

PHASE EQUILIBRIUM IN THE SYSTEM: CYCLOHEXANE-2,3-DIMETHYLPENTANE-
HEPTACOSAFLUOROTRIBUTYLAMINE

by

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PURPOSE

The purpose in carrying out this work was to add previously undetermined phase equilibrium data to the literature, and to investigate with respect to the Scatchard-Hildebrand theory an extractive distillation system utilizing a fluorocarbon as the solvent.

NOMENCLATURE

a	Activity, standard state taken as pure substance
C	Interaction energy
d°	Distance between centers of nearest neighbor molecules
f	Correction factor
I	Ionization potential
K	Constant
ln	Logarithm, base e
P°	Vapor pressure of the pure compound, mm of mercury
q	I_j/I_i
R	Gas constant
s	$d_{jj}^{\circ}/d_{ii}^{\circ}$
T	Absolute temperature, °K
t	Temperature, °C
V	Molal volume, cc
V	Volume, cc
x	Mole fraction in liquid phase
y	Mole fraction in vapor phase

ΔA	Change in Helmholtz Free Energy
ΔE	Change in Internal Energy
ΔG	Change in Gibb's Free Energy
ΔH	Change in Enthalpy
ΔS	Change in Entropy
α	Relative volatility
γ	Activity coefficient, standard state taken as pure substance
δ	Solubility parameter, (calories/cc) ^{1/2}
γ	Total pressure, mm. of mercury
ϕ	Volume fraction

Subscripts

1	More volatile component, cyclohexane
2	Less volatile component, 2,3-dimethylpentane
3	Solvent, heptacosafuorotributylamine
d	Refers to d°
I	Refers to ionization potential
i	i th component
j	j th component

Superscripts

M	Refers to mixing process
V	Refers to vaporization process
'	Refers to ternary system
'	Refers to hydrocarbon phase
"	Refers to fluorocarbon phase
*	Refers to cyclohexane free basis
+	Refers to fluorocarbon free basis
-	Refers to partial molal quantities

INTRODUCTION AND THEORETICAL BACKGROUND

Extractive Distillation

Extractive distillation is defined as distillation in the presence of a nonvolatile solvent which is selected so that the separation between the original components is enhanced (4). This process is especially valuable in industries where separation is desired between two or more miscible liquids which exhibit small differences in their boiling points.

Much experimental work has been done in the past with regard to the choice of solvents for a desired separation (4), (6), (7). This work usually consists of determining the effect of various solvents and solvent concentrations on the vapor-liquid equilibrium relationships of the original components and requires a great deal of time and equipment. Dunn et al. (4), recommended that the testing of various solvent concentrations with a 50-50 mixture of the two original components would shorten the procedure. However, Colburn and Schoenburn (2) have attacked this as not being conclusive. Several investigators have used the empirical approach of selecting solvents for extractive distillation (1), (2), (3), but this procedure still requires a certain amount of experimental data. If a theoretical approach could be found, the advantages would be two fold: first, a true explanation of ternary solution behavior could be presented, and second, the physical properties of the components would be the only necessary data needed to evaluate the effect of a particular solvent.

Solution Behavior

One of the most widely used theories in the field of solution behavior is that which was developed independently by Scatchard and Hildebrand and published in 1931 and 1933 respectively. This theory applies only to solutions which fall in the rather limited classification of "regular solutions". A regular solution was defined by Hildebrand (8), page 46, as a solution which exhibits no segregation tendencies caused by different molecular interactions. Such a solution is considered to have a maximum random distribution of molecules and, therefore, exhibits ideal entropy of mixing. The application of this regular solution theory necessitates four major assumptions:

1. The mutual energy of two molecules depends only upon the distance between them and their relative orientation and not at all on the nature of the molecules around them or the temperature of the system.
2. The distribution of the molecules in position and orientation is random.
3. The change of volume on mixing at constant pressure is zero.
4. The interaction energy between 1-2 pairs of molecules in solution is the geometric mean of the interaction energy between 1-1 and 2-2 pairs or: $C_{12} = (C_{11} C_{22})^{1/2}$

Using the above assumptions and noting that at moderate conditions of pressure and temperature the vapor in equilibrium with a liquid solution obeys the ideal gas law, Scatchard (8), page 124, presented the following equation for the energy change due to mixing for a

regular binary solution:

$$\Delta E^M = (x_1 v_1 + x_2 v_2) \left[\left(\frac{\Delta E_1^V}{v_1} \right)^{1/2} - \left(\frac{\Delta E_2^V}{v_2} \right)^{1/2} \right]^2 \phi_1 \phi_2 \quad (1)$$

Using assumption 3, above, the heat of mixing may be equated to the energy of mixing:

$$\Delta H^M = \Delta E^M + P \Delta V^M \quad (2)$$

$$\text{or } \Delta H^M = J E^M$$

$$\text{and } \Delta F^M = \Delta E^M - T \Delta S^M \quad (3)$$

The ideal entropy of mixing is:

$$\Delta S^M = -R(x_1 \ln x_1 + x_2 \ln x_2) \quad (4)$$

Then by combination of Equations (1) and (4) an expression for the free energy of mixing in terms of measurable variables results:

$$\Delta F^M = RTx_1 \ln x_1 + RTx_2 \ln x_2 + (x_1 v_1 + x_2 v_2) (\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad (5)$$

The symbol δ in the above equation represents the term $\left(\frac{\Delta E_i^V}{v_i} \right)^{1/2}$ and was defined by Hildebrand (8), page 129, as the solubility parameter. The preceding equation may be rewritten in terms of activity coefficients as follows:

$$\overline{\Delta F}_1 = RT \ln x_1 + v_1 (\delta_1 - \delta_2)^2 \phi_2^2 = RT \ln a_1 = RT \ln \gamma_1 x_1 \quad (6)$$

$$\text{or } RT \ln \gamma_1 = v_1 (\delta_1 - \delta_2)^2 \phi_2^2 \quad (7)$$

$$\text{and } RT \ln \gamma_2 = v_2 (\delta_1 - \delta_2)^2 \phi_1^2 \quad (8)$$

In order to apply the Scatchard-Hildebrand theory to extractive distillation studies Kyle (11) has derived an equation for the ratio of the activity coefficients of the two original components in the presence of a solvent:

$$RT \ln \frac{\gamma_1}{\gamma_2} = v_1 (\delta_3 - \delta_1)^2 \phi_3^2 - v_2 (\delta_3 - \delta_2)^2 \phi_3^2 \quad (9)$$

It can be seen that the equation was derived with the assumption that the interaction of 1-2 pairs of molecules is negligible. This assumption was made on the basis that the solvent concentration would be great enough so that only 1-3 and 2-3 interactions would occur appreciably.

Since the purpose of extractive distillation is to separate compounds which cannot be separated by ordinary distillation methods, the prime concern is to increase the value for the relative volatility of the binary components. The relative volatility is defined as:

$$\alpha_{12} = \frac{\gamma_1 \frac{P_1^0}{P_2^0}}{\gamma_2 \frac{P_1^0}{P_2^0}} = \frac{y_1}{x_1} \cdot \frac{x_2}{y_2} \quad (10)$$

Thus the definition of relative volatility indicates that for α_{12} to be a maximum the ratio $\frac{\gamma_1}{\gamma_2}$ must also be a maximum since ratio of the pure component vapor pressures $\frac{P_1^0}{P_2^0}$ varies little with temperature for most binary systems. The function of an effective solvent in extractive distillation would be to increase the ratio of the activity coefficients in the binary system where separation is desired.

If the molal volumes of 1 and 2 can be assumed to be nearly

the same, then Equation (9) may be written in the following form:

$$\ln \frac{\sqrt{1}}{\sqrt{2}} = \frac{2 \phi_3^2}{RT} V_1 (\delta_1 - \delta_2) \left(\frac{\delta_1 + \delta_2}{2} - \delta_3 \right) \quad (11)$$

Equation (11) may be applied to two cases of the binary system. If component one is the more volatile but the least polar component, then $\delta_1 < \delta_2$ and $(\delta_1 - \delta_2) < 0$. With these conditions, according to Equation (11), δ_3 must be larger than $\frac{\delta_1 + \delta_2}{2}$ in order that $\frac{\sqrt{1}}{\sqrt{2}}$ be greater than unity.

In the second case component one is the more volatile and also the more polar component, therefore, $\delta_1 > \delta_2$ and $(\delta_1 - \delta_2) > 0$. In order for the ratio $\frac{\sqrt{1}}{\sqrt{2}}$ to be greater than unity in this case δ_3 should be less than $\frac{\delta_1 + \delta_2}{2}$.

In Equation (11) it can be seen that the ratio $\frac{\sqrt{1}}{\sqrt{2}}$ greatly depends on the volume fraction of the solvent ϕ_3 ; therefore, the effect of the solvent on the activity coefficient ratios will be greatest at high solvent concentrations. This was observed experimentally by Fenske et al. (5) and Dunn et al. (4). As mentioned above, Equation (11) indicates that for the case of the more volatile component being the least polar component a polar solvent should enhance the separation. This was also observed experimentally by Fenske et al. (5) and Griswold et al. (6). This leaves the case of the more volatile component being the more polar component where Equation (11) suggests a relatively non-polar compound as a solvent. Experimental work along this line has been carried out by Kyle (11) and Tetlow (20).

This thesis will present a study of the vapor-liquid equilibrium data for the binary system cyclohexane-2,3-dimethylpentane. The boiling point difference between these two compounds is approximately 9°C., and the components are similar to those for which a separation is desired in the petroleum or petrochemical industry. This system corresponds to the second case previously considered; the more volatile component is also the more polar component. Pure cyclohexane has a boiling point of 80.5°C. and has a solubility parameter of 8.19 (calories/cc)^{1/2} at 25°C., while 2,3-dimethylpentane boils at 89.8°C. and has a solubility parameter of 7.24 (calories/cc)^{1/2} at 25°C. Therefore, by applying the Scatchard-Hildebrand equation as written by Kyle, Equation (11), a "non-polar" solvent should be the most effective extractive distillation agent for this system.

Solution Behavior Applied to Fluorocarbons

The term "polar" is rather vague, but is usually used as a measure of the extent of molecular interaction in the form of dipole-dipole interactions (orientation effects). Since fluorocarbons, a relatively new class of compounds, have been found to have very weak molecular interactions, they have been classed as non-polar. Their low solubility parameters as given by Hildebrand (8), Appendix I, illustrate this point. In view of the other requirements of solvents for extractive distillation such as non-corrosiveness and non-toxicity, it appears that fluorocarbons and chlorofluorocarbons offer great possibilities for this type of system.

Fluorocarbons and chlorofluorocarbons are usually defined as

completely or partially halogenated hydrocarbons or hydrocarbon derivatives. The development of these compounds has taken place extensively since World War II. While much work has been done with these compounds concerning their properties and their behavior in solutions (27), (28), (29), (30), (31), (34), little has been done regarding their applicability as solvents for extractive distillation until recently by Kyle (11) and Tetlow (20).

A paper by Scott (15), published in 1958, summarizes the work done on solution behavior in systems containing fluorocarbons. He points out that, although several theories and empirical relations have been proposed which seem to explain certain classes of fluorocarbon-fluorocarbon or fluorocarbon-hydrocarbon systems, no satisfactory explanation has been given for solution behavior in all classes of solutions.

Solutions of fluorocarbons and hydrocarbons have been found to exhibit greater positive deviations from Raoult's Law and much lower mutual solubilities than would be predicted from the Scatchard-Hildebrand theory. Several attempts have been made to account for and to correct the Scatchard-Hildebrand theory for this irregular behavior when applied to fluorocarbon-hydrocarbon systems. Hildebrand suggested that in such solutions the solubility data could best be fitted by arbitrarily shifting the hydrocarbon solubility parameters; however, this is an empirical approximation, and a theoretical explanation would be much more acceptable. Simons and Dunlap rederived the Scatchard-Hildebrand equation and omitted the assumption of no volume change in mixing.

Hildebrand (8), page 139, has shown that ΔF^M at constant pressure is essentially ΔA^M at constant volume. An expression for the activity coefficients is derived as follows:

$$\Delta E^M = \Delta A^M + T \Delta S^M \quad (\text{at constant temperature}) \quad (12)$$

combining with Equations (1) and (4) gives:

$$\Delta A^M = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 + TR(x_1 \ln x_2 + x_2 \ln x_1) \quad (13)$$

but since ΔF^M at constant pressure = ΔA^M at constant volume,

$$\Delta F^M = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 + TR(x_1 \ln x_1 + x_2 \ln x_2) \quad (14)$$

writing Equation (14) in terms of partial molal quantities:

$$\bar{\Delta F}_1 = V_1(\delta_1 - \delta_2)^2 \phi_2^2 + RT \ln x_1 \quad (15)$$

$$\text{and } \bar{\Delta F}_2 = V_2(\delta_1 - \delta_2)^2 \phi_1^2 + RT \ln x_2 \quad (16)$$

$$\text{where } \bar{\Delta F}_1 = RT \ln x_1 = RT \ln \gamma_1 x_1 = RT(\ln \gamma_1 + \ln x_1) \quad (17)$$

therefore:

$$RT \ln \gamma_1 = V_1(\delta_1 - \delta_2)^2 \phi_2^2 \quad (18)$$

which is the same expression derived earlier, Equation (7). Therefore, it can be seen that the excess free energy of mixing will be affected very little by the assumption of no volume change on mixing. However, entropy of mixing (ΔS^M) and heat of mixing (ΔH^M) cannot be determined using this assumption without the introduction of a considerable error. This follows from Scott (15) who maintains that

solution behavior should be correlated on the basis of excess free energy instead of excess enthalpy or entropy.

Reed (14) rederived Equation (5) omitting the assumptions regarding the geometric mean of the interaction energies and no volume change on mixing. Since ΔF^M is insensitive to ΔV^M , Equation (5) was rederived omitting only the geometric mean assumption:

$$RT \ln \sqrt{1} = v_1 [(\delta_1 - \delta_3)^2 + 2 \delta_1 \delta_3 (1-f_{13})] \beta_3^2 \quad (19)$$

$$RT \ln \sqrt{2} = v_2 [(\delta_2 - \delta_3)^2 + 2 \delta_2 \delta_3 (1-f_{23})] \beta_3^2 \quad (20)$$

The factor f has been applied to solution behavior studies as explained in the section, Predicted Ternary Activity Coefficients.

The correction factor, f , as used in the above equations, is the product of two theoretical expressions:

$$f_{ij} = f_I f_d \quad (21)$$

where

$$f_I = \frac{2a^{1/2}}{1+q} \quad (22)$$

and

$$f_d = \left[\frac{2s^{1/2}}{1+s} \right]^3 \quad (23)$$

where $s = d_{22}^0 / d_{11}^0$ and $q = I_2 / I_1$. Tetlow (20) recently extended the use of this correction factor to ternary systems by developing the following expressions from Hildebrand's ternary equations (8), page 201:

$$RT \ln \sqrt{1} = V_1 \left\{ (\delta_1 - \delta_2)^2 \phi_2^2 + [(\delta_1 - \delta_3)^2 + 2(1-f_{13}) \delta_1 \delta_3] \phi_3^2 + 2 [\delta_1(\delta_1 - \delta_2) + \delta_3(f_{23} \delta_2 - f_{13} \delta_1)] \phi_2 \phi_3 \right\} \quad (24)$$

$$RT \ln \sqrt{2} = V_2 \left\{ (\delta_1 - \delta_2)^2 \phi_1^2 + [(\delta_2 - \delta_3)^2 + 2(1-f_{23}) \delta_2 \delta_3] \phi_3^2 + 2 [\delta_2(\delta_2 - \delta_1) + \delta_3(f_{13} \delta_1 - f_{23} \delta_2)] \phi_1 \phi_3 \right\} \quad (25)$$

In the preceding derivation it was assumed that $f_{12} = 1.0$. If it is further assumed that $f_{13} = f_{23} = f$, then Equation (9) may be rewritten in the following form:

$$RT \ln \frac{\sqrt{1}}{\sqrt{2}} = V_1(\delta_1 - \delta_2)^2 \phi_2^2 + V_1(\delta_1 - \delta_3)^2 \phi_3^2 + 2 V_1(1-f) \delta_1 \delta_3 \phi_3^2 + 2 V_1(\delta_1 - \delta_2)(\delta_1 - f \delta_3) \phi_2 \phi_3 - V_2(\delta_1 - \delta_2)^2 \phi_1^2 - V_2(\delta_2 - \delta_3)^2 \phi_3^2 - 2 V_2(1-f) \delta_2 \delta_3 \phi_3^2 - 2 V_2(\delta_2 - \delta_1)(\delta_2 - f \delta_3) \phi_1 \phi_3 \quad (26)$$

The relevance to extractive distillation studies of this theory and the accompanying equations will be discussed further in the following sections of this thesis.

BINARY EQUILIBRIUM IN THE SYSTEM: CYCLOHEXANE-2,3-DIMETHYLPENTANE

Experimental Procedure

Since the vapor-liquid equilibrium data for the binary system cyclohexane-2,3-dimethylpentane could not be found in the literature, it was obtained as part of the experimental work of this thesis.

The hydrocarbons used in this work were obtained from the Phillips Petroleum Company. The cyclohexane was reported to be 99 mole % pure and the 2,3-dimethylpentane 95 mole % pure.* A chromatogram of the 2,3-dimethylpentane showed a small peak preceding the main peak which indicated a small amount of impurity. This small amount was estimated to be less than 1 mole % and was neglected. A chromatogram of the cyclohexane showed only one smooth peak indicating a high degree of purity.

A modified still, similar to that used by Othmer (12), was used to determine the vapor-liquid equilibrium data for the binary system. The upper portion of the still was insulated and wound with a heating element. However, due to the belief that conduction of heat from the heating element to the still could cause an error in the temperature measurement and that at steady state conditions the heat loss from the upper walls of the still was negligible, the jacket heater was not used. This still was the same used by Tetlow (20) with very good results.

The still was charged with the binary solution of desired concen-

* More information concerning the properties and purity of the chemicals used in this thesis are contained in Appendix II.

tration. Heat was applied by means of an internal resistance heater while the mixture was constantly agitated with a magnetic stirrer. The boil-up rate was adjusted so that superheating would be at a minimum (10-15 drops of condensate collected per minute). The still was operated at a constant pressure (760 mm of mercury) maintained with a cartesian type manostat. After the system had attained steady state, as evidenced by the temperature of the pot mixture remaining constant for about 30 minutes, the heat was removed and the still allowed to cool. Liquid and vapor samples were taken from the appropriate locations. Each run took about 2-3 hours.

These samples were analyzed with an Abbe¹ refractometer which was capable of determining the refractive index to a precision of ± 0.0001 . This precision in the refractive index resulted in an analysis error of ± 0.4 wt % cyclohexane or ± 0.48 mole % cyclohexane. A calibration curve was constructed for the binary system cyclohexane-2,3-dimethylpentane by weighing known samples on the analytical balance to a precision of ± 0.0001 gram and determining the refractive index of each known sample at 25°C. The data for this calibration is shown in Table 1 and Figure 6.

First attempts to measure the equilibrium temperature in the still were made with a thermocouple immersed in the boiling liquid; however, much discrepancy in the temperature was apparent when the composition of the still pot was changed only slightly. This problem was solved by measuring the boiling point of the pot mixture at the end of a run. This was done by transferring about 40 ml. of the pot mixture to a dynamic boiling apparatus similar to that used by

Quiggle et al. (13). This temperature was measured with a chromel-alumel thermocouple at a constant pressure of 760 mm of mercury controlled by the same system used to control the equilibrium still pressure. The procedure for the calibration of the thermocouple appears in Appendix I of this thesis.

Discussion of Experimental Results

The binary equilibrium data for the system cyclohexane-2,3-dimethylpentane are plotted in the form of a boiling point curve and an x-y diagram and appear in Figures 1 and 2, and the data are listed in Table 5. The plots indicate that no azeotrope occurs in the binary system. The data plotted in this form appear smooth and consistent.

The activity coefficients were calculated from the experimental data using the following expression:

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^0} \quad (27)$$

The magnitude and nearly random distribution of the activity coefficients suggested that the system was very close to ideal. The activity coefficients for cyclohexane varied from 1.0 to 1.07, and the activity coefficients for 2,3-dimethylpentane varied from 0.98 to 1.05. It was believed that slight errors in temperature measurement caused the activity coefficients for 2,3-dimethylpentane to dip slightly below unity. The effectiveness of the addition of a solvent to this system were analyzed on the basis of x-y data; however, this is not the only method of comparison. Relative

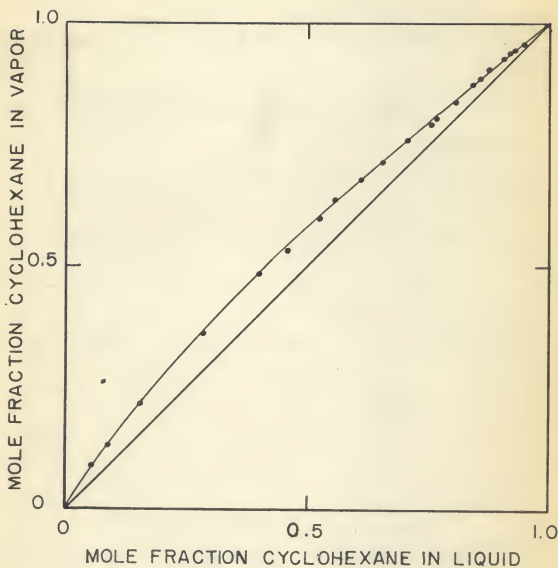


Figure 1. Boiling point-composition diagram at 760 mm. of mercury, total pressure, for the system: cyclohexane-2,3-dimethylpentane.

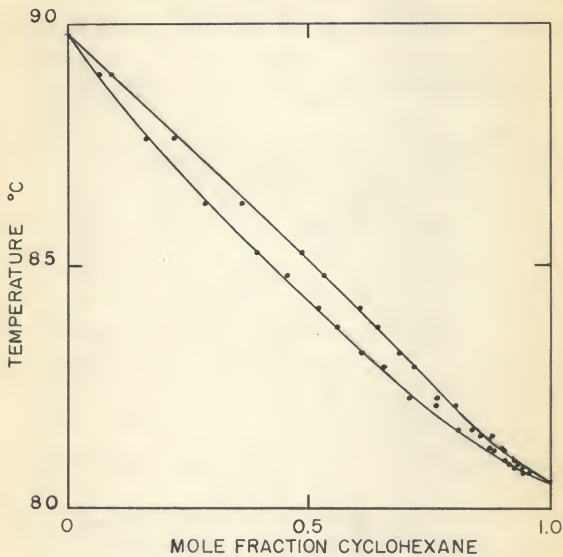


Figure 2. Binary x-y data for the system: cyclohexane-2,3-dimethylpentane.

volatility may also be used, but since it is very sensitive to slight experimental errors, the data was not evaluated on this basis.

However, an average value of 1.35 was determined for the relative volatility of this system.

Prediction of Binary Solution Behavior

A solubility parameter function, K , was determined using the liquid-liquid solubility data of the two binary systems containing the fluorocarbon from the following expression:

$$RT \ln \gamma_1 = V_1 (K_{13}) \phi_3^2 \quad (28)$$

$$RT \ln \gamma_2 = V_2 (K_{23}) \phi_3^2 \quad (29)$$

Since the activity of a component is equal in all phases in which the component is present in a system ($x_1^I \gamma_1^I = x_1^N \gamma_1^N$), each of the above equations may be very easily rearranged to the following form:

$$K_{13} = \frac{\ln(x_1^N/x_1^I)}{(V_1/RT) [(\phi_3^I)^2 - (\phi_3^N)^2]} \quad (30)$$

and a similar expression for K_{23} . In the above equation the x_1^I and x_1^N were determined at a constant temperature from the liquid-liquid solubility curve for the binary system. From the values for K_{13} and K_{23} at 25°C. the values for K_{12} were determined. Using these values and Equations (28) and (29) the x-y data for the binary hydrocarbon system was calculated using a trial and error method.

The solubility parameter as a function of temperature was

determined for each component from their respective physical properties. These values were then used in conjunction with Equations (7) and (8) to evaluate the activity coefficients and predict the x-y diagram theoretically from the regular solution theory.

The prediction of the binary x-y data, using both the empirical K values and the solubility parameters evaluated from the physical properties of the chemicals, gave good agreement with the experimental data. The x-y curves from all three methods, experimental, empirical and theoretical, can be superimposed to illustrate this agreement.

TERNARY EQUILIBRIUM IN THE SYSTEM: CYCLOHEXANE-
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Solubility Relationships

Solubility data is useful in that empirical solubility parameters may be evaluated from such binary data. The liquid-liquid solubility data for the heptacosafuorotributylamine-cyclohexane system was determined by using a heavy walled glass tube fitted with brass flanges and a thermocouple. A detailed description of the apparatus and the thermocouple calibration was given by Tetlow (20).

Each solubility point was determined by weighing the desired amount of each component accurately on the analytical balance and placing the mixture in the glass tube. The flanges were bolted together, sealing the tube, and the apparatus was immersed in a water bath. The temperature of the bath was raised until the two liquid phases disappeared; the bath was then allowed to cool until the liquid in the tube became cloudy. This cloudiness marked the point of unmixing and the temperature at this point was taken as the unmixing temperature. The phenomena of opalescence was observed a few degrees above the unmixing temperature. This was also observed by Kyle (11) and Tetlow (20) in similar systems. This light scattering effect was thought to be caused by agglomerating or clustering of molecules (8), page 457.

Since air was present in the tube during this determination of the unmixing temperature, a solution saturated with air was one of the conditions or restrictions of the data. However, Kyle (11) made a

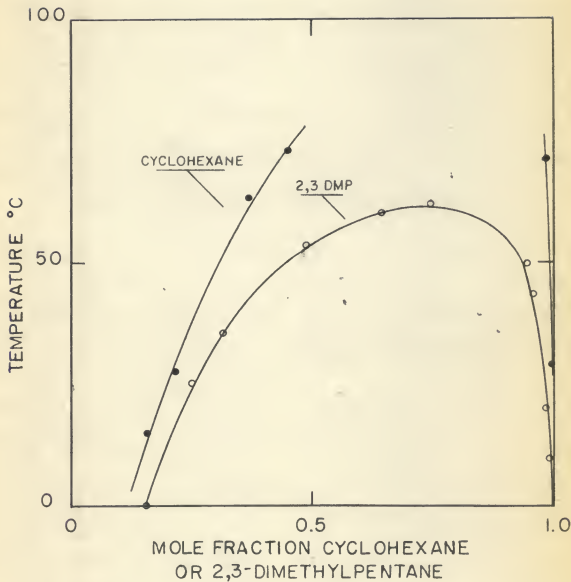


Figure 3. Binary solubility curves for heptacosafuorotributylamine systems.

test run with a similar system (toluene-perfluorocyclic oxide) in the absence of air and found very little difference in the unmixing temperatures.

The solubility data for the system heptacosafuorotributylamine-cyclohexane is shown in Table 4. The solubility curves for this system and the system heptacosafuorotributylamine-2,3-dimethylpentane, as obtained by Tetlow (20), are shown plotted in Figure 3.

Analysis of the Ternary System

One of the main objections to the investigations of ternary systems has been the difficulty of analyses. A binary system requires the measurement of only one physical property of the system, such as refractive index or density, to fix the composition. However, a ternary system requires two such measurements which entails a great deal more work and multiplies the chance for error by a factor of two.

It can be seen that gas-liquid chromatography would lend itself quite readily to the analysis of such systems. However, in order that the desired separations result, a satisfactory partitioning liquid or stationary phase must be found. Tetlow (20) experimented with 18 such compounds without satisfactory results. Several additional compounds were tested during the experimental work of this thesis and 1-naphthylamine was found to give satisfactory results when deposited on acid washed celite and packed in a column about 20 feet long.

The column packing was made by weighing out acid washed Johns-Manville celite, mesh size 35/80, and 1-naphthylamine in a weight

ratio of 3:1 respectively. The 1-naphthylamine was dissolved in about 50 cc of acetone and thoroughly mixed into the celite in order to completely coat each particle. As soon as the acetone had evaporated and the coated celite flowed freely, it was carefully packed into 20 feet of $\frac{1}{4}$ " copper tubing and bent into a coil.

The chromatograph used was designed by B. G. Kyle of Kansas State University and built by student labor. It makes use of a Gow-Mac thermal conductivity cell and accompanying circuit and a Minneapolis-Honeywell recording potentiometer. Optimum operating conditions were found to be a column temperature of 200°F and a carrier gas flow rate of about 50 cc/min. Helium was used as a carrier gas. A detailed theory and explanation of gas-liquid chromatography may be found in Keulemans (10).

Heptacosafuorotributylamine-hydrocarbon systems formed two liquid phases at room temperature; therefore, injecting a sample of this system into the chromatograph presented considerable difficulty. If the sample was heated to the point where only one phase was present, there was a chance cooling below the unmixing temperature might occur in the injecting device (hypodermic syringe calibrated in microliters). The problem was solved by adding a fourth compound, Kel-F Alkane, until only one phase was present. This compound gave a peak which did not interfere with any of the other three and, therefore, was ignored in the analysis. The precision of this chromatographic analysis was estimated to be between 0.5 and 1.0 mole per cent. Details of the calibration of the chromatograph appear in Appendix I.

Ternary Vapor-Liquid Equilibrium

Vapor-liquid data for the ternary system cyclohexane-2,3-dimethylpentane-heptacosafuorotributylamine were determined in an equilibrium still similar to that used by Wilson (22) and Tetlow (20). This still was very versatile in that the overhead condensate flowed directly back into the still pot with no holdup in the receiver which permitted the use of either one or two liquid phase systems. The return leg was long enough so that the density difference between the pot liquid and the condensate did not affect the operation of the still. The upper portion of the still was insulated and equipped with a jacket heater; however, this heater was not used for the same reasons given in the Binary Experimental Procedure section. An internal resistance heater similar to that used in the binary still was used to supply heat to the boiling mixture. It was found that if a magnetic stirrer was employed to agitate the pot mixture during a run, equilibrium was attained faster and superheating was kept to a minimum.

An equilibrium point was obtained by charging a desired pot mixture to the still, applying heat and allowing time for the system to reach equilibrium. It was observed that after about one hour the temperature of the pot mixture reached a constant value. At this point a liquid and a vapor sample were taken while the still remained in operation. The liquid sample was drawn off first. Since the pot mixture was rich in fluorocarbon, the least volatile component, the composition of the system would not be changed appreciably by taking

the bottom sample first. The samples were carefully sealed and placed in a refrigerator to prevent loss of the volatile components until the analysis could be run. The analysis was carried out according to the procedure discussed in the preceding section.

The boiling temperature of the ternary system was measured with a chromel-alumel thermocouple in a thermowell immersed in the boiling liquid. Although this procedure proved unsatisfactory when tried with the binary system, Tetlow (20) found that even greater deviations in temperature resulted when the ternary mixture was placed in the boiling point still. This was evidently due to the large difference between the bubble point of the pot mixture and the dew point of the resulting vapor.

All of the ternary data were taken at a constant pressure of 760 millimeters of mercury controlled with the same manostat used to control the pressure for the binary equilibrium runs. The pressure was read from an absolute manometer to a precision of 0.1 millimeter of mercury.

The ternary data were taken by holding the composition of the fluorocarbon constant and varying the relative compositions of the two hydrocarbons over the entire composition range. The main portion of the vapor-liquid equilibrium data taken for this thesis was obtained using a heptacosafuorotributylamine liquid composition of 71 - 74 mole per cent. Three test runs were also taken at a fluorocarbon liquid composition of 80 - 81.3 mole per cent. The temperature-composition data appear in Table 6 and the x-y diagram on a solvent free basis appears in Figure 4.

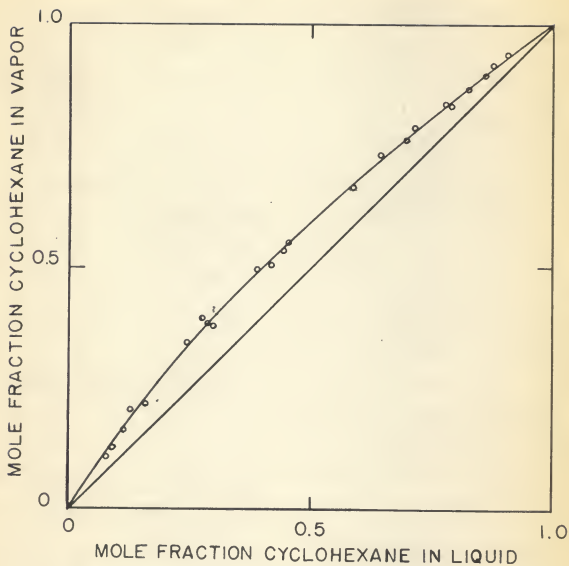


Figure 4. Binary x-y data for the hydrocarbon portion of the system: cyclohexane-2,3-dimethylpentane-heptacosafuorotributylamine at a constant heptacosafuorotributylamine composition of 0.71-0.74 mole fraction and at a constant pressure of 760 mm. of mercury. (Coordinates on heptacosafuorotributylamine free basis)

The physical properties and purities of the compounds used in this section appear in Appendix II of this thesis.

Experimental Ternary Activity Coefficients

The activity coefficients for the hydrocarbons in the ternary system were calculated using Equation (27). These data are shown in Table 7 and Figure 5. The test runs at 80 mole per cent fluorocarbon were not significantly different from the other ternary runs and, therefore, were not plotted on the graphs. Tetlow (20) attempted to test similar data for thermodynamic consistency, but the results were inconclusive because several of the assumptions required by the method could not be met by the experimental data. Since the temperature measurements were very hard to obtain with a high degree of accuracy for this system and since the composition of the fluorocarbon was not constant for all runs, it was thought that a test for thermodynamic consistency would not be particularly advantageous. Failure of experimental data to withstand a test for thermodynamic consistency does not necessarily mean the data is invalid since all of the assumptions made for the particular method must be met by the conditions under which the data were obtained.

Predicted Ternary Activity Coefficients

As previously mentioned, the solubility parameters were calculated for each component from the physical properties and a K value was determined from the binary solubility data. By combining these data and using Equations (19) and (20), the correction factors

f_{12} and f_{23} were evaluated from:

$$(\delta_1 - \delta_3)^2 + 2 \delta_1 \delta_3 (1-f_{13}) = K_{13} \quad (31)$$

$$(\delta_2 - \delta_3)^2 + 2 \delta_2 \delta_3 (1-f_{23}) = K_{23} \quad (32)$$

The following methods were used to predict the activity coefficients of the hydrocarbon portion of the ternary system:

1. The activity coefficients were calculated from Hildebrand's ternary equations (8), page 200, using the solubility parameters evaluated from the physical properties of each compound:

$$\ln \gamma_1' = \frac{V_1}{RT} [(\delta_1 - \delta_2) \phi_2 + (\delta_1 - \delta_3) \phi_3]^2 \quad (33)$$

$$\ln \gamma_2' = \frac{V_2}{RT} [(\delta_2 - \delta_1) \phi_1 + (\delta_2 - \delta_3) \phi_3]^2 \quad (34)$$

2. The activity coefficients were predicted using the same above equations except that the values of K , as determined from Equation (30), were substituted in place of $(\delta_1 - \delta_3)^2$.
3. Equations (24) and (25) were used with the values of f and the solubility parameters, as evaluated from the physical properties, to predict the activity coefficients for the hydrocarbon portion of the ternary system.

Since the f factors were determined from the solubility data, they were not theoretical, as proposed by Reed (14), but were semi-empirical. The results obtained from the K values were strictly empirical which leaves only the results calculated from the physical properties to be purely theoretical. From Figure 5 it can be seen

that the empirical approach using K values gave good results while the semi-empirical approach using the f factors appeared to give even better results. The theoretical method, using only the physical properties of the compounds, predicted activity coefficients considerably lower than the values observed experimentally. The f values were determined at 25°C. which was considerably below the atmospheric boiling temperature of the ternary system. However, according to Kyle (11), f values determined at low temperature are more valid.

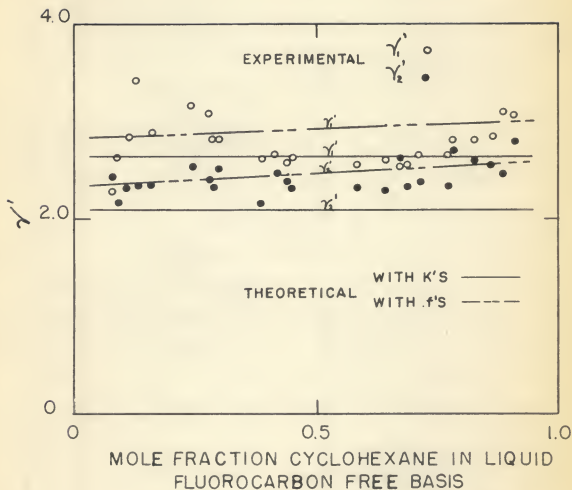


Figure 5. Cyclohexane and 2,3-dimethylpentane activity coefficients for the system: cyclohexane-2,3-dimethylpentane-heptacosfluorotributylamine at a constant heptacosfluorotributylamine composition of 0.71-0.74 mole fraction.

CONCLUSIONS

The magnitude of the activity coefficients calculated from the experimental data for the system cyclohexane-2,3-dimethylpentane indicated that the solution was very nearly ideal. This was substantiated by the application of Equations (7) and (8), using both K values and physical properties, which predicted activity coefficients and x-y data in agreement with experimental values.

Some enhancement of the relative volatility of cyclohexane to 2,3-dimethylpentane due to the addition of the solvent was observed experimentally. This was illustrated by comparing the x-y data for the original binary hydrocarbon system with the x-y data for the same system after the addition of the solvent. The average relative volatility of the binary hydrocarbon system after the addition of the solvent was found to be about 1.50 as compared with an average value of 1.35 for the original system with no solvent. This increase was satisfactorily predicted by Equation (11) which gave a value of 1.64 for the hydrocarbon system (cyclohexane to 2,3-dimethylpentane) after the addition of the solvent. Equations (24) and (25) predicted the solution behavior of the ternary system very well as did Equations (33) and (34) using the empirically determined K values.

While this work substantiates some phases of the modified theory of solution behavior, more work should be done, particularly with non-ideal systems. This additional work should be done in order to evaluate the role of fluorocarbons as solvents for extractive distillation more satisfactorily and to substantiate which branch of the theory should be used in connection with studies on extractive distillation.

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A P P E N D I X I

CALIBRATIONS

Thermocouple Calibrations

A chromel-alumel thermocouple was used in the binary and ternary equilibrium stills and the boiling point apparatus. The thermocouple was calibrated by measuring the boiling point in millivolts of three compounds known to be pure: n-hexane, n-heptane and cumene. These data appear in Table 2. These three points enabled the use of a three constant equation such as:

$$A + Bt + Ct^2 = \text{millivolts}$$

where

$$A = -0.07175, B = +0.0433454 \text{ and } C = -1.2267 \times 10^{-5}.$$

The calibration of the thermocouple used for the determination of the solubility data was described by Tetlow (20).

Calibration of the Chromatograph

The construction of the chromatography column used in this work has been described in the section, Ternary Analysis.

The column was calibrated for the ternary system by injecting a known sample into the chromatograph and measuring the areas under each peak drawn for the component by the recording potentiometer. These areas were measured with a Keuffel and Esser Planimeter. Two calibration curves were constructed from this data: a plot of area fraction fluorocarbon versus mole fraction fluorocarbon on a cyclohexane free basis (Figure 8, calibration curve "B") and a plot of

area fraction 2,3-dimethylpentane versus mole fraction 2,3-dimethylpentane on a fluorocarbon free basis (Figure 6, calibration curve "A"). The composition of an unknown sample was then determined by the following equations:

$$x_3 = \frac{x_3^+ x_2^+}{x_3^+ x_2^+ - x_3^+ + 1} \quad (35)$$

$$x_2 = \frac{x_3(1 - x_3^+)}{x_3^+} \quad (36)$$

$$x_1 = 1 - x_3 - x_2 \quad (37)$$

where the subscripts 3, 2, and 1 refer to ternary mole fractions of fluorocarbon 2,3-dimethylpentane and cyclohexane respectively and

$$x_3^+ = \frac{x_3}{x_3 + x_2}, \quad x_2^+ = \frac{x_2}{x_2 + x_1}.$$

The values for x_3^+ and x_2^+ were obtained by using the peak area fraction as determined from the potentiometer chart and the calibration curves.

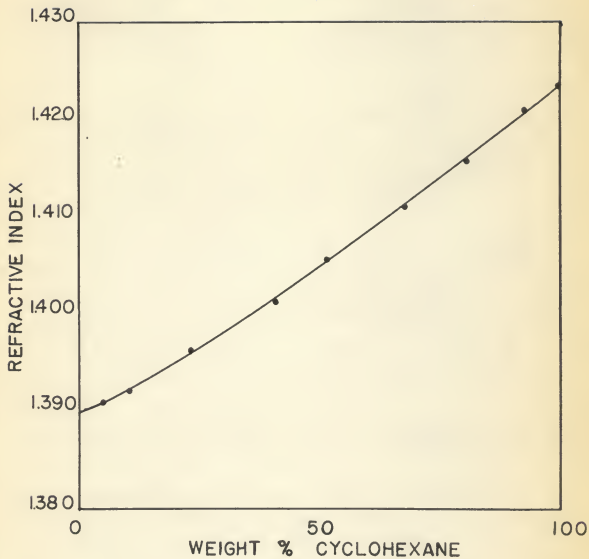


Figure 6. Refractive index at 25°C. for the system: cyclohexane-2,3-dimethylpentane.

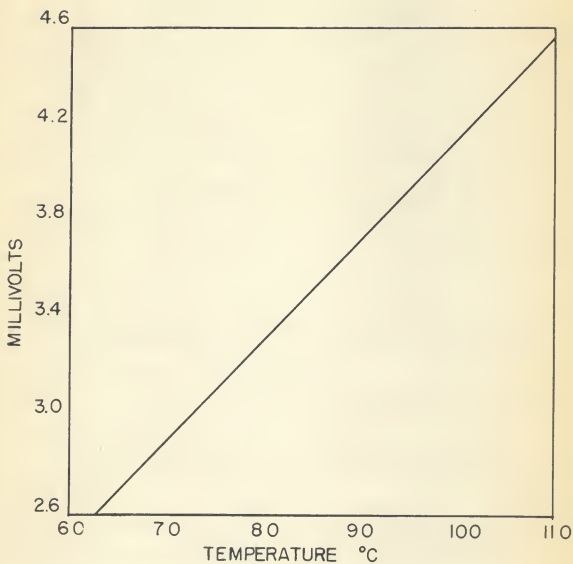


Figure 7. Calibration curve for the chromel-alumel thermocouple used in determining vapor-liquid equilibrium data.

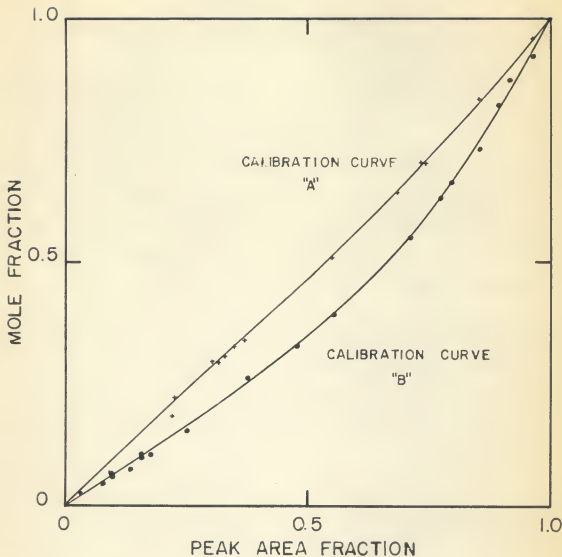


Figure 8. Conversion of chromatograph peak area fractions to mole fraction. Calibration curve A applies to the system: cyclohexane-2,3-dimethylpentane and calibration curve B applies to the system: heptacosafuorotributylamine-2,3-dimethylpentane. Conditions: column temperature - 200°F, helium flow rate - 50 cc/min. Stationary phase - 1-naphthylamine. (Coordinates refer to 2,3-dimethylpentane and heptacosafuorotributylamine)

A P P E N D I X I I

PHYSICAL PROPERTIES OF CHEMICALS

The cyclohexane used in the experimental work was Phillips Petroleum Company "pure" grade reported to be 99 mole % pure. The 2,3-dimethylpentane was also a product of Phillips, but the "technical" grade, which was reported to be 95 mole % pure. A chromatogram of the cyclohexane with a column of 1-naphthylamine on celite showed a single peak; therefore, it was not purified further. A chromatogram of the 2,3-dimethylpentane showed a small peak preceding the main peak indicating a small amount of impurity; however, this impurity was estimated to be less than one mole per cent and the compound was not purified.

The heptacosafuorotributylamine was obtained from the Minnesota Mining and Manufacturing Company under the name of FC-43. The 3M Company reports the composition to be $(C_4F_9)_3N$ (9); however, it was believed that the commercial product contains several isomers due to the boiling range exhibited upon distillation. The middle fractions having a maximum boiling point difference of $3.07^\circ C$ were used in this work. A chromatogram of the purified compound showed only one peak.

Table 3 shows the densities, refractive indices and boiling points of the various compounds. Since the boiling points compared favorably to those found in the literature, the vapor pressure data were not determined experimentally.

A P P E N D I X I I I

TABLES

Table 1. Refractive indices of cyclohexane-2,3-dimethylpentane mixtures at 25°C.

Weight fraction cyclohexane	:	Refractive index
	:	
0.0000		1.3897
0.0567		1.3910
0.1070		1.3925
0.1365		1.3935
0.1809		1.3949
0.2338		1.3962
0.2610		1.3972
0.3088		1.3989
0.3608		1.4002
0.4079		1.4017
0.4503		1.4031
0.5115		1.4055
0.5371		1.4062
0.5945		1.4083
0.6755		1.4110
0.7035		1.4121
0.7511		1.4138
0.7923		1.4155
0.8013		1.4157
0.8632		1.4182
0.9280		1.4210
0.9565		1.4220
1.0000		1.4237

Table 2. Calibration points for chromel-alumel thermocouple.

Compound	Pressure	Boiling point	
		experimental	literature
	mm of mercury	(millivolts)	°C.
n-Hexane	731.3	2.799	67.5197*
n-Heptane	733.3	4.028	97.2620*
Cumene	736.0	6.200	151.5196*

* Values reported by API Tables (see reference 16).

Table 3. Physical properties of chemicals.

Property	Cyclohexane		2,3-dimethylpentane		Heptacosafuoro- tributylamine	
	exper.	lit.	exper.	lit.	exper.	lit.
Density at 25°C.		0.7738 ¹	0.69184 ³	0.69091 ¹	1.92409 ³	1.872 ²
Refractive index at 25°C.	1.4235	1.42354 ¹	1.3897	1.39196 ¹		1.2910 ²
Boiling point at 1 atm.	80.56	80.738 ¹	89.85	89.784 ¹	176.83- 180.9	170-180 ²

1. Values reported by API Tables (reference 16).
2. Values reported by Minnesota Mining and Manufacturing Company for FC-43 (reference 9).
3. Values reported by Tetlow (reference 20).

Table 4. Solubility data for the system:
Heptacosafuorotributylamine-cyclohexane.

Unmixing temperature °C.	Mole fraction cyclohexane
14.920	0.15481
27.671	0.21620
63.226	0.37060
73.041	0.45000
83 +	0.67
83 +	0.74
83 +	0.94
71.635	0.99420
29.152	0.99710

Table 5. Vapor-liquid equilibrium data for the system:
cyclohexane-2,3-dimethylpentane at a total pressure
of 760 mm of mercury.

Temperature °C.	:	Mole fraction cyclohexane liquid	:	vapor
88.95		0.069		0.094
87.60		0.152		0.220
86.30		0.288		0.362
85.25		0.399		0.486
84.87		0.458		0.532
84.15		0.520		0.602
83.75		0.558		0.640
83.20		0.608		0.682
82.90		0.653		0.716
82.25		0.707		0.761
82.15		0.758		0.798
82.10		0.761		0.810
81.65		0.805		0.840
81.50		0.854		0.882
81.22		0.877		0.903
81.20		0.875		0.903
81.00		0.901		0.923
80.95		0.918		0.936
80.85		0.925		0.945
80.75		0.947		0.958

Table 6. Vapor-liquid equilibrium data for the system:
 cyclohexane-2,3-dimethylpentane-heptacosafuorotributylamine
 at a constant total pressure of 760 mm of mercury and at a
 constant heptacosafuorotributylamine composition of 72 mole %.

Temperature °C.	Mole fraction (C ₄ F ₉) ₃ H		Mole fraction cyclohexane	
	liquid	vapor	liquid	vapor
104.40	0.728	0.026		
103.80	0.712	0.026	0.022	0.089
103.11	0.726	0.025	0.025	0.127
103.00	0.732	0.026	0.029	0.160
	0.732	0.040	0.040	0.215
100.72	0.748	0.026	0.065	0.327
100.10	0.736	0.025	0.070	0.381
	0.721	0.036	0.075	0.373
99.41	0.719	0.027	0.082	0.364
98.40	0.734	0.027	0.109	0.480
97.65	0.722	0.026	0.110	0.487
96.75	0.722	0.029	0.125	0.522
94.60	0.719	0.050	0.125	0.533
93.17	0.704	0.025	0.164	0.632
92.63	0.713	0.028	0.191	0.714
	0.715	0.027	0.195	0.706
	0.720	0.025	0.197	0.743
91.50	0.732	0.029	0.201	0.768
90.91	0.706	0.026	0.211	0.806
90.22	0.722	0.027	0.228	0.813
86.95	0.703	0.025	0.229	0.847
86.35	0.713	0.022	0.256	0.870
85.55	0.716	0.024	0.252	0.898
105.90*	0.804	0.028	0.258	0.911
105.70*	0.813	0.033	0.057	0.389
98.69*	0.807	0.022	0.080	0.494
			0.151	0.825

* Data taken at a constant fluorocarbon composition of 80 mole %.

Table 7. Experimental activity coefficients for the system:
cyclohexane-2,3-dimethylpentane-heptacosafuorotributylamine.

Temperature °C.	Mole fraction of cyclohexane in hydrocarbon portion of liquid	Activity Coefficients	
		1	2
104.40	0.075	2.277	2.419
103.80	0.087	2.628	2.165
103.11	0.107	2.833	2.302
	0.125	3.407	2.387
103.00	0.151	2.858	2.327
	0.240	3.155	2.522
100.72	0.278	3.083	2.400
101.10	0.285	2.796	2.333
	0.295	2.798	2.518
99.41	0.387	2.629	2.176
98.40	0.415	2.679	2.476
97.65	0.440	2.586	2.360
96.75	0.450	2.664	2.334
94.60	0.583	2.574	2.369
93.17	0.645	2.606	2.261
	0.678	2.527	2.613
94.30	0.690	2.522	2.307
93.10	0.715	2.670	2.361
90.91	0.775	2.662	2.346
91.50	0.785	2.812	2.737
90.22	0.825	2.809	2.596
86.95	0.862	2.841	2.548
86.35	0.875	3.120	2.479
85.55	0.906	3.089	2.795
105.90*	0.307	2.686	2.313
105.70*	0.430	3.350	2.735
98.69*	0.780	3.704	3.476

* Refers to runs made at a constant fluorocarbon composition of 0.80 mole fraction.

PHASE EQUILIBRIUM IN THE SYSTEM: CYCLOHEXANE-2,3-DIMETHYLPENTANE-
HEPTACOSAFLUOROTRIBUTYLAMINE

by

THOMAS HENRY COUR

B. S., Kansas State University, 1959

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

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OF AGRICULTURE AND APPLIED SCIENCE

1960

Vapor-liquid equilibrium data were obtained for the binary system: cyclohexane-2,3-dimethylpentane and the ternary system: cyclohexane-2,3-dimethylpentane-heptacosafuorotributylamine. In addition liquid-liquid solubility data were obtained for the system: cyclohexane-heptacosafuorotributylamine. The purpose in determining the vapor-liquid equilibrium data for the ternary system was to evaluate the effectiveness of heptacosafuorotributylamine as a solvent for extractive distillation. The binary solubility data were taken as an aid in evaluating the behavior of the ternary system.

Some enhancement was observed in the relative volatility of the original binary hydrocarbon system when the fluorocarbon was added as a solvent. The average relative volatility of the original binary solution was about 1.35 while that for the same system after the addition of the solvent was found to be 1.50. A modification of the Scatchard-Hildebrand equations for the behavior of "regular" solutions was used to predict a relative volatility of the hydrocarbon system in the presence of the fluorocarbon solvent of 1.64. The empirical and semi-empirical modifications of the Scatchard-Hildebrand theory were found to predict the solution behavior of the ternary system very well in terms of activity coefficients. However, the pure theory using only the physical properties of compounds used did not give good agreement with the experimentally observed data.