One use of this type of data is to check correlations. The present data have been used to check the Chao–Seader (*4*) and Grayson–Streed (*7*) correlations. The Chao–Seader correlation represents the K values of methane in methane + n-decane with an absolute average deviation of 14%. The deviation is the largest at the highest temperature. The average error of K_M for the three lower isotherms is less than 8%. The K values of n-decane are correlated to within 11%. For methane + benzene mixtures Chao–Seader represents the K values of both components with an average deviation of 8%. For methane + toluene mixtures we find an average error of 8% for methane and 15% for toluene. The Grayson–Streed correlation gives much larger deviations for methane but slightly smaller deviations for the solvents.

Glossary

K	vaporization equilibrium ratio $\equiv y/x$
p	pressure, atm
t	temperature, °C
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Subscripts

B	benzene
M	methane
D	n-decane
T	toluene

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Gas–Liquid Equilibrium in Binary Mixtures of Methane with Tetralin, Diphenylmethane, and 1-Methylnaphthalene

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Compositions of saturated equilibrium liquid and vapor phases are determined in a flow apparatus for mixtures of methane + tetralin at 190, 270, 350, and 390 °C and for methane + diphenylmethane and methane + 1-methylnaphthalene at 190, 270, 350, and 430 °C. The pressure extends to 250 atm or near the criticals of the mixtures, starting from 20 atm or from above the vapor pressure of the solvent.

Introduction

There is a scarcity of experimental information on the equilibrium phase behavior of mixtures of methane + heavy aromatic hydrocarbons at conditions of elevated temperatures and pressures. Such information on the saturated liquid represents solubility data of methane in the heavy solvents, and the data on the saturated vapor give dew point information. Both types of information are needed for process design and analysis.

In this work we determine the compositions of saturated equilibrium liquid and vapor phases of binary mixtures of methane with tetralin, diphenylmethane, and 1-methylnaphthalene, respectively. No previous data on mixtures of methane + tetralin have been reported. Henry constants for methane in diphenylmethane and in 1-methylnaphthalene were measured by Chappelow and Prausnitz (*1*) at 25–200 °C. The dew points of the same two systems were recently studied by Kaul and Prausnitz (*2*) at 50–170 °C and 9–80 atm. Stepanova (*6*) reported the solubility of methane in 1-methylnaphthalene at 0–60 °C at low pressures.

Experimental Section

The experimental apparatus and procedure of this study have been described (*4*).

The equilibrium temperature is measured by a chromel–alumel thermocouple that has been calibrated against a National Bureau of Standards certified platinum resistance thermometer. The temperatures are accurate to ±0.1 °C. Pressures above 30 atm are measured by a Heise gauge that reads pressures up to 340 atm. Lower pressures are measured by a Heise gauge that reads pressures up to 34 atm. Both gauges are accurate to ±0.1% of full scale.

Since our apparatus is of the flow type we have paid attention to the attainment of equilibrium in the apparatus. We have made several tests and all gave positive results to within the uncertainty of the experiments (*3–5, 7*).

Methane gas was obtained from Matheson with a minimum purity of 99%. The hydrocarbon solvents were all purchased

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Table I. Methane + Tetralin Gas-Liquid Equilibrium Data

p, atm	x_M	y_M	K_M	K_T
		188.7 °C		
20.71	0.0310	0.9634	31.08	0.0378
30.58	0.0483	0.9735	20.16	0.0278
49.63	0.0772	0.9809	12.71	0.0207
99.10	0.1494	0.9841	6.59	0.0187
149.6	0.2174	0.9835	4.52	0.0211
199.3	0.2822	0.9801	3.47	0.0277
247.6	0.3397	0.9761	2.87	0.0362
		269.6 °C		
20.03	0.0293	0.8112	27.69	0.1945
30.03	0.0464	0.8628	18.59	0.1439
49.96	0.0787	0.9064	11.52	0.1016
100.1	0.1613	0.9303	5.77	0.0831
149.0	0.2379	0.9335	3.92	0.0873
198.5	0.3151	0.9304	2.95	0.1016
250.0	0.3918	0.9183	2.34	0.1343
		350.0 °C		
30.56	0.0383	0.5477	14.30	0.470
50.09	0.0806	0.6917	8.58	0.335
99.56	0.1805	0.7757	4.30	0.274
149.8	0.2793	0.7995	2.86	0.278
198.6	0.3915	0.7883	2.01	0.348
223.1	0.4732	0.7415	1.57	0.491
		391.4 °C		
49.84	0.0741	0.4950	6.68	0.545
99.17	0.1934	0.6128	3.17	0.480
148.8	0.3514	0.5593	1.59	0.680
155.8	0.3615	0.4191	1.16	0.910

Table II. Methane + Diphenylmethane Gas-Liquid Equilibrium Data

p, atm	x_M	y_M	K_M	K_D
		189.3 °C		
19.89	0.0335	0.9893	29.53	0.011 07
30.10	0.0493	0.9933	20.15	0.007 05
49.83	0.0792	0.9949	12.56	0.005 54
99.23	0.1508	0.9953	6.60	0.005 53
149.3	0.2139	0.9947	4.65	0.006 74
200.0	0.2731	0.9938	3.64	0.008 53
249.7	0.3235	0.9918	3.07	0.012 12
		269.0 °C		
19.83	0.0339	0.9350	27.58	0.0673
30.24	0.0516	0.9533	18.47	0.0492
49.97	0.0848	0.9661	11.39	0.0370
98.83	0.1636	0.9753	5.96	0.0295
149.9	0.2339	0.9759	4.17	0.0315
196.8	0.2992	0.9738	3.25	0.0374
248.7	0.3618	0.9700	2.68	0.0470
		350.5 °C		
19.83	0.0320	0.7290	22.78	0.280
30.04	0.0519	0.8029	15.47	0.208
49.84	0.0912	0.8673	9.51	0.1460
99.65	0.1845	0.9059	4.91	0.1154
149.2	0.2679	0.9156	3.42	0.1153
199.5	0.3535	0.9127	2.58	0.1350
249.7	0.4388	0.9001	2.05	0.1780
		429.7 °C		
30.51	0.0448	0.4407	9.83	0.586
49.83	0.0961	0.5982	6.22	0.445
100.3	0.2228	0.7132	3.20	0.369
150.4	0.3576	0.7230	2.02	0.431

Table III. Methane + 1-Methylnaphthalene Gas-Liquid Equilibrium Data

p, atm	x_M	y_M	K_M	K_{MN}
		191.0 °C		
20.74	0.0281	0.9858	35.08	0.014 61
31.02	0.0411	0.9891	24.07	0.011 37
50.24	0.0651	0.9915	15.23	0.009 09
99.16	0.1254	0.9928	7.92	0.008 23
150.9	0.1803	0.9922	5.50	0.009 52
199.4	0.2322	0.9906	4.27	0.012 24
247.6	0.2787	0.9884	3.55	0.016 08
		270.4 °C		
20.38	0.0275	0.9071	32.99	0.0955
30.55	0.0421	0.9317	22.13	0.0713
50.32	0.0697	0.9526	13.67	0.0510
99.99	0.1360	0.9648	7.09	0.0407
149.3	0.1992	0.9664	4.85	0.0420
200.0	0.2598	0.9643	3.71	0.0482
248.0	0.3184	0.9603	3.02	0.0582
		351.3 °C		
20.23	0.0246	0.6463	26.27	0.363
30.55	0.0408	0.7476	18.32	0.263
50.66	0.0746	0.8252	11.06	0.1889
100.40	0.1512	0.8784	5.81	0.1433
149.0	0.2275	0.8892	3.91	0.1434
199.2	0.3045	0.8917	2.93	0.1557
247.7	0.3798	0.8777	2.31	0.1972
		430.8 °C		
30.07	0.0286	0.3523	12.32	0.667
50.24	0.0716	0.5215	7.28	0.515
100.25	0.1797	0.6603	3.67	0.414
148.8	0.2951	0.6750	2.29	0.461
172.9	0.3724	0.6481	1.74	0.561
181.3	0.4016	0.6429	1.60	0.597
185.7	0.4544	0.6341	1.395	0.671

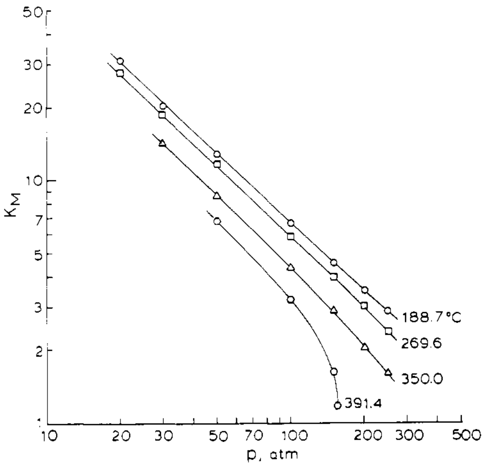

Figure 1. *K* value of methane in methane + tetralin.

from Aldrich Chemical Co. with reported purities of 99% for tetralin and diphenylmethane and 97% for 1-methylnaphthalene. The purchased 1-methylnaphthalene was purified by vacuum fractional distillation under nitrogen before use. Samples of the condensate from the cell effluents of both gas and liquid streams of all the runs were analyzed by gas chromatography. No impurities from thermal decomposition were detected. Samples of gas from the cell effluents of some runs were analyzed by gas chromatography to check the possible presence of decomposition products such as hydrogen. Only negative results were obtained.

Results

Experimental equilibrium data are presented in Table I for the methane + tetralin system at four temperatures from 188.7 to 391.4 °C and at pressures up to 250 atm. Each value of composition in the table is the mean of two or three samples. The reproducibility of the duplicate samples is generally within

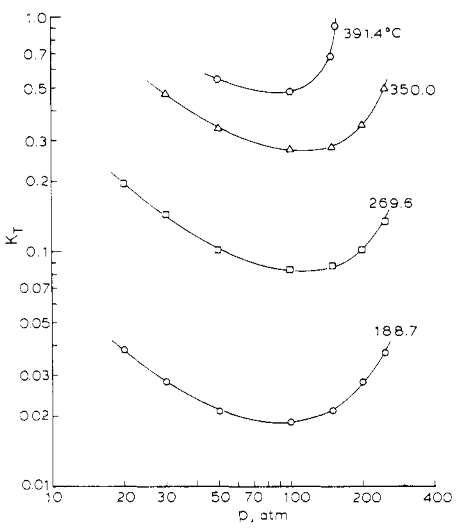

Figure 2. *K* value of tetralin.

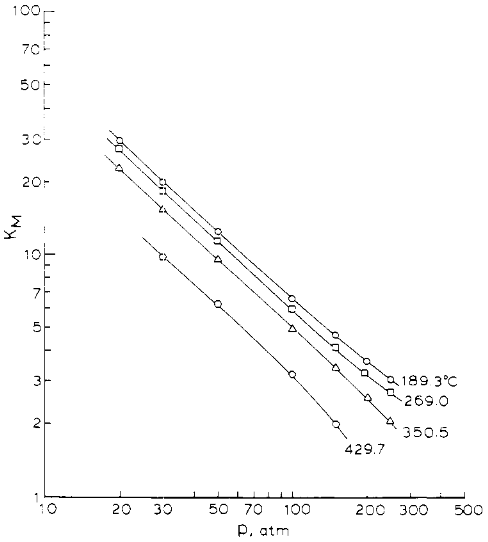

Figure 3. *K* value of methane in methane + diphenylmethane.

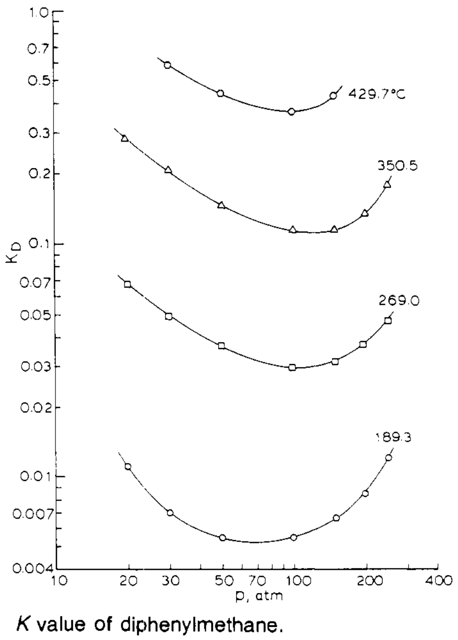

Figure 4. *K* value of diphenylmethane.

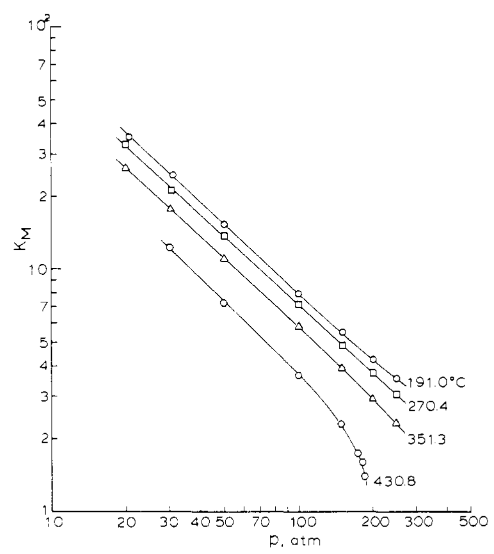

Figure 5. *K* value of methane in methane + 1-methylnaphthalene.

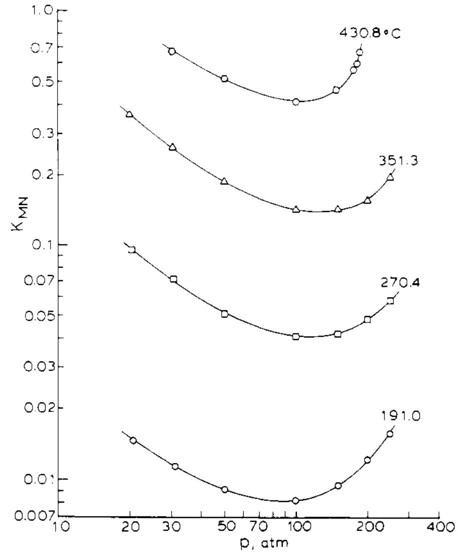

Figure 6. *K* value of 1-methylnaphthalene.

2%. The averaged values of *x* and *y* were then used to compute the vaporization equilibrium ratios $K \equiv y/x$. Isothermal *K* values as a function of total pressure are shown in Figure 1 for methane and Figure 2 for tetralin. An abrupt change of slope of the *K*-value isotherm is observed in the high-pressure region at the highest temperature, indicating approach to the critical state of the mixture.

Table II presents the experimental results for methane + diphenylmethane in the temperature range 189.3–429.7 °C. The equilibrium ratios are shown in Figures 3 and 4. For methane + 1-methylnaphthalene, the data are reported in Table III at four temperatures from 191.0 to 430.8 °C and the *K* values are shown in Figures 5 and 6. Measurements were made at seven pressures from 20 to 250 atm for the three lower temperatures. At the highest temperatures, the lower pressure limit of our measurement was controlled by the vapor pressure of the solvent and the higher pressure limit by the impending critical state of the mixture. These limits are different from one system to the other.

Glossary

K	vaporization equilibrium ratio $\equiv y/x$
p	pressure, atm
t	temperature, °C
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Subscripts

M	methane
D	diphenylmethane
MN	1-methylnaphthalene
T	tetralin

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NEW COMPOUNDS

Syntheses of Trans Alken-1-ols as Candidates for Insect Sex Attractants

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The syntheses of 21 acetylenic alcohols of the general formula $CH_3(CH_2)_mC{\equiv}C(CH_2)_nOH$, where m = 0–6 and n = 3–6, 8–11, were accomplished by both solution and solid-phase methods. Conversion of the acetylenic alcohols to the geometrically pure trans alken-1-ols was done. The IR and NMR spectra and some physical properties of the alkynols and alkenols are given.

Studies directed toward the determination of the insect sex attractants of a host of forest and orchard pests (*1*) have led to the synthesis (*2–4*) of a large number of candidate pheromones suitable for field testing and laboratory assays. Most of the alkynols and trans alkenols described herein were previously unknown or incompletely characterized.

Alkynols **4–11** were prepared by our solid-phase method (*5–8*) (method I) and alkynols **14–26** by previously reported solution methods (*9*) (method II). In method I, polymer-bound diol monomesylates (**1**, n = 4, 6, 8, 9) [Ⓟ-Tr- represents a 2% divinylbenzene–styrene copolymer containing trityl groups] react with 1-lithioalkynes (**2**, m = 0–4, 6) [or with lithioacetylide and alkyl halide treatment in a two-step reaction (*7*)] to give the polymer-bound alkynes (**3**, m = 0–4, 6; n = 4, 6, 8, 9). Cleavage of **3** with acid yielded alkynols **4–11**, respectively (Scheme I). In method II, tetrahydropyranyl (THP) ethers of ω-bromo- or ω-chloroalkanols (**12**, X = Br, Cl; n = 3–6, 10, 11) react with 1-lithio-1-alkynes (**2**, m = 1–5) to give the tetrahydropyranyl ethers of the alkynols (**13**, m = 1–5; n = 3–6, 10, 11) which on acid hydrolysis yield alkynols **14–26**. The alkynols **4–11** and **14–26** were converted to their tetrahydropyranyl ethers where necessary, reduced with sodium in liquid ammonia and THF (*9*, *10*), and treated with acid to give exclusively the trans alkenols (**27–47**) (Scheme I). The geometrical purities of **27–47** were confirmed by vapor-phase chromatography (VPC) and high-pressure liquid chromatography (LC). Trans alkenols **28**, **37**, **39**, and **41** were converted to their acetates **28a**, **37a**, **39a**, and **41a**, respectively. Previous syntheses of sex attractants on solid phases yielded millimole quantities of attractants. We describe here the scaled up synthesis on solid phases of gram quantities of sex attractants in a modified procedure (method I). The physical and spectral properties of **4–11**, **14–26**, **27–47**, **28a**, **37a**, **39a**, and **41a** are recorded in Tables I–V, respectively.

Experimental Section

A Bausch and Lomb Abbê 3L refractometer was used to record the refractive indices. Infrared spectra were recorded on a Unicam SP1000 IR spectrophotometer as neat films between NaCl disks unless otherwise specified. Nuclear magnetic resonance spectra were recorded on a Varian EM360 spectrometer using deuteriochloroform as solvent and tetramethylsilane as internal standard.

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