(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.

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# 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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**Table I. Solid-Liquid-Vapor Three-Phase Smoothed Data: Ethane-2-Methylnaphthalene Binary System**

| temp, K | pressure, atm | liquid-phase compn (mole fraction 2MN) | liquid-phase molar volume, mL/g-mol |
|---|---|---|---|
| 300.0 | 8.6 | 0.925 | 136.4 |
| 290.0 | 19.2 | 0.759 | 121.9 |
| 280.0 | 24.7 | 0.525 | 103.2 |
| 276.5[a] | 25.1 | 0.421[b] | 93.2[b] |
| 276.5[a] | 25.1 | 0.049 1[c] | 76.0[c] |
| 270.0 | 21.8 | 0.022 3 | 73.6 |
| 260.0 | 17.2 | 0.012 9 | 70.4 |
| 250.0 | 13.2 | 0.008 41 | 67.7 |
| 240.0 | 9.8 | 0.005 45 | 65.4 |
| 230.0 | 7.0 | 0.003 54 | 63.2 |
| 220.0 | 5.0 | 0.002 22 | 61.2 |

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

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

| temp, K | pressure, atm | liquid-phase compn (mole fraction naphthalene) | liquid-phase molar volume, mL/g-mol |
|---|---|---|---|
| 350.0 | 12.1 | 0.927 | 126.4 |
| 345.0 | 27.1 | 0.826 | 119.2 |
| 340.0 | 36.3 | 0.714 | 111.2 |
| 335.0 | 58.5 | 0.576 | 104.1 |
| 332.0 | 71.5 | 0.473 | 95.1 |
| 309.9[a] | 51.6 | 0.006 44 | |
| 308.0 | 49.8 | 0.007 26 | 108.3 |
| 305.0 | 46.8 | 0.008 15 | 98.4 |
| 302.0 | 44.1 | 0.008 41 | 94.4 |
| 299.0 | 41.5 | 0.008 53 | 90.9 |
| 295.0 | 38.1 | 0.008 38 | 87.4 |
| 290.0 | 34.4 | 0.007 80 | 84.1 |
| 285.0 | 31.0 | 0.007 00 | 81.3 |
| 280.0 | 27.8 | 0.006 25 | 78.5 |
| 270.0 | 22.1 | 0.004 78 | 73.6 |
| 260.0 | 17.1 | 0.003 51 | 70.2 |
| 250.0 | 13.1 | 0.002 47 | 67.1 |
| 240.0 | 10.1 | 0.001 66 | 64.4 |

[a] K point (V-L critical point in the presence of solid) for the lower compositional branch of the S-L-V locus.

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

| temp, K | pressure, atm | liquid-phase compn (mole fraction $nC_{10}$) | liquid-phase molar volume, mL/g-mol |
|---|---|---|---|
| 240.0 | 0.33 | 0.828 | 166.8 |
| 235.0 | 0.60 | 0.599 | 136.4 |
| 230.0 | 0.69 | 0.432 | 120.6 |
| 225.0 | 0.66 | 0.306 | 107.7 |
| 220.0 | 0.58 | 0.212 | 96.3 |
| 215.0 | 0.47 | 0.144 | 88.3 |
| 210.0 | 0.38 | 0.095 2 | 82.4 |
| 205.0 | | 0.062 0 | 78.1 |
| 200.0 | | 0.040 4 | 74.5 |
| 195.0 | | 0.026 2 | 72.4 |
| 190.0 | | 0.016 7 | 70.9 |
| 185.0 | | 0.010 5 | 69.9 |
| 180.0 | | 0.006 67 | 69.0 |

**Table IV. Solid-Liquid-Vapor Three-Phase Smoothed Data: Propane-*n*-Dodecane System**

| temp, K | pressure, atm | liquid-phase compn (mole fraction $nC_{12}$) | liquid-phase molar volume, mL/g-mol |
|---|---|---|---|
| 250.0 | 1.29 | 0.410 8 | 134.7 |
| 245.0 | 1.27 | 0.274 5 | 114.3 |
| 240.0 | 1.19 | 0.183 6 | 101.1 |
| 235.0 | 1.06 | 0.119 1 | 91.8 |
| 230.0 | 0.89 | 0.075 8 | 84.9 |
| 225.0 | 0.74 | 0.047 5 | 80.4 |
| 220.0 | 0.61 | 0.030 0 | 77.7 |
| 215.0 | 0.50 | 0.019 2 | 75.5 |
| 210.0 | 0.41 | 0.012 1 | 73.8 |
| 205.0 | 0.35 | 0.007 50 | 72.6 |
| 200.0 | | 0.004 61 | 71.6 |

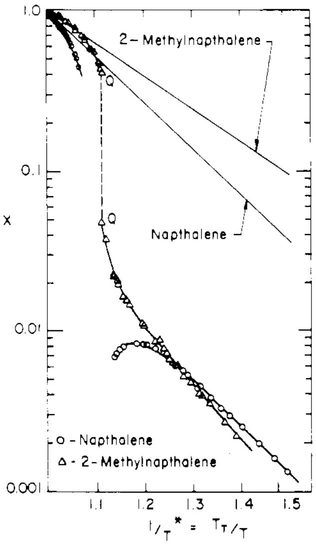

**Figure 1.** The experimental solute mole fraction vs. reduced reciprocal temperature as compared with ideal predictions for both ethane systems studied. The heavy lines are the smoothed data presented in Tables I and II, while the light lines are the ideal composition loci for both systems.

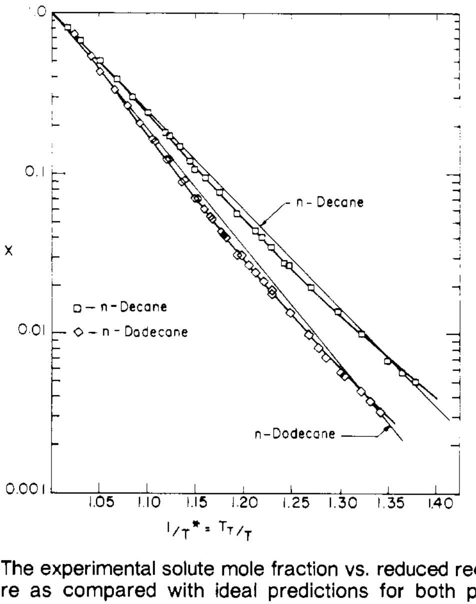

**Figure 2.** The experimental solute mole fraction vs. reduced reciprocal temperature as compared with ideal predictions for both propane systems studied. The heavy lines are the smoothed data presented in Tables III and IV, while the light lines are the ideal composition loci for both systems.

prior to tabulation by use of the same procedure as was reported for the earlier ethane systems (*2*, *5*).

In the case of the ethane-2-methylnaphthalene system, there were runs taken at six different cell loadings—a total of 41 raw data points. The standard deviation between the smoothed compositions in Table I and the raw data was 2.95%. There were 36 raw data points taken in four different cell loadings on the ethane-naphthalene system, and the standard deviation of the smoothed compositions of Table II and the raw data was 1.52%. There were 25 raw data points taken in three different cell loadings on the propane-*n*-decane system, and the standard deviation of the smoothed compositions of Table III and the raw data was 1.95%. There were 36 raw data runs taken in four different cell loadings on the propane–$n$-dodecane systems, and the standard deviation of the smoothed compositions of Table IV and the raw data was 1.85%.

The raw data corresponding to the two ethane–solvent systems are shown in Figure 1, and the raw data for the two propane–solvent 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 at values of $1/T^*$ larger than 1.40 for the systems with ethane as a solvent and larger than 1.35 for the systems with propane as a solvent. 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.

The discontinuities in both ethane solvent binary systems in Figure 1 were not exhibited by any of the previously studied ethane systems. These discontinuities are caused by the fact that the triple point of both solutes exceeds that of the critical point of the solvent. For the 2-methylnaphthalene–solute 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 locus. For the naphthalene–solute system, an even higher solute triple-point temperature causes a temperature range in which no liquid phase exists. Noteworthy in the composition behavior of this naphthalene–solute system is the maximum in the composition which occurs at the high-temperature end of the low-composition branch of the S–L–V locus. At this point the system, already extremely dilute in hydrocarbon solute, is approaching the vicinity of the critical point of pure ethane. Apparently the increase in molar volume of the liquid phase effects a decrease in composition, in contrast to what one experiences at lower temperatures. This phenomenon has been observed before in the binary systems methane–$n$-octane and methane–cyclohexane (*3*).

## Glossary

| | |
|---|---|
| $L_1$ | ethane-lean liquid phase |
| $L_2$ | ethane-rich liquid phase |
| $T$ | temperature in K |
| $T_T$ | triple point temperature in K: 307.73 K for 2-methylnaphthalene, 353.2 K for naphthalene, 243.51 K for $n$-decane, 263.61 K for $n$-dodecane |
| $T^*$ | $T/T_T$ |
| $x$ | 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.

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# Activity Coefficients from Solid–Liquid and Vapor–Liquid Equilibria of Some Associated Solutions

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**Solid–liquid and low-pressure vapor–liquid equilibria were experimentally determined for binary solutions of acetic acid and carbon tetrachloride, benzene, or chloroform. Activity coefficients from vapor–liquid data reduction, taking into account vapor-phase dimerization of acetic acid, were compared with those derived from the solubility of solid acetic acid in the liquid solvent.**

## Introduction

Information on the activity coefficients in liquid solutions can be obtained from data reduction of vapor–liquid equilibria and of solubilities of solids in liquids. Therefore, in principle, the activity coefficients obtained from either of the two-phase equilibria could be used for the prediction of the other equilibrium and vice versa. However, for isobaric equilibria it is necessary to know the heat of mixing, mainly in the case of large temperature ranges or in the case of high thermal effects.

In this note vapor–liquid and solid–liquid equilibrium data are reported for solutions of an associated component, namely, acetic acid, and a common solvent such as carbon tetrachloride, benzene, or chloroform.

The scope of the work is the comparison of the sets of activity coefficients obtained from both types of data. This comparison also allows an indirect check of consistency of the procedure which evaluates vapor-phase nonidealities of associated systems.

The choice of acetic acid is due to its melting temperature (16.6 °C), which allows measurements of solubilities at temperatures close to ambient.

Measurements of vapor–liquid equilibrium data are carried out at pressures of the order of 100 mmHg, to approach the temperature ranges pertaining to both equilibria.

## Experimental Section

Solubilities of solid acetic acid in the liquids were determined by analyzing samples of the liquid phase in equilibrium with the solid.

To this purpose, liquid–solid systems were agitated in a thermostatic bath (±0.1 °C). After equilibrium was reached,

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