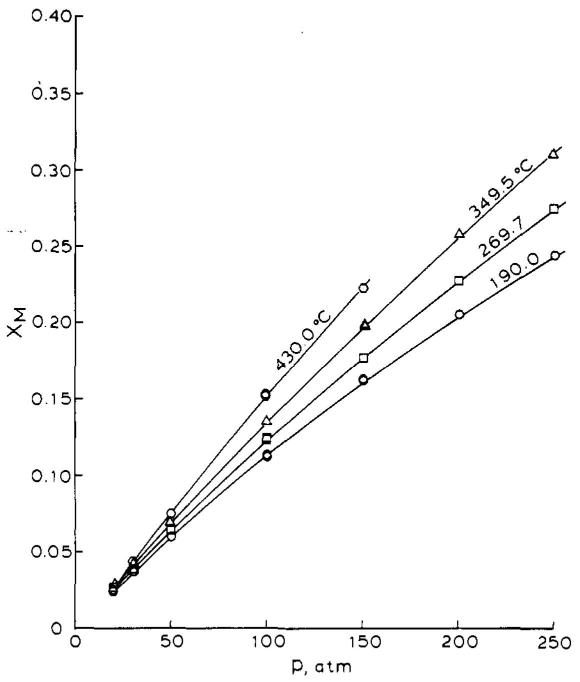

Figure 2. Solubility of methane in 9,10-dihydrophenanthrene liquid.

Condensates of cell effluents were collected from all experiments and analyzed by gas chromatography with a flame ionization detector. No significant products from chemical reactions were detected at the three lower temperatures studied. However, at the highest temperature, phenanthrene was found in the samples to the extent of 1~3% at the lower pressures and up to ~5% at 150 atm. The experiment was thus discontinued at this pressure. We report the data at 430 °C in spite of the known chemical changes in the belief that equilibrium conditions are not substantially altered in view of the closely similar properties of NTDP and phenanthrene. It is nevertheless clear that the data at 430 °C are less accurate.

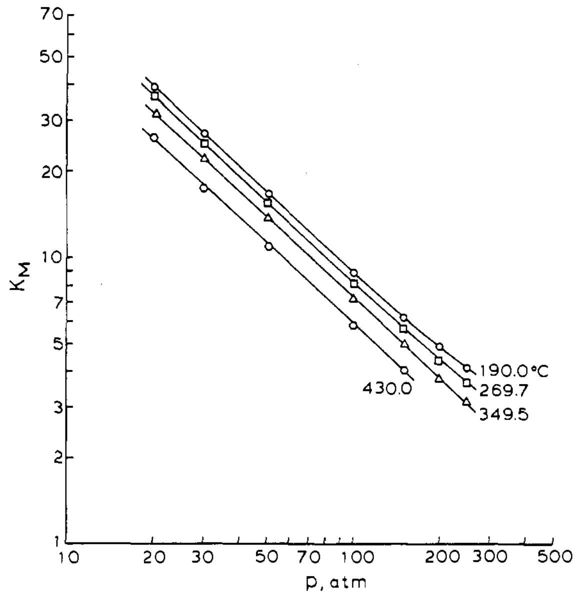

Figure 3. *K* values of methane.

Table I. Methane plus 9,10-Dihydrophenanthrene Vapor-Liquid Equilibrium Data

p, atm	x_M	y_M	K_M	K_D
		190.0 °C		
20.09	0.0255	0.99760	39.12	0.002 46
30.22	0.0371	0.99834	26.91	0.001 72
50.5	0.0600	0.99884	16.65	0.001 23
99.6	0.1132	0.99871	8.82	0.001 45
150.3	0.1628	0.99849	6.13	0.001 80
200.3	0.2058	0.99806	4.85	0.002 44
250.0	0.2445	0.99757	4.08	0.003 22
		269.7 °C		
20.04	0.0268	0.9781	36.50	0.022 50
30.18	0.0396	0.9841	24.85	0.016 56
50.2	0.0642	0.9886	15.40	0.012 18
99.8	0.1227	0.9912	8.08	0.010 03
150.1	0.1768	0.9914	5.61	0.010 45
199.9	0.2278	0.9908	4.35	0.011 91
249.7	0.2744	0.9893	3.61	0.014 75
		349.5 °C		
20.45	0.0284	0.8925	31.43	0.110 6
30.19	0.0421	0.9224	21.91	0.081 0
49.9	0.0693	0.9461	13.65	0.057 9
100.0	0.1353	0.9629	7.12	0.042 9
150.7	0.1972	0.9665	4.90	0.041 7
200.1	0.2576	0.9666	3.75	0.045 0
249.2	0.3115	0.9643	3.10	0.051 9
		430.0 °C		
20.04	0.0252	0.6623	26.28	0.346 4
30.01	0.0429	0.7477	17.43	0.263 6
50.5	0.0763	0.8301	10.88	0.183 9
99.7	0.1537	0.8889	5.78	0.131 3
150.7	0.2246	0.9105	4.05	0.115 4

Results

Figures 1 and 2 show the compositions of the saturated vapor and liquid phases, respectively, at four temperatures from 190 to 430 °C as a function of pressure. The measurements were made at seven pressures from 20 to 250 atm at each temperature except the highest where the pressures were measured up to 150 atm.

At least two samples were taken at a fixed condition of temperature and pressure for both *x* and *y*. The duplicate points plotted in the figures represent the individual samples when they can be distinguished. The reproducibility of the multiple samples is within 1% in mole fraction of methane. The average values