the diffusivity decreases very rapidly as concentration increases in the dilute region, but becomes much less dependent on concentration in the concentrated region.

Refractive indices of nickel ammonium sulfate solutions were measured at 25° C. with an Abbé refractometer. The instrument was capable of measuring refractive index with a precision of ±0.00005 (Table II).

Densities were determined by the density bottle method, as described by Findlay (*1*), over the temperature range 10° to 35° C. The precision of these measurements (*1*) is estimated to be ±0.1%.

Viscosities of the solutions were measured with an Ostwald viscometer, as described by Findlay (*1*), over the temperature range 10° to 35° C. The estimated precision is ±0.3%. The density and viscosity results are recorded in Table III.

The solubility of nickel ammonium sulfate in water was measured over the temperature range 10° to 49° C. by approaching equilibrium from the under- and oversaturated states. The solutions contained in stoppered flasks were immersed in a thermostatically controlled bath (±0.1° C.) and shaken at intervals over 48 hours. Samples were withdrawn through a filter and their concentrations determined by measuring the density at a temperature about 5° above the saturation temperature.

The results (Table IV) do not agree very well with those recorded in the handbooks (*2, 5*) or with the early work of Tobler (*6*). It is, of course, difficult to explain differences between results from various sources without knowledge of the techniques used, but certain comments can be made. Two of the references (*2, 5*) are data handbooks, one of which (*2*) quotes no literature source. Neither gives any experimental detail. The work of Tobler (*6*) makes no mention of the purity of the salt or solvent, and saturation was approached only from the undersaturated state. The present investigation has shown that up to 48 hours is needed to approach equilibrium.

The detailed measurements of solubility in the range 37.5° to 49° C. were made in an attempt to detect any possible phase change. None was found in this region.

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Vapor-Liquid Equilibria of the Methane-Toluene System at Low Temperatures and High Pressures

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The system methane-toluene exhibits limited liquid-liquid miscibility at temperatures below the critical for methane. A quadruple point involving the two immiscible liquids, a solid phase, and a gas phase has been located visually at −149.7° F. and 358 p.s.i.a. Experimental data shown on the pressure-temperature projections permit one to classify the system as one with a Type *K* critical point and one with qualitatively similar behavior in all respects to the methane-heptane system. Experimental techniques were developed to sample and analyze with good precision the equilibrium gas phases containing as little as 0.001 mole % toluene. Thus, toluene *K* values as low as 2×10^{-5} can be reported with confidence. Binary *K* values for methane and toluene are reported at intervals of 20° from 0° to − 100° F. for pressures from 100 to 3500 p.s.i.a. The results are reported numerically and illustrated graphically.

STUDIES on the low temperature phase behavior of the methane-*n*-paraffin binaries have appeared since the review of the vapor-liquid equilibria of light hydrocarbons by Price and Kobayashi (*9*). The equilibrium ratios and the low temperature phase behavior of the methane-*n*-hexane (*8*), methane-*n*-heptane (*2, 6*), methane-*n*-octane (*7*), methane-*n*-nonane (*11*), and methane-*n*-decane (*12*) systems have been investigated in the last few years. There are very few reports made on the study of methane-aromatic and methane-naphthenic systems up to the present time. Elbishlawi and Spencer (*5*) reported vapor-liquid equilibrium ratios of methane-toluene and methane-benzene systems at 150° F. in 1951. Sabbina and Velikovski (*10*) reported some results for the methane-toluene system from 40° to 150° C. in 1956. Clark (*4*) studied methane-cyclohexane and methane-methylcyclohexane at 150° F. in 1949. The methane-cyclohexane system has also been reported by Stepanov and Vybornov (*13*) at temperatures from 32° to 140° F.

The objectives of this study were to: obtain vapor-liquid equilibria data on the methane-toluene system which could be related to the methane-*n*-heptane (*2*) and methane-methylcyclohexane systems (*3*) recently studied, all systems with a different solvent type of the same carbon number; and provide basic data on binary systems which would

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Table I. Observed Three- and Four-Phase Conditions of the Methane–*n*-Heptane, Methane-Methylcyclohexane, and Methane-Toluene Systems

	Methane–*n*-Heptane		Methane-Methylcyclohexane		Methane-Toluene	
Phases	*T*, ° F.	*P*, p.s.i.a.	*T*, ° F.	*P*, p.s.i.a.	*T*, ° F.	*P*, p.s.i.a.
L_1L_2G	...	...	...	...	-117.0	650
L_1L_2G	-126.0	570	-155.0	318	-125.0	570
L_1L_2G	-130.0	519	-177.5	190	-131.0	502
L_1L_2G	-140.0	435	-194.0	125	-139.0	443
L_1SG	-136.7	155	-207.0	50	-142.5	144
L_1SG	-139.5	98	-209.5	65	-143.5	203
L_2SG	...	...	-216.0	66	...	...
L_2SG	...	...	-223.0	53	-168.6	246
L_1L_2S	...	...	-213.5	100	...	...
L_1L_2S	...	...	-214.0	400	...	...
L_1L_2SG	-154.2	331	-213.5	73	-149.7	358
K_{sing}[a]	-114.7	694	-113.8	687	-115.9	671

[a] K_{sing} = Type *K* singular point.

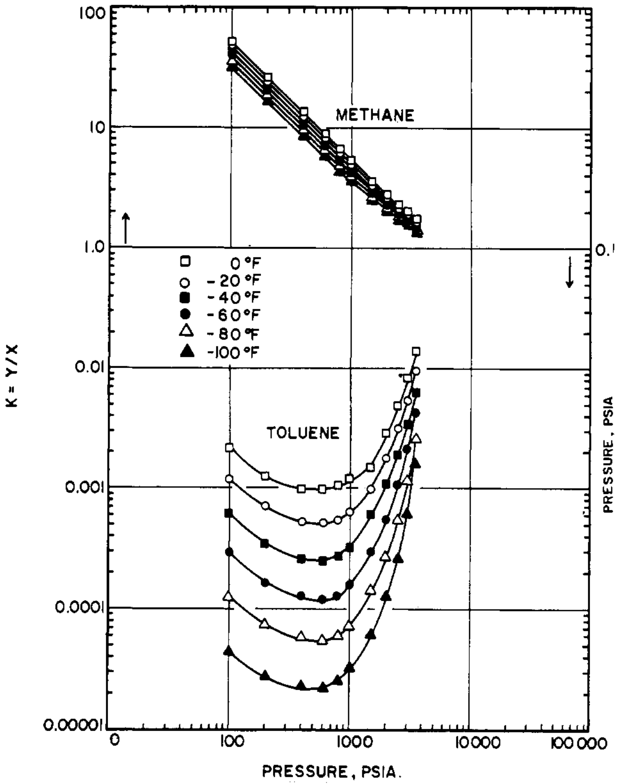

Figure 1. *K* value vs. pressure for methane-toluene system

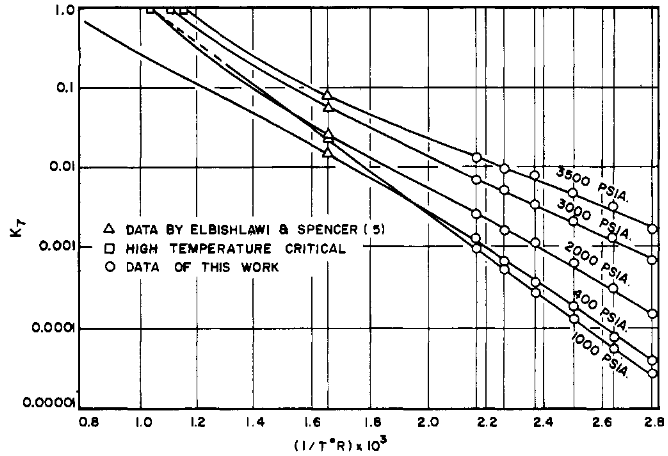

Figure 2. *K* value of toluene vs. 1/*T* for the methane-toluene system

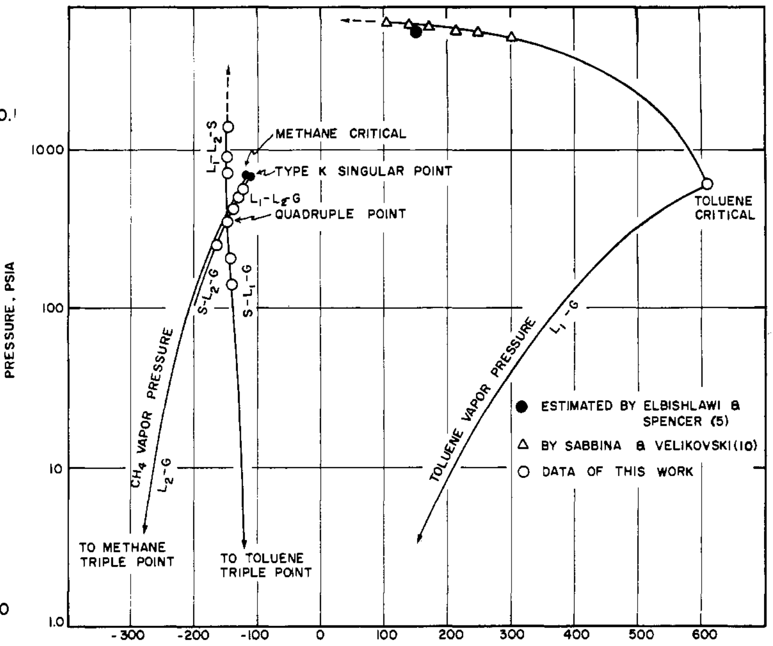

Figure 3. Pressure-temperature projection for the methane-toluene system

serve as a basis for multicomponent vapor-liquid equilibrium studies at both infinitesimal and finite concentrations of the intermediate components by gas-liquid partition chromatography methods.

PHASE BEHAVIOR IN THE METHANE-TOLUENE BINARY

As previously noted (*2*) the binary phase behavior of methane with other *n*-paraffin hydrocarbons through *n*-decane offers three types of phase behavior: complete liquid phase miscibility, limited liquid phase miscibility, and intersection of the solubility curve with the critical locus. This study showed that the low temperature phase behavior of the methane-toluene system falls in the middle category and is quite similar to the methane–*n*-heptane binary system, which is characterized by liquid-liquid

Table II. Vapor-Liquid Equilibrium Data for the Methane-Toluene System

P, P.S.I.A.	y_7	x_7	K_1	K_7	P, P.S.I.A.	y_7	x_7	K_1	K_7
		0.0° F.					−60.0° F.		
100.0	0.0021	0.9807	51.75	0.00215	100.0	0.00030	0.9749	39.80	0.00029
200.0	0.0012	0.9610	26.00	0.00122	200.0	0.00017	0.9501	20.00	0.00018
400.0	0.0009	0.9260	13.20	0.00097	400.0	0.00011	0.9028	10.30	0.00013
600.0	0.0009	0.8880	8.92	0.00097	600.0	0.00010	0.8575	7.00	0.00012
800.0	0.0009	0.8505	6.68	0.00105	800.0	0.00010	0.8080	5.25	0.00013
1000.0	0.0010	0.8139	5.36	0.00121	1000.0	0.00012	0.7672	4.25	0.00016
1250.0	0.0010	0.7770	4.48	0.00135	1250.0	0.00015	0.7160	3.51	0.00021
1500.0	0.0011	0.7340	3.75	0.00150	1500.0	0.00019	0.6700	3.00	0.00029
1750.0	0.0014	0.6960	3.28	0.00204	1750.0	0.00025	0.6240	2.62	0.00040
2000.0	0.0018	0.6500	2.85	0.00284	2000.0	0.00032	0.5802	2.36	0.00055
2500.0	0.0027	0.5670	2.30	0.00480	2500.0	0.00052	0.5021	2.00	0.00105
3000.0	0.0041	0.5050	2.01	0.00810	3000.0	0.00089	0.4330	1.75	0.00210
3500.0	0.0063	0.4600	1.84	0.0137	3500.0	0.00160	0.3749	1.58	0.00430
		−20.0° F.					−80.0° F.		
100.0	0.0012	0.9791	47.82	0.00119	100.0	0.00012	0.9713	34.90	0.00012
200.0	0.0007	0.9590	24.43	0.00070	200.0	0.00007	0.9449	18.14	0.00007_4
400.0	0.0005	0.9185	12.25	0.00052	400.0	0.00005	0.8939	9.40	0.00005_8
600.0	0.0004	0.8789	8.25	0.00050	600.0	0.00005	0.8395	6.30	0.00005_5
800.0	0.0004	0.8391	6.20	0.00054	800.0	0.00005	0.7949	4.88	0.00006_0
1000.0	0.0005	0.8011	5.00	0.00064	1000.0	0.00006	0.7490	3.99	0.00007_3
1250.0	0.0006	0.7535	4.10	0.00080	1250.0	0.00007	0.6946	3.27	0.00010
1500.0	0.0007	0.7100	3.42	0.00099	1500.0	0.00009	0.6465	2.80	0.00014
1750.0	0.0009	0.6700	3.00	0.00137	1750.0	0.00011	0.5985	2.49	0.00019
2000.0	0.0011	0.6350	2.71	0.00173	2000.0	0.00015	0.5500	2.21	0.00027
2500.0	0.0017	0.5550	2.21	0.00315	2500.0	0.00025	0.4700	1.88	0.00054
3000.0	0.0026	0.4900	1.91	0.0053	3000.0	0.00045	0.3988	1.66	0.00113
3500.0	0.0041	0.4350	1.70	0.0095	3500.0	0.00087	0.3381	1.50	0.00258
		-40.0° F.					−100.0° F.		
100.0	0.0006	0.9770	43.06	0.00061	100.0	0.00004	0.9678	31.05	0.00004_5
200.0	0.0003	0.9548	22.12	0.00037	200.0	0.00003	0.9379	16.10	0.00003_0
400.0	0.0002	0.9133	11.53	0.00026	400.0	0.00002	0.8816	8.44	0.00002_3
600.0	0.0002	0.8704	7.70	0.00025	600.0	0.00002	0.8249	5.70	0.00002_3
800.0	0.0002	0.8271	5.78	0.00027	800.0	0.00002	0.7721	4.39	0.00002_6
1000.0	0.0002	0.7850	4.65	0.00032	1000.0	0.00002	0.7255	3.62	0.00003_2
1250.0	0.0003	0.7372	3.80	0.00045	1250.0	0.00003	0.6699	3.10	0.00004_3
1500.0	0.0004	0.6901	3.23	0.00060	1500.0	0.00004	0.6168	2.60	0.00006_0
1750.0	0.0005	0.6460	2.82	0.00080	1750.0	0.00005	0.5650	2.26	0.00008_7
2000.0	0.0006	0.6049	2.51	0.00107	2000.0	0.00006	0.5180	2.04	0.00012
2500.0	0.0010	0.5350	2.15	0.00186	2500.0	0.00011	0.4290	1.75	0.00026
3000.0	0.0016	0.4685	1.88	0.00337	3000.0	0.00021	0.3551	1.55	0.00060
3500.0	0.0026	0.4180	1.71	0.00632	3500.0	0.00045	0.2924	1.40	0.00160

immiscibility and a quadruple point involving the coexistence of four phases. The four three-phase lines emanating from the quadruple point are L_1-L_2-S, L_1-L_2-G, L_1-S-G, and L_2-S-G. The $L_2 \equiv G$ critical locus runs from the critical of pure toluene to the "three phase critical" in which $L_1 \equiv L_2$ with solid toluene present. A study of the phase behavior indicated that the $L_2 \equiv G$ critical locus is higher in pressure than would be the case if the critical locus proceeded from the critical point of pure toluene to the critical point of pure methane. Also, the critical locus of the methane-toluene system is much higher than the methane–*n*-heptane system, but the low temperature phase behavior of these two systems is qualitatively similar. The higher critical pressures can be explained qualitatively by the difference in vapor pressure of *n*-heptane and toluene and the positive deviation from ideal solution laws exhibited by the methane-aromatic system.

Comparisons of the observed three- and four-phase conditions of the methane-toluene system with the methane–*n*-heptane and methane-methylcyclohexane systems are shown in Table I. The Type K singular points for the three systems are quite close, but the quadruple point of the methane-methylcyclohexane system is far below the other two systems. An explanation of these phenomena is presented elsewhere (*3*).

EXPERIMENTAL

The experimental equipment, an error analysis, and the analytical techniques have been described by Chang *et al.* (*2*). The equipment is discussed in detail by Chang (*1*). The error analysis gave a maximum percentage error in the heavy component to be less than 5% of the amount present.

MATERIALS USED

The methane was purchased from the Matheson Co., Inc., with a certified purity of 99.99 mole %, the toluene was obtained from the Phillips Petroleum Co. with a reported purity of 99.96 mole %. Methane was passed through drying tubes packed with silica gel, activated charcoal, and Ascarite before it was introduced into the equilibrium cell. The toluene was used without further purification.

EXPERIMENTAL RESULTS AND DISCUSSION

Equilibrium measurements were made on a large number of mixtures involving methane and toluene for the temperatures from 0° to −100° F. and pressures from 100 to about 3500 p.s.i.a. Table 1 presents a comparison of the observed three- and four-phase conditions of the methane-toluene and methane-n-heptane and methane-methylcyclohexane binaries. Table II presents a complete tabulation of all binary phase compositions and K values determined in this investigation at the experimental conditions. Plots of K value *vs.* pressure for the six isotherms studied are presented in Figure 1. Minimum K values of toluene are at approximately 600 p.s.i.a. as shown in Figure 1. A plot of the K values of toluene *vs.* the reciprocal absolute temperature is shown in Figure 2. The critical locus in Figure 3 is estimated using the toluene critical point and the data of Elbishlawi and Spencer (*5*) and Sabbina and Velikovski (*10*). Great care was taken to have the experimental conditions at even temperature and pressure increments (Table II).

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Vapor-Liquid Equilibria of the Methane-Methylcyclohexane System at Low Temperatures and High Pressures

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The methane-methylcyclohexane system exhibits limited liquid miscibility at temperatures below the critical of methane. A quadruple point involving a gas phase, two liquid phases, and a solid phase has been located visually at −213.5° F. and 73 p.s.i.a. Experimental data on the pressure-temperature projection show that the low temperature phase behavior of this system is qualitatively similar to the methane–n-heptane system with the exception that a minimum point appears in the critical locus. Binary K values of methane and methylcyclohexane are reported at intervals of 20° from 0° to −100° F. for pressures from 100 p.s.i.a. to the critical of the system. The lowest K value of methylcyclohexane determined was 0.000044 at 100 p.s.i.a. and −100° F.

THE EQUILIBRIUM ratio and the low temperature phase behavior of the several methane-n-paraffin binary systems studied in the last few years have recently been reviewed (*2*). There are only a few references on the study of methane-aromatic or methane-naphthenic systems (*7, 8, 11*). The only literature data found for the methane-methylcyclohexane system was the study by Clark (*6*) in 1949.

The objectives of this study were: to obtain vapor-liquid equilibrium data on the methane-methylcyclohexane system over a temperature range comparable with that made for the methane-n-heptane (*4*) and the methane-toluene (*5*) systems—i.e., from 0° to −100° F. inclusive— and to reveal the effect of solvent types on the vapor-liquid equilibrium behavior of these systems; to provide basic data on binary systems which would serve as a basis for subsequent multicomponent vapor-liquid equilibrium studies at both infinitesimal and finite concentrations of the intermediate components both by classical and gas-liquid partition chromatography methods; and to provide basic data to permit theoretical studies on the effects of molecular size and structure of the solvent on the vapor-liquid equilibria behavior of hydrocarbon systems at low temperatures and elevated pressures (*2, 3*).

PHASE BEHAVIOR IN METHANE-METHYLCYCLOHEXANE BINARY SYSTEM

The binary phase behavior of methane with other n-paraffin hydrocarbons through n-decane offers three types of phase behavior: complete liquid phase miscibility, limited liquid miscibility, and the intersection of the three-phase solid-liquid-gas solubility curve locus with the gas-liquid critical locus, which causes an interruption in the latter. This study showed that the low temperature phase behavior of methane-methylcyclohexane system falls in the middle category and is qualitatively similar to methane–n-heptane binary system, which is characterized by liquid-liquid immiscibility and a quadruple point involving the coexistence of four phases, G-L_1-L_2-S. The four three-phase

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