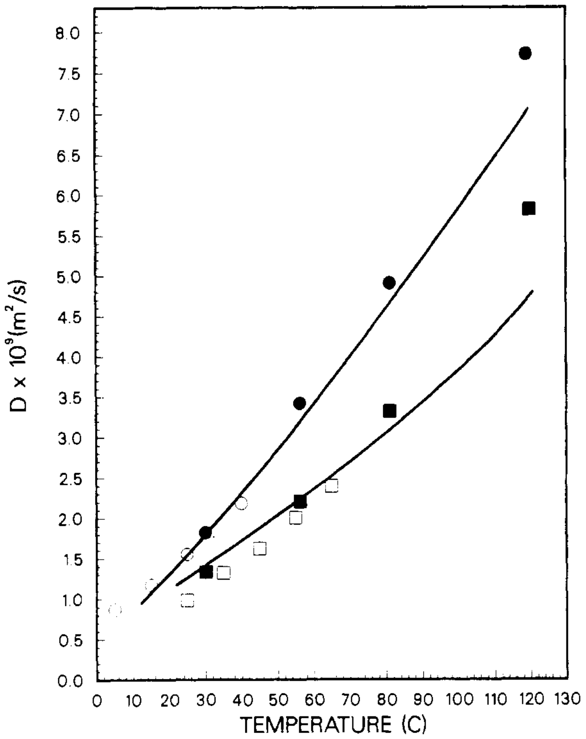

Figure 1. Infinte dilution diffusion coefficients of methanol and 2-propanol in water: (●) methanol, this work; (■) 2-propanol, this work; (○) methanol, ref *5*; (□) 2-propanol, ref *4*; (—) predictions of Othmar and Thakar (*6*).

used the Taylor dispersion method to make their measurements. Esteal and Woolf used a magnetically stirred diaphragm cell technique. Our low-temperature data agrees well within experimental accuracy with data of Pratt and Wakeham and Esteal and Woolf.

Diffusion in water as been well correlated with the Othmar and Thakar equation (*5*). For diffusion in water this empirical correlation reduces to

$$D_{12} = 14.0 \times 10^{-5} \eta_2^{-1.1} V_1^{-0.6} \tag{1}$$

where the water viscosity η_2 is in centipoise, the molar volume of the alcohol is in cm^3/(g mol), and the diffusivity is in cm^2/s. This equation is also plotted in Figure 1. As can be seen from the figure, the agreement is good at low temperatures; however, there is a significant deviation from the data at high temperatures. Clearly there is a danger in extrapolating this predictive equation beyond its temperature range.

Glossary

D_{12}	diffusivity of solute 1 in solvent 2
V_1	molar volume of solute, cm^3/(g mol)
η_2	solvent viscosity

Registry No. Methanol, 67-56-1; 2-propanol, 67-63-0; water, 7732-18-5.

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Vapor–Liquid Equilibria of Nitrogen–Hydrocarbon Systems at Elevated Pressures

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The phase equilibria behavior of nitrogen + hydrocarbon binary, ternary, and quaternary systems was studied. Measurements were made over the temperature range from 305.4 K (90 °F) to 373.2 K (212 °F) at pressures up to 35.85 MPa (5200 psia). The binary systems studied included nitrogen + *n*-heptane, nitrogen + *n*-octane, nitrogen + *n*-nonane, nitrogen + *n*-decane, nitrogen + *n*-dodecane, nitrogen + benzene, and nitrogen + toluene. The methane + *n*-butane + *n*-decane, nitrogen + *n*-butane + *n*-decane, and nitrogen + methane + *n*-butane + *n*-decane systems are also reported. Comparisons with binary data from the literature show good agreement and consistency of a new experimental vapor–liquid equilibrium (VLE) measurement design.

Introduction

Nitrogen has been widely used in oilfield operations for reservoir pressure maintenance, gas cycling, and gas lift. In recent years, the use of nitrogen for enhanced oil and gas recovery has become an attractive method for some high-pressure reservoirs.

A thorough understanding of the phase behavior of the nitrogen gas and the crude oil is essential for applications of nitrogen in enhanced oil recovery. The equilibrium phase diagram of nitrogen–crude oil systems can be used to establish whether a miscible or immiscible condition will occur.

Ideally, the phase behavior of complex systems can be predicted by using equations of state (EOS) such as the Soave–Redlich–Kwong (SRK) or Peng–Robinson (PR) EOS. However, the use of EOS for the prediction of these multicomponent systems will face a possible problem—the lack of experimental phase behavior information needed to optimize these equations of state for more accurate predictions.

Most of the information on this subject in the literature is about binary nitrogen–light alkane systems. Binary system studies involving nitrogen and methane, ethane, or propane have been concentrated mostly on operations under cryogenic conditions. Most data for ternary and a few quaternary systems

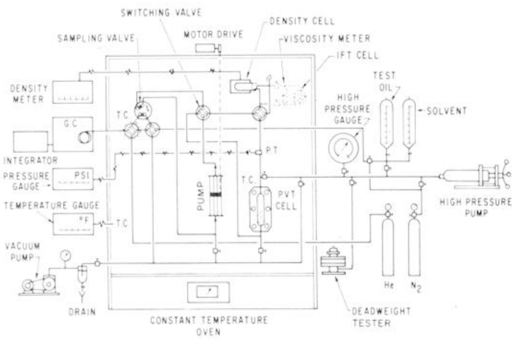

Figure 1. Flow diagram for volumetric and VLE measurement apparatus.

have concentrated on mixtures containing nitrogen and methane at low-temperature conditions. Under these conditions, VLE and vapor–liquid–liquid equilibrium (VLLE) information has been reported.

Intermediate- and high-temperature studies involving nitrogen and alkanes ranging from butane up to octane (*1*, *2*, *7*–*11*, *15*, *19*) as well as mixtures with benzene (*12*–*14*) and toluene (*6*, *16*) are also available, with a few data reported for systems containing components heavier than *n*-decane (*3*, *5*, *13*). The ternary study by Azarnoosh et al. (*4*) presents the nitrogen + methane + *n*-decane VLE data at high temperatures and pressures. Data for nitrogen-containing quaternary and multicomponent systems under such conditions are scarce.

These simpler systems serve as the basis for understanding the behavior of multicomponent systems through analysis of simpler systems represented by light, intermediate, and heavy components. Information generated from these VLE studies will help to determine binary interaction parameters in equations of state for more accurate representation of nitrogen + hydrocarbon oil phase behavior.

This paper presents results on the equilibrium composition of binary, ternary, and quaternary systems of nitrogen + hydrocarbons at elevated pressures. The binary systems of nitrogen and *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-dodecane, benzene, and toluene were studied to provide additional VLE information on these binaries and to check the consistency of the experimental techniques and procedures with data in the literature. The temperatures and pressures used in this study are in the range of reservoir conditions. The ternary systems of methane + *n*-butane + *n*-decane and nitrogen + *n*-butane + *n*-decane were studied at 352.6 K (175 °F) and 27.58 MPa (4000 psia) to provide information on the phase diagram of the quaternary system of nitrogen + methane + *n*-butane + *n*-decane. This latter system shows the effect of methane on the behavior of the nitrogen + *n*-butane + *n*-decane mixture.

Experimental Equipment and Procedure

The experimental work was performed with an apparatus designed to facilitate sampling of both liquid and vapor phases at high pressures and temperatures using a flow switching technique. A schematic diagram of the experimental apparatus is shown in Figure 1.

The VLE apparatus consists of a 100-cm^3 Ruska high-pressure, windowed *PVT* cell. The system was designed to handle high pressure studies (up to 41.37 MPa (6000 psia)). A Ruska magnetic pump was used to circulate each phase to ensure thorough mixing and to pump the circulation fluid through the sample valve for the chromatographic sampling. A Valco switching valve was used to direct the flow of each phase to provide both liquid- and vapor-phase sampling. Sampling was done using an inline high-pressure sampling valve with a volume of 1–5 μL. The analysis of phase samples was convenient, fast, and accurate. The entire apparatus was housed in an oven with temperature controlled to ±0.1 °F. *PVT* cell temperature was measured by means of thermocouple leads connected to a digital temperature readout. Frequent thermocouple calibrations were made to ensure no temperature shifts occur. System pressure was directly measured by means of a pressure transducer with an accuracy of ±0.03 MPa (±5 psia). The pressure calibrations were performed by means of a dead-weight tester.

Compositions of the vapor and liquid samples were determined with a Hewlett-Packard 5890A gas chromatograph equipped with both thermal conductivity and flame ionization detectors. The chromatograph was equipped with a Porasil-C column. Peak areas were determined with an HP 3392A electronic integrator.

The nitrogen used was Linde High Purity grade with a stated purity of 99.9 mol %. The methane used was Linde Ultra High Purity grade with a stated purity of 99.97 mol %. The propane and butane used were Linde Instrument grade with a stated purity of 99.5 mol %. The solutes used (*n*-heptane, *n*-octane, *n*-nonane, *n*-decane, benzene, and toluene) were all of stated purity of 99+ wt % from Alfa Products. These materials were used without further purification.

The system was preflushed with *n*-pentane or petroleum ether and then dried under vacuum at 352.6 K (175 °F). After drying under vacuum, the system was purged with nitrogen to ensure that the last traces of solvents were removed. The system was evacuated overnight and then ready for use. During the experimental run, a measured amount of the heaviest hydrocarbon was injected into the *PVT* cell under vacuum. The secondary solvents (butane and methane) were then added to the system as needed. Finally, the system was pressurized with nitrogen (or primary solvent) to the desired pressure. The magnetic circulation pump was then turned on to circulate the vapor phase to achieve equilibrium. Nitrogen was then introduced sparingly, to maintain the desired operating pressure until the pressure stabilized.

After the system reached apparent equilibrium, vapor samples were then collected in the sampling valve and carried by helium into the gas chromatograph for analysis. Sampling of the vapor phase continued until a stable compositional value was achieved (typically after three to four samples). Upon completing the gas-phase sampling, the switching valve was then switched for liquid-phase circulation to route liquid to the sampling valve. The sampling lines were heated above the boiling point of the sample with an electric heating coil to vaporize the liquid sample. Liquid-phase sampling injections and analysis were repeated four or five times.

Experimental Results

The experimental results for the binary systems are given in Table I. These results cover a range of temperatures from 305.4 K (90 °F) to 373.2 K (212 °F) as well as pressures from 3.45 MPa (500 up) to 35.16 MPa (5100 psia). The pressure–composition diagrams of two of these binaries are shown in Figures 2 and 3. As shown in the figures, the experimental work agrees very well with the works of Azarnoosh et al. (*3*) for the nitrogen + *n*-decane system, and Miller et al. (*14*) for the nitrogen + benzene system. These comparisons provide an acceptable measure of the internal consistency of the experimental setup and procedure.

The results of the vapor–liquid equilibrium studies of the ternary systems of methane + *n*-butane + *n*-decane and nitrogen + *n*-butane + *n*-decane and the quaternary system of nitrogen + methane + *n*-butane + *n*-decane are given in Tables II and III, and are shown on the triangular phase diagrams in Figures 4, 6, and 7. No literature information was available for comparison for nitrogen-containing systems. Figure 5 is a comparison of the methane + butane + decane

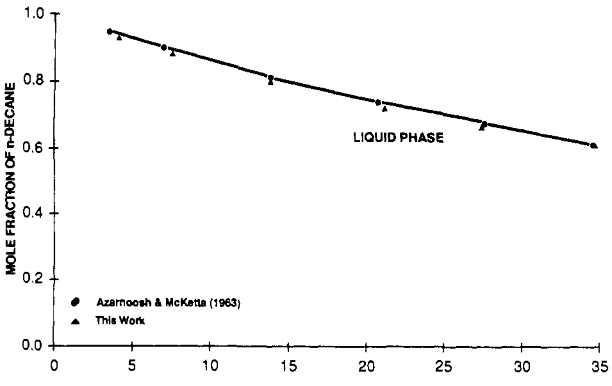

Figure 2. Pressure vs *n*-decane mole fraction in the liquid phase for the binary system nitrogen + *n*-decane at 344.3 K (160 °F).

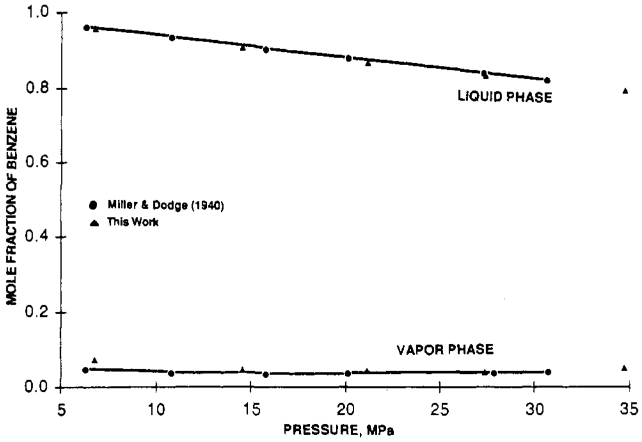

Figure 3. Pressure vs benzene mole fraction for the binary system nitrogen + benzene at 373.2 K (212 °F).

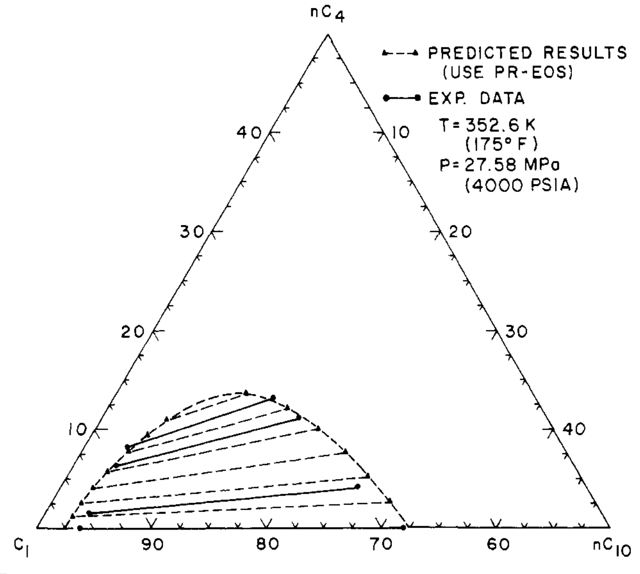

Figure 4. Phase envelope for the ternary system methane + *n*-butane + *n*-decane at 352.6 K (175 °F) and 27.58 MPa (4000 psia).

system with data from literature (*17*, *18*). Figures 4, 6, and 7 also show a comparison of the experimental results with the Peng–Robinson equation-of-state predictions. The binary interaction parameters for the equation of state were determined by the best fit of the binary data. As shown in the figures, deviations of the experimental and predicted results occur near the critical region.

The phase envelope of a ternary system can be represented by a triangular phase diagram, but for quaternary or multicomponent systems, because of the extra degree of freedom, the system components must be lumped into three pseudocomponents to be represented on the triangular phase diagram. In the study of the system of nitrogen + methane + *n*-butane +

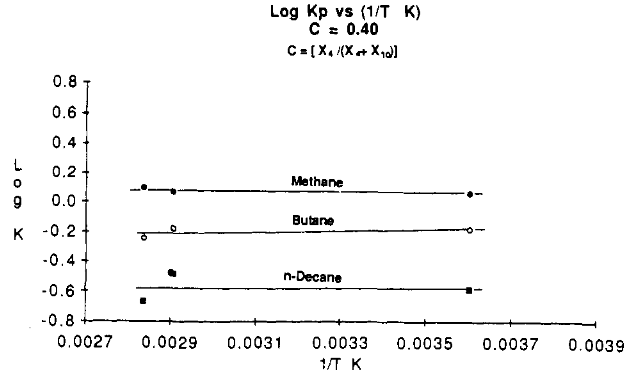

Figure 5. Comparison of experimental data of this work ($1/T < 0.0029$) and data from literature (*17*, *18*) for the ternary system methane + *n*-butane + *n*-decane at 27.58 MPa (4000 psia).

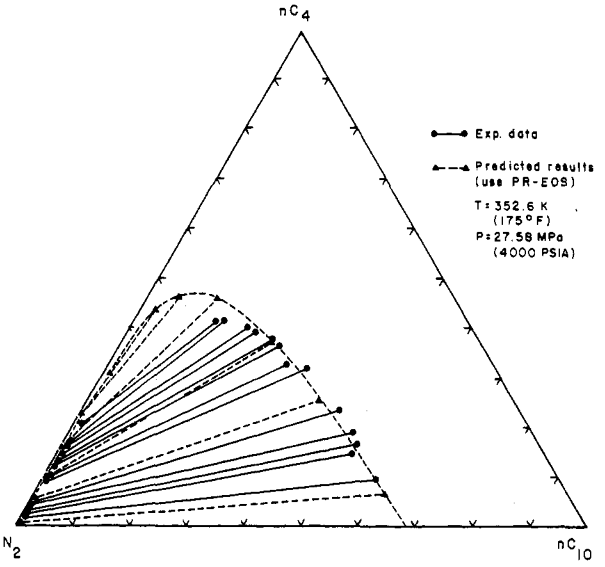

Figure 6. Phase envelope for the ternary system nitrogen + *n*-butane + *n*-decane at 352.6 K (175 °F) and 27.58 MPa (4000 psia).

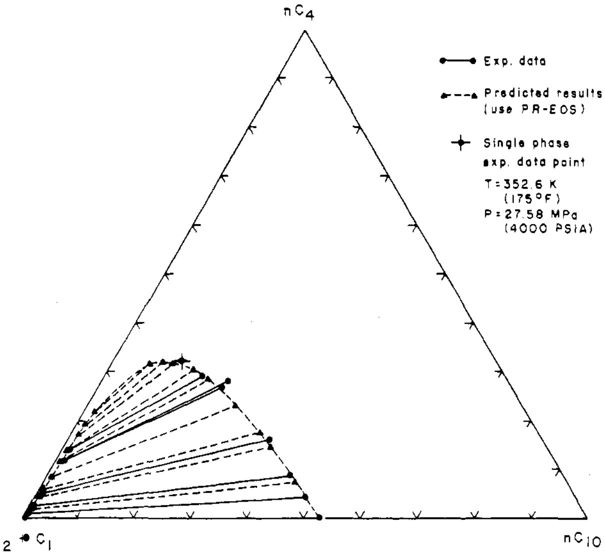

Figure 7. Pseudoternary phase diagram for the quaternary system nitrogen + methane + *n*-butane + *n*-decane at 352.6 K (175 °F) and 27.58 MPa (4000 psia).

Table I. Measured Equilibrium Compositions of Nitrogen-Hydrocarbon Binary Systems

Nitrogen–*n*-Heptane

press., MPa (psia)	mole fractn of *n*-heptane in liq	press., MPa (psia)	mole fractn of *n*-heptane in liq	press., MPa (psia)	mole fractn of *n*-heptane in liq	press., MPa (psia)	mole fractn of *n*-heptane in liq
T = 305.4 K (90 °F)		*T* = 324.3 K (124 °F)		*T* = 352.6 K (175 °F)		*T* = 366.5 K (200 °F)	
6.38 (925.0)	0.910	5.50 (797.0)	0.944	6.88 (998.0)	0.916	5.97 (866.0)	0.909
12.42 (1802.0)	0.845	10.41 (1510.0)	0.881	13.76 (1995.0)	0.823	12.94 (1877.0)	0.824
19.31 (2800.0)	0.801	19.39 (2812.0)	0.797	20.87 (3027.0)	0.761	19.20 (2784.0)	0.747
26.72 (3875.0)	0.726	25.29 (3668.0)	0.748	27.20 (3945.0)	0.696	27.47 (3984.0)	0.661
31.72 (4600.0)	0.704	29.70 (4308.0)	0.711	34.34 (4980.0)	0.628	33.96 (4925.0)	0.603
34.94 (5068.0)	0.684	34.23 (4965.0)	0.665				

Nitrogen–*n*-Octane

press., MPa (psia)	mole fractn of *n*-octane in liq	press., MPa (psia)	mole fractn of *n*-octane in liq	press., MPa (psia)	mole fractn of *n*-octane in liq	press., MPa (psia)	mole fractn of *n*-octane in liq
T = 322.0 K (120 °F)				*T* = 344.3 K (160 °F)			
4.24 (615.0)	0.940	21.28 (3086.0)	0.781	3.23 (468.0)	0.957	17.53 (2542.0)	0.799
9.00 (1306.0)	0.897	28.35 (4112.0)	0.727	4.23 (614.0)	0.945	24.69 (3581.0)	0.735
14.91 (2162.0)	0.839			7.12 (1033.0)	0.917	35.04 (5082.0)	0.653
				10.47 (1519.0)	0.874		

Nitrogen–*n*-Nonane

press., MPa (psia)	mole fractn of *n*-nonane in liq	press., MPa (psia)	mole fractn of *n*-nonane in liq	press., MPa (psia)	mole fractn of *n*-nonane in liq	press., MPa (psia)	mole fractn of *n*-nonane in liq
T = 322.0 K (120 °F)				*T* = 344.3 K (160 °F)			
3.92 (568.0)	0.952	20.98 (3043.0)	0.790	3.72 (540.0)	0.950	20.82 (3020.0)	0.777
7.49 (1086.0)	0.914	28.06 (4070.0)	0.738	7.34 (1065.0)	0.908	27.69 (4016.0)	0.718
14.55 (2110.0)	0.840	34.65 (5025.0)	0.698	14.02 (2033.0)	0.832	34.74 (5038.0)	0.668

Nitrogen–*n*-Decane

press., MPa (psia)	mole fractn of *n*-decane in liq	press., MPa (psia)	mole fractn of *n*-decane in liq	press., MPa (psia)	mole fractn of *n*-decane in liq
T = 344.3 K (160 °F)					
4.02 (583.0)	0.931	13.81 (2003.0)	0.804	27.39 (3972.0)	0.675
7.47 (1083.0)	0.884	21.13 (3065.0)	0.727	34.64 (5024.0)	0.620

Nitrogen–*n*-Dodecane

press., MPa (psia)	mole fractn of *n*-dodecane in liq	press., MPa (psia)	mole fractn of *n*-dodecane in liq	press., MPa (psia)	mole fractn of *n*-dodecane in liq
T = 327.6 K (130 °F)		*T* = 344.3 K (160 °F)		*T* = 366.5 K (200 °F)	
4.91 (712.0)	0.942	3.53 (512.0)	0.945	3.10 (450.0)	0.952
11.49 (1667.0)	0.864	10.18 (1476.0)	0.862	9.40 (1364.0)	0.878
17.92 (2599.0)	0.804	15.23 (2209.0)	0.788	16.29 (2363.0)	0.824
24.17 (3505.0)	0.752	21.70 (3147.0)	0.742	22.96 (3330.0)	0.762
29.37 (4260.0)	0.720	27.84 (4038.0)	0.693		
33.78 (4900.0)	0.684	34.69 (5031.0)	0.651		

Nitrogen–Benzene

press., MPa (psia)	mole fractn of benzene		press., MPa (psia)	mole fractn of benzene		press., MPa (psia)	mole fractn of benzene	
	in liq	in vapor		in liq	in vapor		in liq	in vapor
T = 303.2 K (86 °F)			*T* = 348.2 K (167 °F)			*T* = 373.2 K (212 °F)		
6.77 (982.0)	0.969	0.011	7.34 (1065.0)	0.961	0.030	6.74 (977.0)	0.959	0.073
13.16 (1908.0)	0.943	0.010	13.93 (2021.0)	0.925	0.028	14.51 (2105.0)	0.910	0.046
19.99 (2900.0)	0.919	0.009	20.35 (2952.0)	0.894	0.029	21.10 (3060.0)	0.872	0.045
29.16 (4230.0)	0.892	0.012	27.35 (3967.0)	0.862	0.027	27.35 (3967.0)	0.838	0.043
34.89 (5060.0)	0.878	0.013	35.65 (5170.0)	0.827	0.030	34.72 (5036.0)	0.799	0.052

Nitrogen–Toluene

press., MPa (psia)	mole fractn of toluene in liq	press., MPa (psia)	mole fractn of toluene in liq	press., MPa (psia)	mole fractn of toluene in liq	press., MPa (psia)	mole fractn of toluene in liq
T = 323.2 K (122 °F)				*T* = 348.2 K (167 °F)			
3.64 (528.0)	0.982	21.17 (3070.0)	0.912	4.15 (602.0)	0.973	23.27 (3375.0)	0.889
7.04 (1021.0)	0.968	27.75 (4025.0)	0.891	6.52 (945.0)	0.966	27.60 (4003.0)	0.870
14.17 (2055.0)	0.938	35.35 (5127.0)	0.861	14.02 (2033.0)	0.929	34.78 (5044.0)	0.841

n-decane, the proportion of nitrogen to methane in the feed was fixed at equimolar ratio.

For each of the ternary and quaternary experimental runs, at least four samples were analyzed for each phase. The equilibrium compositions were determined by using both a thermal conductivity detector (TCD) and a flame ionization detector (FID), which were connected in a series with the GC column. The nitrogen and methane compositions were determined by using the TCD, whereas the other hydrocarbons were determined by using the FID. The average uncertainty of the determined response factor is ±0.5%.

Discussion

The system of nitrogen + methane + *n*-decane studied by Azarnoosh and McKetta (*4*) at 344.3 K (160 °F) shows a large two-phase region (Figure 8). Additional experimental runs were made on this system to check the consistency of the experi-

Table II. Experimental Results of Ternary Vapor-Liquid Equilibria

Methane + *n*-Butane + *n*-Decane
T = 352.6 K (175 °F) and 27.58 MPa (4000 psia)

mole fraction of methane in		mole fraction of *n*-butane in	
vapor	liquid	vapor	liquid
0.8801	0.7299	0.0817	0.1309
0.8987	0.7171	0.0644	0.1121
0.9466	0.6995	0.0152	0.0417
0.9621	0.6793	0.0000	0.0000

Nitrogen + *n*-Butane + *n*-Decane
T = 352.6 K (175 °F) and 27.58 MPa (4000 psia)

mole fraction of nitrogen in		mole fraction of *n*-butane in	
vapor	liquid	vapor	liquid
0.9763	0.3194	0.0159	0.0951
0.9680	0.3354	0.0253	0.1455
0.9602	0.3186	0.0332	0.1635
0.9579	0.3159	0.0348	0.1772
0.9483	0.3115	0.0439	0.1883
0.9437	0.3158	0.0491	0.2308
0.9000	0.3300	0.0899	0.3127
0.8877	0.3514	0.1023	0.3261
0.8868	0.3542	0.1225	0.3636
0.8559	0.3586	0.1329	0.3761
0.8525	0.3682	0.1355	0.3779
0.8423	0.3720	0.1454	0.3803
0.8377	0.3803	0.1498	0.3905
0.8275	0.3919	0.1595	0.3953
0.8270	0.3885	0.1594	0.3995
0.8139	0.4243	0.1733	0.4115
0.7781	0.4401	0.2053	0.4104

Table III. Experimental Results of Quaternary Vapor-Liquid Equilibria

Nitrogen + Methane + *n*-Butane + *n*-Decane
T = 352.6 K (175 °F) and 27.58 MPa (4000 psia)

mole fraction of nitrogen in		mole fraction of methane in		mole fraction of *n*-butane in	
vapor	liquid	vapor	liquid	vapor	liquid
0.5063	0.1627	0.4864	0.3080	0.0000	0.0000
0.4934	0.1653	0.4861	0.3093	0.0111	0.0434
0.4921	0.1857	0.4444	0.2923	0.0506	0.1630
0.4888	0.2305	0.3768	0.2652	0.1173	0.2826
0.4848	0.1722	0.4813	0.3102	0.0240	0.0887
0.4567	0.2480	0.3717	0.2788	0.1461	0.2966
0.4495	0.2216	0.4034	0.2919	0.1216	0.2710
0.4340	0.2248	0.3944	0.2947	0.1255	0.2562
0.2737[a]		0.2837[a]		0.3201[a]	

[a] Single-phase region.

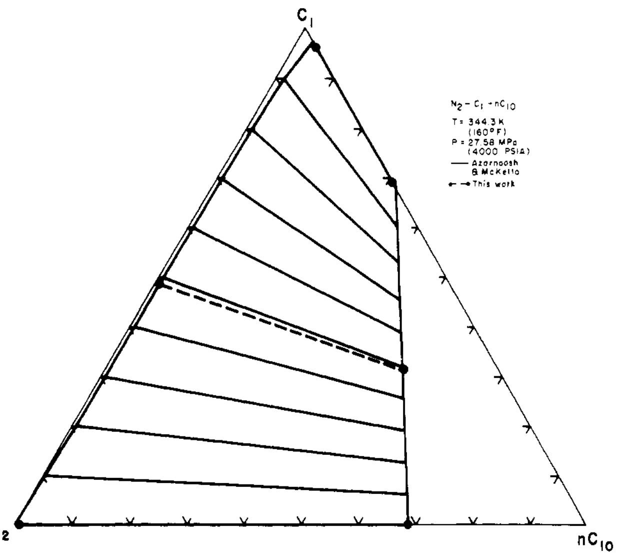

Figure 8. Phase envelope for the ternary system nitrogen + methane + *n*-decane at 344.3 K (60 °F) and 27.58 MPa (4000 psia).

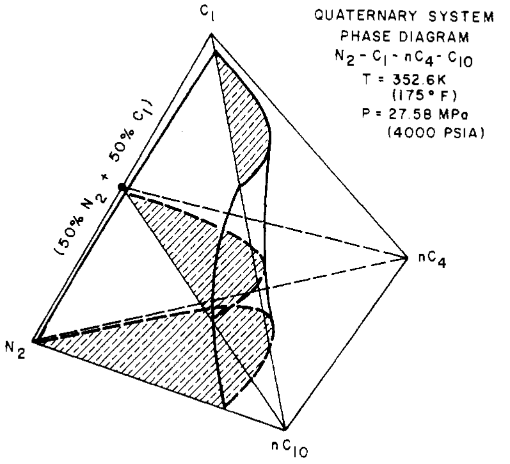

Figure 9. Phase diagram for the quaternary system nitrogen + methane + *n*-butane + *n*-decane at 352.6 K (175 °F) and 27.58 MPa (4000 psia).

mental work at the ternary level, which was previously confirmed with the binary studies. The nitrogen + *n*-decane and methane + *n*-decane binaries show two-phase behavior at 344.3 K (160 °F) and 27.58 MPa (4000 psia). The methane + *n*-decane binary exhibits a larger one-phase region compared to the nitrogen + *n*-decane binary. This shows that increasing the methane composition in the ternary nitrogen + methane + *n*-decane system decreases the size of the two-phase region.

For the ternary system of methane + *n*-butane + *n*-decane, the addition of *n*-butane to the methane + *n*-decane reduces the immiscible phase region. The limit of the phase envelope is at about 14 mol % of *n*-butane before the system becomes completely miscible at 352.6 K (175 °F) and 27.58 MPa (4000 psia) (Figure 4). If the methane is completely replaced by nitrogen, the relative size of the two-phase region is larger, immiscible up to about 42 mol % of *n*-butane, as shown in Figure 6. On the other side, the ternary system of nitrogen + methane + *n*-butane is completely miscible at the same temperature and pressure. The addition of *n*-butane to the nitrogen + methane binary would not promote any two-phase regions at these conditions.

As shown in Figure 9, the quaternary system of nitrogen + methane + *n*-butane + *n*-decane has four ternary system constituents: nitrogen + methane + *n*-decane, methane + *n*-butane + *n*-decane, nitrogen + *n*-butane + *n*-decane, and nitrogen + methane + *n*-butane.

The quaternary system reflects all the effects of the constituent ternaries. At the limits of near-negligible amounts of nitrogen in the feed, the predominant phase behavior is that of the small phase envelope methane + *n*-butane + *n*-decane ternary system, whereas the phase boundary of nitrogen + *n*-butane + *n*-decane dominates the behavior at low methane concentrations. The phase envelope of the quaternary nitrogen + methane + *n*-butane + *n*-decane system can be represented by a pseudoternary phase diagram (figure 7), which is shown as an inclined surface in Figure 9. The addition of a fourth component to a ternary system would produce a two-phase volume in a tetrahedral phase diagram, as shown in Figure 9.

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Registry No. N_2, 7727-37-9; *n*-heptane, 142-82-5; *n*-octane, 111-65-9; *n*-nonane, 111-84-2; *n*-decane, 124-18-5; *n*-dodecane, 112-40-3; benzene, 71-43-2; toluene, 108-88-3; methane, 74-82-8; *n*-butane, 106-97-8.

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Solubilities of D-Xylose and D-Mannose in Water–Ethanol Mixtures at 25 °C

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Solubilities of D-xylose and D-mannose were measured in water–ethanol mixtures at 25 °C, in the concentration range of 0–100 wt % ethanol. Sugar solutions were analyzed by two methods: direct refractometry and high-pressure liquid chromatography.

Introduction

D-Xylose ($C_5H_{10}O_5$), commonly called wood sugar, and D-mannose ($C_6H_{12}O_6$) are monosaccharides. D-Xylose is mainly used as a nonnutritive sweetener. It provides a source of energy for diabetics because it can be metabolized without insulin in humans (*1*). It is widely distributed in plant materials, but its commercial production turns out to be difficult. Its selective separation from aqueous extracts of plants, containing in particular D-mannose, represents one of the main problems.

A French patent (*2*) deals with a method of isolating crystalline D-xylose from an aqueous plant extract by precipitating it with methanol. Due to the toxicity of methanol, salting out from ethanol could be preferably envisaged but the feasibility of this process cannot be quite appreciated from the available literature data.

Here are reported some new experimental data concerning D-xylose–water–ethanol and D-mannose–water–ethanol phase equilibria. The solubility of each carbohydrate has been investigated at 25 °C for water–ethanol mixtures of several compositions.

Experimental Method

A common experimental method for the solubility determinations was used. It consists in maintaining at a fixed temperature a stirred solution containing some excess of solid solute until equilibrium is reached, after which the concentration of the solution is measured. In this work two methods were used to analyze the solutions: direct refractometry, and a combined chromatography and refractometry techniques.

The carbohydrates were supplied by Sigma Chemical Co. (purity >99%). They were dried over P_2O_5 at room temperature. Ethanol used for preparation of the mixed solvents was 99.85 vol % pure. The water was deionized grade. The experimental apparatus was a water bath equipped with a vibrating device holding 12 100-cm^3 Erlenmeyer flasks. The temperature of the water bath could be controlled with an accuracy of 0.02 °C.

Liquid and solid phases were assumed to be in equilibrium when the difference between the refractive indexes of liquid samples withdrawn at about 24-h intervals was smaller than 0.000 07. Several days of intimate contact were required depending on the viscosity of the solution which was affected by the ethanol concentration.

The sampling procedure was as follows. The equilibrium mixture was allowed to stand still for 1 h or more at a constant temperature to enable any finely dispersed solids to settle down. Three samples of the clear supernatant liquid were carefully withdrawn by means of Pasteur pipets slightly hotter than the solution in order to avoid any precipitation.

Concerning the first method of analysis (direct refractometry), a linear relationship was established, for all experimental water–ethanol weight ratios, between sugar concentration of a solution close to saturation and its refractive index. A Zeiss refractometer fitted with thermoprisms was used. The temperature of the measurements was fixed at 30 ± 0.03 °C by means of a thermostatic circulating bath. This method proved to be very accurate but very tedious and time consuming.

The second one brings into play a high-pressure liquid chromatograph (HPLC) equipped with a separator column of HPX 87 P and bidistilled water as a solvent (*3*). The components emerging from the column are detected by a differential refractometer. The output signal is recorded on a strip chart and processed by an integrating device. The preparation procedure of the sample solution was as follows. The solution was transferred to 0.2-cm^3 flasks and weighed to ±0.1 mg. Moreover, high concentrations of sugar require appreciable dilution of the samples which might increase experimental errors. Injection volumes of 0.02 cm^3 were employed. Quan-

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