

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

By

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B. S., Kansas State University, 1957

A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
OF AGRICULTURE AND APPLIED SCIENCE

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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
d°	Distance between centers of nearest-neighbor molecules
f	Correction factor
h	Linear scale reading
I	Ionization potential
K	Constant
ln	Logarithm base e
log	Logarithm base 10
P°	Vapor pressure of pure component mm. of Mercury
Q	Thermodynamic function
R	Gas constant
T	Absolute temperature, $^{\circ}\text{K}$.
t	Temperature, $^{\circ}\text{C}$.
v	Potential, mv.
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

ΔF	Change in Gibbs 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, $(\frac{\text{calories}}{\text{cc}})^{\frac{1}{2}}$
Π	Total pressure, mm of mercury
ϕ	Volume fraction

Subscripts

1	More volatile component, benzene
2	Less volatile component, 2,3-dimethylpentane
3	Solvent, Heptacosfluorotributylamine
d	Refers to d°
I	Refers to ionization potential
i	i^{th} component
P	Refers to constant pressure process
V	Refers to constant volume process

Superscripts

M	Refers to mixing process
V	Refers to vaporisation process

THEORETICAL BACKGROUND

Extractive Distillation

It is frequently desired to separate mixtures for which normal distillation methods are not practical. This situation may arise due to the formation of azeotropes or to a very low relative volatility over a wide concentration range. The technique of extractive distillation often overcomes these difficulties (24). Extractive distillation is defined as distillation in the presence of a solvent that is relatively nonvolatile compared to the other components in the mixture. This technique is particularly effective when applied to a mixture of components having a small difference in boiling points, but exhibiting a relatively large deviation from Raoult's law.

Most previous studies of solution behavior in extractive distillation systems have been limited to the determination of the relative volatilities of the components to be separated at various solvent concentrations (6)(7)(8) (9). These studies usually have to be carried out for several different ternary systems before a suitable solvent can be selected. It would be desirable to be able to predict the solution behavior in ternary systems from the properties of the pure components. If this were possible the selection of extractive distillation solvents could be based upon the physical properties, eliminating the need for a large part of the equilibrium data now necessary. Several authors have utilized empirical relationships to correlate ternary extractive distillation data (28)(2). These empirical methods may accurately predict the solution behavior for individual systems, but a theoretical analysis is necessary for the true understanding of solution behavior in ternary systems.

The benzene-2,3-dimethylpentane system represents a typical mixture of aromatic and paraffinic hydrocarbons where the aromatic is the more volatile component. The difference in boiling points of these hydrocarbons is approx-

imately ten centigrade degrees. This thesis presents the results of an investigation of the solution behavior of the system benzene-2,3-dimethylpentane-heptacosfluorotributylamine, where the perfluoroamine was added as an extractive distillation solvent. It should be recognized that heptacosfluorotributylamine is a "nonpolar" compound whereas all previous investigations of extractive distillation systems have utilized "polar" compounds as solvents.

The distinction between "polar" and "nonpolar" compounds is somewhat vague, but the term "polar" is generally applied to compounds having strong intermolecular forces such as phenol or ethylene glycol. Fluorocarbons and chlorofluorocarbons are classified as "nonpolar" compounds since their intermolecular forces are very weak. Fluorocarbons and chlorofluorocarbons have just been developed over the past ten years, and although several investigators (25) have studied their solution behavior, they have not been previously applied as extractive distillation solvents.

Analysis of Solution Behavior

Perhaps the most widely used theory of nonelectrolytic solution behavior is one developed independently by Scatchard and by Hildebrand (10) in 1932. This theory, known as the "regular" solution theory, has achieved considerable success in predicting the properties of hydrocarbon systems.

By making four simple assumptions Scatchard and Hildebrand were able to write the following expression for the energy of mixing in a binary system:

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

The expression $\left(\frac{\Delta E^v}{v} \right)^{\frac{1}{2}}$ occurs so frequently in "regular" solution calculations that it has been termed the "solubility parameter", δ . The four assumptions made in arriving at the above expression were:

- 1) The energy of a system can be expressed as the summation of the interaction energies of all possible molecular pairs. The molecular interaction energy was assumed to depend only on the distance between molecules.
- 2) The molecules are distributed randomly with respect to position and orientation.
- 3) There is no volume change on mixing at constant pressure.
- 4) The interaction energy between 1-2 pairs of molecules is the geometric mean of 1-1 and 2-2 pairs.

It is further assumed that the entropy of mixing is ideal the free energy of mixing and the activity coefficients may be written as follows:

$$\Delta F^M = RT(x_1 \ln x_1 + x_2 \ln x_2) + (x_1 v_1 + x_2 v_2)(d_1 - d_2)^2 \phi_1 \phi_2 \quad (\text{Eq. 2})$$

$$RT \ln \gamma_1 = v_1 (d_1 - d_2)^2 \phi_2^2$$

$$RT \ln \gamma_2 = v_2 (d_1 - d_2)^2 \phi_1^2 \quad (\text{Eq. 3})$$

"Solubility parameters" can be used qualitatively as a measure of the "polarity" of a compound since large "solubility parameters" are associated with "polar" compounds.

The ratio of activity coefficients of two components in the presence of a solvent has been derived (17):

$$RT \ln \gamma_1 / \gamma_2 = v_1 (d_1 - d_3)^2 \phi_3^2 - v_2 (d_2 - d_3)^2 \phi_3^2 \quad (\text{Eq. 4})$$

where subscript 3 refers to the solvent and subscript 1 refers to the more volatile component. In deriving the above expression two independent binary systems (only 1-3 and 2-3 interactions) were assumed. This is equivalent to assuming no interaction effects between components 1 and 2.

The relative volatility, α , is defined as

$$\alpha = \frac{P_1^s Y_1}{P_2^s Y_2} \quad (\text{Eq. 5})$$

It can be seen from its definition that the maximum value of the relative volatility occurs when the ratio v_1/v_2 is at its maximum. The ratio P_1^s/P_2^s is constant at constant temperature and in nearly all cases changes only slightly with temperature change.

Equation 4 indicates that the maximum enhancement in the relative volatility due to the addition of an extractive distillation solvent occurs when the volume fraction of the solvent approaches unity, since v_1/v_2 reaches its maximum at this point. This effect has been observed experimentally by Fenske, et. al. (7). Equation 4 also indicates that a "polar" solvent would increase the relative volatility in binary systems in which the less volatile component is more "polar", since the ratio v_1/v_2 would be increased by the large "solubility parameter" of the "polar" solvent. Experimental evidence substantiates this reasoning (7)(9). Conversely, a "nonpolar" solvent should increase the relative volatility in binary systems in which the more volatile component is more "polar".

The "solubility parameters" for benzene and 2,3-dimethylpentane at 80 C. are 8.30 and 6.63 respectively. Therefore, on the basis of equation 4 a "nonpolar" solvent should increase the relative volatility of the benzene-2,3-dimethylpentane system because benzene is more volatile than 2,3-dimethylpentane and the "solubility parameters" indicate that benzene is more "polar".

Since 1950 a considerable amount of work has been done on fluorocarbon-hydrocarbon systems. Scott (25) has published a comprehensive summary of the results of these investigations. The results of almost all these investigations show that fluorocarbon-hydrocarbon systems exhibit far greater positive

deviations from Raoult's law than predicted by the "regular" solution theory. These deviations are so great in most of the systems studied that incomplete miscibility at room temperature is exhibited.

In attempting to account for the anomalous behavior of fluorocarbon-hydrocarbon systems, Simons and Dunlap (26) rederived equation 1 omitting the assumption of no volume change on mixing. Reed (23) later found that in fluorocarbon-hydrocarbon systems the interaction energy between unlike pairs of molecules is not equal to the geometric mean of like pairs. He rederived equation 1 omitting the assumption of the geometric mean and the assumption of no volume change. Using this derivation he was able to calculate reliable values of the heats of mixing for the systems reported by Simons and Dunlap (26) and Simons and Mausteller (27).

Hildebrand (11) has shown that ΔF^M at constant pressure is virtually equal to ΔA^M at constant volume. Therefore, the assumption of constant volume mixing introduces a negligible error in the calculation of activity coefficients. If, however, it is desired to know ΔE^M or ΔS^M the assumption of no volume change can introduce errors of considerable magnitude.

Reed (23) rewrote equation 3 introducing a correction factor, f :

$$RT \ln \gamma_1 = V_1 \left[(\delta_1 - \delta_3)^2 + 2\delta_1\delta_3(1 - f_{13}) \right] \left| \frac{\phi_1^2}{\phi_3} \right| \quad (\text{Eq. 6})$$

$$RT \ln \gamma_2 = V_2 \left[(\delta_2 - \delta_3)^2 + 2\delta_2\delta_3(1 - f_{23}) \right] \left| \frac{\phi_2^2}{\phi_3} \right|$$

This factor takes into consideration the ratio of the ionization potentials of hydrocarbons and fluorocarbons and the ratio of d° values for hydrocarbons and fluorocarbons, d° being the distance from the center of a molecule to the first maximum in the density distribution of other molecule centers located around the first molecule. Kyle (18) has extended the application of the correction factor, f , to ternary systems:

$$\text{RTln } \gamma_1 = v_1 \left\{ (\omega_1 - \omega_2)^2 \phi_2^2 + \left[(\omega_1 - \omega_3)^2 + 2(1 - f_{13})\omega_1\omega_3 \right] \phi_3^2 \right. \\ \left. + 2 \left[\omega_1(\omega_1 - \omega_2) + \omega_3(f_{23}\omega_2 - f_{13}\omega_1) \right] \phi_2\phi_3 \right\}$$

$$\text{RTln } \gamma_2 = v_2 \left\{ (\omega_1 - \omega_2)^2 \phi_1^2 + \left[(\omega_2 - \omega_3)^2 + 2(1 - f_{23})\omega_2\omega_3 \right] \phi_3^2 \right. \\ \left. + 2 \left[\omega_2(\omega_2 - \omega_1) + \omega_3(f_{13}\omega_1 - f_{23}\omega_2) \right] \phi_1\phi_3 \right\} \quad (\text{Eq. 7})$$

In the derivation of equation 7 it was assumed that $f_{12} = 1$. If it is further assumed that $f_{13} = f_{23} = f$, equation 7 may be combined to give equation 8:

$$\text{RTln } \frac{\gamma}{\bar{v}} = v_1(\omega_1 - \omega_2)^2 \phi_2^2 + v_1(\omega_1 - \omega_3)^2 \phi_3^2 + 2v_1(1 - f)\omega_1\omega_3 \phi_3^2 \\ + 2v_1(\omega_1 - \omega_2)(\omega_1 - f\omega_3) \phi_2\phi_3 - v_2(\omega_1 - \omega_2)^2 \phi_1^2 - v_2(\omega_2 - \omega_3)^2 \phi_3^2 \\ - 2v_2(1 - f)\omega_2\omega_3 \phi_3^2 - 2v_2(\omega_2 - \omega_1)(\omega_2 - f\omega_3) \phi_1\phi_3 \quad (\text{Eq. 8})$$

In addition to the inclusion of the correction factor, f , equation 8 does not rely upon the assumption of no 1-2 interaction as does equation 4. The applicability of equations 7 and 8 to the benzene-2,3-dimethylpentane-heptacosfluorotributylamine extractive distillation system is discussed under the heading "DISCUSSION OF TERNARY DATA".

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

Experimental Data

The hydrocarbons used in this work were obtained commercially in a reasonable degree of purity, as shown by chromatographic analysis, so they were not further purified. For a listing of the physical properties of these hydrocarbons see Appendix I.

The binary equilibrium data were determined in a modified Othmer equilibrium still (20). The upper part of the Othmer still was wound with heating wire and insulated with asbestos so that the walls could be maintained at the boiling point of the pot liquid. The operation of the still was checked with the heptane-toluene system, and the data* were found to agree satisfactorily with that reported by Hipkin and Myers (13).

The still was charged with the desired mixture and put into operation. After the still had operated a sufficient length of time (several hours) for equilibrium to be definitely established, the pot heater was turned off and samples of the liquid and vapor were obtained after the pot mix ceased to boil. These liquid and vapor samples were subsequently analyzed for composition by the method of refractive index. An Abbe type refractometer was utilized to determine the refractive indices to a precision of 0.0001. A change of this magnitude in value of the refractive index represented a change in composition of approximately 0.05 mole percent. A curve relating composition to refractive index was constructed by measuring the refractive indices of some mixtures of known composition. The mixtures of known composition were prepared by weighing on an analytical balance. These data are shown in Table 1 and are plotted in Figure 1.

*See Appendix III

Table 1. Refractive indices of benzene-2,3-dimethylpentane mixtures at 20 C.

Mole fraction benzene	Refractive index	Mole fraction benzene	Refractive index
0.0000	1.3919	0.5882	1.4393
0.0448	1.3946	0.6586	1.4475
0.0897	1.3972	0.7075	1.4539
0.1488	1.4010	0.7178	1.4564
0.1825	1.4035	0.7523	1.4602
0.2522	1.4085	0.7971	1.4669
0.3363	1.4150	0.8306	1.4718
0.3511	1.4164	0.8669	1.4779
0.3977	1.4203	0.9054	1.4833
0.4679	1.4270	0.9330	1.4882
0.5497	1.4350	1.0000	1.5009

The boiling temperature of each run was found by withdrawing a liquid sample at equilibrium and boiling it in a dynamic boiling apparatus similar to one described by Quiggie, et al. (21). The boiling temperatures were measured in the dynamic boiling apparatus with a calibrated thermocouple.

The usual method of determining the equilibrium temperature consists of reading a thermometer or thermocouple placed directly in the vapor tube of the Othmer still. This method has the advantage of convenience, however, it was found that the temperatures read by this method were directly proportional to the rate of boiling in the still pot. This effect has previously been recorded by Canjar and coworkers (4)(5). Since the boiling range of the benzene-2,3-dimethylpentane system is somewhat narrow, this variation could cause serious variances in the boiling point data, therefore the equilibrium temperatures were obtained by the method described above.

The total pressure over the system was 760 mm. of mercury for all the runs. The pressure was controlled by a manostat and was read to 0.1 mm. with an absolute manometer.

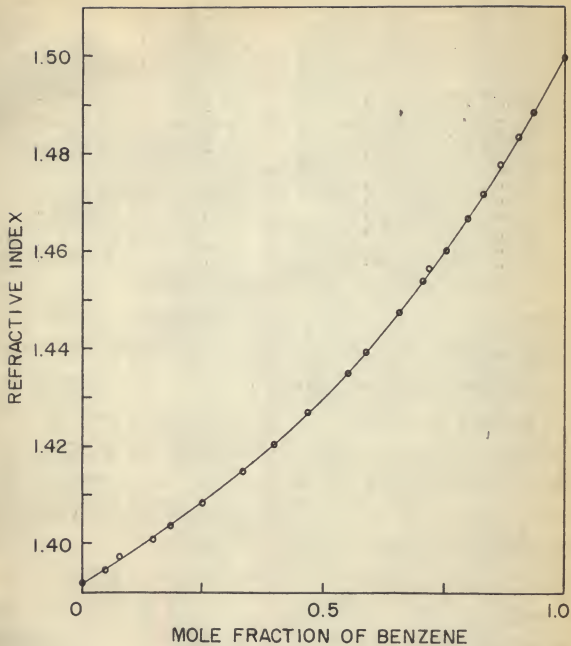


Figure 1. Refractive index at 20 C. for system: benzene-2,3-dimethylpentane.

A minimum boiling azeotrope was found at a composition of 82.5 mole per cent benzene and a temperature of 79.44 C. A composition of 83.0 mole per cent benzene and a temperature of 79.2 C. had been previously reported (14).

The equilibrium data are listed in Table 2, and the boiling point and x-y diagrams appear on Figures 2 and 3.

Table 2. Vapor-liquid equilibrium in the benzene-2,3-dimethylpentane system at 760 mm. of mercury total pressure.

Temperature C.	Mole fraction benzene	
	liquid	vapor
	0.980	0.972
79.80	0.972*	
	0.944	0.933
79.70	0.943*	
79.59	0.930*	
	0.913	0.900
	0.908	0.897
79.55	0.905*	
	0.882	0.873
79.51	0.862*	
79.48	0.845	0.842
79.47	0.842*	
79.44	0.825	0.825
79.53	0.776	0.788
79.66	0.754	0.770
79.72	0.714	0.744
79.90	0.675	0.716
80.29	0.614	0.675
80.48	0.585	0.655
80.91	0.535	0.620
81.35	0.486	0.585
81.88	0.445	0.548
82.79	0.373	0.493
84.65	0.247	0.360
85.80	0.181	0.285
87.10	0.125	0.218
87.25	0.115	0.191
88.30	0.072	0.132
89.10	0.036	0.068

* These runs made in the dynamic boiling apparatus only.

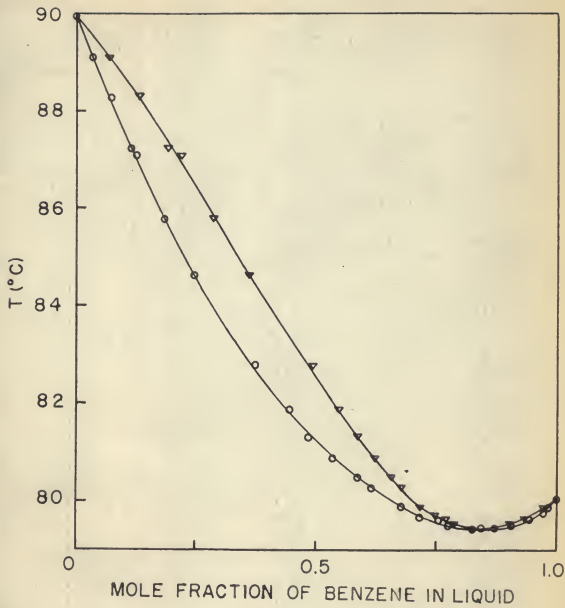


Figure 2. Boiling point-composition diagram at 760 mm. of mercury for system: benzene-2,3-dimethylpentane.

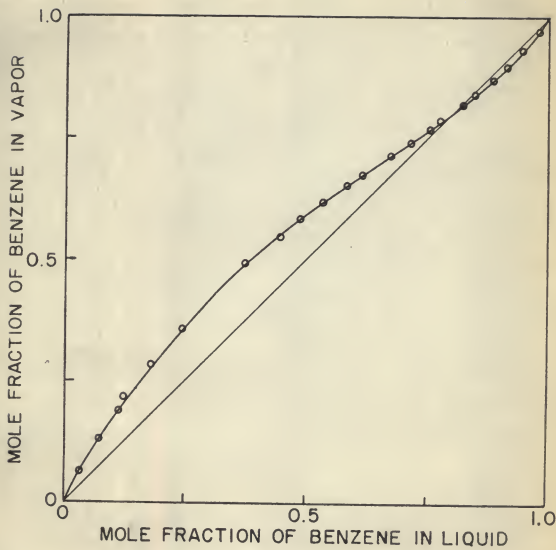


Figure 3. Binary x-y diagram for system: benzene-2,3-dimethylpentane.

Activity Coefficients

Activity coefficients were determined from the equilibrium data by the usual expressions:

$$\gamma_1 = \frac{y_1 P}{x_1 P_1} \quad (\text{Eq. 9})$$

In order to use equation 9 it was assumed that the vapors behaved as ideal gases. The activity coefficients are listed in Table 3 and plotted on Figure 4.

Table 3. Activity coefficients in the benzene-2,3-dimethylpentane system.

Mole fraction benzene in liquid	Benzene activity coefficients	2,3-Dimethylpentane activity coefficients
0.036	1.444	0.99*
0.072	1.433	0.98*
0.115	1.340	0.99*
0.181	1.326	0.98*
0.247	1.270	0.99*
0.373	1.215	1.000
0.445	1.166	1.033
0.486	1.158	1.042
0.535	1.131	1.069
0.585	1.106	1.101
0.614	1.093	1.122
0.675	1.068	1.179
0.714	1.055	1.216
0.754	1.036	1.271
0.776	1.033	1.291
0.825	1.020	1.368
0.845	1.015	1.393
0.882	1.008	1.471
0.908	1.005	1.526
0.913	1.003	1.567
0.944	1.002	1.626
0.980	1.000	1.885

* These values are obviously slightly low since the activity coefficients cannot be less than one. It should be noted, however, that errors in temperature measurement of 0.1 are more than sufficient to cause errors of this magnitude in the activity coefficients.

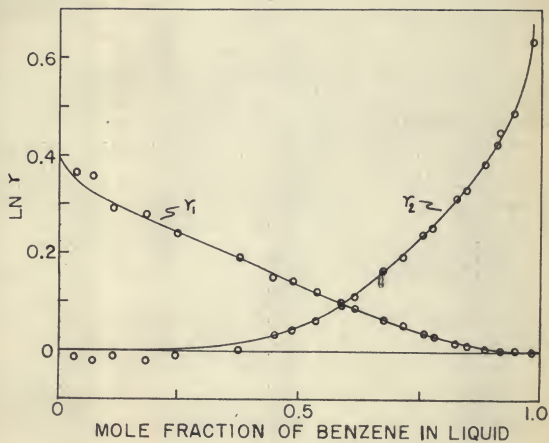


Figure 4. Activity coefficients for system: benzene-2,3-dimethylpentane.

Thermodynamic Consistency of Binary Data

The binary data were tested for thermodynamic consistency by the methods of Redlich, et. al. (22), and Black (3).

The Redlich, et. al. consistency test requires that

$$\int_0^1 \log \frac{r_1}{r_2} dx = 0$$

In other words, a plot of $\log r_1/r_2$ vs. x_1 should yield equal areas above and below the abscissa axis. This condition is strict only for constant temperature data, however when the boiling range of the system is relatively small the area test may also be applied to constant pressure data. Fulfillment of the area test denotes thermodynamic consistency of the x-y data.

The test devised by Black requires that a plot of $(\log r_1)^{\frac{1}{2}}$ vs. $(\log r_2)^{\frac{1}{2}}$ yield a good correlation. In other words, the data should plot as a smooth curve when plotted in this manner. This test checks the consistency of the temperature-pressure data.

Figure 5 and Figure 6 show the above conditions applied to the experimental activity coefficients. It can be seen from these plots that the data are thermodynamically consistent.

Activity Coefficients Predicted by "Regular" Solution Theory

Equations 3, page 4, were used to calculate activity coefficients for the binary mixtures. The calculated values are compared to the experimental values on Figure 7. The maximum deviation of the theoretical curve from the experimental curve is less than ten percent. This indicates that the benzene-2,3-dimethylpentane system behaves as the original "regular" solution theory predicts.

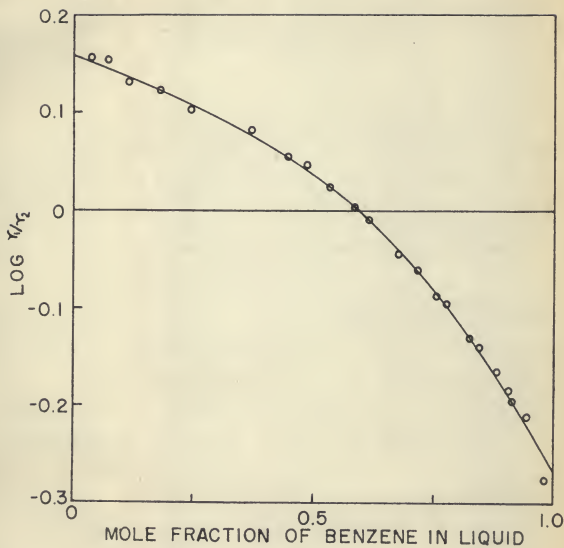


Figure 5. Thermodynamic consistency of x-y data for system: benzene-2,3-dimethylpentane.

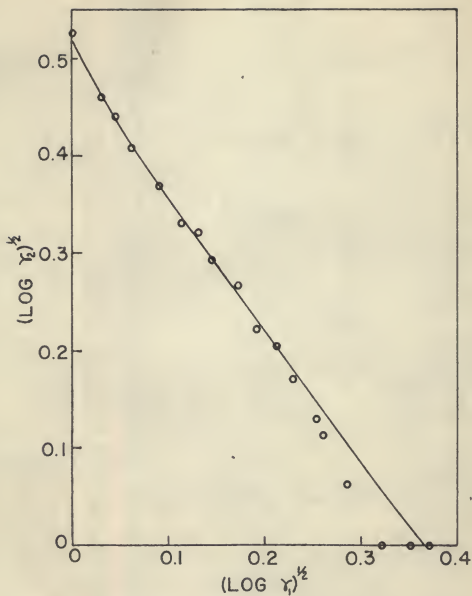


Figure 6. Consistency of P-T data for system: benzene-2,3-dimethylpentane.

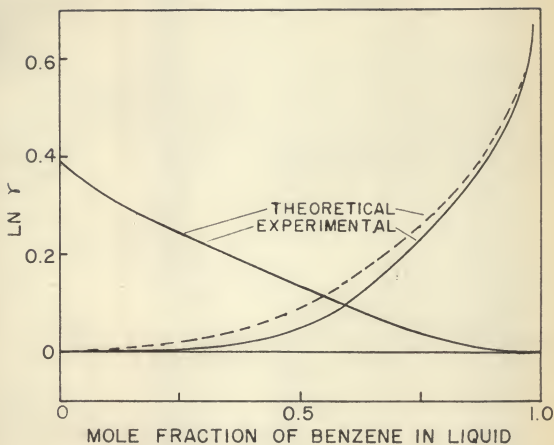


Figure 7. Comparison of theoretical and experimental activity coefficients for system: benzene-2,3-dimethylpentane.

TERNARY EQUILIBRIUM IN THE SYSTEM: BENZENE-2,3-DIMETHYLPENTANE-
HEPTAFLUORO-3-TERT-BUTYLAMINE

Solubility Relationships

Solubility data were determined for the binary hydrocarbon-fluorocarbon systems and in the ternary system to make it possible to analyze ternary mixtures and to assist in the calculation of theoretical activity coefficients in the ternary system. The data were determined at temperatures ranging from 0°C. to 80°C. The physical properties and degree of purity of the chemicals used are listed in Appendix I.

The experimental method was based upon the fact that the fluorocarbon, $(C_4F_9)_3N$, and the hydrocarbons are only partially miscible at room temperatures. The unmixing temperature of a known binary or ternary mixture was determined by raising the temperature of the mixture to such a point that only one phase existed. Then the solution was slowly cooled, and the temperature at which a second phase appeared was noted; the appearance of the second phase being marked by a distinct cloudiness in the mixture. Sometimes an opalescence, thought to be due to molecular clustering (12), was observed a few degrees above the unmixing temperature. This made the determination of the unmixing temperature somewhat dependent upon the judgment of the observer, but reproducible results were obtained after a very little practice.

The apparatus used to determine unmixing temperatures consisted of a heavy walled Pyrex tube bolted between two brass flanges. A teflon gasket was fitted in the upper flange to make the apparatus leak proof. An iron-constantan thermocouple passed through the upper flange into the tube. Figure 8 consists of a drawing of this apparatus.

Since air was trapped in the solubility cell, unmixing temperatures determined by the above procedure pertain to the mixtures saturated with air

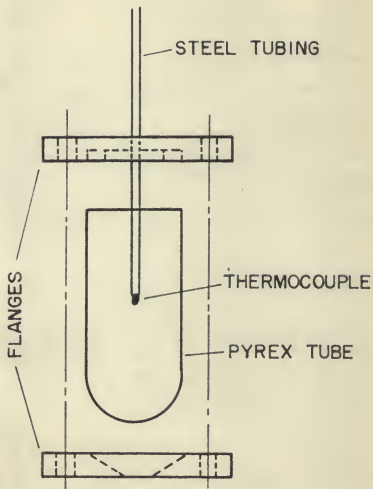


Figure 8. Solubility cell.

and at pressures in excess of the equilibrium vapor pressure. Kyle (16) showed that this fact had no discernible effect upon the accuracy of the values obtained for other fluorocarbon-hydrocarbon mixtures.

The solubility data are listed in Tables 4 and 5, and the solubility curves obtained from this data are shown in Figures 9 and 10.

Table 4. Binary solubility data in heptacosafuorotributylamine systems.

Mole fraction of benzene	Unmixing temperature °C.	Mole fraction of 2,3-dimethylpentane	Unmixing temperature °C.
0.015	0.0*	0.157	0.0*
0.252	57.9	0.250	25.4
0.370	81.2	0.314	35.9
0.998	60.8	0.488	53.7
0.999	41.7	0.643	60.2
		0.748	62.1
		0.942	50.1
		0.959	43.3
		0.984	20.4
		0.989	10.3

Table 5. Ternary solubility data in the benzene-2,3-dimethylpentane-heptacosafuorotributylamine system.

Mole fraction of (C ₄ F ₉) ₃ N	Mole fraction of benzene	Unmixing temperature °C.
0.892	0.057	0.0*
0.752	0.195	45.7
0.750	0.132	35.3
0.770	0.042	22.1
0.670	0.259	60.5
0.662	0.178	49.5
0.655	0.063	41.0
0.607	0.308	70.4
0.604	0.311	70.2
0.565	0.230	63.8
0.519	0.088	55.0
0.518	0.379	84.3
0.472	0.278	73.0
0.470	0.096	59.5

* The unmixing temperatures at 0°C. were not determined in the solubility cell, but were arrived at by adding hydrocarbon drop by drop to a weighed amount of fluorocarbon at 0°C. The volume of hydrocarbon added was measured to the nearest one hundredth of one cubic centimeter. The weight of hydrocarbon added was then calculated from density data.

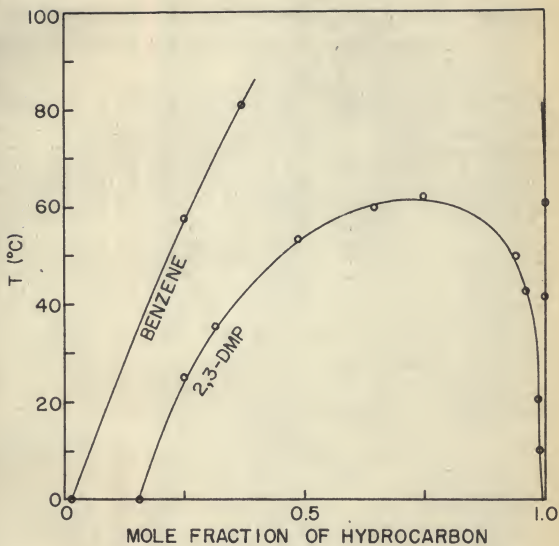


Figure 9. Binary solubilities in heptacosfluorotributylamine systems.

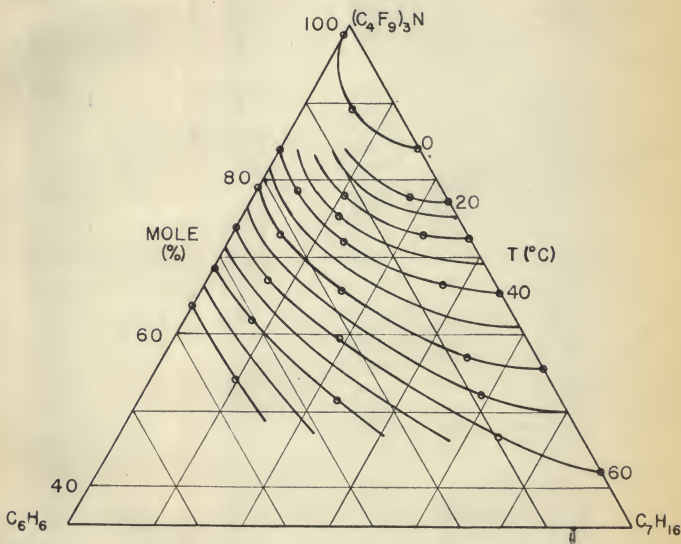


Figure 10. Solubility relationships for system: benzene-2,3-dimethylpentane-heptacosafuorotributylamine.

Method of Analysis

Before equilibrium data could be obtained for the ternary system it was necessary to develop a suitable analysis procedure.

Gas-liquid chromatography was the first method considered since it is convenient and applicable to most liquid mixtures. However, before this method can be applied a suitable partitioning liquid must be found. A total of 18 different partitioning columns were investigated with respect to the benzene-2,3-dimethylpentane-heptacosafuorotributylamine system, but none were found to be suitable.

A procedure utilizing semi-micro distillation was also investigated. First, the percent of fluorocarbon in the sample was to be determined from solubility relationships. Then the hydrocarbon portion of the sample was to be removed by semi-micro distillation and analyzed by refractive index. It was found that heptacosafuorotributylamine forms binary azeotropes with benzene and 2,3-dimethylpentane so the method could not be utilized.

The procedure adopted for the liquid and vapor samples follows:

- 1) The unmixing temperature of the liquid sample was determined.
- 2) The liquid and vapor samples were cooled to a temperature such that the fluorocarbon and the hydrocarbons were practically immiscible, and sufficient time was allowed for equilibrium to be established.
- 3) The relative volumes of the hydrocarbon and fluorocarbon phases comprising the vapor sample were measured to 0.02 c.c. in a graduated tube.
- 4) The binary hydrocarbon phases separated from the fluorocarbon phases in step 2 were drawn off the liquid and vapor samples. These hydrocarbon portions of the samples were analyzed for binary composition by gas-liquid chromatography.

- 5) The ternary liquid composition was determined from the solubility relationships plotted on Figure 10.
- 6) The percent fluorocarbon in the vapor was determined from the volume ratio noted in step 3 and the molar volumes of the components.
- Complete immiscibility was assumed in step 6.

The temperatures necessary to obtain virtually complete separation in step 2 were determined in the following manner. Hydrocarbon mixtures of various benzene-2,3-dimethylpentane compositions were mixed with heptacosafuorotributylamine to make ternary mixtures containing 60 and 70 mole percent fluorocarbon. These mixtures were cooled to a certain temperature and allowed to come to equilibrium. Then the hydrocarbon phases were drawn off and analyzed by gas-liquid chromatography. The results of the analysis on the separated phases were compared to the results of an analysis of the original hydrocarbon mixtures. Data obtained in this way appear in Table 6.

Table 6. Effect of heptacosafuorotributylamine on the analysis of benzene-2,3-dimethylpentane mixtures.

Mole fraction of (C ₄ F ₉) ₃ N in ternary mix	Mole fraction of benzene in original hc. mix	Separation temperature °C.	Mole fraction of benzene in separated hc. mix
0.70	0.280	0	0.280
0.70	0.515	0	0.530
0.70	0.710	0	0.755
0.70	0.405	-18	0.405
0.70	0.635	-18	0.640
0.70	0.080	-25	0.080
0.70	0.880	-25	0.895
0.60	0.590	-18	0.590
0.60	0.520	-25	0.520
0.60	0.890	-25	0.895

Figure 9 shows that heptacosafuorotributylamine is practically insoluble in both the hydrocarbons at 0 C. Figure 9 also shows that 2,3-dimethylpentane is more soluble in heptacosafuorotributylamine than is benzene. This

indicates that lower separation temperatures would be required to separate ternary mixtures of a given mole fraction of fluorocarbon, when the hydrocarbon portion is richer in benzene, since a given small quantity of dissolved 2,3-dimethylpentane would represent a greater percent of the 2,3-dimethylpentane present in this case. This reasoning is borne out by data in Table 6.

Table 6 shows that a lower separation temperature was necessary as the mole fraction of fluorocarbon increased. This is obviously due to the fact that when more fluorocarbon is present, more hydrocarbon can remain dissolved. The vapor samples contained such small amounts of fluorocarbon that they did not need to be cooled below 0°C ., however, the liquid samples contained approximately 70 mole percent fluorocarbon so lower temperatures were in order for them.

Referring again to Table 6, it can be seen that 70 percent fluorocarbon samples whose hydrocarbon portion did not contain more than 30 mole percent benzene were amenable to separation at 0°C . Likewise, 70 percent fluorocarbon samples whose hydrocarbon portion did not contain more than 70 mole percent benzene could be separated at -18°C .

Temperatures lower than -18°C . were not used to separate mixtures whose hydrocarbon portion contained more than 70 mole percent benzene due to the fact that the hydrocarbon phase froze if these samples were cooled below a certain temperature depending upon the percent benzene in the sample. Samples whose hydrocarbon portion contained more than 85 mole percent benzene froze if cooled to -18°C ., while samples whose hydrocarbon portion contained more than 75 mole percent benzene froze if cooled to -25°C . The analysis was modified slightly to accommodate liquid samples whose hydrocarbon portion was high in benzene. No change was necessary in the vapor analysis due to the low amount of fluorocarbon present.

The following modification, used only when the hydrocarbon portion of the liquid sample contained more than 70 mole percent benzene, was applied after step 1 and before step 2. The modification consisted of:

- a) The liquid sample was weighed, and a weighed amount of 2,3-dimethylpentane was added. This lowered the binary percent benzene to less than 70, and the ternary percent fluorocarbon to approximately 60.
- b) The unmixing temperature of the diluted sample was determined.

The remaining steps of the analysis were carried out on the diluted sample. The composition of the original sample was calculated, with no loss in accuracy, from the composition of the diluted sample plus the information gained in a and b. Then the final result was checked against the unmixing temperature determined in step 1 to insure against errors.

The modified analysis was checked experimentally in the same manner as the original analysis and an example verifying the validity of the modification is now shown:

A hydrocarbon mixture composed of 90 mole percent benzene and 10 mole percent 2,3-dimethylpentane was prepared on the analytical balance. A 70 mole percent fluorocarbon ternary mixture was made by adding 0.4110 grams of the 90 percent hydrocarbon mixture to 7.8320 grams of $(C_2F_6)_3N$. This ternary mixture represented a typical liquid sample. Sufficient 2,3-dimethylpentane (0.2645 grams) was then added to lower the fluorocarbon content to 60 mole percent. The diluted mixture was cooled to $-18^\circ C$. and the hydrocarbon phase drawn off. Analysis of the separated hydrocarbon plus the above mentioned calculations indicated 90 mole percent benzene, which proved the method.

Gas-liquid chromatography was found to be suitable for the analysis of the binary hydrocarbon portion of the samples. Chromatography was used instead of refractive index because minute amounts of fluorocarbon were frequently carried into the hydrocarbon portion of the sample during the draw-off operation of step 4. This had no adverse effect upon analysis by chromatography, but the refractive index was changed.

A curve (shown in Figure 11) relating peak area fraction to mole fraction

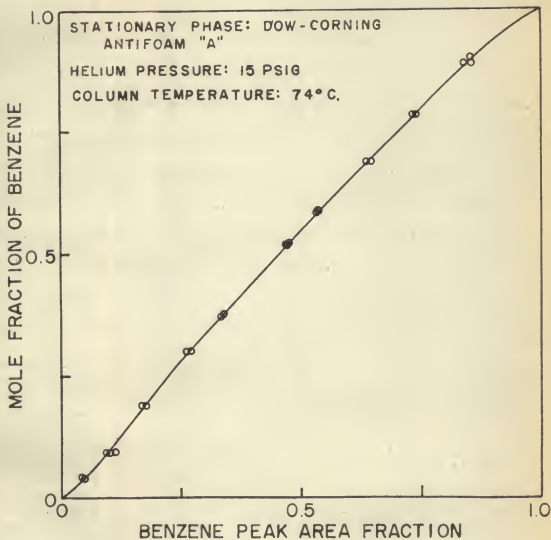


Figure 11. Conversion of chromatograph peak area fraction to mole fraction for system: benzene-2,3-dimethylpentane.

was constructed by determining the area fractions of some samples of known composition. Peak areas were measured by drawing the tangents to the points of inflection of the peak sides, and then multiplying the length between the intersections of the tangents with the base line times the peak height.

The calibration data shown on Figure 11 indicated that a precision of 0.01 with respect to binary mole fraction could be expected. Considering the several steps of the analysis, it is felt that the compositions of the liquid and vapor samples were determined to an accuracy of ± 1 mole percent.

Ternary Equilibrium Data

The physical properties and degree of purity of the chemicals used are listed in Appendix I.

The ternary equilibrium data were determined in an equilibrium still similar to one described by Wilson, et. al., (29). Figure 12 is a drawing of the still. This still could be used for single or two liquid phase systems, and it was for this reason that it was used for the ternary system instead of the Othmer still. The vapor return leg of the still used for the ternary system was quite long, making it possible to run systems having a large difference in density between the liquid and vapor phases*. A magnetic stirrer was used in conjunction with the still to insure complete and rapid mixing of the returning vapor with the pot liquid. The upper portion of the still body was wound with heating wire and insulated with asbestos so that the walls could be kept at a temperature above the condensing temperature of the vapor. The operation of the still was checked with the heptane-toluene system, and the data** were found to be consistent with that reported by Hipkin and Myers (13).

* The ratio of the densities of the liquid and condensed vapor phases of the benzene-2,3-dimethylpentane-heptacosaflluorotributylamine system when the liquid phase contains 70 mole percent fluorocarbon is approximately 2:1.

** See Appendix III.

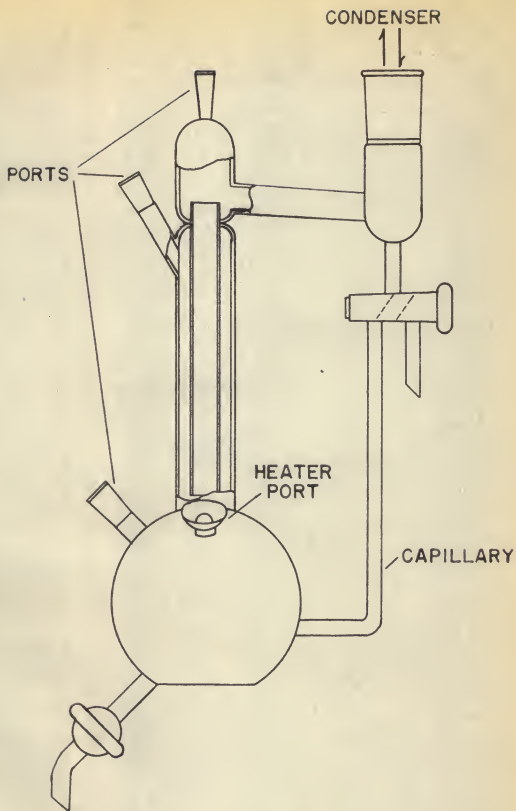


Figure 12. Equilibrium still used for ternary data.

The still was charged with the desired ternary mixture and put into operation. It was assumed that vapor-liquid equilibrium had been established when temperature equilibrium was apparent. The temperatures came to equilibrium in less than one hour. Liquid and vapor samples were taken after the attainment of equilibrium, and were subsequently analyzed by the method described in the preceding section.

Boiling points were obtained from a thermocouple immersed in the boiling liquid. Since the pot liquid was vigorously stirred and the boiling rate was kept low, it is felt that the boiling points read in this manner reflected very little if any superheating. The thermocouple was originally placed in the vapor tube of the still, as is usually the case, however the temperatures read at this position were found to be strongly dependent upon the boiling rate and the amount of heat supplied to the still jacket. This same effect was noted for the Othmer still during the binary equilibrium determinations. It was attempted to obtain the boiling points by boiling a liquid sample in the dynamic boiling apparatus, as was done for the binary system, but the dynamic boiling apparatus was not suitable for the ternary mixtures since there was a large difference between the boiling and condensing temperatures of the liquid and vapor respectively.

The total pressure over the system was held at 760 mm. of mercury for all runs. The pressure was maintained by a manostat and read with an absolute manometer to 0.1 mm.

All the data were obtained for pot mixtures composed of 69-71 mole percent heptacosafuorotributylamine. The binary compositions of the hydrocarbon portion of the mixtures covered the entire range of benzene-2,3-dimethylpentane concentrations. The equilibrium data appear in Table 7 and the hydrocarbon

x-y diagram and the boiling point-composition diagram appear on the following pages as Figures 13 and 14. Since the third component, heptacosafuorotributylamine, was held at a nearly constant composition ternary plots would serve no purpose and accordingly were not included.

Table 7. Vapor-liquid equilibrium data for the benzene-2,3-dimethylpentane-heptacosafuorotributylamine system at 70 mole percent heptacosafuorotributylamine.

Boiling point C.	Mole fraction : of $(C_4F_9)_3N$: in liquid	Mole fraction : of benzene : in liquid	Mole fraction : of $(C_4F_9)_3N$: in vapor	Mole fraction : of benzene : in vapor
104.2	0.715	0.018	0.045	0.119
102.0	0.713	0.040	0.040	0.202
	0.690	0.041	0.055	0.210
101.1	0.700	0.051	0.040	0.245
	0.700	0.052	0.055	0.246
	0.710	0.070	0.034	0.333
97.0	0.700	0.105	0.020	0.478
96.5	0.710	0.120	0.030	0.505
93.5	0.700	0.157	0.030	0.586
92.7	0.710	0.169	0.030	0.636
90.2	0.695	0.204	0.030	0.695
90.6	0.705	0.208	0.045	0.710
89.5	0.700	0.216	0.035	0.755
89.1	0.700	0.225	0.040	0.755
87.8	0.708	0.229	0.040	0.802
86.7	0.695	0.258	0.045	0.840
86.0	0.700	0.254	0.030	0.865
84.7	0.705	0.278	0.030	0.921

Experimental Activity Coefficients

Activity coefficients were determined for benzene and 2,3-dimethylpentane, utilizing equation 9, page 14. These activity coefficients are tabulated in Table 8 and are shown on Figure 15.

It was attempted to prove the thermodynamic consistency of the ternary data by a method devised by Krishnamurty and Rao (15). This method is somewhat similar to the method of Redlich, Kister and Turnquist used for the binary

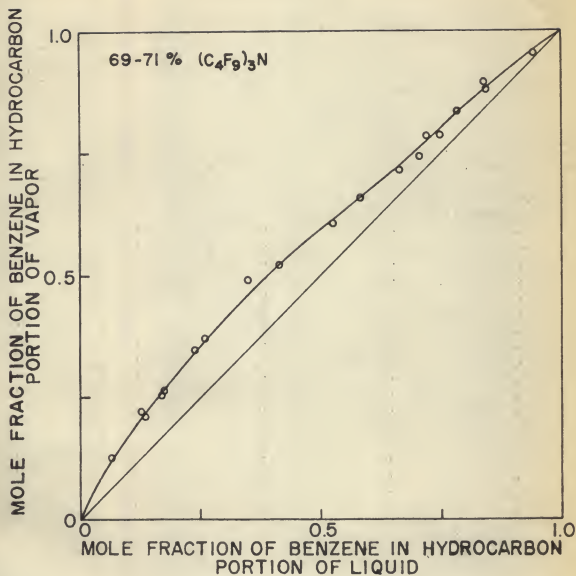


Figure 13. Binary x-y diagram of hydrocarbon portion for system: benzene-2,3-dimethylpentane-heptacosafuorotributylamine.

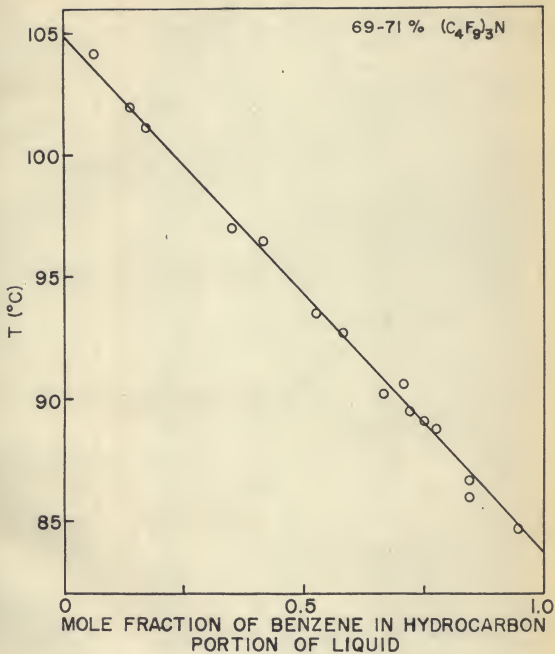


Figure 14. Boiling temperatures of 70 mole percent heptafluoro-tributylamine mixtures.

data. The method of Krishnamurty and Rao requires that

$$\int_{Q'}^{Q''} dQ = \int_{x_1'}^{x_1''} \ln \frac{Y_1}{Y_2} dx_1 \quad \text{where } x_3 \text{ is constant over the entire } x_1 \text{ composition}$$

range. The quantity Q is defined as $x_1 \ln \gamma_1 + x_2 \ln \gamma_2 + x_3 \ln \gamma_3$. This method is derived from the Gibbs-Duhem equation (as is the Redlich, Kister and Turnquist method) so it is strict only at constant temperature.

It was found to be impossible to prove thermodynamic consistency of the ternary data by the method of Krishnamurty and Rao. This may have been due to several reasons:

- 1) The data were not obtained at constant temperature. This method can be applied to constant pressure data if the variation in temperature is small, but it is felt that the temperature range in this case (20 C.) was too large.
- 2) The data were not obtained at a strictly constant fluorocarbon composition. The mole fraction of heptacosafuorotributylamine varied from 0.69 to 0.71 whereas the test requires that one component be at a constant composition.
- 3) The values obtained for the concentration of fluorocarbon in the vapor samples did not possess sufficient accuracy. Small errors in the determination of the mole fraction of fluorocarbon in the vapor had a large effect upon the calculated fluorocarbon activity coefficients.

It should be pointed out that the failure of the ternary activity coefficients to satisfy the consistency test does not necessarily mean that the equilibrium data is invalid.

Table 8. Activity coefficients for benzene and 2,3-dimethylpentane in the benzene-2,3-dimethylpentane-heptacosafuorotributylamine system at 70 mole percent heptacosafuorotributylamine.

Mole fraction of benzene in hydrocarbon portion of liquid	Activity coefficient of benzene	Activity coefficient of 2,3-dimethylpentane
0.065	3.23	2.09
0.132	2.72	1.97
0.140	2.68	2.17
0.170	2.62	2.08
0.173	2.64	2.08
0.240	2.71	2.16
0.350	2.75	2.06
0.414	2.61	2.22
0.524	2.52	2.40
0.582	2.59	2.54
0.667	2.52	2.73
0.707	2.50	2.78
0.720	2.66	2.43
0.750	2.58	2.85
0.785	2.80	2.70
0.845	2.69	2.71
0.845	2.85	2.55
0.944	2.91	2.79
1.000	2.80*	

* This point was determined from binary solubility data. It was assumed that the benzene activity coefficient for the binary benzene-heptacosafuorotributylamine system could be represented by $\ln \gamma_1 = K \phi_1^2$, where K was a constant dependent upon temperature. K may be considered as the logarithm of the activity coefficient of benzene at infinite dilution. The boiling point of a 30 mole per cent benzene mixture of benzene and heptacosafuorotributylamine was found from Figure 14 to be 84°C. From Figure 9 it was determined that the amount of benzene soluble in heptacosafuorotributylamine was 39 mole percent and that the amount of fluorocarbon soluble in benzene was negligible at 84°C. The benzene activity in each phase was equal (in this case $a_1 = a'_1 = 1$), so the activity coefficient at $x_1 = 0.39$ was obtained as

$\gamma_1 = 1/0.39$, since $a_1 = \gamma_1 x_1$. A value of $K = 1.27$ was computed from this

value of γ_1 and the value of ϕ_3 at $x_1 = 0.39$ and 84°C. A value of $\gamma_1 = 2.8$

was then calculated from $\ln \gamma_1 = 1.27 \phi_3^2$ at $x_1 = 0.30$ and 84°C.

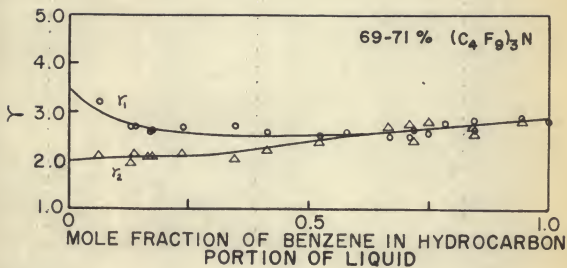


Figure 15. Benzene and 2,3-dimethylpentane activity coefficients for system: benzene-2,3-dimethylpentane-heptacosafuorotributylamine.

DISCUSSION OF TERNARY DATA

Comparison of Relative Volatilities

In order to ascertain the value of heptacosafuorotributylamine as an extractive distillation solvent for the benzene-2,3-dimethylpentane system it was necessary to compare the hydrocarbon portion of the ternary equilibrium data (Figure 13) with the binary equilibrium data (Figure 3). A convenient way to compare these data was to compare the relative volatilities. The hydrocarbon relative volatilities, with respect to benzene, in both the binary and ternary systems are shown in Figure 16.

The comparison of the relative volatilities showed that heptacosafuorotributylamine is not a good extractive distillation solvent for benzene 2,3-dimethylpentane mixtures. The relative volatility was not improved for mixtures containing less than 50 mole percent benzene. For mixtures containing more than 50 mole percent benzene the relative volatility was improved only slightly, and although this improvement was sufficient to destroy the binary azeotrope, it was not great enough to facilitate easy separation of the components. It can therefore be concluded that heptacosafuorotributylamine is not a suitable extractive distillation solvent for benzene-2,3-dimethylpentane mixtures because the solvent effect is not great enough.

It is interesting to examine the manner in which the solvent effected the relative volatilities. Recalling the definition of relative volatility (equation 5, page 6), the overall solvent effect can be attributed to the effect upon the activity coefficient ratio and the effect upon the vapor pressure ratio. The activity coefficient ratios with and without the solvent are shown in Figure 17.

Inspection of Figure 17 reveals that nearly all of the change in relative volatility was due to the effect of the solvent on the activity coefficient

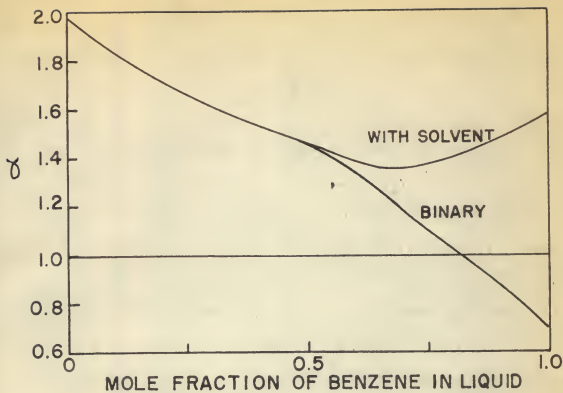


Figure 16. Comparison of relative volatilities.

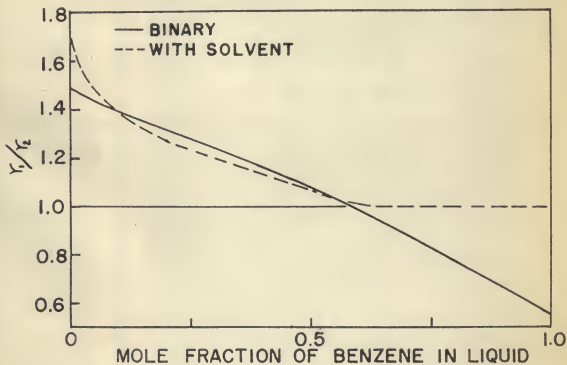


Figure 17. Comparison of binary and ternary activity coefficient ratios.

ratio. The curves comparing activity coefficient ratios are quite similar to those comparing the relative volatilities. The small remainder of the change in relative volatility was due to a slight change in the vapor pressure ratio. The vapor pressure ratio was changed slightly because the ternary system had a higher range of boiling temperatures than the binary system. If the boiling ranges had been identical the entire change in relative volatility would have been due to the change in the activity coefficient ratio.

Theoretical Activity Coefficients

Theoretical activity coefficients for the benzene-2,3-dimethylpentane-heptacosfluorotributylamine system were calculated using equations 7, page 7. Prior to using equations 7 it was necessary to determine values of f_{13} and f_{23} . These values were obtained from the solubility data plotted on Figure 9.

The values of f_{13} and f_{23} were determined at 60°C., the highest temperature at which they could be obtained. Although f is considered to be independent of temperature, f_{13} and f_{23} were obtained at a temperature as near to the boiling range of the ternary mixtures as possible.

Equations 6 were used to calculate the f values. Separate calculations were required to compute f_{13} and f_{23} since they were determined from two separate binary systems. The calculations were identical for f_{13} and f_{23} so are explained for the fluorocarbon-2,3-dimethylpentane system only.

Equation 6 was written separately for the hydrocarbon phase and the fluorocarbon phase:

$$RT \ln \gamma_2 = v_2 \left[(\delta_2 - \delta_3)^2 + 2\delta_2\delta_3(1 - f_{23}) \right] \phi_3^2$$

$$RT \ln \delta_2^1 = v_2 \left[(\delta_2 - \delta_3)^2 + 2\delta_2\delta_3(1 - f_{23}) \right] \phi_3^2$$

These expressions were combined to yield

$$RT \ln \gamma_2 / \gamma_2' = V_2 \left[(\delta_2 - \delta_3)^2 + 2\delta_2\delta_3(1 - f_{23}) \right] \left[\phi_3^2 - \phi_3'^2 \right]$$

The activity coefficient is defined by equation 10:

$$a_1 = x_1 \gamma_1 \quad (\text{Eq. 10})$$

Since each component existing in separate phases at equilibrium has equal activity in each phase $x_2 \gamma_2 = x_2' \gamma_2'$ and $\gamma_2 / \gamma_2' = x_2' / x_2$. Substituting this into the combined equations 6 yielded

$$RT \ln x_2 / x_2' = V_2 \left[(\delta_2 - \delta_3)^2 + 2\delta_2\delta_3(1 - f_{23}) \right] \left[\phi_3^2 - \phi_3'^2 \right]$$

The value for f_{23} was found from this expression since all the other quantities were known. Values of 0.970 and 0.950 were calculated for f_{13} and f_{23} respectively by the method explained above.

It should be realized that f values determined in the above manner are empirical and are not necessarily equal to the theoretical values. Reed (23) defined

$$f = f_I f_d \quad (\text{Eq. 11})$$

$$f_I = \frac{2(I_1 I_2)^{\frac{1}{2}}}{I_1 I_2} \quad (\text{Eq. 12})$$

$$f_d = \left[\frac{2(d_{11} d_{22})^{\frac{1}{2}}}{d_{11} d_{22}} \right]^3 \quad (\text{Eq. 13})$$

Values of f_{d13} and f_{d23} were estimated from the molar volumes to be 0.932 and 0.968 respectively. Since the ionization potential of heptacosfluorotributylamine is unknown it was not possible to arrive at values of f_I , however it is known that for fluorocarbon-hydrocarbon mixtures f_I must be less than 0.99. Substituting the empirical values of f and the estimated theoretical values

of f_d into equation 11 yielded $f_{I_{13}} = 1.041$ and $f_{I_{23}} = 0.981$. The unreasonably high value for f_{13} indicates that more theoretical work needs to be done concerning the physical significance of f .

The empirically determined values of f were used in equations 7 to predict activity coefficients for the ternary system. These predicted activity coefficients are compared to the experimental coefficients on Figure 18. The theoretical activity coefficients agree to within approximately twenty percent of the experimental values. This shows that equations 7 predicted the activity coefficients with a fair degree of accuracy. However, these values were not determined on a purely theoretical basis since f_{13} and f_{23} were determined empirically. In other words, empirical factors were used in the theoretical expressions. Purely theoretical values of f_{13} and f_{23} might give substantially different results.

Although the activity coefficients determined above can not be considered to be purely theoretical they are of a more theoretical nature than coefficients determined by purely empirical expressions such as the ternary van Laar equations (30). The van Laar expressions, and other strictly empirical methods, utilize empirical constants in empirical formulas to determine activity coefficients.

The ratio of the activity coefficients determined by equations 7 is compared to the experimental ratio on Figure 19. Since f_{13} and f_{23} are practically equal equation 8 would give substantially the same results. From Figure 19 it can be seen that the predicted ratio does not agree satisfactorily with the experimental ratio. On the basis of this predicted ratio a substantial improvement in the relative volatility would have been expected and heptacosafuorotributylamine would have been assumed to be a suitable extractive distillation solvent. Therefore expressions that predict reasonably accurate

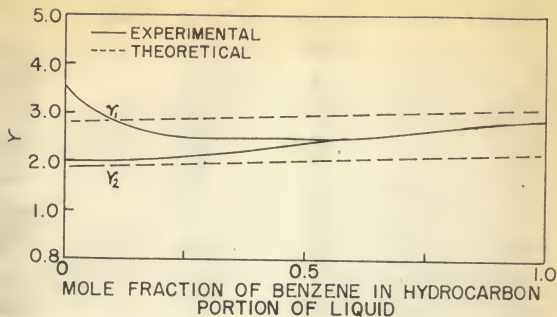


Figure 18. Comparison of ternary theoretical and experimental activity coefficients.

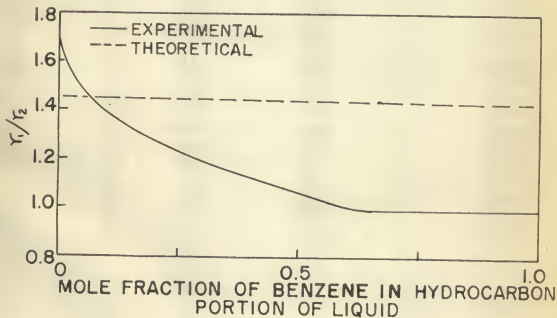


Figure 19. Comparison of theoretical and experimental activity coefficient ratios.

values of the activity coefficients may or may not predict sufficiently accurate values of the activity coefficient ratio, depending upon both the magnitude and direction of the errors in the predicted coefficients.

It can be concluded from the above results that the prediction of good extractive distillation solvents is a severe test of the method used. Further data on other systems needs to be obtained in order to determine if the "regular" solution theory can be used to predict extractive distillation solvents.

ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. Benjamin G. Kyle whose advise and consultation have contributed very greatly to the completion of this work.

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APPENDICES

APPENDIX I

PHYSICAL PROPERTIES OF CHEMICALS

The benzene used in this work was Phillips' 99 mole percent "pure" grade. The 2,3-dimethylpentane was Phillips' 95 mole percent "technical" grade. These hydrocarbons exhibited single peaks when subjected to chromatographic analysis so were not further purified.

Heptacosafuorotributylamine, $(C_4F_9)_3N$, is the principle constituent of Minnesota Mining & Manufacturing Company's fluorochemical FC-43. The FC-43 was vacuum distilled in a fractionating column. The outside fractions were discarded and the central fractions, having a 2.4°C. boiling range, were combined. This gave the heptacosafuorotributylamine an acceptable degree of purity. It is thought that the remaining impurities were isomers.

The densities, refractive indices and boiling points appear in the following table.

Table 9. Physical properties of chemicals used.

Property	Benzene		2,3-Dimethylpentane		Heptacosafuoro- tributylamine	
	exper.	lit.	exper.	lit.	exper.	lit.
Density at 25°C.	0.87341	0.87370 ¹	0.69184	0.69091 ¹	1.92409	1.872 ²
Refractive index at 20°C.	1.5009	1.50112 ¹	1.3919	1.39196 ¹		1.2910 ² (25°)
Boiling point at 1 atm.	80.06	80.100 ¹	90.16	89.784 ¹	177.4- 179.8	170-180 ²

1. Values reported in API tables (see reference 1).
2. Values reported by Minnesota Mining and Manufacturing Company for FC-43. These values should not be taken as standards of purity for heptacosafuorotributylamine.

Vapor Pressures were determined for the 2,3-dimethylpentane and heptacosafuorotributylamine used. Due to the good agreement between the experimental and reported boiling points for benzene, vapor pressure data were not obtained experimentally. For values of the vapor pressure of benzene the Antoine equation, $\log P_1^{\circ} = 6.90565 - \frac{1211.033}{220.79 + t}$ (1), was used. The vapor pressure data determined experimentally appear in Tables 10 and 11 and on Figure 20.

Table 10. Vapor pressure of 2,3-dimethylpentane.

Temperature °C.	90.16	88.85	88.45	87.90	87.00	86.10	85.00	83.90
Pressure mm. Hg.	760	734	724	714	696	676	657	636
Temperature °C.	82.75	81.80	80.76	79.19				
Pressure mm. Hg.	613	595	578	550				

Table 11. Vapor pressure of heptacosafuorotributylamine

Temperature °C.	178.78	177.67	176.83	175.79	174.81	173.68	172.62
Pressure mm. Hg.	760	739	720	700	680	659	640
Temperature °C.	171.49	170.41	169.21	168.08	166.64	163.94	160.42
Pressure mm. Hg.	620	601	581	560	540	500	450
Temperature °C.	156.54	152.39	147.50	141.51	135.24	127.40	116.87
Pressure mm. Hg.	400	352	300	245	198	148	100

The experimental densities were determined by the use of a pycnometer described by Lipkin (19). The refractive indices were determined with an Abbé type refractometer manufactured by Bausch & Lomb. The boiling points and vapor pressures were determined in a dynamic boiling apparatus similar to one described by Quiggle, Tongberg and Fenske (21).

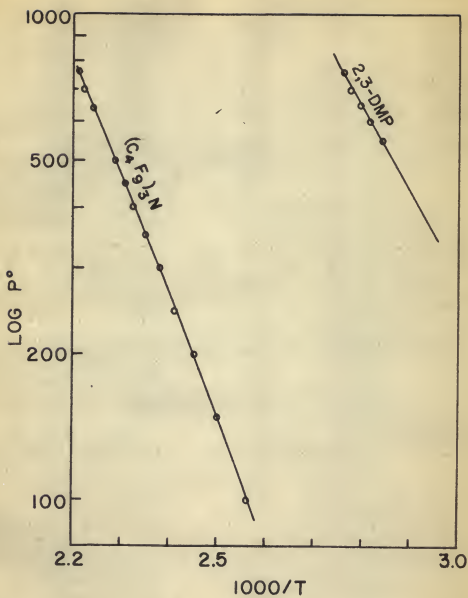


Figure 20. Vapor pressure data for 2,3-dimethylpentane and for heptacosafuorotributylamines.

APPENDIX II

CALIBRATIONS

Thermocouple Calibration

The thermocouple used in the equilibrium stills and ebullimeter was made of iron-constantan, and was calibrated in a constant temperature bath against a platinum resistance thermometer calibrated by the National Bureau of Standards. The following expressions relating temperature ($^{\circ}\text{C}.$) to potential (mv.) were determined by the method of least-squares:

$$t = 19.6991v - 0.2304v^2 + 0.0184v^3 - 0.0007v^4$$

$$\pm 0.15 \quad (0-185 \text{ C.})$$

$$\pm 0.05 \quad (120-185 \text{ C.})$$

$$t = 20.1317v - 0.5315v^2 + 0.0613v^3$$

$$\pm 0.05 \quad (0-90 \text{ C.})$$

The solubility cell thermocouple was also of the iron-constantan type. This thermocouple was checked against the thermocouple used in the equilibrium stills. It was found to give substantially the same potential readings as the calibrated thermocouple so the expression

$$t = 20.1317v - 0.5315v^2 + 0.0613v^3$$

was used for this thermocouple.

A Leeds & Northrup model 8662 potentiometer was used to measure the potentials of both thermocouples to ± 0.001 millivolts. It was found that both thermocouples followed the conversion table published by Leeds & Northrup quite closely in the range $0-80^{\circ}\text{C}.$

Pycnometer Calibration

The pycnometer was immersed in a constant temperature bath and filled with distilled mercury to three different scale readings. The amount of mercury at each level was determined by weighing on an analytical balance. Volumes vs. scale readings were obtained from the density of mercury at the bath temperature. The weighings were barometrically corrected. The method of least-squares was used to determine an expression relating volume to scale reading:

$$V = 4.22626 + 0.00772h \quad (\text{at } 25 \text{ C.})$$

APPENDIX III

EQUILIBRIUM STILL TESTS

The operation of both the Othmer still (20) and the still used for the ternary data (29) were checked with the heptane-toluene system. The data obtained are compared with the data reported by Hipkin and Myers (13) on Figure 21. The test data agreed well with the reported data.

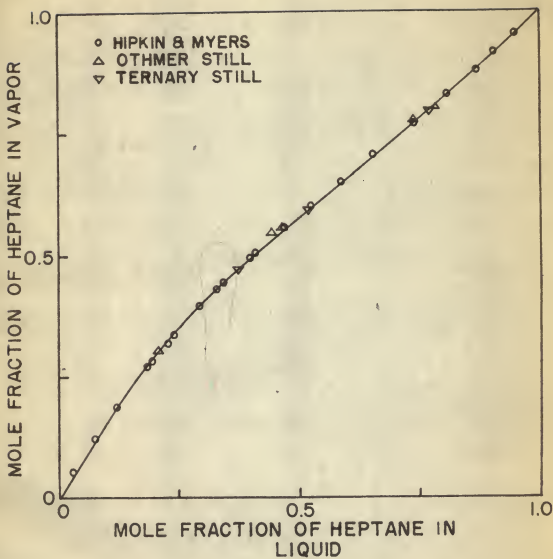


Figure 21. Equilibrium still test data.

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

by

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B. S., Kansas State University, 1957

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemical Engineering

KANSAS STATE UNIVERSITY
OF AGRICULTURE AND APPLIED SCIENCE

1959

Vapor-liquid equilibrium data were determined at a constant pressure of one atmosphere in the binary benzene-2,3-dimethylpentane system over the complete composition range, and in the ternary benzene-2,3-dimethylpentane-heptacosafuorotributylamine system at compositions having 70 mole percent fluorocarbon. These data were used to evaluate heptacosafuorotributylamine as an extractive distillation solvent for the binary system. Heptacosafuorotributylamine was evaluated for its solvent effect because it is a relatively high boiling "nonpolar" compound. Certain qualitative aspects of the Scatchard-Hildebrand "regular" solution theory indicated that a "nonpolar" compound would be a suitable extractive distillation solvent for this system.

It was found that heptacosafuorotributylamine is not a suitable extractive distillation solvent for the benzene-2,3-dimethylpentane system. This solvent did not affect the relative volatility of the binary mixtures containing less than 50 mole percent benzene. The relative volatility of benzene-2,3-dimethylpentane mixtures containing more than 50 mole percent benzene was increased enough to destroy an azeotrope found in the binary hydrocarbon system at 82.5 mole percent benzene and 79.44°C., but it was not increased enough to afford easy separation of the components.

It was attempted to predict the solution behavior in the binary and ternary systems by means of the Scatchard-Hildebrand theory of "regular" solutions. The theory was used to predict activity coefficients in the binary system that agreed with the experimental data to within ten percent.

The "regular" solution theory as amended by Reed was used to predict activity coefficients in the ternary system. These predicted activity coefficients agreed with the experimental values to about twenty percent accuracy, however the ratio of these activity coefficients disagreed markedly with the experimental ratio and erroneously predicted that heptacosafuorotributylamine was a good solvent for the system.