Vapor-Liquid Equilibrium in the Methane—n-Hexane—Nitrogen System

ROBERT S. POSTON and JOHN J. McKETTA

University of Texas, Austin, Texas

Because varying amounts of nitrogen are found in hydrocarbon mixtures, a knowledge of vapor-liquid equilibrium ratios for hydrocarbon-nitrogen systems is needed for petroleum reservoir studies and refinery calculations. Presented here are results of a quantitative investigation which shows how the *K* values of methane and *n*-hexane change when varying amounts of nitrogen are added to mixtures of the two hydrocarbons.

Analyses of equilibrium phases at different conditions of temperature and pressure in order to completely describe the phase equilibria of the system are presented. Temperature intervals of 60°F., starting at 100°F., and going up to 340°F. were used. At each temperature equilibrium samples were taken at 500 lb./sq.in.abs. and the pressure increased in 500 lb./sq.in.abs. intervals with samples taken at each interval up to 5,000 lb./sq.in.abs. or the critical pressure, whichever was lower.

EXPERIMENTAL

A stainless steel windowed glass cell with a volume of 35 cc. was charged with the research grade reagents, and equilibrium was established by recirculating the vapor from the top of the cell through a magnetic pump into the bottom of the cell for two hours. Near the critical region, a period of four hours was used for recirculation. Two to four hours were found adequate for phase separation, depending on how close the particular run was to the critical.

The equilibrium cell was immersed in a 16-gal. oil bath and the magnetic pump was located in an air bath which was maintained at, or slightly above, the oil bath temperature. The experiments were performed at constant temperatures. Pressure was controlled by the amount of reagent or mercury added to or taken from the cell.

Isobaric, isothermal equilibrium samples were varied by the removal of one and the addition of the other volatile component until the critical composition or essentially pure binary composition was reached. This procedure completely defined the phase behavior for the system.

The experimental apparatus and operating procedures are described further by Roberts (*4*).

ANALYTICAL

Both the liquid and vapor phase at each equilibrium experimental point were sampled for analysis. The reader is referred to Roberts (*4*) for a detailed discussion of sampling procedure. Roberts' sampling technique was modified only slightly to prevent condensation of the hexane as sampling took place. This was accomplished by placing heating tapes around the liquid sample lines exterior to the experimental apparatus and by placing a heating mantle around the 500-cc. glass flask in which the sample was trapped for analysis. Thermocouples were inserted around the sample lines and the lowest temperature was found to be 150°F., well above the boiling point for hexane at the partial pressure of hexane in any sample.

The composition of the coexisting liquid and vapor phases was determined on a Beckman GC-2A gas chromatograph which had been calibrated using the pure components. A special column arrangement was used which permitted a complete analysis for the composition of a sample in one step. No pressure or volume measurements were necessary and corrections were obtained from the chromatogram for any air leak into the chromatographic system. The columns consisted of an 8-ft. ansul ether column (30% by weight on firebrick support) in series with a 3.5-ft. molecular sieve column. A sample, upon reaching the ansul ether column, separated the natural gases (nitrogen, oxygen, and methane) from the *n*-hexane, allowing the natural gases to pass without retention into the molecular sieve column where oxygen was first released. Then nitrogen and finally the methane came off and the three respective responses were received on a strip chart recorder from the thermal conductivity detector. After the natural gases were off the column and their responses recorded, the hexane which was still in the ansul ether column was diverted through a capillary restrictor away from the molecular sieve column directly into the detector. The 0.005-in. I.D. capillary restrictor compensated for the pressure drop through the mo-

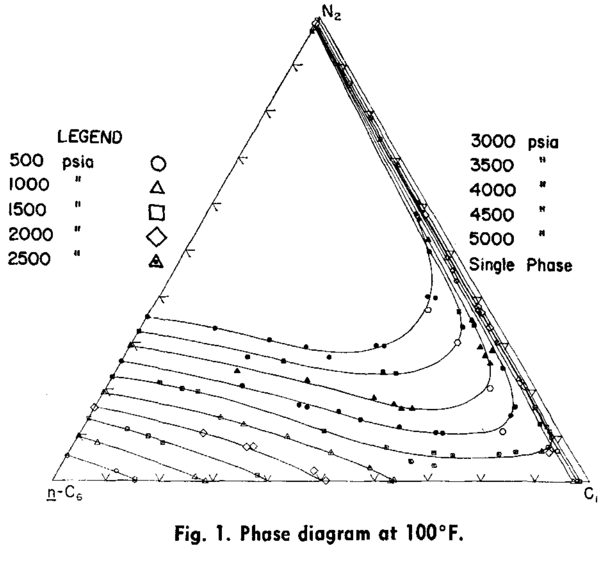

Fig. 1. Phase diagram at 100°F.

Robert S. Poston is with Sinclair Oil and Gas Company, Tulsa, Oklahoma.

TABLE 1. TERNARY EXPERIMENTAL DATA

Temp., °F.	Press., lb./sq. in. abs.	Mole fraction			
		Vapor phase		Liquid phase	
		N_2	n-C_6	N_2	n-C_6
100	500	.374	.016	.020	.870
	1000	.674	.018	.080	.876
		.071	.020	.009	.726
	1500	.787	.011	.113	.804
		.685	.013	.097	.771
		.603	.012	.084	.754
		.066	.021	.016	.613
	2000	.361	.022	.078	.598
		.335	.016	.074	.588
		.066	.021	.020	.519
		.578	.014	.105	.666
	2500	.223	.020	.061	.449
		.376	.016	.099	.511
		.486	.016	.124	.582
		.580	.018	.145	.614
	3000	.740	.018	.199	.629
		.780	.018	.202	.658
		.852	.013	.216	.690
		.159	.020	.071	.342
		.127	.030	.062	.257
		.109	.019	.044	.310
		.094	.020	.060	.134
		.118	.019	.058	.222
		.075	.033	single phase	
	3500	.450	.026	.160	.442
		.434	.030	.165	.457
		.340	.044	.151	.389
		.283	.038	.133	.360
		.246	.039	.132	.265
		.248	.026	.118	.291
		.160	.058	.104	.232
		.142	.075	.104	.221
		.110	.103	single phase	
	4000	.293	.055	.168	.280
		.272	.056	.158	.271
		.349	.042	.184	.309
		.256	.054	.160	.249
		.670	.018	.239	.539
		.522	.035	.218	.418
		.203	.082	single phase	
	4500	.372	.052	.238	.263
		.334	.067	.235	.246
		.579	.033	.257	.439
		.689	.018	.270	.500
		.308	.095	single phase	
	5000	.400	.084	.296	.246
		.495	.046	.268	.349
		.568	.037	.293	.377
		.671	.021	.304	.442
		.400	.099	.295	.231
		.811	.020	.331	.528
		.372	.113	single phase	
160	500	.241	.061	.013	.891
		.757	.057	.041	.925
	1000	.228	.047	.042	.801
		.796	.042	.080	.870
	1500	.406	.039	.070	.721
		.719	.033	.114	.802
	2000	.182	.050	.047	.582
		.586	.040	.103	.676
		.753	.031	.146	.752
	2500	.216	.057	.072	.510
		.449	.044	.114	.606
		.640	.041	.158	.672
		.763	.037	.175	.713
		.804	.044	.194	.739
	3000	.056	.126	.039	.286
		.087	.083	.052	.319
		.072	.109	.041	.319
		.100	.082	.064	.339
		.127	.083	.071	.366
		.277	.067	.112	.466
		.438	.055	.175	.588
		.896	.043	.232	.727
		.050	.144	single phase	
	3500	.777	.046	.249	.646
		.556	.056	.190	.509
		.362	.068	.166	.433
		.343	.051	.149	.391
		.278	.066	.151	.328
		.220	.089	.138	.299
		.174	.137	single phase	
	4000	.740	.047	.273	.573
		.540	.064	.236	.481
		.413	.095	.217	.414
		.297	.152	.222	.301
		.255	.196	single phase	
	4500	.740	.062	.313	.539
		.477	.114	.289	.364
		.454	.126	.293	.341
		.360	.197	single phase	
	5000	.908	.049	.375	.600
		.794	.060	.373	.509
		.576	.105	.350	.392
		.517	.137	.363	.333
		.516	.137	.364	.332
		.429	.221	single phase	
220	500	.491	.125	.025	.926
	1000	.264	.090	.031	.805
		.528	.089	.056	.854
220	1500	.811	.073	.118	.841
		.544	.079	.086	.793
		.269	.092	.049	.727
	2000	.160	.096	.045	.583
		.378	.085	.086	.662
		.592	.076	.121	.733
		.748	.074	.162	.759
	2500	.158	.101	.058	.488
		.319	.102	.106	.563
		.393	.096	.129	.584
		.573	.090	.159	.652
		.719	.077	.187	.712
		.786	.074	.208	.720
	3000	.796	.080	.260	.670
		.509	.098	.198	.561
		.288	.107	.150	.481
		.219	.141	.124	.414
		.185	.146	.107	.379
		.173	.143	.103	.357
		.143	.176	single phase	
	3500	.437	.134	.224	.476
		.412	.147	.220	.436
		.358	.153	.226	.399
		.233	.330	.319	.199
		.556	.114	.255	.515
		.854	.085	.338	.647
		.300	.215	single phase	
	4000	.618	.123	.337	.473
		.577	.133	.326	.452
		.503	.173	.324	.413
		.485	.173	.327	.387
		.427	.206	.336	.336
		.563	.140	.338	.431
		.367	.262	single phase	
	4500	.699	.135	.413	.457
		.611	.161	.423	.391
		.599	.173	.419	.379
		.639	.151	.408	.429
		.568	.205	.414	.385
		.549	.244	single phase	
	5000	.760	.143	.488	.424
		.695	.161	.516	.357
		.670	.188	.524	.341
		.640	.194	single phase	
280	500	.417	.248	.027	.929
	1000	.293	.168	.039	.830
		.500	.168	.061	.859
	1500	.715	.145	.147	.798
		.474	.147	.088	.778
		.298	.151	.064	.737
	2000	.098	.181	.038	.569
		.520	.156	.129	.714
		.670	.146	.173	.741
		.720	.139	.181	.753
	2500	.696	.156	.239	.685
		.570	.163	.215	.633
		.295	.194	.143	.531
		.218	.217	.118	.510
		.173	.231	.102	.488
		.164	.238	.098	.473
		.138	.249	.095	.443
		.116	.265	single phase	
	3000	.741	.153	.317	.611
		.636	.168	.289	.589
		.492	.199	.271	.519
		.450	.212	.246	.515
		.400	.233	.246	.475
		.370	.255	.252	.422
		.334	.279	single phase	
	3500	.550	.237	.370	.465
		.535	.240	.387	.424
		.524	.244	.380	.429
		.584	.226	.373	.480
		.705	.189	.385	.536
		.460	.307	.418	.359
	4000	.775	.212	.489	.501
		.711	.242	.495	.462
		.716	.232	.484	.473
		.650	.274	.507	.429
		.589	.319	single phase	
340	500	.061	.468	.001	.910
		.136	.458	.008	.940
		.256	.434	.021	.933
	1000	.032	.326	.005	.801
		.280	.318	.053	.840
		.483	.297	.080	.866
		.550	.290	.085	.863
	1500	.015	.333	.008	.639
		.074	.308	.028	.660
		.137	.299	.049	.673
		.257	.275	.080	.703
		.681	.243	.171	.800
		.698	.240	.188	.786
	2000	.477	.304	.193	.681
		.227	.364	.139	.589
		.174	.408	.121	.544
		.140	.470	single phase	
	2500	.628	.317	.328	.633
		.488	.376	.333	.562
		.409	.422	single phase	

lecular sieve column, so that little baseline disturbance occurred when the flow of the carrier gas was altered.

The instrument was calibrated with the pure components and with known compositions of methane and n-hexane to ascertain linear response. Checks were made on the mass spectrometer and agreemnt to within 1 mole % was attained.

RESULTS

Analyses of the ternary equilibrium samples obtained in this investigation are shown in Table 1 and illustrated in familiar ternary phase diagrams in Figures 1 and 2. Each phase diagram contains only the experimental data for the indicated constant temperature.

The ternary data approached binary data as the ternary composition became lean in one of the volatile components (3). Also, reasonable comparison to limited interpolated data from Boomer (1) was made for the liquid samples. However, greater deviation from Boomer's data was found in the vapor phase compositions.

The experimental data were graphically smoothed using a y-x diagram for each of the five isotherms. K values for each component were then calculated from the smoothed equilibrium data. Then the familiar log K vs. log P graphs shown in Figures 3 and 4, with constant nitrogen content in the vapor phase serving as the parameter, were prepared for each isotherm.

Organick and Brown (2) stated that for ternary systems composed of components with similar chemical nature, the K values for each volatile component increased as the volatile composition of the overall system increased.

Figures 3 and 4 substantiate Organick for this system, except for the methane at 100°F. at low pressures. At 100°F., the region of low pressures (around 500 lb./sq.in.abs.), the addition of nitrogen to the system at constant pressure causes methane to be preferentially dissolved in the liquid phase. The liquid phase at low pressures is composed principally of n-hexane. Therefore, methane at low pressures is more soluble in n-hexane than is nitrogen. However, at pressures of 1,000 lb./sq.in.abs. or more the physical and chemical properties of methane and nitrogen approach one another and their solubilities in the liquid phase are as expected. The K values of methane increased with the addition of nitrogen in the vapor phase for all other conditions.

In Figure 1, the curvature in the bubble point composition locus illustrates the fact that the solubility of the volatile components is greater than ideal solution theory would predict. However, this graph does not show which, if any, component is preferentially dissolved. No curvature in the bubble point locus is visible at higher temperatures.

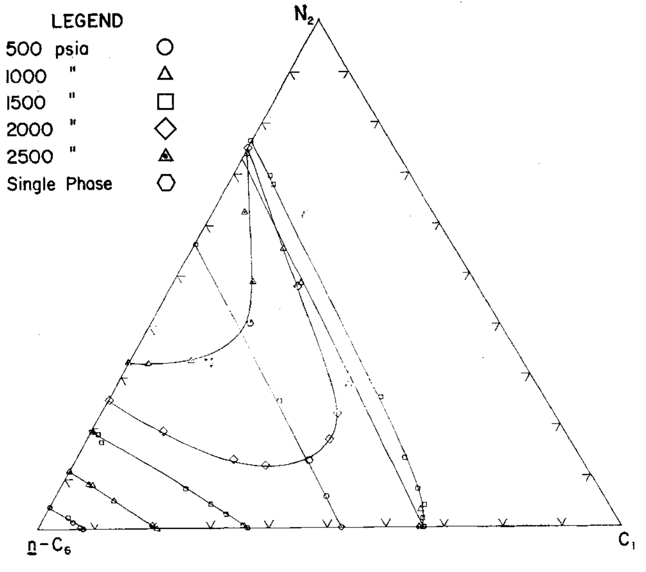

Fig. 2. Phase diagram at 340°F.

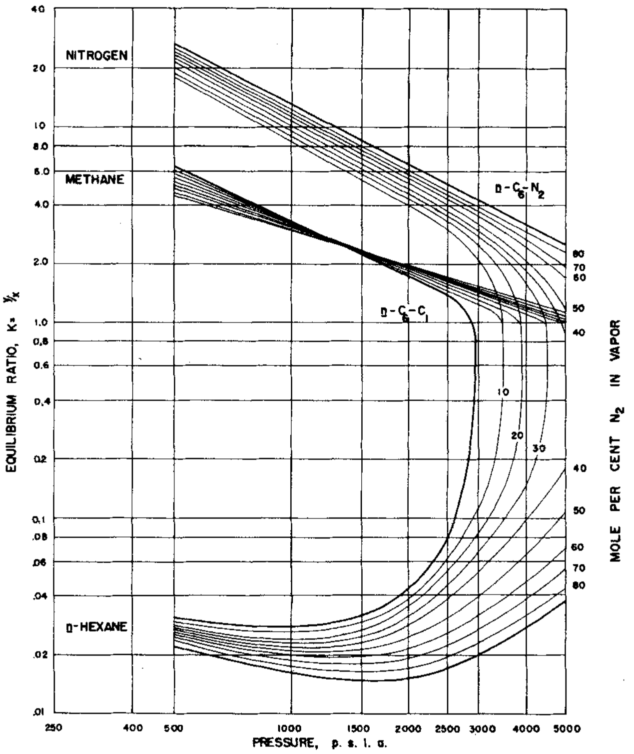

Fig. 3. K values at 100°F.

Accuracy

The overall analytical procedure is thought to be reliable to ± 0.002 mole fraction of the smoothed experi-

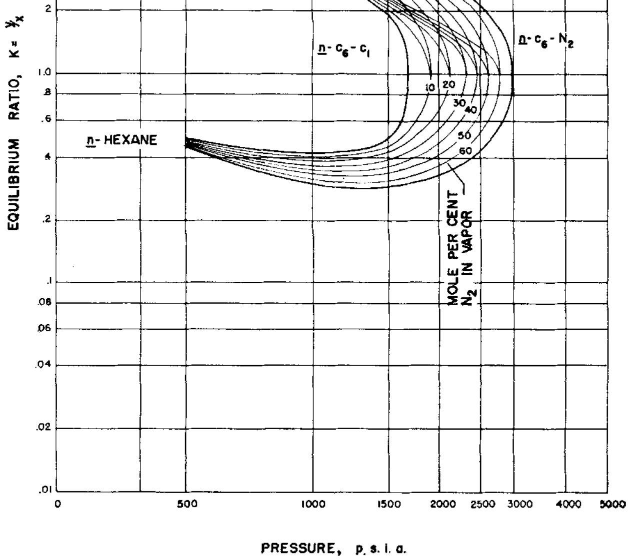

Fig. 4. K values at 340°F.

mental data. Variations within the cell were ± 0.2°F. during circulation and ± 2 lb./sq.in.abs. during circulation, settling, and sampling.

Materials Used

The methane and *n*-hexane were of research grade with stated purity of 99.9%. The nitrogen was dry research grade with a purity of 99.85%. Independent analyses on the mass spectrometer and the gas chromatograph confirmed these purities.

ACKNOWLEDGMENT

This work was carried out under a National Science Foundation Grant, for which the authors are very grateful. Also, Phillips Petroleum Company provided the research grade hydrocarbons.

LITERATURE CITED

1. Boomer, E. H., and C. A. Johnson, *Can. J. Res.*, 16, 319-396 (1938).
2. Organick, E. I., and G. G. Brown, *Chem. Eng. Progr. Symposium Ser. No.* 2, 48, 97-111 (1952).
3. Poston, R. S., and J. J. McKetta, to be submitted for publication.
4. Roberts, L. R., and J. J. McKetta, *A.I.Ch.E. J.*, 7, No. 1, 173-174 (1961).

Manuscript received February 5, 1965; revision received May 24, 1965; paper accepted May 26, 1965.

Correlations of Selectivity Parameters for Separations Extractions of Hydrocarbons with Fluorochemicals

M. S. B. MUNSON

Esso Research and Engineering Company, Baytown, Texas

The equation $\ln \beta^1{}_2 = \epsilon^1{}_2\, x_S{}^2/T$ adequately represents the variation of the separation factors for the extraction of hydrocarbon mixtures with fluorochemicals. The selectivity parameter $\epsilon^1{}_2$ is a measure of the selectivity of a solvent for hydrocarbons 1 and 2 which is independent of the experimental conditions. With a given solvent it is possible to develop a correlation between $\epsilon_j{}^i$ for pairs of hydrocarbons and the heats of vaporization of these hydrocarbons. A group contributions method is also successful in correlating the selectivity parameters. The three fluorochemicals in these experiments, $(C_4F_9)_3N$, C_7F_{14}, and $C_8F_{16}O$, had essentially the same selectivity for hydrocarbon separation which one would expect on the basis of their essentially identical solubility parameters.

If we consider that, at equilibrium between two phases of a multicomponent system, the activity of each component must be the same in both phases, then, by definition

$$a_{1j} = x_{1j}\gamma_{1j} = a_{1i} = x_{1i}\gamma_{1i} \qquad (1)$$

For the two compounds to be separable by liquid-liquid extraction, the ratios of the distribution coefficients for the two compounds between the two phases must be different than unity.

$$(x_{1i}/x_{1j})/(x_{2i}/x_{2j}) = \beta_2{}^1 \neq 1 \qquad (2)$$

For convenience we may say that in order to extract component 1 from component 2, with a given solvent, $\beta_2{}^1 > 1$. This quantity β is sometimes called the selectivity (*16*), but it seems somewhat better to refer to the quantity ln β (or log β) as the selectivity (*1*), since with this definition a nonselective solvent has a selectivity of zero rather than one.

Substituting the first set of equations into the definition of the separation factor β one obtains

$$\beta_2{}^1 = (x_{1i}/x_{1j})/(x_{2i}/x_{2j}) = (\gamma_{1j}/\gamma_{1i})/(\gamma_{2j}/\gamma_{2i}) \qquad (3)$$

Here β is defined in terms of the activity coefficients of the two compounds to be separated in the two phases. If one considers the extraction of a mixture of hydrocarbons with a solvent, one phase *b* will be predominantly hydrocarbon and the other *a* will be predominantly solvent. To a reasonable approximation hydrocarbons form ideal mixtures and the activity coefficients of the hydrocarbons 1 and 2 in the predominantly hydrocarbon phase *b*, γ_{1b}, and γ_{2b} will be of the order of unity, as will be their ratio. This ratio also will be an insensitive function of the concentration of the solvent in the predominantly hydrocarbon phase *b*, so that

$$\beta_2{}^1 \cong 1/(\gamma_{1a}/\gamma_{2a}) \qquad (4)$$

That is, the separation factor is the inverse ratio of the activity coefficients of the two components to be separated in the predominantly solvent phase *a*.

Many equations can express the dependence of activity coefficients on concentration of single-phase binary mixtures; they are generally of the form

$$T \ln \gamma_{1j} = A_{1j} x^2_{2j} F(x_2, x_1) \qquad (5)$$

although the temperature is not always explicity given. The lowest power of the concentration which can occur and satisfy the Gibbs-Duhem equation is x^2 (*9*) and this term is the only one occurring in the "zeroth approximation" of Guggenheim (*8*) for which random mixing is