H *n*-heptane

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Vapor-Liquid Equilibrium Study of the H_2-CH_4 System at Low Temperatures and Elevated Pressures

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The *K* values for the H_2-CH_4 system were measured at 10 different temperatures and up to the respective critical pressures for five of those temperatures, -90, -100, -110, -120, and -130 °C. For the other lower temperatures, -140, -150, -155, -160, and -165 °C, *K* values were measured up to 20.684 or 27.579 MPa. Henry's constants for hydrogen in methane at each of the above temperatures were evaluated and reported.

Introduction

In view of the increasing interest in the recovery of hydrogen from coal liquefaction processes, the data on vapor-liquid equilibria (VLE) of the H_2-CH_4 system reported in the literature (*1*, *4*, *5*, *10*, *12*, *13*, *18*, *22-24*) must be critically examined and augmented. The data points were found to be scarce and show considerable inconsistencies so that reasonable interpolation, extrapolation, and parametric extraction lead to inaccuracies. The purpose of this work is to obtain self-consistent, extensive VLE data on the H_2-CH_4 system for the temperature and pressure ranges of interest in synthetic natural gas (SNG) processes.

Experimental Section

The apparatus and the experimental procedure used in this investigation are essentially the same as those discussed by Mraw et al. (*16*) in the methane-carbon dioxide studies. The equilibrium cell, the magnetic circulating pump, and sampling valves were immersed in a cryostat with commercial-grade isopentane and a eutectic mixture of isopentane and isohexane as the bath fluids. The bath temperature was controlled to better than 0.01 °C of the reported value. Liquid nitrogen was used as the coolant. The fine temperature control was achieved by using a small (50 W) heater which injected heat into the system through a Thermotrol proportional controller. The temperature was measured with a Leeds and Northrup certified platinum resistance thermometer (serial no. 1331413) calibrated against a National Bureau of Standards reference.

Before the experiments were started, the entire system was evacuated and then flushed with methane. After thermal equilibrium had been achieved, methane was charged into the cell up to the desired liquid level. Hydrogen was then added to obtain the desired pressure. Further pressure adjustments were needed during early stages of the equilibration process to compensate for the hydrogen dissolution in the methane-rich liquid.

The equilibrium composition of liquid and vapor samples were measured chromatographically. A thermal conductivity detector manufactured by Tracor Instruments, Inc., was used. A 6-ft long, $^1/_8$-in. o.d., stainless-steel tubing packed with 120-mesh molecular sieve 5A was used to achieve the base-line separation of H_2 and methane. The gas-chromatographic conditions were as follows: oven temperature, ambient temperature (22 °C); carrier gas, gas mixture of 8.5% H_2 and 91.5% He; flow rate, 59.2 cm^3/min; detector, 240 Ma at 67 °C. The signal from the detector was integrated by a Spectra Physics Autolab Minigrator and recorded on a Hewlett Packard 7100B strip chart recorder.

The selection of carrier gas for chromatographic analysis of both hydrocarbon and hydrogen posed some difficulties. The anomalous behavior of hydrogen when helium is used as the carrier gas has long been known (*14*). Pietsch (*19*) discovered that a helium-hydrogen mixture has a minimum thermal conductivity at ~8 mol % hydrogen. Purcell and Ettre (*20*) demonstrated that, when a H_2-He gas mixture containing more than 8 mol % hydrogen can be used as the carrier gas, the hydrogen response becomes totally negative with respect to other compounds, thus changing the polarity of the detector giving a positive response for the quantitative analysis of hydrogen. Commercially available H_2-He gas mixtures with 8.5% H_2 and the balance helium were thus chosen as a carrier gas. However, the similarity in thermal conductivity between H_2 and its carrier gas makes the detection of hydrogen at low concentration very difficult (if not impossible).

Mixtures with known concentrations of H_2 and CH_4 were prepared by using two precision positive displacement pumps. These mixtures were used to calibrate the thermal conductivity detector (TCD) response for various concentrations of both components. The procedure for preparation and analysis of these calibration mixtures was described by Mraw et al. (*15*). The calibration curve of the TCD response, registered as peak area, vs. mole fraction of each component was prepared. Four commercially prepared calibration mixtures containing 20, 40, 60, and 80 mol % methane were found to be consistent with the calibration curve.

With the proper arrangement of the gear systems of the two precision displacement pumps, the calibration gas mixtures with the hydrogen concentration as low as 0.0051 mole fraction could be made. The calibration curve of methane is linear for the whole range with a maximum accuracy of 0.1%. In order to effectively use our existing analytical setup, we prepared an

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Table I. Experimental Vapor-Liquid Equilibrium Data for the Methane-Hydrogen System

	mole fraction of CH_4			
press., MPa	vapor	liquid	K_{CH_4}	K_{H_2}
	T = 183.12 K (−90.04 °C)			
3.639	1.0000[a]	1.0000[a]		
3.916	0.9662	0.9932	0.9728	4.971
4.016	0.9521	0.9893	0.9623	4.477
4.016	0.9511	0.9893	0.9613	4.570
4.199	0.9411	0.9883	0.9522	4.775
4.344	0.9211	0.9827	0.9728	4.587
4.488	0.9093	0.9797	0.9281	4.468
4.926	0.8708	0.9672	0.9004	3.939
5.619	0.8294	0.9471	0.8757	3.225
6.309	0.8032	0.9260	0.8674	2.650
6.343	0.8093	0.9266	0.8734	2.598
6.902	0.7972	0.9006	0.8852	2.040
7.105	0.8010	0.8916	0.8984	1.836
7.342	0.8007	0.8766	0.9124	1.622
7.412	0.8104	0.8731	0.9282	1.494
7.433	0.8115	0.8743	0.9282	1.506
7.539	0.8183	0.8513	0.9612	1.222
			critical point	
	T = 173.25 K (−99.91 °C)			
2.616	1.0000[a]	1.0000[a]		
3.064	0.9118	0.9913	0.9198	10.140
3.644	0.8245	0.9804	0.8410	8.954
4.237	0.7578	0.9673	0.7834	7.407
4.906	0.7049	0.9558	0.7375	6.677
5.533	0.6636	0.9410	0.7052	5.702
6.205	0.6344	0.9255	0.6854	4.907
6.995	0.6034	0.9027	0.6685	4.076
8.374	0.5740	0.8642	0.6642	3.140
9.756	0.5771	0.8315	0.6940	2.509
10.342	0.5837	0.8059	0.7243	2.144
11.032	0.6051	0.7728	0.7830	1.738
11.400	0.6379	0.7513	0.8490	1.456
11.483	0.6371	0.7377	0.8636	1.384
11.625	0.6918		critical point	
	T = 163.17 K (−109.99 °C)			
1.806	1.0000[a]	1.0000[a]		
2.168	0.8808	0.9937	0.8864	18.921
2.444	0.8082	0.9889	0.8172	17.279
2.872	0.7314	0.9812	0.7454	14.287
4.040	0.5848	0.9597	0.6094	10.303
5.616	0.4869	0.9312	0.5230	7.458
6.995	0.4420	0.9030	0.4894	5.772
8.374	0.4175	0.8778	0.4756	4.767
9.753	0.4053	0.8505	0.4765	3.977
11.132	0.4038	0.8198	0.4925	3.309
12.511	0.4076	0.7845	0.5195	2.749
13.820	0.4255	0.7494	0.5678	2.293
15.199	0.4710	0.6905	0.6821	1.709
15.544	0.4844	0.6717	0.7215	1.571
15.889	0.5173	0.6339	0.8196	1.319
15.958	0.5267	0.6200	0.8494	1.246
15.992	0.5535		critical point	
	T = 153.21 K (−119.95 °C)			
1.200	1.0000[a]	1.0000[a]		
3.616	0.4435	0.9643	0.4599	15.588
4.137	0.4046	0.9557	0.4234	13.440
4.137	0.4084	0.9554	0.4275	13.260
5.237	0.3570	0.9378	0.3807	10.338
6.205	0.3268	0.9256	0.3531	9.048
6.374	0.3248	0.9205	0.3529	8.493
7.591	0.3027	0.9026	0.3354	7.159
8.274	0.2985	0.8933	0.3342	6.575
8.963	0.2895	0.8798	0.3291	5.911
10.342	0.2823	0.8583	0.3289	5.065
11.721	0.2802	0.8326	0.3365	4.300
13.789	0.2886	0.7929	0.3640	3.435
15.513	0.3024	0.7575	0.3992	2.877
17.237	0.3224	0.7157	0.4505	2.383
19.099	0.3594	0.6615	0.5388	1.901
19.891	0.3857	0.6227	0.6195	1.627
20.271	0.4027	0.6036	0.6671	1.507
20.512	0.4230	0.5869	0.7207	1.397
20.719	0.4432	0.5566	0.7963	1.256
20.822	0.4843		critical point	
	T = 143.48 K (−130.08 °C)			
0.751	1.0000[a]	1.0000[a]		
1.386	0.6012	0.9921	0.6060	50.481
3.451	0.3038	0.9634	0.3153	19.022
4.154	0.2693	0.9539	0.2823	15.850
5.526	0.2303	0.9343	0.2457	11.715
6.891	0.2091	0.9158	0.2283	9.3931
8.274	0.1938	0.8981	0.2208	7.8675
8.618	0.1967	0.8933	0.2202	7.5286
10.342	0.1917	0.8717	0.2199	6.3000
13.789	0.1937	0.8206	0.2360	4.4919
17.237	0.2099	0.7634	0.2750	3.3394
20.684	0.2391	0.7017	0.3407	2.5508
22.408	0.2606	0.6673	0.3905	2.2224
24.132	0.2898	0.6212	0.4665	1.8749
25.865	0.3553	0.5392	0.6589	1.3991
26.303	0.3833	0.5108	0.7504	1.2606
26.407	0.3954		critical point	
	T = 133.14 K (−140.21 °C)			
0.442	1.0000[a]	1.0000[a]		
2.754	0.2200	0.9732	0.2261	29.104
3.551	0.1839	0.9624	0.1911	21.704
4.140	0.1688	0.9564	0.1765	19.064
5.519	0.1457	0.9396	0.1551	14.144
6.860	0.1337	0.9262	0.1444	11.738
6.953	0.1342	0.9224	0.1455	11.150
9.642	0.1249	0.8932	0.1398	8.193
13.755	0.1289	0.8512	0.1514	5.854
17.237	0.1411	0.8028	0.1758	4.356
20.739	0.1590	0.7615	0.2088	3.526
24.132	0.1799	0.7041	0.2555	2.772
27.580	0.2106	0.6435	0.3273	2.214
	T = 123.05 K (−150.05 °C)			
0.237	1.0000[a]	1.0000[a]		
4.516	0.0912	0.9561	0.09539	20.701
5.516	0.08483	0.9446	0.08981	16.520
5.895	0.08220	0.9389	0.08755	15.020
6.895	0.07944	0.9309	0.08534	13.322
6.895	0.07890	0.9307	0.08477	13.290
8.618	0.07830	0.9159	0.08549	10.960
10.342	0.07675	0.8963	0.08563	8.902
13.845	0.08069	0.8589	0.09395	6.515
13.858	0.08170	0.8598	0.09502	6.550
17.202	0.09020	0.8276	0.1090	5.277
20.615	0.1005	0.7854	0.1280	4.192
	T = 118.19 K (−155.03 °C)			
0.168	1.0000[a]	1.0000[a]		
4.171	0.07165	0.9614	0.0747	24.052
5.543	0.06460	0.9482	0.06813	18.058
6.922	0.06028	0.9338	0.06455	14.195
10.342	0.05903	0.9025	0.06540	9.650
13.824	0.06475	0.8696	0.07451	7.177
17.237	0.07146	0.8389	0.08518	5.764
20.684	0.08133	0.8075	0.1007	4.772
20.650	0.08189	0.8059	0.1016	4.730
	T = 113.14 K (−160.02 °C)			
0.1145	1.0000[a]	1.0000[a]		
2.820	0.0660	0.9760	0.06762	38.9166
4.164	0.0510	0.9648	0.05286	26.9602
5.530	0.0457	0.9541	0.0479	20.7888
6.909	0.0428	0.9406	0.04545	16.1153
8.591	0.0431	0.9248	0.04662	12.7247
10.356	0.0443	0.9100	0.0487	10.6192
13.734	0.0498	0.8811	0.0566	7.9937
17.271	0.0552	0.8515	0.0648	6.3623
20.684	0.0639	0.8208	0.0779	5.2238
24.614	0.0735	0.7926	0.0927	4.4672
28.406	0.0840	0.7665	0.1096	3.9225

Table I (*Continued*)

press., MPa	mole fraction of CH_4 vapor	mole fraction of CH_4 liquid	K_{CH_4}	K_{H_2}
	T = 108.13 K (−165.03 °C)			
0.0752	1.0000[a]	1.0000[a]		
3.5852	0.03693	0.9720	0.0380	34.396
4.179	0.03533	0.9673	0.0365	29.505
5.536	0.03317	0.9565	0.0347	22.228
6.929	0.03182	0.9454	0.0337	17.724
7.894	0.03127	0.9378	0.0334	15.590
8.570	0.03096	0.9316	0.0332	14.167
9.653	0.03188	0.9238	0.03451	12.706
13.789	0.03698	0.8944	0.04135	9.1193
17.030	0.04185	0.8655	0.04835	7.1238
20.474	0.04850	0.8409	0.0577	5.9816

[a] Vapor pressure of CH_4 calculated from equation in ref 6.

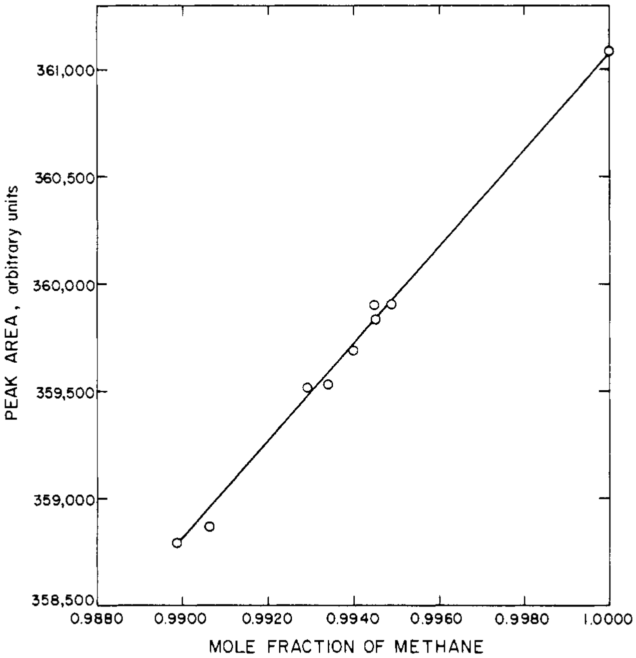

Figure 1. Calibration curve for low hydrogen concentration.

additional, special calibration curve (Figure 1) with emphasis on the low hydrogen concentration region (0.01–0.0051 mole fraction) from which both hydrogen and methane concentrations were obtained. When this was done, the maximum analytical error in measuring hydrogen (at the lowest hydrogen concentration) became as large as 8.3% of the amount of hydrogen present, all other hydrogen concentration errors being appreciably less, on the order of a few tenths of a percent.

The calibrations were checked before and after each analysis, because the peak response was found to be sensitive to the flow rate of carrier gas and its fluctuations during the course of analysis.

The pressure of the system was indicated by three Heise gauges (0–500, 0–2000, 0–6000 psia), which have an accuracy of 0.1% of the full scale reading.

Material

High-pressure hydrogen (6000 psia) with a purity of 99.995% and hydrogen–methane mixtures with nominal compositions of 20, 40, 60, and 80 mol % methane were purchased from Linde Specialty Gases and from Matheson Gas Products, respectively. High-purity methane (99.999 mol %) and the chromatographic carrier gas (8.5% H_2, 91.5% He) were also obtained from Matheson Gas Products Co.

Results

Experimental results for 10 isotherms are tabulated in Table I. The *K* values were measured from low pressure (2.062 MPa) up to the critical pressures for −90, −100, −110, −120, and −130 °C. For the other five lower temperatures, −140, −150, −155, −160, and −165 °C, because of limitations of the equilibrium cell, data points were obtained only up to 27.579 MPa (4000 psia) at −140 and −160 °C or 20.684 MPa (3000 psia) at −150, −155, and −165 °C.

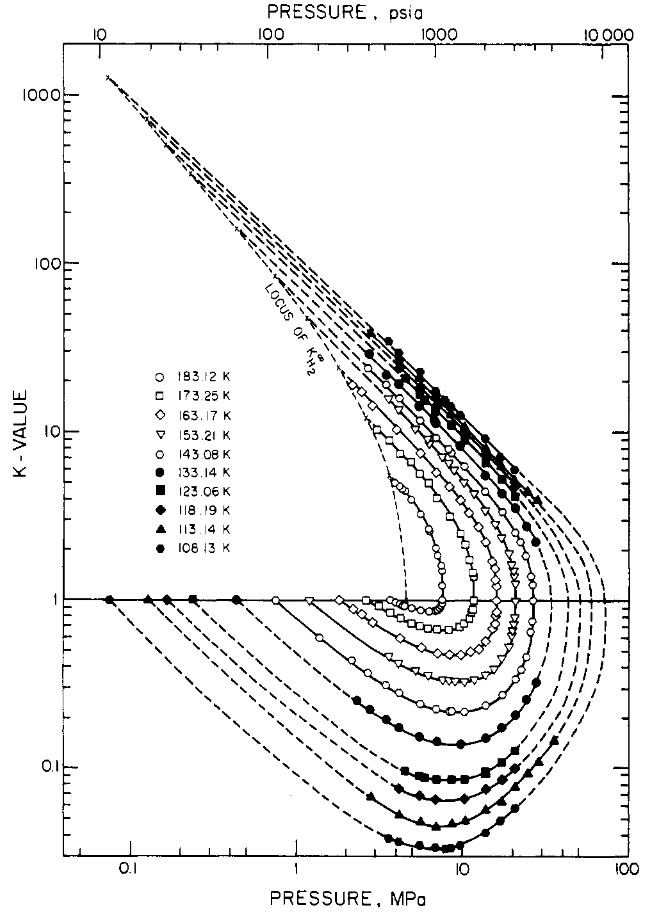

Figure 2. *K* value vs. pressure for hydrogen–methane system from −90 to −165 °C.

Diagrams of the *K* value and the products of the *K* value and the pressure vs. pressure are presented for both hydrogen and methane in Figures 2 and 3, respectively.

The Henry's law constants at each temperature were evaluated by using the Krichevsky–Kasarnovsky equation (*11*). The fugacity coefficients needed to apply the Krichevsky–Kasarnovsky equation were obtained by two different approaches. Method I utilizes the virial equation of state, truncated after the second virial coefficient, *B*, at lower total pressures. Method II utilizes the modified Redlich–Kwong equation of state developed by Gray et al. (*7*) through calculation of the vapor-phase fugacity coefficients (*9*) calculated with interaction parameters adjusted and optimized with respect to the experimental VLE data of this study given in Table I.

In method I, the virial coefficients of hydrogen and methane were taken from Dymond and Smith (*3*). The vapor-phase fugacity coefficient may be expressed by

$$\ln \phi_i = (2\sum_j y_j B_{ij} - B_m)[P/(RT)] \qquad (1)$$

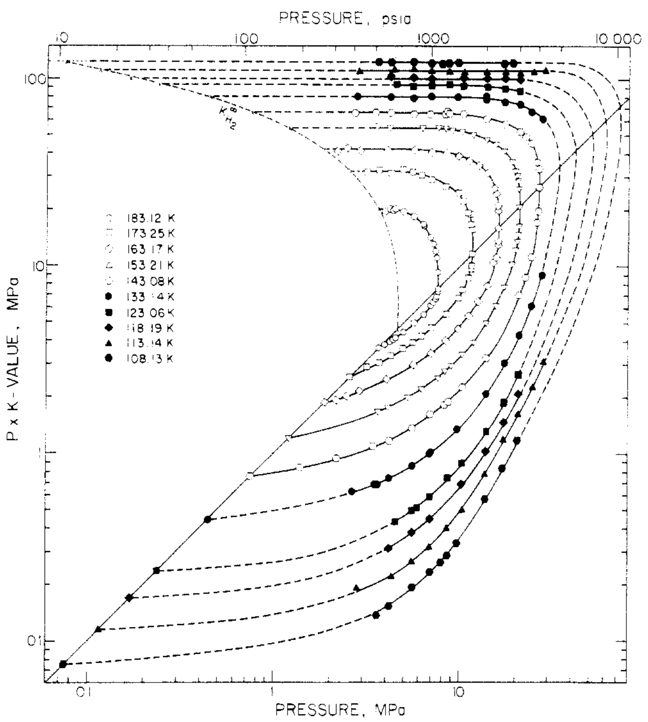

Figure 3. (Pressure × K value) vs. pressure for hydrogen-methane system from -90 to -165 °C.

where the mixture interaction virial B_{ij} values are taken in the form of

$$B_{ij} = B_i y_i + B_j y_j \tag{2}$$

and the mixture coefficient (*21*)

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \tag{3}$$

In method II, the parameters from the modified Redlich-Kwong equation are identified in the following relationships:

$$a_m = \sum_{ij} y_i y_j a_{ij} \tag{4}$$

where $a_{ii} = a_i$, and

$$a_{ij} = (a_i a_4)^{1/2}(1 - C_{ij}) \tag{5}$$

The Henry's constants obtained by methods I and II do not agree at the higher temperatures, 153, 163, 173, and 183 K, or as one approaches the critical conditions of methane, owing to the truncated virial expression used in method I. The Henry's law constants obtained in this study and in the literatures are reported in Table II. Large discrepancies in the reported values point to the difficulties in evaluating Henry's law constants as one approaches the solvent critical temperature.

Hayduk and Laudie (*8*) observed that all gas solubilities in a given solvent have a common value as the solvent critical temperature is approached. Beutier and Renon (*2*) demonstrated thermodynamically that there may be a limiting law for gas solubilities in liquids at their solvent critical point. This prediction suggests that a plot of a reduced Henry's constant (H divided by $P_c^{CH_4}$) vs. reduced temperature (T divided by $T_c^{CH_4}$) should give a curve with a slope of infinite value at the critical point of the solvent.

Figure 4 presents the Henry's law constants calculated by methods I and II and by other authors (*1*, *13*, *17*, *18*). The constants obtained by method II are believed to be more in accord with the criterion for the Henry's law constant behavior at the critical point set forth by Beutier and Renon (*2*).

Table II. Comparison of Henry's Constants (H) on H_2/CH_4 System

T, K	H, MPa (this work) method I	H, MPa (this work) method II
183.12	16.25	32.23
173.25	30.51	40.98
163.17	43.51	49.30
153.21	57.86	55.87
143.08	68.24	64.91
133.14	79.28	74.66
123.06	92.11	85.46
118.19	99.78	92.11
113.14	109.18	96.83
108.13	123.10	105.95

T, K	H, MPa (lit.)	ref
90	184.82	*18*
110	104.97	*18*
110	98.29	*18*
127	84.91	*18*
144	63.84	*18*
110.16	104.9	*17*
127.16	79.74	*17*
158.16	46.61	*17*
168.16	42.05	*17*
178.16	22.80	*17*
110.16	115.51	*17*[a]
127.16	85.11	*17*[a]
158.16	49.11	*17*[a]
168.16	39.52	*17*[a]
178.16	26.34	*17*[a]

[a] Calculated from equilibrium composition (*1*, *4*, *12*) which is calculated from fugacity by using BWR equation.

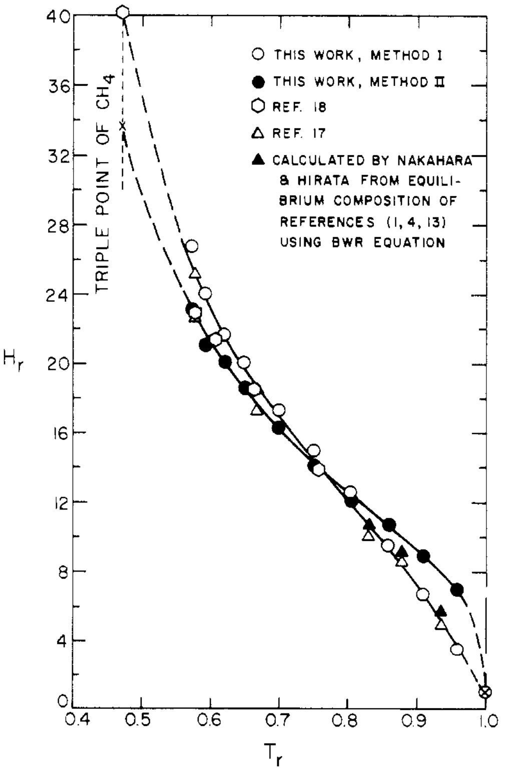

Figure 4. Reduced Henry's constant vs. reduced temperature.

Conclusions

In conclusion, the vapor-liquid equilibria of binary systems consisting of hydrogen and methane were measured over a wide temperature and pressure range. The experimental results show good internal consistency. Volumetric data are not available to rigorously determine the Henry's law constant as the pressure approaches the solvent critical point. Therefore, in this exercise, the fugacity coefficients calculated by using a modified Redlich-Kwong equation of state (*7*) consistent with the vapor-liquid equilibria data of this study were used to yield values of the Henry's law constant more consistent with the criteria set forth by Renon et al. (*2*).

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Ternary Equilibrium for the System Water/Methyl Isobutyl Ketone/2-Ethyl-2-(hydroxymethyl)-1,3-propanediol

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Liquid-liquid equilibrium has been determined for the ternary system water/methyl isobutyl ketone/2-ethyl-2-(hydroxymethyl)-1,3-propanediol at 25 and 70 °C. The latter compound is known commercially as trimethylolpropane.

Cyclohexanol (*1*) has been tested as a solvent for extracting 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP), but the two liquid phase region for this system is not very large. It is the purpose of the present paper to show the behavior of another solvent in the extraction of TMP.

Experimental Procedure

The water was purified by distilling it in the presence of potassium permanganate. The methyl isobutyl ketone was supplied by Merck as a spectroscopic reagent. The TMP was purified by extracting impurities with methyl isobutyl ketone followed by drying at 100 °C for 24 h. The melting point for the final TMP was 57-57.5 °C.

The experiments were carried out in a small glass stirring vessel of 100-mL volume, provided with a circulating jacket. The circulating-water temperature was controlled by a recirculating bath. A PTFE-covered magnetic bar was used for stirring.

The points on the binodal curve were first obtained by using the titration method. Tie lines were obtained secondly by preparing overall mixtures of the three components, which would yield an overall composition within the two liquid phase region, stirring them for 4 h, and allowing the mixture to settle for 6 h. At the end of each experiment, samples were taken from both phases and weighed, and then both water and solvent were

Table I. Liquid-Liquid Equilibrium Composition Data ($T = 25$ °C)

binodal curve (wt fraction)		
water	TMP	MIBK
0.981		0.019
0.877	0.097	0.026
0.779	0.195	0.026
0.675	0.290	0.035
0.568	0.380	0.052
0.467	0.464	0.069
0.358	0.536	0.106
0.253	0.584	0.163
0.166	0.585	0.249
0.081	0.495	0.424
0.046	0.382	0.572
0.033	0.291	0.676
0.028	0.195	0.777
0.029	0.097	0.874
0.021		0.979

tie lines (wt fraction)						distribution coeff, ketone/water
water-rich phase			ketone-rich phase			
water	TMP	MIBK	water	TMP	MIBK	
0.869	0.110	0.021	0.021	0.008	0.971	0.071
0.573	0.378	0.049	0.019	0.037	0.944	0.097
0.477	0.458	0.065	0.022	0.048	0.930	0.105
0.282	0.574	0.144	0.022	0.078	0.900	0.136
0.168	0.582	0.250	0.025	0.122	0.853	0.210
0.119	0.556	0.325	0.024	0.186	0.790	0.335
0.073	0.487	0.440	0.027	0.227	0.746	0.466
0.034	0.316	0.650	0.028	0.247	0.725	0.782

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