Phase Equilibria Data for Helium–Methane System

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Helium–methane phase equilibria data are presented to 1000 psia for eight isotherms from 124–190.6° K. Data were obtained by a vapor recirculation method and analyzed with a high-precision thermal conductivity analyzer. The slope (*dP/dT*), of the critical curve for helium–methane mixtures leaving the methane critical point is positive. The 190.6° K isotherm is shown to be in the fluid-fluid region.

The data reported here concludes our work on the helium-methane system. Earlier work by Rhodes, DeVaney, and Tully (*5*) on this system for pressures from 1000–3800 psia and temperatures from 94–192° K, verified that helium–methane mixtures exhibit fluid-fluid behavior.

A pure component above its critical temperature is generally referred to as a fluid, rather than a gas or vapor. Even under extreme pressures, where the density can exceed that of the normal liquid, the substance is said to be in a fluid state, because the pressure-volume relationship does not resemble that of a liquid.

For the helium–methane system, the critical temperature of the heavier component is 190.53° K (*3*). At 190.6° K, we observed what appeared to be coexisting vapor and liquid phases, but because of the supercritical temperature, it is more technically correct to refer to this behavior as fluid-fluid equilibria.

In this study, 39 experimental conditions were investigated at temperatures of 124°, 154°, 164°, 174°, 184°, 189°, 190.3°, and 190.6° K for pressures from near the vapor pressure of pure methane to 900 psia. Sinor, Schindler, and Kurata (*7*) investigated six isotherms between 93° and 188° K for pressures to 2000 psia. Heck and Hiza (*2*) investigated seven isotherms at 15° intervals from 95° to 185° K for pressures to 3000 psia. The region studied in the present investigation fills in some of the gaps in earlier works and extends the data into the fluid-fluid region.

EXPERIMENTAL

The experimental apparatus used in this investigation has been described elsewhere (*1*, *8*). Minor modifications to the equipment mentioned in (*5*) also apply in this study. The apparatus consists of an optical beryllium-copper phase cell suspended in a gas bath cryostat controlled at a temperature slightly below that of the experiment. The temperature of the cell is controlled to within 0.001° K during a run.

System pressure was measured with a 0–1000 psia strain-gage pressure transducer. The transducer was calibrated before and after data acquisition with a dead weight piston gage whose accuracy is 0.015% of reading or better, and whose calibration can be traced to NBS. A quadratic least squares regression analysis of the transducer calibrations gave 0.11 and 0.31 psi, respectively, for one standard error of estimate. A shift of about 1 psi was observed between the calibrations.

The temperature of the cell was measured by a platinum resistance thermometer located about ¼ in. from the cell cavity. This thermometer was vendor-calibrated. It was compared with another platinum resistance thermometer which had been recently calibrated by NBS on IPTS-48 and IPTS-68 (*4*), at several temperatures in the range of this study. The largest difference observed was 0.003° K. The constants A_4 and C_4, used in the deviation function for determining temperatures on IPTS-68, were calculated for the thermometer that was used. The temperatures reported in this investigation are on IPTS-68.

The procedures used were essentially the same as used in the helium-nitrogen study reported earlier (*8*). Briefly, the windowed phase cell was cooled below the operating temperature using liquid nitrogen in direct contact with the cell. The cell was warmed to within a few hundredths of a degree of the operating temperature before it was charged. After raising the pressure to the level desired, during which time some liquid (or fluid) was formed, the vapor recirculating pump was started. Two hours were allowed for equilibration. If the pressure of the closed system remained constant, it was assumed that equilibrium had been established. The vapor recirculating pump was blocked-off from the cell, and its contents were analyzed 10 times. The pump was restored to operating pressure before opening it to the cell. The 10 liquid samples were withdrawn while a regulator maintained relatively constant pressure.

Equilibrium phase samples were analyzed for methane with a high-precision thermal conductivity analyzer (*6*), which was calibrated by using 11 weighed primary standards of methane in helium. The standard error of estimate for a cubic least squares fit to the calibration data was 0.02 mol % methane. The analyzer was checked periodically

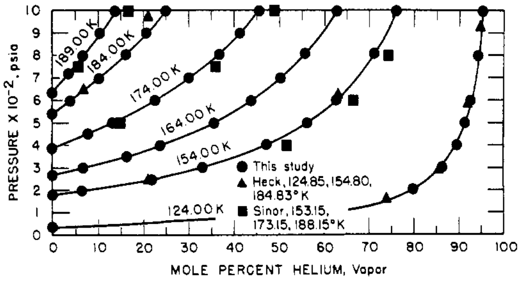

Figure 1. Pressure-composition diagram, vapor phase, helium–methane system

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Table I. Experimental Vapor-Liquid Data for Helium-Methane System

Vapor phase		Liquid phase		Equilibrium ratio	
P, psia	Mol % helium	P, psia	Mol % helium	Helium	Methane
124.00° K					
36.8	0.0	36.8	0.0		1.0
203	79.96	202	0.15	533	0.201
302	86.43	302	0.24	360	0.136
401	89.63	400	0.31	289	0.104
499	91.55	499	0.35	262	0.0848
600	92.82	596	0.44	211	0.0721
798	94.52	796	0.60	158	0.0551
1005[a]	95.44	1001	0.79	121	0.0459
154.00° K					
180.8	0.0	180.8	0.0		1.0
200	6.44	200	0.01	644	0.936
251	21.97	251	0.14	157	0.781
303	33.21	303	0.28	119	0.670
403	47.42	397	0.50	94.8	0.528
501	56.40	496	0.72	78.3	0.439
603	62.85	598	0.98	64.1	0.375
808	71.21	805	1.48	48.1	0.292
1002[a]	76.18	999	1.92	39.7	0.243
164.00° K					
271.3	0.0	271.3	0.0		1.0
303	6.83	303	0.06	114.0	0.932
353	16.43	352	0.26	63.2	0.838
401	23.80	402	0.46	51.7	0.765
501	35.78	500	0.78	45.9	0.647
600	44.04	596	1.08	40.8	0.566
699	50.50	700	1.39	36.3	0.502
808	55.94	808	1.81	30.9	0.449
999[a]	63.00	999	2.38	26.5	0.379
174.00° K					
390.7	0.0	390.7	0.0		1.0
453	7.96	452	0.27	29.5	0.923
501	13.32	501	0.57	23.4	0.872
599	22.74	597	1.05	21.7	0.781
700	30.28	701	1.50	20.2	0.708
174.00° K cont.					
806	36.92	806	2.00	18.5	0.644
901	41.49	902	2.46	16.9	0.600
999[a]	45.80	997	2.91	15.7	0.558
184.00° K					
543.2	0.0	543.2	0.0		1.0
600	3.93	598	0.38	10.3	0.964
701	10.39	700	1.22	8.52	0.907
806	16.26	798	1.96	8.30	0.854
903	20.92	902	2.80	7.47	0.814
999[a]	25.18	1000	3.53	7.13	0.776
186.00° K					
597.7	0.0	597.7	0.0		1.0
700	6.99	700	1.10	6.35	0.941
188.00° K					
617.2	0.0	617.2	0.0		1.0
700	3.98	698	0.88	4.52	0.969
189.00° K					
637.4	0.0	637.4	0.0		1.0
722	3.63	721	1.00	3.63	0.973
801	6.79	800	1.96	3.46	0.951
904	10.64	902	3.16	3.37	0.923
999[a]	13.99	1000	4.29	3.26	0.899
190.30° K					
664.9	0.0	664.9	0.0		1.0
800	4.35	799	2.15	2.02	0.978
903	7.36	901	3.68	2.00	0.962
1000[a]	10.19	998	5.11	1.99	0.946
190.60° K					
801	3.31	802	2.56	1.29	0.992
901	5.96	900	4.29	1.39	0.983
999[a]	8.73	999	5.87	1.49	0.970

[a] Data point from ref. *5*.

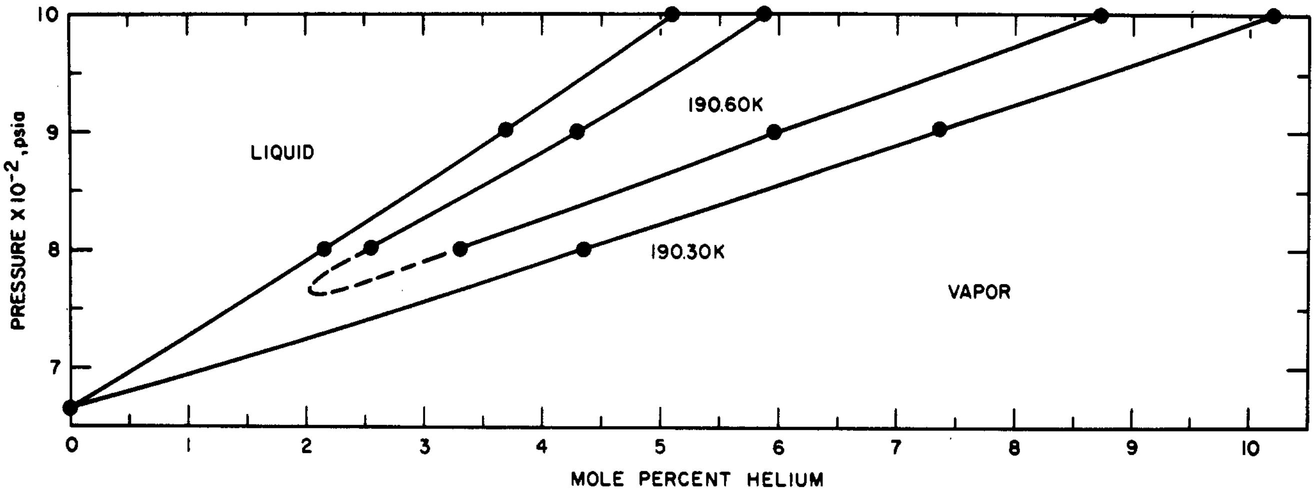

Figure 2. Pressure-composition diagram, helium–methane system

during data acquisition by analyzing one of the standard mixtures. These analyses had a mean that was 0.017 mol % higher in helium than the standard, and a standard deviation of 0.014 mol %.

The methane used in this study was an ultrapure grade being at least 99.99% methane with the impurities being primarily oxygen and nitrogen. The helium used was Bureau of Mines high-purity helium containing less than 10 ppm impurities, the major contaminant being neon. Several mixtures of helium in methane were prepared in compressed gas cylinders. Mixture compositions were adjusted when required to remain inside the dewpoint-bubblepoint locus.

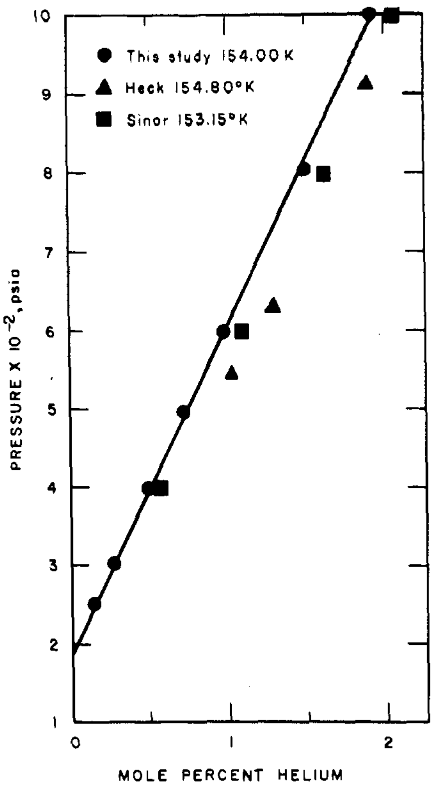

Figure 3. Comparison of Sinor's 153.15° K and Heck's 154.80° K liquid phase data, helium-methane system

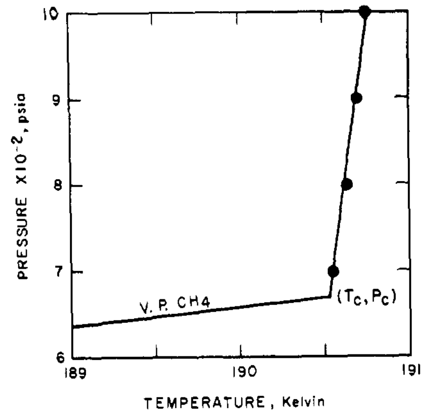

Figure 5. Critical curve, helium-methane system

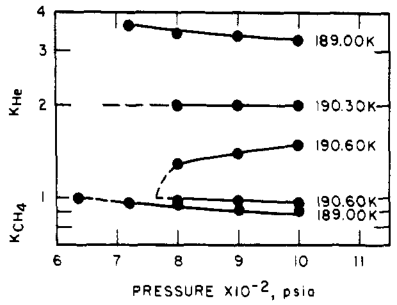

Figure 6. Equilibrium ratios for helium-methane system

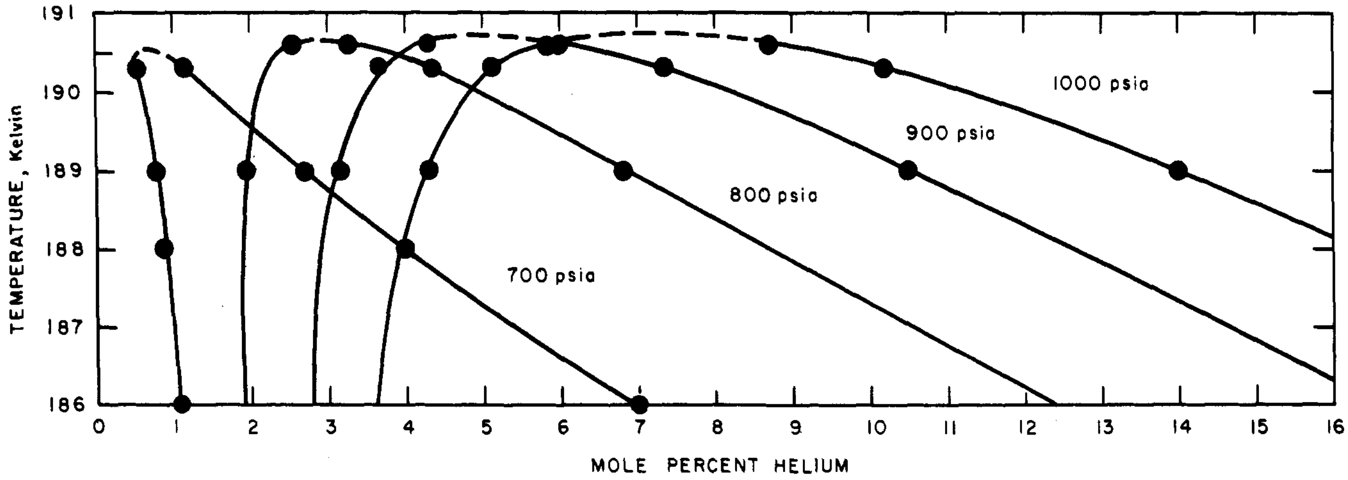

Figure 4. Temperature-composition diagram, helium-methane system

Conservative estimates of uncertainties in pressure, temperature, and composition are 1 psi, 0.01° K, and 0.05% He, respectively.

RESULTS AND DISCUSSION

Vapor-liquid equilibrium behavior of the helium-methane system was investigated at eight temperatures from 124–190.6° K and at pressures to 1000 psia. Experimental results are presented in Table I, along with vapor pressure values of methane calculated from an expression given by van Itterbeek (*9*). The equilibrium constants, $K = y/x$, for helium and methane were calculated from the experimental data and are also included.

The vapor phase composition as a function of pressure is shown in Figure 1. The data of Sinor (*7*) and Heck (*2*) are compared with our results, and, in general, the agreement is good to excellent. The liquid phase is not presented because of the relatively low concentration of helium in methane and the isothermal crossovers.

Figure 2 is a pressure-composition diagram for the 190.3° and 190.6° K isotherms. The 190.3° K isotherm is shown to be in the vapor-liquid region with the vapor and liquid lines intersecting the zero helium axis at the methane vapor pressure (665 psia). The vapor and liquid lines for the 190.60° K isotherm, being above the methane critical (190.53° K), have been extrapolated to an estimated critical point of 765 psia for a 2% helium mixture. A recent paper by Jansoone (*3*) has reported the critical temperature of methane to be 190.498° K (IPTS-48) or 190.531° K (IPTS-68).

Our 154.00° K liquid phase isotherm is compared with Sinor's (*7*) 153.15° K and Heck's (*2*) 154.80° K isotherm in Figure 3. The data of Heck are shown to be in good agreement with our results because the helium content in the liquid phase increases with temperature. The data of Sinor, being approximately 1° below ours, appear to be high in helium.

Figure 4 is a temperature-composition diagram for the 700, 800, 900, and 1000 psia isobars above 184° K. It can be seen from this diagram that the cricondentherm loci starts at the methane critical with a positive slope and increases with pressure. An estimate of the critical temperatures, based on extrapolation of the vapor and liquid curves for each isobar, is 190.55°, 190.64°, 190.70°, and 190.74° K, for 700, 800, 900, and 1000 psia, respectively. The pressure-temperature diagram, Figure 5, obtained from Figure 4 shows that the critical curve for helium–methane mixtures leaves the critical point of methane with a positive slope.

Figure 6 is a plot of K-values for helium and methane for the higher isotherms. It is interesting to note the change in the K-values of helium as the system goes from vapor-liquid to fluid-fluid equilibria. The slope of the 189.00° K isotherm is negative at the lower pressures, decreasing with increasing pressure. The 190.30° K isotherm has a very small negative slope at the lower pressures and, when considered with higher pressure data from (*5*), appears to pass through a minimum at about 1000 psia and then increases with increasing pressure. The 190.60° K isotherm, which is in the fluid-fluid region, originates at about 765 psia with a very steep positive slope which then decreases rapidly with increasing pressure. No unusual behavior is seen in the methane K's. The 190.30° K isotherm for methane was omitted for clarity.

LITERATURE CITED

(1) DeVaney, W. E., Rhodes, H. L., Tully, P. C., *Cryog. Technol.*, **7** (1971).
(2) Heck, C. K., Hiza, M. J., *A.I.Ch.E. J.*, **13**, 593 (1967).
(3) Jansoone, V., Gielen, H., DeBoelpaep, J., *Physica*, **46**, 213 (1970).
(4) *Metrologia*, **5**, 35 (1969).
(5) Rhodes, H. L., DeVaney, W. E., Tully, P. C., *J. Chem. Eng. Data*, **16**, in press, 1971.
(6) Rhodes, H. L., Tully, P. C., "Helium Symposia Proceedings in 1968—A Hundred Years of Helium," compiled by H. W. Lipper, *Bur. Mines Inf. Circ.*, 8417, 1969, pp 79-92.
(7) Sinor, J. E., Schindler, D. L., Kurata, Fred, *A.I.Ch.E. J.*, **12**, 353 (1966).
(8) Tully, P. C., DeVaney, W. E., Rhodes, H. L., *Cryog. Eng. Conf.*, June 17-19, 1970, paper I-5.
(9) Van Itterbeek, A., Staes, K., Verbeke, O., Theeuwes, F., *Physica*, **30**, 1896 (1964).

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Methyl and Monoglycol Esters of Hydroxymethylabietanoic Acid and Their Derivatives

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A convenient and quantitative method is described for making the methyl and monoglycol esters of 12-hydroxymethylabietan-18-oic acid (I-1). A simple synthesis, starting from the glycol ester, for abietanyl diamines and diisocyanates is described. Several other new derivatives of I-1 are reported.

The Naval Stores Research Laboratory has been engaged for a number of years in making polyfunctional derivatives of resin acids. New glycols, hydroxy acids, amines, amino acids, amino alcohols, diamines, and diisocyanates have been reported (*1, 6, 7, 10, 11*).

This paper has three objectives: viz. to report a convenient quantitative route to resin acid esters; to point out a new simple route to abietanyl diamines and diisocyanates applicable to other similar derivatives described in the literature; and to give data on a number of new compounds prepared in connection with unpublished work.

A convenient method for converting 12-hydroxymethylabietan-18-oic acid (I-1) to a diisocyanate, and probably the simplest of published methods, was to prepare the dry sodium salt in dioxane (*6*), react the salt with ethylene chlorohydrin in dimethylsulfoxide (DMSO), react the glycol ester with tosyl chloride, and treat the ditosylate with ammonia to get the diamine. The diamine dihydrochloride was then converted to diisocyanate with phosgene (*11*).

A similar glycol ester was obtained by reacting a crude mixture of dihydro isomers of 12-hydroxymethylabietenoic acid and ethylene oxide by the method used by Lewis and Hedrick (*5*) and successfully converted to a diamine.

DISCUSSION

It is a well-known fact that the direct esterification of resin acids and rosin is difficult. Quantitative esterifications can usually be achieved by reacting the sodium salt with an alkyl halide. Dissolving rosin in dioxane, neutralizing with aqueous sodium hydroxide, and drying by distilling a water azeotrope gave a dry, crystalline salt which reacts readily with alkyl halides. Dioxane is a particularly good solvent for this reaction. This reaction works well with rosin and resin acids, but reactions with alkyl halides are not complete when the abietanyl moiety is substituted by hydroxyl groups that result from the addition of hydroxymethyl groups by reaction with formaldehyde (*1, 6, 8*) or oxonation of rosin (*4*). With compounds of this type

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