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

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Pressure, temperature, liquid-phase molar volumes, and liquid-phase compositions are presented along the solid–liquid–vapor locus for three *n*-alkane 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 liquid compositional data when represented as a logarithm of composition vs. T_T/T (where T_T = triple point 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 1.26% for *n*-octane, 1.10% for *n*-decane, and 2.06% for *n*-dodecane.

Introduction

Solid solubility data of hydrocarbon components in low molecular weight solvents are rare compared to the amount of data available on the vapor–liquid behavior of such systems. These three-phase solid–liquid–vapor data 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, primarily in the low solute concentration range.

In an earlier paper, Kohn et al. (*6*) studied the solubility of the same *n*-alkane solutes studied here with ethane as a common solvent by cryoscopic means. The data were taken along the three-phase solid–liquid–vapor locus for each binary system. In the same spirit as ref 6, we have undertaken the present study to add to existing knowledge of hydrocarbon solubility behavior 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. Furthermore, the cryoscopic approach avoids some of the difficulties that would hamper traditional sampling methods of liquid-phase analysis in solid–liquid–vapor systems. This problem is discussed in detail in ref 5 and 14.

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 are not only readily applicable but form a basis from which the solubility of hydrocarbons in multicomponent systems with ethylene can be predicted. Luks et al. (*11*) developed procedures for predicting solid solubility in multicomponent systems based upon experimental data on the constitutive binary systems. These procedures are discussed thoroughly in ref 5 and were recently revised and expanded by Orozco et al. (*12*).

Experimental Section

The ethylene used in this study was Matheson CP Grade with a minimum purity of 99%. Small amounts of ethane, propylene, and propane and traces of methane were present as impurities. A 0 °C isotherm determined on the gas indicated a difference

between the bubble-point and the dew point pressure of less than 0.2 atm, and the vapor pressure at 50 volume % liquid was within 0.1 atm of the data reported in Din (*1*). The critical point temperature and pressure were measured to be 9.48 °C and 49.8 atm, respectively. These values are within 0.3 °C and 0.1 atm of those given by ref 2. The ethylene was used without further purification.

The three *n*-alkane solutes *n*-octane, *n*-decane, and *n*-dodecane were all Humphrey-Wilkinson "pure grade" petroleum-derived products with a stated purity of 99%. The purity of these hydrocarbons was further checked by use of a Gow-Mac Series 550 thermal conductivity gas chromatograph and a Bausch and Lomb Abbe-3L refractometer. Only trace impurities were found by injecting the samples through the GC column at 160 °C. The column was packed with 20 000 molecular weight Carbowax on Chromosorb P. The refractive indices of the *n*-alkanes agreed with literature values within the accuracy of the instrument (±0.0001) at 20 °C.

A reasonably good and direct estimation of the purity of the solutes can be calculated by measuring the freezing points of the compounds and using the simple version of the Van't Hoff isochore equation given in the following section. (See eq 1 and 2.) In this case, $\gamma = 1.0$ since the level of impurity is very low. Using this method, the *n*-octane and *n*-dodecane were found to be essentially pure and the *n*-decane was 99.1% pure. All three hydrocarbon solutes were used without further purification.

The apparatus used in this study was identical with that reported by Lee and Kohn (*9*) which was used in other cryoscopic studies (*4–8, 10*). Briefly, the procedure involved charging a carefully weighed amount of liquid solute at room temperature to a borosilicate glass equilibrium cell which had an inside volume from 10 to 24 mL and was calibrated for volumetric readings, either by visual means or by use of a cathetometer. The air was vented from the cell by repeated flushing with ethylene. The cell was thermostated in a liquid bath confined in a Dewar flask; the bath could be chilled by means of a cascade refrigerator or liquid N_2 or both. Ethylene was added to the cell from a reservoir using a calibrated positive displacement mercury pump. The bath was cooled slowly while agitation of the cell contents was effected by a steel ball actuated by an override magnet. The temperature was lowered until crystals formed and then was raised until only a trace of crystals remained. Alternately, the equilibrium cell was thermostated at a temperature at which there were crystals, and then small incremental amounts of ethylene were added as a superheated gas until only a trace of crystals remained in equilibrium with the vapor and liquid phases. Both cryoscopic techniques were employed interchangably without increasing the reported standard deviations significantly. It was possible visually to detect as little as a few tenths of a milligram of crystals in the cell. This was regarded as an equilibrium crystal point with known liquid-phase solute composition. Addition of more ethylene would lead to dissolution of the remaining crystals. The temperature would then be lowered until crystals again appeared, and the above procedure followed for establishing the new equilibrium crystal point. When the cell filled with liquid phase, the "run" was terminated. Measurements on each solute were done with at

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

Temp, K	Pressure, atm	Liquid-phase comp (mole fraction C_8)	Liquid-phase molar volume, mL/g-mol
210	2.52	0.704 5	119.8
205	3.30	0.511 9	100.1
200	3.42	0.339 7	84.0
195	3.18	0.207 7	72.2
190	2.69	0.118 7	63.7
185	2.16	0.067 37	58.6
180	1.66	0.039 70	55.4
175	1.27	0.024 43	53.2
170	0.96	0.014 95	51.8
165	0.72	0.009 23	51.0
160	0.54	0.005 63	50.2
155	0.44	0.003 42	49.5
150	0.36	0.002 06	48.8
145	0.32	0.001 22	48.2
140	0.31	0.000 705	47.5

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

Temp, K	Pressure, atm	Liquid-phase comp (mole fraction C_{10})	Liquid-phase molar volume, mL/g-mol
235	6.96	0.592 4	133.9
230	8.55	0.418 0	110.2
225	8.91	0.261 6	89.6
220	8.28	0.142 6	73.4
215	7.42	0.069 62	65.6
210	6.36	0.038 52	61.3
205	5.28	0.022 39	58.5
200	4.35	0.013 48	56.6
195	3.52	0.008 22	55.3
190	2.81	0.005 11	54.3
185	2.21	0.003 12	53.5
180	1.72	0.001 86	52.7
175	1.35	0.001 09	52.0

least four 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. With the aid of ethylene vapor compressibility data (*1–3*, *15*), liquid-phase compositions and molar volumes could be readily computed.

Temperatures were taken on a platinum resistance thermometer which was accurate to at least ±0.03 °C of the 1968 IPTS scale. Pressures were taken on a calibrated Heise bourdon tube gauge which was accurate to at least ±0.07 atm. Liquid-phase volumes could generally be read to ±0.02 mL.

Results

Tables I, II, and III present the smoothed experimental data for the three systems studied. The pressures are precise to ±0.1 atm, the temperatures to ±0.2 °C, and the liquid molar volume to ±0.6 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 (*6*, *10*). In this procedure, 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:

$$\ln x_I = \frac{\Delta H_{FUS}}{RT_T}(1 - 1/T^*) \tag{1}$$

where $T^* = T/T_T$, ΔH_{FUS} = enthalpy of fusion of the solute, and T_T = triple point temperature of the solute. The enthalpies of fusion and the triple point temperatures were taken from

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

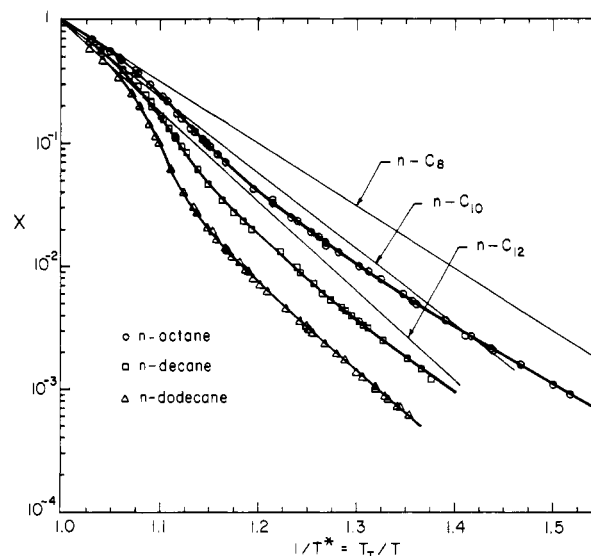| Temp, K	Pressure, atm	Liquid-phase comp (mole fraction C_{12})	Liquid-phase molar volume, mL/g-mol
255	12.02	0.561 4	147.2
250	15.47	0.388 9	120.6
245	16.71	0.238 5	97.0
240	16.01	0.110 6	76.8
235	14.39	0.045 83	68.1
230	12.58	0.022 82	64.6
225	10.82	0.013 25	62.3
220	9.23	0.008 03	60.6
215	7.80	0.004 92	59.1
210	6.51	0.002 99	57.9
205	5.36	0.001 80	56.8
200	4.38	0.001 06	55.9
195	3.60	0.000 614	55.0

Figure 1. The experimental solute mole fraction vs. reduced reciprocal temperature as compared with ideal predictions. The heavy lines are the smoothed data presented in Tables I–III, while the light lines are the ideal composition loci for the three systems studied.

Rossini (*13*). The ratio of the ideal solubility to the experimental solubility is the estimated activity coefficient of the solute.

The activity coefficients were plotted as log γ vs. $1/T^*$ and smoothed by eye. Then smoothed values of the mole fraction of solute component x were computed from

$$x = x_I/\gamma \tag{2}$$

where x_I is calculated from eq 1. These are the composition values listed in Tables I, II, and III. In the case of the ethylene-*n*-octane system, there were runs taken at six different cell loadings—a total of 43 raw data points. The standard deviation between the smoothed compositions in Table I and the raw data was 1.26%. There were 35 raw data points taken in four different cell loadings on the ethylene-*n*-decane system, and the standard deviation of the smoothed compositions of Table II and the raw data was 1.10%. There were 42 raw data points taken in four different cell loadings on the ethylene-*n*-dodecane system, and the standard deviation of the smoothed compositions of Table III and the raw data was 2.06%. 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 1.30. This, in fact, is the region in which Henry's law might be expected to hold for the solute. Thus extrapolation of the data into even

more dilute regions would be likely to be reasonably accurate.

It is interesting to compare these results with those for the same n-alkane solutes with ethane as a common solvent (6). The pressures along the three-phase solid–liquid–vapor locus for all three of these binary systems are higher than the pressures for the comparable ethane binary systems. Also, the pressure maximum occurs at about the same temperature. The solid solubilities of the solute components are slightly less in ethylene than in ethane at the same temperatures and these solubility differences are more pronounced at the lower temperatures.

Glossary

R	universal gas law constant = 1.987 cal/(g-mol K)
T	temperature in K
T_T	triple point temperature in K: 216.38 K for n-octane, 243.51 K for n-decane, 263.61 K for n-dodecane
T^*	T/T_T
x	solute mole fraction
x_1	ideal solute mole fraction, computed from eq 1
γ	activity coefficient of solute $\equiv x_1/x$
ΔH_{FUS}	enthalpy of fusion of pure solute component, cal/g-mol

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Mutual Diffusion Coefficients in Binary Mixtures of Carbon Tetrachloride and Alcohols at 20 °C

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The mutual diffusion coefficients at 20 °C were measured for three associated binary mixtures: CCl_4–CH_3OH, CCl_4–n-C_3H_7OH, CCl_4–n-C_4H_9OH. A limited-diffusion method was used with concentration differences being measured by holographic interferometry. The experimental results are compared with values derived by various predictive methods.

In a previous article (15) we showed that the limited-diffusion method of Harned and French (7) could be adapted for measuring mutual diffusion coefficients in binary organic mixtures. This adaptation involved the use of holographic interferometry to measure the concentration differences. Since the results obtained were satisfactory, with an estimated error in the diffusion coefficient of 1.5%, we extended the work by applying the same method to mixtures of tetrachloromethane with a series of normal alcohols (methanol, 1-propanol, 1-butanol), at a temperature of 20 °C and throughout the entire range of concentration. The mixture tetrachloromethane–ethanol had been previously studied (15).

The diffusion coeficients measured in this work add new information to the values already existing in the literature (1, 9, 11), which were mostly obtained at other temperatures.

Numerous equations, either empirical or theoretical, have been proposed to predict diffusion coefficients in binary liquid mixtures throughout the whole range of composition (5, 10, 13, 18). Most of these equations are applicable in the case of nearly ideal or regular mixtures. We ourselves, in a recent paper (14), have

also proposed an empirical relationship that can be applied equally well to either regular or associated mixtures.

The second part of this work will be concerned with a comparison between the experimental results for a series of aliphatic alcohols from CH_3OH to C_4H_9OH in CCl_4 and the results calculated from these various equations. It is obvious that such a comparison is not entirely fair since most of the earlier equations were not originally intended to be applied to associated systems. However, there seems to be no alternative, since no other simple equations applicable to associated systems have yet been proposed.

Prediction of Diffusion Coefficients

The prediction of the variation with concentration of the mutual diffusion coefficient in binary liquid mixtures is a problem that has stimulated a great deal of interest, both theoretical and practical.

From a practical point of view the desired aim is to obtain a relationship giving the mutual diffusion coefficient at any chosen concentration as a function of system properties which are readily accessible. It is from this point that we shall approach the subject. On the basis of various theoretical equations so far proposed, none of which is entirely satisfactory for binary mixtures, a few empirical or semiempirical models have given rise to a number of equations intended for practical use.

Among those equations requiring the fewest data, we find the following relationships, proposed respectively by Caldwell and Babb (4), Vignes (18), and Rathbun and Babb (13):