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Vapor-Liquid Equilibrium Constants at Infinite Dilution Determined by Gas Chromatography: Ethane, Propane, and *N*-Butane in the Methane-Decane System

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The gas chromatography technique has been extended to determine the *K*-values of ethane, propane, and *n*-butane at infinite dilution in the methane-decane system at 70, 40, 0, and −20° F. from near atmospheric pressure to 2000 p.s.i. The *K*-value of *n*-butane at infinite dilution in the methane-decane system has also been measured at 160° F. from near atmospheric pressure to 460 p.s.i.

GAS-LIQUID partition chromatography (GLPC) has been used to determine vapor-liquid equilibrium data under certain conditions by several investigators. Porter, Deal, and Stross (*9*), Anderson (*2*), and Anderson and Napier (*1*) found substantial agreement between partition coefficients determined by gas-liquid chromatography and those obtained from static methods of measurement. Several authors (*7, 13*) have calculated activity coefficients from GLPC elution data and found these values in agreement with values measured by static means. These previous studies were conducted at near atmospheric pressure using an elution gas such as nitrogen, hydrogen, or helium that was insoluble in the particular non-volatile liquid phase considered. The partition coefficients so determined were for the solute at essentially infinite dilution in a one component liquid phase.

In the work described in this paper the technique of gas-liquid chromatography has been extended to determine over a wide range of pressure and temperature the equilibrium K or y/x values of a solute at essentially infinite dilution in a vapor-liquid system in which the liquid phase contains appreciable quantities of two components, one essentially non-volatile. In particular, the K values of ethane, propane, and n-butane at infinite dilution in the methane-decane system have been measured at 70, 40, 0, and −20° F. from near atmospheric pressure to 2000 p.s.i. The K-value of n-butane at infinite dilution in the methane-decane system has also been measured at 160° F. from near atmospheric pressure to 460 p.s.i.

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EXPERIMENTAL PROCEDURE

The apparatus used is similar to a conventional gas-liquid chromatograph except that it has been modified for the packed column to operate at high pressures. Tubing, valves, and fittings are of stainless steel with all connections for ⅛ inch stock to minimize dead space.

A vapor solute sample was introduced by diverting the high pressure elution gas flow through a sample tube. A Wilkens six port linear sample valve accomplished the sample introduction. O-rings fitted on a sliding stem partitioned off various parts of the valve body. Depending on whether the stem was in the up or down position, gas flow was either straight through the valve or diverted through the sample tube. The sample introduction valve was located outside the liquid temperature bath in which the GLPC column was immersed, since small, abrasive particles in the bath kept working past the stem to damage the O-rings.

Pressure regulation in the GLPC column was achieved with a sensitive diaphragm regulator placed just upstream from the sample introduction valve. Flow rate through the column and reference side of the system was controlled with microneedle valves which also served to break the elution gas pressure down to atmospheric. These valves were also placed outside the temperature bath, because at some of the lower bath temperatures slight condensation of the elution gas tended to occur upon expansion through the valve. Elution gas flow rate was accurately measured at atmospheric conditions with a calibrated soap bubble flowmeter and stop watch.

The thermal conductivity detector was a conventional hot wire model. It was mounted in the system past the microneedle flow control and pressure breakdown valves and was operated at atmospheric pressure.

The chromatographic columns used in this investigation were ¼ inch stainless tubes from 6 inches to 3 feet in length packed with decane impregnated firebrick. The decane was placed on the firebrick and the impregnated firebrick packed in the column following procedures previously described (*5*). Frequent checks were made to redetermine the amount of non-volatile liquid on the column packing.

Above 50 p.s.i.g., column pressure was measured with a Heise gauge graduated in 2 p.s.i. increments. Below 50 p.s.i.g. a mercury manometer was used for pressure measurement. Temperature was controlled and measured to ±0.1 F.

Briefly, the experimental procedure was to adjust the methane elution gas flow to approximately 50 cc./minute at STP after setting the column pressure and temperature and to allow sufficient time for the flowing methane to reach equilibrium with the decane in the GLPC column. A ¼ cc. STP sample of gaseous solute was then introduced and the time for its peak concentration to be detected in the column effluent was measured. The measurement of elution gas flow rate at room conditions then allowed the solute retention volume to be calculated at standard conditions. A complete description of apparatus and experimental procedure may be found in the original work of this study (*11*).

MATERIALS

Methane was donated by the Tennessee Gas Transmission Co. and The Associated Oil and Gas Co. and was taken from a dehydration station near El Campo, Texas. After passing through a dryer this gas was found to be 99.7 per cent methane, 0.2 per cent nitrogen, and 0.1 per cent other gases, mainly ethane, by mass spectrograph analysis.

Other hydrocarbons used were obtained from Phillips Petroleum Co. Both the ethane and propane used as solute samples were 99 mole per cent minimum stock, the *n*-butane was Instrument grade, and the *n*-decane was Research Grade 99.35 mole per cent stock.

The column packing material used as a support for the hydrocarbon liquid phases was a screened 30–50 mesh, acid washed C-3 firebrick purchased from Curtin Co.

DISCUSSION AND RESULTS

Several authors have presented theoretical derivations relating the retention volume of a solute to its equilibrium partition coefficient (*8, 14*). This relation is:

$$V_{R_i} = V_g + V_L/H_k \qquad (1)$$

For a one component elution gas that is appreciably soluble in the liquid impregnated on the GLPC packing, Equation 1 may be modified to give the solute K-value (*11, 12*).

$$K_k = \frac{y_k}{x_k} = \frac{Z_1 RTW}{P(V_{R_k} - V_g)(1 - 1/K_1)} \qquad (2)$$

Besides assuming pointwise equilibrium of the solute as it elutes through the column, the derivation of Equation 2 also assumes a constant partition coefficient at all points along the length of the column as well as the introduction of a negligibly small sample volume. In this work both the sample volume and the minimum dilution of solute sample with elution gas were experimentally determined which satisfied the above assumptions; *i.e.*, further reduction of sample volume or further dilution of solute sample with elution gas caused no noticeable change in the measured solute retention volume. Use of Equation 2 also requires that the total moles of non-volatile component (decane) on the column packing, the compressibility factor and K-value of the elution gas (methane), and the "free" gas volume of the column available for elution gas flow be known.

"Free" gas volume was estimated both by measuring the retention volume of an inert solute such as helium and by substracting the non-porous solid firebrick volume and liquid phase volume from the empty column volume. Unfortunately, the agreement between these two methods was not very good, the results differing sometimes by as much as 10 per cent. This uncertainty in the determination of "free' gas volume should cause a correspondingly larger error in the K-value calculated from Equation 2 for lighter solutes with smaller values of retention volume (*12*).

Methane compressibility factors for use in Equation 2 were taken from Brown, Katz, Oberfell, and Alden (*4*). The error made in estimating elution gas compressibility does not cause a correspondingly large error in the calculated K-value. Since retention volume was actually measured at atmospheric pressure and room temperature and had to be converted to column conditions, the quantity substituted into Equation 2 for V_{R_k} would also contain Z_1. This would lead to a partial cancellation of compressibility factor in the numerator and denominator with Z_1 only remaining as the denominator of the V_g term. Thus, as with V_g the error made in estimating Z_1 would cause a correspondingly larger error the more volatile the solute (*12*).

Methane K-values used in Equation 2 were extrapolated from the methane-decane data of Sage and Lacey (*10*) using the methane-*n*-heptane data of Kohn (*6*) to guide the extrapolation.

Values of partial molar volume of methane were taken from the work of Sage and Lacey (*10*) and the volume increase of the liquid phase caused by solution of methane was computed at each pressure and temperature investigated. This value was substracted from the value of V_g determined at low pressures to give the actual "free' gas volume used in Equation 2.

In this work it is felt that the moles of effective decane on the column packing were probably known at all times to within 5 per cent. The original amount of liquid placed on the packing was determined as the difference between total liquid-solid packing material weight and amount of solids involved. At the higher pressures and lower temperatures the combined error in the V_g/Z_1 term may cause a few per cent error in the calculation of butane K's and as high

Table I. Comparison of Infinite Dilution, Atmospheric, Liquid Phase Activity Coefficients for *n*-Butane in Methane *n*-Decane System

Temp., °F.	Chromatographic	Bronsted & Koefoed
160	0.898	0.935
70	0.963	0.960
40	0.980	0.973
0	0.987	0.973
−20	0.990	0.976

Table II. K-Values for Ethane at Infinite Dilution in the Methane-Decane System

Pressure P.S.I.A.	K-Methane[a]	K-Ethane	Pressure P.S.I.A.	K-Methane[a]	K-Ethane
	70° F.			40° F.	
39.5	67.0	10.36	21.1	100	15.10
75.3	35.6	5.34	41.1	59	6.97
103	26.3	3.65	61.1	40.5	4.93
145	19.0	2.73	62.8	39.0	4.80
205	13.8	2.04	66.7	37.4	4.46
305	9.7	1.45	112	23.7	2.67
317	9.4	1.41	158	16.3	1.93
456	6.8	1.06	207	12.6	1.53
461	6.73	1.05	311	8.70	1.13
618	5.25	0.853	461	6.18	0.845
804	4.25	0.739	607	4.86	0.701
997	3.58	0.689	822	3.82	0.604
1382	2.00	0.628	996	3.27	0.563
1966	2.22	0.607	1403	2.55	0.521
			1738	2.22	0.525
	0° F.			−20° F.	
16.3	120	12.41	16.5	120	8.82
26.3	80	7.59	25.9	74	5.60
27.3	78	8.78	37.5	51	3.86
36.5	58	5.89	39.7	48	3.98
36.9	53	5.19	57.8	33.0	2.56
67.8	31	2.75	71.8	26.7	2.19
68.8	31	3.29	103	18.7	1.45
90.8	23.5	2.10	107	18.0	1.51
109.3	19.5	1.98	109	17.5	1.49
149	14.4	1.31	157	12.4	1.02
161	13.5	1.37	165	11.7	1.03
203	10.8	1.01	210	9.4	0.790
210	10.6	1.07	309	6.6	0.583
316	7.15	0.705	325	6.3	0.563
452	5.23	0.564			
590	4.20	0.497	449	4.73	0.466
775	3.40	0.436	457	4.50	0.454
988	2.85	0.423	589	3.80	0.414
			795	3.06	0.359
1395	2.28	0.420	1011	2.59	0.371
1935	1.90	0.469	1365	2.14	0.380
			1798	1.82	0.456

[a] K-Value of methane used in Equation 2, also see texts.

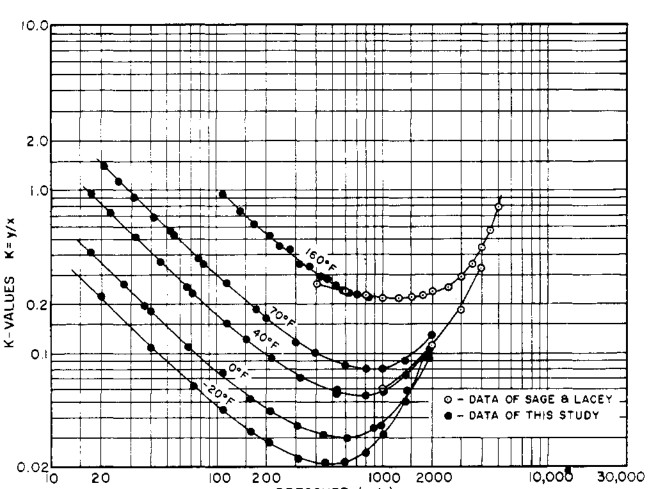

Figure 1. K-values for n-butane at infinite dilution in the system methane-n-decane

Table III. K-Values for Propane at Infinite Dilution in the Methane-Decane System

Pressure P.S.I.A.	K-Methane[a]	K-Propane	Pressure P.S.I.A.	K-Methane[a]	K-Propane
	70° F.			40° F.	
39.5	67	2.78	21.2	100.0	3.35
77.8	34.2	1.40	41.1	59.0	1.64
103	26.3	1.06	62.8	39.0	1.12
145	19.0	0.784	65.8	37.5	1.10
205	13.8	0.593	112	23.7	0.656
305	9.7	0.433	158	16.3	0.476
401	7.6	0.371	207	12.6	0.382
456	6.8	0.327	303	8.9	0.288
609	5.3	0.278	421	6.65	0.226
812	4.2	0.243	611	4.84	0.189
1014	3.56	0.235	795	3.90	0.174
1372	2.83	0.249	1001	3.27	0.169
1960	2.22	0.281	1367	2.62	0.184
			1885	2.12	0.219
	0° F.			−20° F.	
17.3	120	2.36	19.94	96	1.39
27.1	78	1.42	39.7	48	0.640
36.9	53	1.01	71.8	26.7	0.367
67.8	31	0.599	109	17.5	0.260
110	19.5	0.384	165	11.7	0.188
161	13.5	0.266	205	9.5	0.162
210	10.6	0.208	309	6.6	0.122
307	7.35	0.166	449	4.73	0.100
311	7.26	0.172	589	3.80	0.0961
441	5.33	0.141	795	3.06	0.0947
463	5.15	0.138	1011	2.59	0.105
609	4.07	0.125	1365	2.14	0.139
803	3.33	0.127	1798	1.82	0.218
984	2.87	0.127	...	...	...
1385	2.28	0.155	...	...	...
1895	1.91	0.215	...	...	...

[a] K-Value of methane used in Equation 2, also see text.

as 10–12 per cent error in the calculation of ethane K's. The influence of the error made in estimating K_1 becomes larger at higher pressures as the value of K_1 becomes smaller. When $K_1 \geqq 10$, an error of 20 per cent in its estimation would cause an error of less than 3 per cent in the calculated value of K_k.

The authors feel that n-butane K's of this work may have an experimental error of 3–5 per cent and the ethane K's may have an experimental error of 10–15 per cent. The higher errors are more likely at the higher pressures studied.

K-values for ethane, propane, and n-butane at infinite dilution in the methane-decane system that were calculated from Equation 2 using the raw experimental data of this study are given in Tables II, III, and IV. The methane K values used in the calculation are also shown in these tables. As improved K-values for methane in n-decane become available it should be possible to obtain improved values for the infinite dilution K-values from Equation 2.

In Figure 1 a comparison is made at 160 and 40° F. between the butane K-values of this work and values reported or derived from the work of Sage and Lacey *(10)* who used a static equilibrium cell technique. Agreement is generally quite good between the two sets of data indicating equilibrium results have been obtained by the chromatographic technique. At 160° F., 400 p.s.i. there is serious disagreement between the K-values of the two sources. However, if the Sage and Lacey curve were extrapolated back to low pressures using this point and an activity coefficient calculated from the extrapolated K-value, a value that is abnormally low for this type system would be obtained. Table I compares atmospheric pressure activity

Table IV. *K*-Values for *n*-Butane at Infinite Dilution in the Methane-Decane System

Pressure P.S.I.A.	*K*-Methane[a]	*K*-Butane	Pressure P.S.I.A.	*K*-Methane[a]	*K*-Butane
	160° F.			70° F.	
119	26.5	0.920	19.9	100	1.46
138	23.2	0.726	25.4	100	1.18
168	19.0	0.615	32.0	84	0.919
209	15.5	0.515	42.2	63	0.701
239	13.8	0.444	55.5	48	0.539
275	12.2	0.414	76.7	35	0.388
318	10.7	0.353	80.8	33	0.357
360	9.5	0.334	83.7	32	0.366
415	8.4	0.313	115	23.9	0.274
460	7.7	0.295	175	16.0	0.191
515	7.0	0.262	255	11.5	0.141
575	6.35	0.238	202	14.0	0.156
620	6.0	0.244	398	7.6	0.101
705	5.35	0.240	605	5.4	0.847
805	4.8	0.223	795	4.3	0.0811
			1002	3.6	0.0804
			1379	2.8	0.0915
			1985	2.2	0.127
	40° F.			0° F.	
17.7	100	0.988	17.3	120	0.407
23.2	100	0.745	27.2	78	0.257
32.6	75	0.523	36.9	53	0.196
35.7	70	0.450	67.8	31	0.115
46.7	54	0.365	109	19.5	0.0750
58.8	42	0.274	161	13.5	0.0518
66.7	37.5	0.253	210	10.6	0.0436
69.8	35.5	0.259	307	7.35	0.0348
72.8	34.0	0.237	463	5.15	0.0295
82.8	30.0	0.198	614	4.02	0.0293
96.8	25.5	0.185	885	3.08	0.0337
117	21.5	0.152	995	2.83	0.0353
153	16.7	0.124	...	...	...
157	16.3	0.116	1411	2.27	0.0573
216	12.2	0.0953	...	...	...
321	8.45	0.0709	1934	1.90	0.0941
530	5.47	0.0584	...	...	...
532	5.45	0.0570	...	...	...
799	3.9	0.0545	...	...	...
800	3.9	0.0551	...	...	...
1020	3.25	0.0582	...	...	...
1020	3.25	0.0573	...	...	...
1404	2.56	0.0705	...	...	...
1404	2.56	0.0725	...	...	...
1941	2.07	0.108	...	...	...
	−20° F.				
19.9	96	0.221			
39.7	48	0.108			
71.8	26.7	0.0622			
109	17.5	0.0452			
165	11.7	0.0326			
205	9.5	0.0273			
309	6.6	0.0223			
449	4.73	0.0212			
589	3.80	0.0213			
795	3.06	0.0242			
1011	2.59	0.0314			
1365	2.14	0.0512			
1798	1.82	0.102			

[a] *K*-Values of methane used in Equation 2, also see text.

coefficients of *n*-butane calculated from *K*-value data of Table IV with activity coefficients calculated from an empirical relation of Bronsted and Koefoed (*3*) for simple hydrocarbon systems.

For a more complete explanation of the theoretical requirements to be met experimentally as well as the errors and limitations encountered in measuring *K*-values by gas chromatography, the reader is referred to references (*11*) and (*12*).

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NOMENCLATURE

- H_k = equilibrium partition coefficient of solute k, (concentration of k in the liquid phase)/(concentration of k in the gas phase)
- K_k = equilibrium y_k/x_k value for component k
- K_1 = equilibrium y/x value for methane
- P = system pressure
- R = universal gas constant
- T = absolute temperature
- V_g = "free" gas volume or volume available to elution gas flow
- V_L = volume of liquid phase on column packing
- V_{R_k} = retention volume of component k at column P, T
- W = total moles of non-volatile liquid component on column packing
- x_k = mole fraction of component k in the liquid phase
- y_k = mole fraction of component k in the gas phase
- Z_1 = compressibility factor of methane at column P, T

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