Δt	change in temperature of the mixture, °C
T	time through which the current is passed, s

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Three-Phase Solid–Liquid–Vapor Equilibria of the Systems Ethylene–Cyclohexane, Ethylene–*trans*-Decalin, Ethylene–Benzene, and Ethylene–2-Methylnaphthalene

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Pressure, temperature, liquid-phase molar volumes, and liquid-phase compositions are presented along the solid–liquid–vapor loci for four ringed hydrocarbon solutes with ethylene as a common solvent. The data were taken employing cryoscopic techniques over a liquid compositional range from solute-rich solutions to very dilute solute solutions. The data are pictorialized as the logarithm of composition vs. T_T/T to elucidate the nonideality of the liquid phase. The standard deviations of the liquid compositional data are 0.93% for cyclohexane, 1.08% for *trans*-decalin, 1.34% for benzene, and 2.10% for 2-methylnaphthalene.

Introduction

Three-phase, solid–liquid–vapor, solubility data of hydrocarbon components in low molecular weight solvents are important for use in the design of liquefaction, vaporization, and transport systems for liquefied ethylene as well as liquefied natural gas (LNG) and liquefied petroleum gas (LPG). The authors are engaged in an extended program of obtaining such data and recently reported solid–liquid–vapor data for three ethylene–*n*-alkane binary systems (*5*). In an earlier paper, Liu et al. (*4*) studied the solubility of three of these same solutes studied here with ethane as a common solvent by cryoscopic means. The ethane–2-methylnaphthalene system has been investigated and the data are reported in ref 6. In the same spirit as ref 4, we have undertaken the present study to add to existing knowledge of the solubility behavior of aromatic and naphthenic hydrocarbon species in light liquid hydrocarbon solvents. These data will serve as an interesting basis for comparison of ethylene to other solvents, especially ethane, over a wide range of temperatures and solute compositions.

As the U.S. production of ethylene is fifth of all chemicals and first of all petrochemicals, this paper provides useful design data. These binary data not only are readily applicable but also form a basis from which the solubility of hydrocarbons in multicomponent systems with ethylene can be predicted.

Experimental Section

The ethylene used in this study was Matheson CP grade with a minimum purity of 99% and was identical with that used in the previous study (*5*). The cyclohexane used was an Eastman Reagent "ACS" Grade chemical. The benzene was a Mallinckrodt "Spectrar" spectrophotometric grade chemical. The 2-methylnaphthalene was supplied by Aldrich Chemical Co., Inc., with a stated purity of 99+%. The *trans*-decalin was supplied by Columbia Organic Chemicals Co., Inc., and is at least 99% pure. The purity of these hydrocarbons was further checked by a Bausch and Lomb ABBE-3L refractometer and by measuring the freezing point of each of the four compounds. The refractive indices of the hydrocarbons agreed with literature values within the accuracy of the instrument (±0.0001) at 20 °C (at 40 °C for 2-methylnaphthalene). The freezing points measured agreed well with literature values. All four hydrocarbon solutes were used without further purification. The apparatus and procedures used in this study were identical with that reported by Lee and Kohn (*3*) which was used in other cryoscopic studies (*1*, *2*, *4*).

Table I. Solid-Liquid-Vapor Three-Phase Smoothed Data: Ethylene-Cyclohexane Binary System

temp, K	pressure, atm	liquid-phase compn (mole fraction cyclohexane)	liquid-phase molar volume, mL/g-mol
270	1.68	0.9706	104.6
260	3.09	0.9347	101.5
250	3.83	0.8941	98.4
240	4.09	0.8508	95.3
230	4.00	0.8068	92.1
220	3.66	0.7602	89.0
210	3.10	0.7127	85.8
200	2.38	0.6629	82.5
190	1.80	0.6103	79.2
180	1.33	0.4063	69.0
170	0.90	0.1761	58.0
160	0.56	0.07955	52.7
150	0.35	0.03963	50.0
140	0.30	0.02170	48.4

Results

Tables I and II present the smoothed experimental data for the two naphthenic solute systems studied and Tables III and IV present the smoothed experimental data for the two aromatic solute systems studied. The pressures are precise to ±0.1 atm, the temperatures to ±0.2 °C, and the liquid molar volume to

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Table II. Solid-Liquid-Vapor Three-Phase Smoothed Data: Ethylene-*trans*-Decalin Binary System

temp, K	pressure, atm	liquid-phase compn (mole fraction *trans*-decalin)	liquid-phase molar volume, mL/g-mol
235	4.78	0.7988	129.9
230	6.49	0.6757	118.6
225	7.32	0.5526	106.8
220	7.43	0.4220	94.1
215	7.01	0.2900	81.4
210	6.16	0.1427	67.5
205	5.22	0.07243	61.3
200	4.30	0.04553	58.4
195	3.50	0.03112	56.3
190	2.85	0.02195	55.0
185	2.29	0.01575	54.0
180	1.82	0.01153	53.1
175	1.41	0.00844	52.2
170	1.10	0.00617	51.3
165	0.81	0.00448	50.4
160	0.62	0.00323	49.5

Table III. Solid-Liquid-Vapor Three-Phase Smoothed Data: Ethylene-Benzene Binary System

temp, K	pressure, atm	liquid-phase compn (mole fraction benzene)	liquid-phase molar volume, mL/g-mol
270	7.68	0.8510	81.7
260	12.46	0.6888	76.4
250	14.22	0.5206	71.3
240	13.31	0.3363	66.6
230	11.04	0.1976	62.2
220	8.45	0.1185	59.2
210	6.22	0.07558	57.0
200	4.31	0.04978	55.1
190	2.83	0.03297	53.6
180	1.82	0.02177	52.0
170	1.09	0.01428	50.7
160	0.58	0.00912	49.5

Table IV. Solid-Liquid-Vapor Three-Phase Smoothed Data: Ethylene-2-Methylnaphthalene Binary System

temp, K	pressure, atm	liquid-phase compn (mole fraction 2-methyl-naphthalene)	liquid-phase molar volume, mL/g-mol
300	12.1	0.935 5	138.2
290	26.0	0.831 6	129.0
280	35.0	0.637 8	112.5
271.1[a]	39.3	0.364 9[b]	96.4[b]
271.1[a]	39.3	0.013 81[c]	80.8[c]
270	37.8	0.013 32	79.7
260	29.0	0.009 95	71.8
250	22.6	0.007 43	68.0
240	17.4	0.005 49	64.9
230	13.1	0.003 95	62.3
220	9.4	0.002 71	59.8

[a] Quadruple point (S-L_1-L_2-V). [b] L_1 properties. [c] L_2 properties.

±1.0 mL/g-mol. The liquid composition data were smoothed prior to tabulation by use of the same procedure as was reported for the ethane systems (*1*, *4*).

In the case of the ethylene-cyclohexane system, there were runs taken at four different cell loadings—a total of 36 raw data points. The standard deviation between the smoothed compositions in Table I and the raw data was 0.93%. There were 31 raw data points taken in five different cell loadings on the ethylene-*trans*-decalin system, and the standard deviation of the smoothed compositions of Table II and the raw data was 1.08%. There were 31 raw data points taken in three different cell loadings on the ethylene-benzene system, and the standard deviation of the smoothed compositions of Table III and the raw data was 1.34%. There were two different cell loadings resulting in 9 data points for the liquid-1 portion of the ethylene-2-methylnaphthalene system and two different cell loadings resulting in 14 data points for the liquid-2 portion of this system. The standard deviation of the smoothed compositions of Table IV and the raw data was 2.10%.

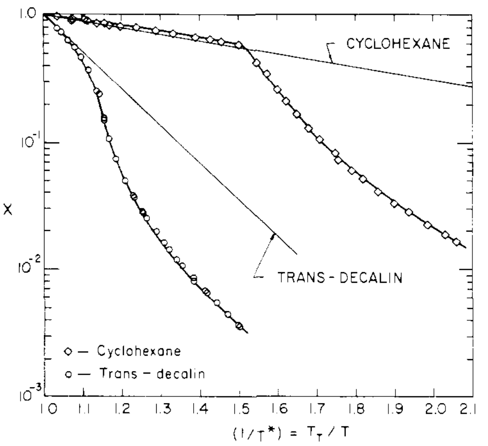

Figure 1. The experimental solute mole fraction vs. reduced reciprocal temperature as compared with ideal predictions for both ethylene-naphthene systems studied. The heavy lines are the smoothed data presented in Tables I and II, while the light lines are the ideal composition loci for both systems.

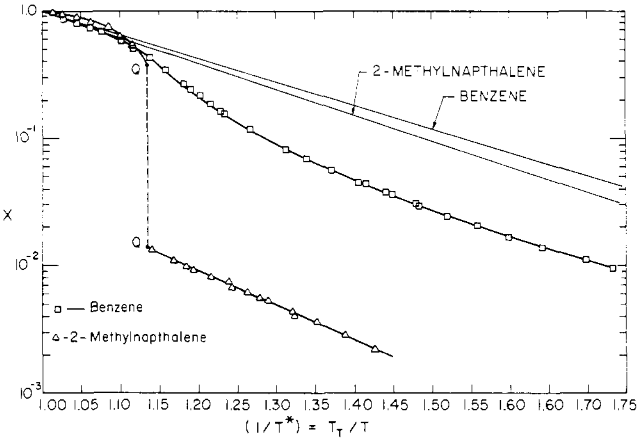

Figure 2. The experimental solute mole fraction vs. reduced reciprocal temperature as compared with ideal predictions for both ethylene-aromatic systems studied. The heavy lines are the smoothed data presented in Tables III and IV, while the light lines are the ideal composition loci for both systems.

The raw data corresponding to the two naphthenic-solute systems are shown in Figure 1, and the raw data for the two aromatic-solute systems are shown in Figure 2. These figures also present the smoothed composition lines and "ideal" solubility lines. From this representation, it appears that there is a high degree of linearity of the composition lines of all binary systems, excluding the cyclohexane system, at $1/T^*$ larger than 1.40. This, in fact, is the region in which Henry's law might be expected to hold. Thus extrapolation of the data into even more dilute regions would be likely to be reasonably accurate. Although the data also appear to have become linear for the solute cyclohexane at $1/T^* > 1.8$, the solute compositions are high enough in this region to make linear extrapolation possibly risky.

All smoothed composition curves are continuous with the exception of the 2-methylnaphthalene-solute system. For this system there is a four-phase solid-liquid 1-liquid 2-vapor point

(Q point). The compositional difference between the liquid-1 and liquid-2 phases causes a discontinuity with respect to composition along the three-phase solid–liquid–vapor loci. The ethane–2-methylnaphthalene binary system demonstrated this same Q-point phenomenon.

Glossary

L_1	ethylene-lean liquid phase
L_2	ethylene-rich liquid phase
T	temperature in K
T_T	triple point temperature in K: 279.83 K for cyclohexane, 242.75 K for *trans*-decalin, 278.69 K for benzene, 307.73 K for 2-methylnaphthalene
T^*	T/T_T
x	solute mole fraction

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Supplementary Material Available: Four tables of raw data corresponding to Tables I–IV (4 pages). Ordering information is given on any current masthead page.

Three-Phase Solid–Liquid–Vapor Equilibria of the Binary Hydrocarbon Systems Ethane–2-Methylnaphthalene, Ethane–Naphthalene, Propane–*n*-Decane, and Propane–*n*-Dodecane

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Pressure, temperature, liquid-phase molar volumes, and liquid-phase compositions are presented along the solid–liquid–vapor loci for binary systems of the solvent ethane with the solutes 2-methylnaphthalene and naphthalene and propane with the solutes *n*-decane and *n*-dodecane. The data were taken employing cryoscopic techniques over a liquid compositional range from solute-rich solutions to very dilute solute solutions. The liquid compositional data when represented as a logarithm of solute composition vs. T_R/T are smooth curves exhibiting three distinct types of solid–liquid–vapor phase behavior, the type depending on the solute. The curves become quite linear in the lower temperature range. The standard deviations of the liquid composition data are 2.95% for the ethane–2-methylnaphthalene system, 1.52% for the ethane–naphthalene system, 1.95% for the propane–*n*-decane system, and 1.85% for the propane–*n*-dodecane system.

Introduction

Solid solubility data of hydrocarbon components in low molecular weight solvents are important for use in the design of liquefaction, vaporization, and transport systems for liquefied natural gas (LNG) and liquefied petroleum gas (LPG). The authors are engaged in an extended program of obtaining such data, primarily in the low solute concentration range.

In earlier papers (*2*, *5*), the authors examined the solubility of six other hydrocarbon species in ethane by cryoscopic means. These data were taken along the three-phase solid–liquid–vapor locus for each binary system. In the same spirit as these previous investigations (*2*, *5*), we have undertaken the present study to add to existing knowledge of the solubility behavior of hydrocarbon species (alkanes, aromatics, and naphthenes) in LNG and LPG components. The binary data form a basis from which the solubility of hydrocarbons in multicomponent systems with ethane or propane can be predicted.

Experimental Section

The ethane used in this study was Matheson CP grade with a minimum purity of 99% and is identical with that used in previous studies (*2*, *5*).

The propane used in this study was Linde "instrument grade" stated to be 99.5 mol % pure. An 253.48 K isotherm determined on the propane indicated a difference between the dew-point and bubble point pressures of less than 0.1 atm. The vapor pressure and liquid-phase molar volume at 50 volume % liquid were within 0.1 atm and 0.2 mL/g-mol, respectively, of the literature values (*1*). The propane was used without further purification.

The 2-methylnapthalene and naphthalene used were Aldrich Chemical Co. Inc., "Gold Label" quality products with a stated minimum purity of 99+%. The *n*-decane and *n*-dodecane were Humphrey-Wilkinson "Pure Grade" petroleum-derived products with a stated purity of 99%. These hydrocarbon solutes were used without further purification.

The apparatus was identical with that reported by Lee and Kohn (*4*) which was used in other cryoscopic studies (*2*, *3*, *5*). The experimental procedure is described in our earlier paper (*6*).

Results

Tables I and II present the smoothed experimental data for the two ethane solvent systems studied and Tables III and IV present the smoothed experimental data for the two propane solvent systems studied. The pressures are precise to ±0.1 atm, the temperatures to ±0.2 °C, and the liquid molar volume to ±1.0 mL/g-mol. The liquid composition data were smoothed

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