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Effect of the Presence of Nitrogen on Solid Solubility of Normal Paraffins in Liquid Methane

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Experimental solid–liquid–vapor three-phase data are presented on the ternary systems methane–nitrogen–*n*-heptane and methane–nitrogen–*n*-octane. These data were taken by employing cryoscopic techniques and are compared with existing binary data on the systems methane–*n*-heptane and methane–*n*-octane to evaluate the effect that small quantities of nitrogen have on the solubility of hydrocarbon solutes in liquid methane.

Introduction

A major problem in the liquefaction processing of liquefied natural gas (LNG) is the precipitation of solids (hydrocarbons and CO_2) from the liquid phase. These solids can coat the surfaces of heat exchangers and foul turbo-expansion devices, requiring liquefaction units to be shut down for cleaning and/or repair. We have been conducting an extensive study of the solid–liquid–vapor three-phase equilibria of binary and ternary prototype systems pertinent to the problem, with the goal of providing data with which to build a successful correlation of the S–L–V phase equilibria behavior of realistic LNG process systems.

In several earlier papers, we have investigated the effect of additive gases on the solubility of certain hydrocarbon solutes in liquid methane. A dramatic enhancement of the solubility of *n*-heptane, *n*-octane, benzene, and cyclohexane in liquid methane was observed with the addition of modest amounts of ethane (*7*, *8*). More pronounced enhancement of *n*-heptane and *n*-octane solubility was reported with the addition of either propane or *n*-butane instead of ethane (*6*). It can be concluded that the less volatile solvent additives will enhance solid hydrocarbon solubility, the degree to which is an increasing function of the carbon number of the additive.

In contrast, the presence of nitrogen should depress the solubility of a hydrocarbon solute in a typical LNG solvent. Hottovy et al. (*2*) examined the effect of nitrogen on the solubility of *n*-octane, *n*-decane, and *n*-dodecane in liquid ethane and reported a decrease in the solute solubility with increasing amounts of nitrogen in the ethane solvent.

In this paper, we report the effect of nitrogen on the solubility of *n*-heptane and *n*-octane in liquid methane. These S-L-V data, which were taken by cryoscopic means, are interpreted in comparison to earlier studies on the binary S-L-V systems methane–*n*-heptane (*8*) and methane–*n*-octane (*4*).

Table I. Solid–Liquid–Vapor Three-Phase Raw Data for the Ternary System Methane-Nitrogen-*n*-Heptane

run	temp, K	press., atm	liquid-phase compn, mole fraction C_1	N_2	C_7	liquid-phase molar vol, mL/(g mol)
1	165.55	24.02	0.9412	0.0496	0.009 23	50.2
	164.32	23.48	0.9406	0.0512	0.008 20	50.0
	162.78	23.27	0.9394	0.0535	0.007 02	49.6
2	160.79	21.43	0.9404	0.0537	0.005 92	48.8
3	169.16	27.08	0.9389	0.0482	0.012 83	52.0
	167.97	26.27	0.9381	0.0507	0.011 19	51.6
	167.00	25.72	0.9379	0.0519	0.010 26	51.2
	166.76	25.52	0.9375	0.0528	0.009 73	51.1
	166.56	25.45	0.9372	0.0535	0.009 27	51.0
4	164.85	22.86	0.9488	0.0423	0.008 95	50.4
	161.56	20.89	0.9479	0.0457	0.006 49	49.3
	163.63	22.18	0.9483	0.0442	0.007 57	49.9
	160.10	20.21	0.9473	0.0469	0.005 81	49.0
	158.47	19.26	0.9449	0.0502	0.004 96	48.4
	156.72	18.13	0.9433	0.0524	0.004 33	47.2

Table II. Solid–Liquid–Vapor Three-Phase Raw Data for the Ternary System Methane-Nitrogen-*n*-Octane

run	temp, K	press., atm	liquid-phase compn, mole fraction C_1	N_2	C_8	liquid-phase molar vol, mL/(g mol)
1	172.65	29.80	0.9573	0.0422	0.000 518	55.23
	167.45	25.48	0.9538	0.0458	0.000 389	50.90
	165.62	24.29	0.9518	0.0479	0.000 330	50.36
2	174.06	30.62	0.9600	0.0395	0.000 504	55.46
3	175.17	32.46	0.9584	0.0412	0.000 479	55.33
	171.66	29.46	0.9542	0.0454	0.000 414	52.88
	167.69	26.20	0.9520	0.0477	0.000 340	50.94
4	168.39	25.38	0.9662	0.0334	0.000 401	51.64
	164.74	22.66	0.9619	0.0378	0.000 302	50.18
	161.43	20.48	0.9619	0.0379	0.000 261	48.75
	159.75	19.39	0.9585	0.0413	0.000 233	47.26
5	185.26	43.75	0.9577	0.0418	0.000 496	70.49
	170.42	27.97	0.9565	0.0431	0.000 397	53.02
	168.02	26.54	0.9556	0.0441	0.000 356	52.13
6	184.05	43.14	0.9461	0.0535	0.000 449	68.67
7	182.64	41.24	0.9495	0.0501	0.000 408	66.33
8	180.08	37.02	0.9577	0.0416	0.000 721	64.87
	170.80	27.90	0.9661	0.0334	0.000 556	54.09
	166.99	24.91	0.9605	0.0390	0.000 438	51.99
	164.24	23.48	0.9603	0.0394	0.000 359	51.73
	160.88	20.89	0.9547	0.0451	0.000 236	47.92
9	178.88	36.88	0.9515	0.0479	0.000 533	60.82
	176.65	34.09	0.9596	0.0398	0.000 528	58.46
	174.23	32.18	0.9509	0.0486	0.000 457	56.68
	171.69	29.74	0.9496	0.0499	0.000 409	54.73
	170.30	28.51	0.9478	0.0518	0.000 363	54.05
10	180.43	38.72	0.9498	0.0498	0.000 485	61.88

Experimental Section

The apparatus used in this study was identical with that reported by Lee and Kohn (*5*). Our experimental procedure of cryoscopically determining the S–L–V equilibria and properties is detailed in ref *2* and *4*. Gaseous feed mixtures of ~20:1 were accurately prepared, and the distribution of methane and nitrogen between the liquid and vapor phases in the presence of solute crystals was determined with the aid of existing literature (*9*) on methane–nitrogen vapor–liquid equilibria as well as vapor–liquid phase equilibria measurements of our own. On occasion, samples of the vapor phase were taken and analyzed

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Table III. Comparison of Estimated Liquid-Phase Solubility of *n*-Heptane in a 20:1 Methane-to-Nitrogen Solvent Mixture and in Pure Methane with Ideal Solubility

temp, K	X_I	X_{C_7} ($C_1/N_2 = \infty$)[a]	X_{C_7} ($C_1/N_2 = 20$)[b]
168	0.4485	0.0197	0.0114
165	0.3736	0.0133	0.008 70
162	0.3091	0.009 74	0.006 76
159	0.2540	0.007 67	0.005 41
156	0.2071	0.005 95	0.004 33

[a] Obtained from ref 8. [b] Obtained from Table I.

Table IV. Comparison of Estimated Liquid-Phase Solubility of *n*-Octane in a 20:1 Methane-to-Nitrogen Solvent Mixture and in Pure Methane with Ideal Solubility

temp, K	X_I	X_{C_8} ($C_1/N_1 = \infty$)[a]	X_{C_8} ($C_1/N_2 = 20$)[b]
180	0.0973	0.000 772	0.000 556
175	0.0655	0.000 664	0.000 478
170	0.0431	0.000 538	0.000 390
165	0.0276	0.000 406	0.000 307
160	0.0172	0.000 288	0.000 228

[a] Obtained from ref 4. [b] Obtained from Table II.

by using a gas chromatograph.

The experience of the authors is that the *solute* composition reported in the *raw* data is uncertain in the third significant figure. The molar volume raw data are uncertain in the third significant figure, to no more than ±0.4% of the molar volume. The feed mixtures could be stoichiometrically prepared to ±0.01% in the ratio of methane to nitrogen. The temperatures reported in Tables I and II are precise to ±0.2 K while the pressures are precise to ±0.1 atm.

The methane used in this study was Linde "ultra pure" grade stated to be 99.97 mol % pure. The gas was run through 13X molecular sieves at 100-atm pressure and room temperature before use. A -85 °C isotherm determined on the treated gas indicated a difference between the bubble-point and the dew-point pressure of 0.2 atm, and vapor pressure of 50 vol % liquid was within 0.1 atm of the data reported by Din (*1*).

The nitrogen was "ultra dry grade", supplied by the Mittler Supply Co. (South Bend, IN) and was rated at 99.5+% pure. The nitrogen was used as is.

The *n*-heptane and *n*-octane were Humphrey-Wilkinson "Pure Grade" petroleum-derived products with a stated purity of 99%. Freezing-point depressions (air-saturated) and refractive indexes supported this claim, and the solutes were used without further purification.

Results

Tables I and II present the raw data for the ternary systems methane-nitrogen-heptane and methane-nitrogen-*n*-octane, respectively. These raw data are shown in Figures 1 and 2, and estimates of the solubility of these solutes in a 20:1 liquid mixture of methane-nitrogen are shown as well as tabulated in Tables III and IV. For comparison, earlier data on the binary systems methane-*n*-heptane and methane-*n*-octane are also presented. The presence of nitrogen in liquid methane significantly lowers the solubility of *n*-octane, e.g., more so in terms of percent decrease than the same amount of nitrogen in liquid ethane does (*2*). A possible explanation is that the methane-*n*-octane system is already highly nonideal (*4*) while the ethane-*n*-octane system is only slightly nonideal (*3*). Ideal solubilities of *n*-heptane and *n*-octane, which would obey eq 1, are presented in Tables III and IV, respectively.

$$\ln X_I = \frac{\Delta h_F}{RT_T}[1 - (1/T^*)] \qquad (1)$$

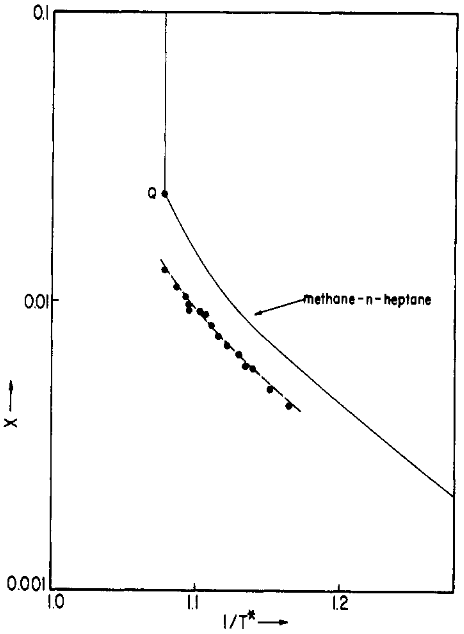

Figure 1. S-L-V data points for the ternary system methane-nitrogen-*n*-heptane. The dashed line is an estimate of the S-L-V locus for a methane-to-nitrogen ratio of 20:1. Also shown for comparison are S-L-V data for the binary methane-*n*-heptane system (*8*), for the branch of the S-L-V locus at temperatures lower than the Q-point.

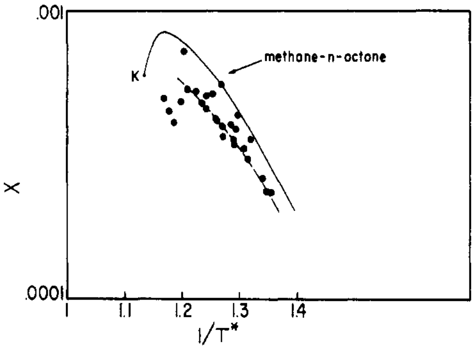

Figure 2. S-L-V data points for the tenary system methane-nitrogen-*n*-octane. The dashed line is an estimate of the S-L-V locus for a methane-to-nitrogen ratio of 20:1. Also shown for comparison are S-L-V data for the binary methane-*n*-octane system (*4*), for the lower temperature branch of the S-L-V locus.

Glossary

Δh_F	heat of fusion at the triple point of the solutes, 3354 cal/(g mol) for *n*-heptane and 4957 cal/(g mol) for *n*-octane
K	K-point, or critical end point, of a S-L-V locus where L and V are critical
L	liquid phase
Q	Q-point, or quadruple point, of a S-L-V locus where one has four phases ($S-L_1-L_2-V$)
R	gas constant, 1.987 cal/(g mol K)
S	solid phase
T	temperature, K
T_T	triple-point temperature of the solutes, 182.57 K for *n*-heptane and 216.38 K for *n*-octane
T^*	$= T/T_T$
V	vapor phase
X	mole fraction
X_I	ideal mole fraction of the solute, calculated from eq 1

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Saturation Properties of Chlorine by the Principle of Corresponding States

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Vapor pressures, saturation densities, and enthalpies of evaporation of chlorine have been estimated from the triple point to the critical point and correlated by appropriate equations. The only reliable experimental data are vapor-pressure measurements below the normal boiling point. The work described here shows that with this limited information a modified corresponding-states technique, where the critical-point parameters and the acentric factor are determined from the reliable vapor-pressure measurements using a nonlinear fitting procedure, gives accurate values.

Introduction

The thermodynamic properties of a fluid at saturation, as well as being of use in themselves, are important in defining an equation of state for use over a wide range in the liquid and gas regions. As part of a study of the properties of the industrially important fluid chlorine, a survey of the experimental data on the saturation curve showed that the only measurements in which the modern correlator can have confidence are restricted to vapor pressures over a limited temperature range. The most comprehensive correlation based on experimental results, by Kapoor and Martin (*1*), predates some of the better data and does not achieve the accuracy that is now attainable. Stein (*2*) has calculated properties based on generalized corresponding states which are useful for some purposes but again do not achieve high accuracy.

Available Data

After a critical evaluation of all of the vapor-pressure data for chlorine available in the literature, the experimental data sets listed in Table I were considered to be the only ones approaching the precision required for accurate correlation.

Table I. Experimental Vapor-Pressure Data

ref	T_R range	date
3	0.41–0.58	1939
4 (series I)	0.49–0.65	1979
4 (series II)	0.8–1.0	1979
5	0.47–1.0	1915
ref	**critical-point values**	
5	417.15 K, 7.7011 MPa	
4	416.76 K, 7.991 MPa	
	416.87 K, 7.974 MPa	
	416.90 K, 7.977 MPa	

Table II. Experimental Saturation Density Data

ref	T_R range	date
	Gas	
5	0.66–0.97	1915
	Liquid	
5	0.47–0.97	1915
7	0.47–0.58	1909
8	0.46–0.84	1890
9	0.50–0.58	1937

The results of Giauque and Powell (*3*) and the series-*I* results of Ambrose et al. (*4*) are in close agreement where they overlap and show little scatter, but the series-II results of Ambrose et al. and those of Pellaton (*5*) are scattered and differ by between 1 and 5%. From the experimental details reported in these references the results of Giauque and Powell and the series-I results of Ambrose et al. were judged to be the most reliable, and a requirement for any new correlation is that these data should be adequately reproduced. The value of the critical point reported throughout the literature is that found by Pellaton. The recent values reported by Ambrose et al. are of at least equal precision. In view of the differences, the critical point must be regarded as uncertain.

The only correlations of vapor pressure based on experimental data are that by Ambrose et al. (*4*), which was fitted only to results from their laboratory, and that by Kapoor and Martin (*1*), which predates the results of Ambrose et al. Tables of properties based on predictive generalized corresponding-states methods have been calculated by Stein (*2*) using the constants of Lee and Kesler (*6*). These are useful for some purposes but can be in error by several percent. This may be due either to the fact that the properties of the reference fluids are based on data for several real fluids which are of low accuracy near the saturation curve or to the fact that the extended BWR equations used by Lee and Kesler have incorrect behavior near saturation.

All of the measurements of saturation densities, which are listed in Table II, are of dubious quality. The results of Pellaton, which were previously thought to be accurate, were carried out at the same time as his vapor-pressure measurements, the reliability of which is now in question. The work of the other experimenters can be criticized on several counts, e.g., purity of samples and accuracy of temperature scale. The usual

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