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Supplementary Material Available: Table I (12 pages). Ordering information is given on any current masthead page.

Three-Phase Solid–Liquid–Vapor Equilibria of Binary-*n*-Alkane Systems (Ethane–*n*-Octane, Ethane–*n*-Decane, Ethane–*n*-Dodecane)

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Pressure–temperature profiles along with liquid compositions and molar volumes are presented for three *n*-alkane solutes with ethane 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 liquid compositional data when represented as logarithm of composition vs. T_{FUS}/T (where T_{FUS} = freezing temperature of each pure solute) are smooth curves which become quite linear in the dilute solute range. The standard deviations of the liquid composition data are 0.67% for *n*-octane, 0.84% for *n*-decane, and 2.04% for *n*-dodecane.

Solid solubility data of hydrocarbon components in low molecular weight solvents are relatively rare compared to the amount of data available on the vapor–liquid behavior of such systems. Solid solubility data are quite important for use in the design of liquefaction, vaporization, and transport systems for liquefied natural gas (LNG) and liquefied petroleum gas (LPG). Kurata (*5*) has reviewed and summarized most of the experimental data on solid solubility of hydrocarbons in liquefied methane. The best recent data on the solid solubility of hydrocarbons in methane are those of Kuebler and McKinley (*2, 3*). Luks et al. (*7*) have developed procedures for predicting solid solubility in multicomponent systems based upon experimental data on all of the constitutive binary systems. Additional experimental data on solid solubility of hydrocarbon components including alkane, naphthene, and aromatic substances in methane, ethane, and propane are necessary. Such data will be used in the design of a variety of cryogenic processes, including the design of the recently proposed slurry pipe lines to transport both LNG and crude oil simultaneously.

Experimental Section

The apparatus was identical with that reported by Lee and Kohn (*6*) which was used in other solid phase studies (*1, 4*). The equilibrium cell was immersed in a bath contained in a 4.0-l. cylindrical Dewar flask which was concentrically mounted inside an 8 in. o.d. cylindrical battery jar. The bottom of the air space between the Dewar flask and the battery jar contained about 100 g of 13A molecular sieves. This prevented the condensation of water on the Dewar flask. At temperatures higher than 156 K the bath liquid was absolute ethyl alcohol. Mixtures of absolute alcohol and *n*-propyl alcohol were found suitable at temperatures down to 140 K. Bath temperatures down to 188 K were achieved by use of a "CRYOCOOL-100" cascade refrigerator whose cooling coil was immersed in the working bath. At temperatures below 188 K liquid nitrogen was metered to a copper coil inside the working bath. Temperatures of the bath were controlled using a Model 94 Bayley Precision temperature controller which generally could achieve temperature control to ±0.05 °C. Temperatures were taken on a platinum resistance thermometer which had a calibration correct at least to ±0.03 °C. Pressures were taken on Heise bourdon tube gauges which were set against a dead weight gauge. The pressure gauges were accurate to about ±0.07 atm. Volumes of the liquid phase inside the cell were taken relative to calibration marks on the outside of the cell. The volume calibration was correct to at least ±0.2% when filled to about 10 ml.

Pure solute liquid was charged to a clean empty equilibrium cell. The mass of the liquid was determined by weighing techniques to at least ±0.2 mg. The cell was chilled to 0 °C and the air was flushed from it by repeated charging to 7 or 8 atm with ethane gas. The cell was then immersed in the Dewar flask and ethane added from a reservoir at constant pressure and temperature by use of mercury displacement pump. The reservoir

Table I. Vapor–Liquid–Solid Three-Phase Smoothed Data: Ethane–*n*-Octane Binary System

Temp (K)	Pressure (atm)	Liquid phase composition (mole fraction C_8)	Liquid phase volume (ml/g mol)
210	1.19	0.701 0	117.7
205	1.53	0.522 1	102.0
200	1.63	0.377 6	89.4
195	1.39	0.266 0	79.1
190	1.00	0.178 9	70.8
185	0.72	0.116 9	64.4
180	...	0.077 82	59.6
175	...	0.051 96	57.6
170	...	0.034 03	55.5
165	...	0.021 81	53.6
160	...	0.013 55	52.2
155	...	0.008 67	51.4
150	...	0.005 53	50.6

Table II. Vapor–Liquid–Solid Three-Phase Smoothed Data: Ethane–*n*-Decane Binary System

Temp (K)	Pressure (atm)	Liquid phase composition (mole fraction C_{10})	Liquid phase volume (ml/g mol)
235	3.55	0.595 3	133.5
230	4.42	0.427 8	112.7
225	4.77	0.299 9	96.0
220	4.35	0.200 0	82.9
215	3.70	0.125 2	73.0
210	2.98	0.076 70	67.0
205	2.48	0.048 39	63.2
200	2.00	0.030 46	60.5
195	1.60	0.019 12	58.9
190	1.21	0.011 96	57.2
185	0.85	0.007 51	56.3
180	...	0.004 67	55.3
175	...	0.002 832	55.0
170	...	0.001 660	54.6
165	...	0.000 938	54.3

Table III. Vapor–Liquid–Solid Three-Phase Smoothed Data: Ethane–*n*-Dodecane Binary System

Temp (K)	Pressure (atm)	Liquid phase composition (mole fraction C_{12})	Liquid phase volume (ml/g mol)
255	5.88	0.555 8	151.1
250	7.80	0.364 1	120.9
245	8.59	0.206 7	96.1
240	8.68	0.119 6	80.9
235	7.99	0.065 27	71.7
230	6.78	0.034 04	66.6
225	5.72	0.018 15	64.2
220	4.81	0.010 01	62.6
215	3.90	0.005 74	60.2
210	3.11	0.003 42	58.8
205	2.58	0.001 93	57.5
200	2.10	0.001 10	56.5
195	1.66	0.000 624	55.9

was connected to the equilibrium cell by a stainless steel capillary line. The volume of ethane delivered to the cell could be estimated to ±0.001 ml. The cell contents were stirred by means of a steel ball inside the cell which was actuated by an override magnet outside the cell. After addition of an arbitrary but accurately known amount of ethane which caused increases in cell pressure and liquid volume, the bath temperature was lowered until crystal formation was observed. Then the temperature was raised at a very slow rate and, under vigorous stirring of the cell contents, the temperature was noted at the disappearance of the last few crystals. The cooling–heating sequence was repeated if there was doubt of whether the heating rate was too rapid. Generally the final crystal point could be duplicated to within ±0.1 °C. The degree of subcooling before crystal formation varied somewhat for each system but was generally from 1 to 2 °C for *n*-octane and *n*-decane and was from 3 to 7 °C for *n*-dodecane. At the temperature of the crystal point the cell pressure, cell liquid volume, vapor volume, and cumulative mass of ethane added to the cell were recorded. Additional ethane was then added to the cell which amount was roughly gauged by the incremental volume change of the liquid phase. Cooling was then started in order to obtain crystal formation and additional lower temperature crystal points. The procedure of addition of ethane and search for crystal points was continued until the cell was filled with liquid. From three to six solubility points were obtained from each run.

Measurements on each solute were done with at least five different initial masses of solute in the equilibrium cell. This provided overlapping data points and permitted a good estimate of the precision of the data.

Results

Tables I, II, and III present the smoothed experimental data for the three systems. Additional data are available; see paragraph at end of paper regarding supplementary material. The pressures are precise to ±0.10 atm, the temperatures to ±0.2 °C, and the liquid molar volumes to ±0.6 ml/(g mol). The liquid compositions have experimental precisions which vary somewhat for the three systems. The multiple run data for each of the systems were smoothed by use of the deviations between ideal solubility and the actual solubility. The ideal solubility for each solute component was determined by use of a simple version of the Van't Hoff isochore for freezing point lowering. It is shown in eq 1

$$\ln x_l = \frac{\Delta H_{FUS}}{RT_{FUS}}(1 - 1/T^*) \qquad (1)$$

where $T^* = T/T_{FUS}$, ΔH_{FUS} = enthalpy of fusion of each pure solute, and T_{FUS} = triple point temperature of each pure solute. The enthalpies of fusions and the triple point temperatures were taken from Rossini (*8*). The ratio of the ideal solubility to the real solubility is the deviation function or liquid phase activity coefficient. These coefficients are all greater than unity but approached unity as the solute compositions approached unity mole fraction. The activity coefficients were plotted against $1/T^*$ and smoothed carefully by eye on large scale. These values of the activity coefficients were then used with eq 1 to produce the values of composition tabulated in Tables I, II, and III. In the case of the ethane–*n*-octane system there were runs taken at five different cell loadings—a total of 16 raw data points. The standard deviation between the smoothed compositions in Table I and the raw data was 0.67%. There were 20 raw data points taken in 5 different cell loadings on the ethane–*n*-decane system, and the standard deviation of the smoothed compositions of Table II and the raw data was 0.84%. There were 18 raw data points taken in 5 different cell loadings on the ethane–*n*-dodecane system, and the standard deviation of the smoothed compositions of Table III and the raw data was 2.04%. The raw data are shown in Figure 1 along with smoothed composition lines and "ideal" solubility lines. Using this representation it appears that there is a high degree of linearity of the composition lines of all three binary systems at $1/T^*$ larger than 1.25. This in fact is the region in which Henry's law might be expected to hold for

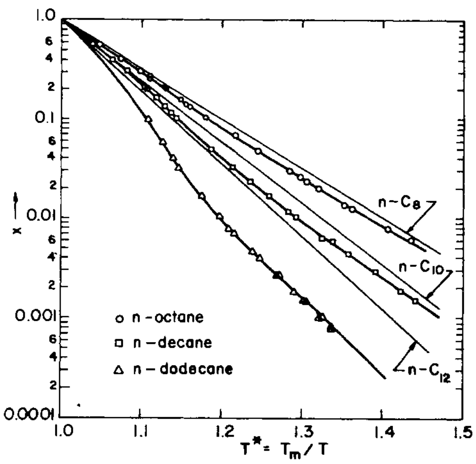

Figure 1. A comparison of the solute mole fraction vs. reciprocal temperature experimental data with ideal predictions. The heavy lines are the smoothed data presentations of Tables I–III, while the light lines are the ideal loci for the three systems studied.

the solute. Thus extrapolation of the data into even more dilute regions would be likely to be reasonably accurate.

Nomenclature

R = universal gas law constant = 1.987 cal/(g mol K)
T = temperature, K
T_{FUS} = freezing temperature (triple point temperature), K
x_i = ideal solubility, mole fraction
ΔH_{FUS} = enthalpy of fusion of pure solute component, cal/(g mol)

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Supplementary Material Available: Vapor–liquid–solid three-phase raw data (3 pages). Ordering information is given on any current masthead page.

Thermodynamic Properties of Some Cycloalkane–Cycloalkanol Systems at 298.15 K. 4. Excess Volumes

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Measurements of excess volumes at 298.15 K are reported for the systems cycloheptane–cyclohexanol, cyclooctane–cyclohexanol, cyclopentane–cycloheptanol, cyclohexane–cycloheptanol, and cyclooctane–cycloheptanol. The results are compared with the excess volumes of other cycloalkane–cycloalkanol systems investigated previously in our laboratory. The volume behavior of cycloalkane–cycloalkanol systems can be attributed qualitatively to the effects of hydrogen bonding and to differences in the sizes of the component molecules.

Previous investigations (*1–3*) of binary cycloalkane–cycloalkanol systems have shown that the shapes of the excess volume curves vary considerably when the ring sizes of the component species are changed. This is in marked contrast to the curves for both the excess enthalpy and excess Gibbs free energy, the shapes of which are relatively insensitive to changes of component ring size.

As an extension of our earlier studies, we have measured excess volumes at 298.15 K for binary mixtures of cyclohexanol with cycloheptane and cyclooctane, and of cycloheptanol with cyclopentane, cyclohexane, and cyclooctane.

Experimental Section

The component liquids were the same as used in our earlier studies. Reference can be made to those publications (*1, 3*) for the methods of purification and for values of the densities, refractive indices, and vapor pressures characterizing the final samples.

The changes in volume which occurred on mixing the component liquids at 298.15 K were measured in a successive dilution dilatometer. A description of the equipment and operating technique is available in the literature (*4*). The results are estimated to be accurate to better than ±1 × 10^{-3} cm^3 mol^{-1}.

Results

Experimental values of the molar excess volume V^E measured for the five cycloalkane–cycloalkanol systems are summarized in Table I. In each case, x_1 is the mole fraction of the cycloalkane. The results are also presented graphically in Figures 1 and 2, where each figure refers to systems containing a common cycloalkanol.

Polynomial forms

$$V^E = x_1(1 - x_1) \sum_{k=1}^{n} c_k(1 - x_1)^{(k-1)/2} \tag{1}$$

in the square root of the cycloalkanol mole fraction were used to smooth the resuls. Least-squares analyses led to the coefficients and standard error of estimate

$$\sigma = \left\{ \sum_{1}^{m} [V^E\,(\text{exptl}) - V^E(\text{eq }1)]^2/(m - n) \right\}^{1/2} \tag{2}$$

given in Table II for each system.