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

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Pressure–temperature profiles along with liquid compositions and liquid molar volumes for binary systems of the solvent ethane with the solutes benzene, cyclohexane, and *trans*-decalin are presented for the solid–liquid–vapor loci. The data were taken using cryoscopic techniques over a liquid compositional range extending from solute-rich solutions to solute-lean solutions. The data are pictorialized as the logarithm of composition vs. reciprocal temperature to elucidate the nonideality of the liquid phase. The standard deviations of the liquid compositional data are 1.37% for benzene, 1.55% for cyclohexane, and 1.53% for *trans*-decalin.

Solid solubility data of hydrocarbons 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 pertinent data, being in the low solute concentration range, are scarce, as can be seen by inspection of Kurata's review (6) of experimental data on the 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 (3, 4), which included n-alkanes and benzene and toluene.

Since additional experimental data on the solid solubility of hydrocarbons (including alkanes, aromatics, and naphthenes) in methane, ethane, and propane are needed, the authors have undertaken an extended study of such systems. In an earlier paper (2), we examined the binary systems of solvent ethane with solutes n-octane, n-decane, and n-dodecane, over a wide range of solute compositions. In this paper, the study is extended to binary systems of solvent ethane with benzene, cyclohexane, and *trans*-decalin as solutes, in an effort to understand the solubility behavior of ringed species in liquid ethane. The data are taken along the solid–liquid–vapor locus for each binary system.

Experimental Section

The apparatus was identical with that reported by Lee and Kohn (7) which was used in other cryoscopic studies (1, 5). The experimental procedure is described in our earlier paper (2). In performing the experiments, all data were taken with only a trace of the solute in solid form. Imposing the assumption that the solute was nonvolatile at the conditions of study, the compositions and molar volumes of the liquid phase were calculated stoichiometrically. Due to supercooling of the liquid phase prior to crystallization, all crystal points were taken as temperature was increased. The degree of supercooling was 1 to 2° for benzene and cyclohexane, and about 4° for *trans*-decalin.

Each experimental run consisted of loading a known amount of hydrocarbon (solute) into the cell and adding known amounts of ethane and observing the crystal points, until the cell was filled with liquid phase. 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.

Materials

The ethane used in this study was Matheson CP grade with a minimum purity of 99%. Small amounts of ethylene, propylene, and propane and traces of methane were present as impurities.

The cyclohexane used was an Eastman reagent "ACS" grade chemical. The benzene was a Mallinckrodt "Spectrar" spectrophotometric grade chemical. The *trans*-decalin was supplied by Columbia Organic Chemicals Co., Inc., and is at least 99% pure.

All chemicals were used without further purification.

Results

Tables I–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 volumes to ±0.4 ml g-mol⁻¹.

The data were smoothed prior to its tabulation by using the deviations between ideal and actual solubilities. 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:

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

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 experimental solubility is the estimated activity coefficient of the solute.

Table I. Vapor–Liquid–Solid Three Phase Smoothed Data: Ethane–Benzene Binary System

Temp (K)	Pressure (atm)	Liquid phase composition (mole fraction C_6)	Liquid phase volume (ml g-mol⁻¹)
265	8.05	0.7648	81.8
260	9.30	0.6522	77.7
255	9.75	0.5308	73.9
250	9.68	0.4096	70.4
245	9.04	0.2983	67.5
240	8.22	0.2128	65.1
235	7.24	0.1577	63.3
230	6.30	0.1201	62.1
225	5.38	0.0924	61.0
220	4.60	0.0721	60.1
215	4.39	0.0573	59.4
210	3.38	0.0455	58.6
205	2.76	0.0362	58.0
200	2.21	0.0287	57.3
195	1.75	0.0227	56.6
190	1.43	0.0179	56.0
185	1.09	0.0140	55.3
180	0.74	0.0109	54.7
175		0.00845	54.0

Table II. Vapor–Liquid–Solid Three Phase Smoothed Data: Ethane–Cyclohexane Binary System

Temp (K)	Pressure (atm)	Liquid phase composition (mole fraction C_6)	Liquid phase volume (ml g-mol^{-1})
255	1.96	0.9030	98.2
250	2.02	0.8941	97.4
245	2.06	0.8754	96.5
240	2.07	0.8561	95.6
235	2.06	0.8355	94.5
230	2.03	0.8135	93.3
225	1.92	0.7944	92.0
220	1.70	0.7698	90.4
215	1.50	0.7456	89.0
210	1.35	0.7203	87.6
205	1.23	0.6983	86.0
200	1 13	0.6728	84.5
195	1.06	0.6575	82.9
190	1.00	0.6275	81.2
185	0.95	0.5746	78.8
180		0.4803	74.9
175		0.3718	68.3
170		0.2781	63.4
165		0.2079	59.7
160		0.1556	57.4
155		0.1168	55.6
150		0.0890	54.1
145		0.0665	52.8

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

Temp (K)	Pressure (atm)	Liquid phase composition (mole fraction C_{10})	Liquid phase volume (ml g-mol^{-1})
240	1.64	0.9287	136.0
235	2.47	0.8041	125.3
230	2.91	0.6829	115.5
225	3.27	0.5682	105.4
220	3.35	0.4625	96.0
215	3 24	0.3628	87.2
210	2.96	0.2701	79.3
205	2.48	0.1898	72.2
200	2.06	0.1287	66.1
195	1.74	0.0861	62.2
190	1 52	0.0616	59.9
185	1.34	0.0444	58.1
180	1.16	0.0323	56.6
175	0.96	0.0238	55.3
170		0.0177	54.2
165		0.0132	53.3
160		0.00979	52.4
155		0.00713	51.5
150		0.00511	50.4

In general the activity coefficients will be $\geqq 1$, but, in the case of cyclohexane, the activity coefficient was less than unity in the range $1. > x > 0.54$. No heat of fusion was found for *trans*-decalin so an ideal curve was constructed as a tangent in ln x vs. $1/T^*$ space to the actual data as $x \rightarrow 1.0$.

The activity coefficients were plotted vs. $1/T^*$ and smoothed. Then the smoothed values of x were computed from

$$x = x_I/\gamma \qquad (2)$$

where x_I is calculated from eq 1. The resulting values of x, and also smoothed values of P and v, are those in Tables I–III. In the case of the ethane–benzene system there were runs taken at six different cell loadings—a total of 32 raw data points. The standard deviation between the smoothed compositions in Table
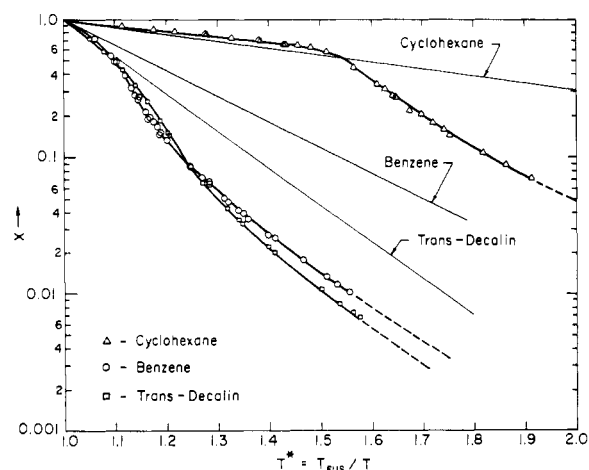

Figure 1. The experimental solute mole fraction vs. reduced reciprocal temperature as compared with ideal predictions. The heavy lines are the smoothed data presented in Tables I–III, while the light lines are the ideal composition loci for the three systems studied.

I and the raw data was 1.37%. There were 26 raw data points taken in five different cell loadings on the ethane–cyclohexane system, and the standard deviation of the smoothed compositions of Table II and the raw data was 1.55%. There were 19 raw data points taken in five different cell loadings on the ethane–*trans*-decalin system, and the standard deviation of the smoothed compositions of Table III and the raw data was 1.53%.

The raw data are shown in Figure 1 along with the smooth composition lines and "ideal" solubility lines. In the case of the solutes benzene and *trans*-decalin, the solute compositions extend to values low enough that linear extrapolation of the data to lower compositions in Figure 1 would be valid; i.e., one might expect Henry's law to hold for the solute when $x < 0.01$. Although the data also appear to have become linear for the solute cyclohexane at $T^{*-1} > 1.8$, the solute compositions are high enough in this region to make linear extrapolation possibly risky.

Glossary

R	universal gas constant (1.987 cal g-mol^{-1} K^{-1})
P	pressure (atmospheres absolute)
T_{FUS}	triple point temperature in K
T	temperature in K
T^*	T/T_{FUS}
v	liquid phase molar volume in ml g-mol^{-1}
x	solute mole fraction
x_I	ideal solute mole fraction, computed from eq 1
γ	activity coefficient of solute $= x_I/x$
ΔH_{FUS}	enthalpy of fusion of pure solute component (cal g-mol^{-1})

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