Perfluorotributylamine as an Extractive Distillation Solvent for a Hydrocarbon Mixture

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FLUOROCARBONS are a relatively new class of compounds whose unusual solution behavior has received much attention in recent years. Most of this attention has been focused on solutions of fluorocarbons and hydrocarbons where extremely large deviations from Raoult's law have been reported. This unique solution behavior has been exploited by Mair (9) who used fluorocarbons as entrainers for the azeotropic distillation of hydrocarbon mixtures. Their successful use in azeotropic distillation suggests a potentiality as solvents for extractive distillation, which is also indicated from theoretical considerations. Vapor-liquid equilibrium data are presented herein for the binary system benzene–2,3-dimethylpentane and the ternary system benzene–2,3-dimethylpentane–perfluorotributylamine.

These data show that the fluorocarbon solvent is not as effective as theoretically predicted.

SOLUTION BEHAVIOR

The relative volatility of component 1 (the more volatile component) over component 2 in the presence of a solvent can be written as the product of the vapor pressure ratio and activity coefficient ratio.

$$\alpha'_{12} = (p_1^0/p_2^0)\,(\gamma'_1/\gamma'_2) \tag{1}$$

The primary effect of adding a solvent to the binary mixture is to alter the value of the activity coefficient ratio. A high boiling solvent will tend to raise the boiling temperature, but the vapor pressure ratio should not be strongly dependent on temperature. If the vapor pressures of components 1 and 2 are approximately equal, then any solvent which causes a large value of either γ'_1/γ'_2 or γ'_2/γ'_1 would be acceptable for extractive distillation. If, however, the vapor pressures of components 1 and 2 differ appreciably, then solvents that cause a large value of γ'_1/γ'_2 would be more desirable than those that produce large values of γ'_2/γ'_1.

An analysis of solution behavior in extractive distillation systems, similar to that employed by Robinson and Gilliland (*14*), can be made in terms of the Scatchard-Hildebrand theory of regular solutions (*6*). If it is assumed that the molal volumes of components 1 and 2 are approximately equal and that the solvent concentration is great enough so that interactions between components 1 and 2 may be neglected, Equation 2 can be used to express the activity coefficient ratio of components 1 and 2 in the ternary mixture as a function of the physical properties of the pure components.

$$\ln \gamma'_1/\gamma'_2 = \frac{(V_1 + V_2)(\delta_1 - \delta_2)}{RT}\left[\frac{\delta_1 + \delta_2}{2} - \delta_3\right]\phi_3^2 \tag{2}$$

The Scatchard-Hildebrand theory in its present state of development presents at best only a qualitative explanation of solution behavior; however, Equation 2 should provide useful information concerning the selection of solvents for extractive distillation. The equation is not expected to apply to solutions containing extremely polar compounds where specific interactions such as hydrogen bonding occur. In Equation 2 the most important variables influencing the activity coefficient ratio are the solubility parameters, δ's. These parameters can be used in a general manner as a measure of the polarity of a compound, because large values of δ are associated with polar compounds.

There are two possible cases which can be analyzed by means of Equation 2. The first case is where component 1 (the more volatile component) is less polar than component 2 ($\delta_1 < \delta_2$). When this situation arises, the term ($\delta_1 - \delta_2$) in Equation 2 is negative and a solvent whose solubility parameter is greater than $(\delta_1 + \delta_2)/2$ is needed to make γ'_1/γ'_2 greater than unity. This case is common, as most commercial extractive distillation processes employ polar solvents. Examples are found in the separation of toluene from a petroleum naphtha fraction using phenol as a solvent (*4*) and the separation of C_4 hydrocarbons employing furfural as an extractive agent (*5*).

The second case is where component 1 is more polar than component 2 ($\delta_1 > \delta_2$). In this situation a nonpolar solvent whose solubility parameter is less than $(\delta_1 + \delta_2)/2$ is needed to make γ'_1/γ'_2 greater than unity. Because fluorocarbons possess the lowest solubility parameters of any class of compounds, they should be potentially good solvents for systems of this type. This study was undertaken to determine whether a fluorocarbon solvent would be effective for this type of hydrocarbon system.

EXPERIMENTAL

Materials. The hydrocarbons used were obtainable commercially in a reasonable degree of purity and were not further purified. These hydrocarbons exhibited single peaks when subjected to chromatographic analysis.

Perfluorotributylamine, $(C_4F_9)_3N$, is the principal constituent of Fluorochemical FC-43 (Minnesota Mining and Manufacturing Co.). This material was distilled in a laboratory fractionating column. The middle fractions covering a boiling range of 2.4° C. were combined for use in this study.

Physical properties of compounds used in this work are presented in Table I along with reported literature values.

Binary Vapor-Liquid Equilibria. The binary vapor-liquid equilibrium data were determined in a modified Othmer equilibrium still. The upper part of the still was wound with resistance wire and insulated so that the wall tempera-

Table I. Physical Properties of Chemicals Used

	Refractive Index, 20° C.		Boiling Point, 1 Atm., ° C.	
Compound	Exptl.	Lit. (*1*)	Exptl.	Lit. (*1*)
Benzene[a]	1.5009	1.50112	80.06	80.100
2,3-Dimethylpentane[a]	1.3919	1.39196	90.16	89.784
Perfluorotributylamine[b]	...	...	178.8	...

[a] Phillips Petroleum Co.
[b] Minnesota Mining & Manufacturing Co.

ture could be controlled. The operation of the still was checked with the *n*-heptane–toluene system, and the data agreed satisfactorily with those reported by Hipkin and Myers (*7*).

The liquid and vapor samples were analyzed by refractive index using an Abbe type refractometer which could be read with a precision of 0.0001 init. A change of this magnitude in the value of the refractive index represented a change in composition of approximately 0.05 mole %.

The temperatures obtained from the Othmer still were proportional to the rate of boiling. This effect has been reported by Canjar and coworkers (*2*, *3*). To determine the equilibrium temperature more closely, about 40 ml. of pot liquid were removed from the Othmer still and placed in a Cottrell apparatus (*12*). The boiling temperature in this apparatus was measured with a thermocouple calibrated against a platinum resistance thermometer calibrated by the National Bureau of Standards. Both the Cottrell apparatus and Othmer still were operated at 760 mm. of mercury pressure. The pressure was controlled by a Cartesian manostat and could be determined to 0.1 mm. by an absolute manometer.

Vapor-liquid equilibrium data for the system benzene–2,3-dimethylpentane are listed in Table II and plotted on Figures 1 and 2. These data were checked and found to be thermodynamically consistent by the method of Redlich, Kister, and Turnquist (*13*). A minimum boiling azeotrope having a boiling point of 79.4° C. and a composition of 82.5 mole % benzene was found. This agrees with a temperature of 79.2° C. and a composition of 83.0 mole % of benzene as reported by Marschner and Cropper (*10*).

Table II. Vapor-Liquid Equilibrium Data for System Benzene–2,3-Dimethylpentane at 760 Mm. of Mercury

Temp., ° C.	Benzene, Mole Fraction	
	Liquid	Vapor
...	0.980	0.972
79.8	0.972[a]	...
...	0.944	0.933
79.7	0.943[a]	...
79.6	0.930[a]	...
...	0.913	0.900
...	0.908	0.897
79.6	0.905[a]	...
...	0.882	0.873
79.5	0.862[a]	...
79.5	0.845	0.842
79.5	0.842[a]	...
79.4	0.825	0.825
79.5	0.776	0.788
79.7	0.754	0.770
79.7	0.714	0.744
79.9	0.675	0.716
80.3	0.614	0.675
80.5	0.585	0.655
80.9	0.535	0.620
81.4	0.486	0.585
81.9	0.445	0.548
82.8	0.373	0.493
84.7	0.247	0.360
85.8	0.181	0.285
87.1	0.125	0.218
87.3	0.115	0.191
88.3	0.072	0.132
89.1	0.036	0.068

[a] Runs made in Cottrell apparatus only.

Solubility Measurements. Unmixing temperatures were determined at several fluorocarbon concentrations for mixtures of the fluorocarbon with benzene, with 2,3-dimethylpentane, and with three benzene–2,3-dimethylpentane mixtures. The experimental technique and apparatus for these measurements are similar to those described by Kyle and Reed (*8*). The solubility data were obtained primarily to provide a means of performing analyses in the ternary system. These data are plotted on Figures 3 and 4.

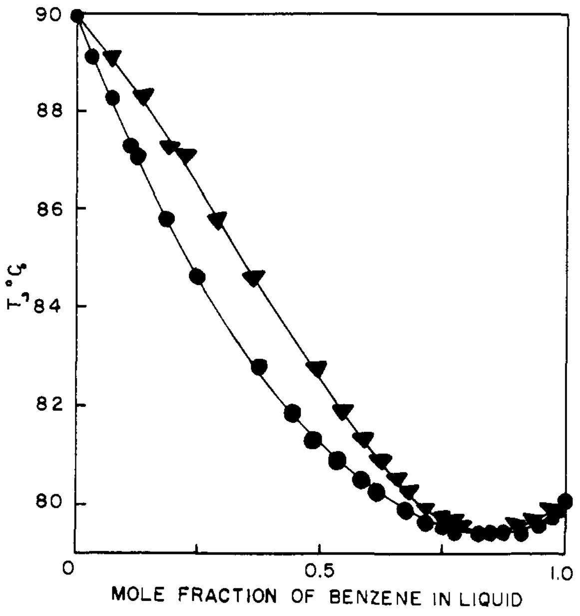

Figure 1. Vapor-liquid equilibrium data system: benzene–2,3-dimethylpentane at 1 atm.

Ternary Analyses. Because liquid samples were rich in fluorocarbon and vapor samples were lean in fluorocarbon, different analysis procedures were employed for liquid and vapor samples.

Liquid samples contained approximately 70 mole % of fluorocarbon and were analyzed from the determination of the unmixing temperature and the hydrocarbon analysis on a fluorocarbon-free basis. The hydrocarbons were separated from the fluorocarbon by cooling to a temperature of about −18° C. and decanting the hydrocarbon phase. The hydrocarbon phase contained a small amount of fluorocarbon which altered the refractive index; therefore, analysis of this hydrocarbon phase was performed chromatographically. A 2-meter long column, containing Dow Corning Antifoam A as a partitioning liquid, was employed, and a calibration curve of mole fraction *vs.* peak area fraction was determined. The chromatographically determined hydrocarbon composition (fluorocarbon-free basis) and the unmixing temperature of the orginal samples were used with Figure 4 to determine the fluorocarbon composition.

The vapor samples contained from 2 to 6 mole % of fluorocarbon. These samples were placed in a graduated

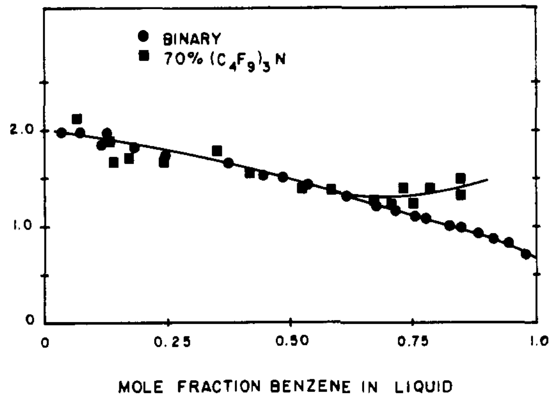

Figure 2. Relative volatility of benzene over 2,3-dimethylpentane *vs.* liquid composition

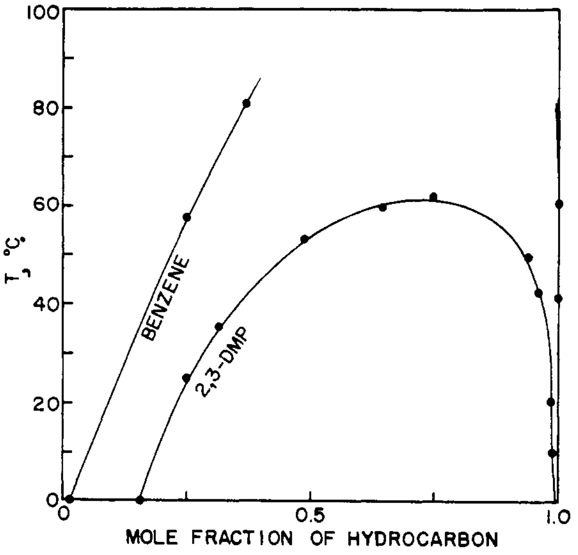

Figure 3. Binary solubility curves of systems containing $(C_4F_9)_3N$

tube and cooled to −18° C. where the volumes of both phases were recorded. The hydrocarbon phase was decanted and analyzed by the chromatographic technique. The fluorocarbon content of the original sample was determined from the recorded volumes of hydrocarbon and fluorocarbon phases at −18° C. assuming complete immiscibility and using available density data. Density of the hydrocarbon phase was calculated from data of API Research Project 44 (*1*), assuming no volume change on mixing. Density data for the fluorocarbon are reported by Minnesota Mining and Manufacturing Co. (*11*).

The vapor and liquid analysis procedures were tested on several prepared ternary mixtures, and compositions could be determined to an accuracy of ±1 mole %.

Ternary Vapor-Liquid Equilibria. The ternary equilibrium data were determined in an equilibrium still similar to the one described by Wilson, Munger, and Clegg (*16*). This still is adaptable for either single- or two-liquid phase systems and for this reason was selected over the Othmer still. Only one liquid phase was present in the pot liquid over the entire composition range, but the condensed vapor formed two liquid phases at high benzene concentrations. A magnetic stirrer was used to ensure complete mixing of the pot liquid. The upper portion of the still was wound with resistance wire and insulated to allow control of the wall temperature.

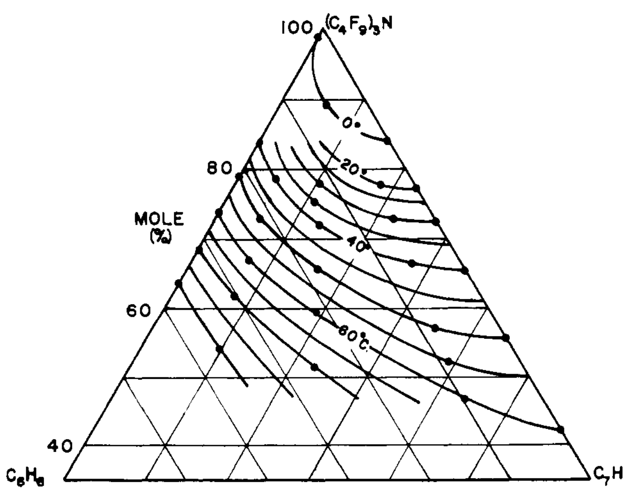

Figure 4. Unmixing temperatures of system: benzene–2,3-dimethylpentane–perfluorotributylamine

The operation of this still was checked with the *n*-heptane–toluene system, and the data agreed with that obtained in the Othmer still and reported by Hipkin and Myers (*7*). Table III contains the test data for both the Othmer still and the Wilson, Munger, and Clegg still. The total pressure was maintained at 760 mm. of mercury for the ternary equilibrium measurements.

Table III. Still Test Data, System: *n*-Heptane–Toluene (*7*)

Pressure, Mm.	Temp., ° C.	Mole Fraction *n*-Heptane, Liquid	Mole Fraction *n*-Heptane, Vapor
	Othmer Still		
734	103.8	0.785	0.805
733	100.0	0.742	0.778
741	101.7	0.445	0.552
739	105.0	0.207	0.302
	Wilson, Munger, and Clegg Still		
760	101.4	0.521	0.595
760	103.2	0.375	0.470
760	99.4	0.770	0.800

The ternary vapor-liquid equilibrium data (Table IV) were obtained at a constant fluorocarbon mole fraction (69 to 72 mole %) in the liquid phase. The entire range of binary hydrocarbon compositions was covered. The relative volatility of benzene over 2,3-dimethylpentane is plotted *vs.* composition in Figure 2 for both the binary and ternary systems.

Table IV. Vapor-Liquid Equilibrium Data for the System Benzene–2,3-Dimethylpentane–Perfluorotributylamine at 1 Atm.

	$(C_4F_9)_3N$, Mole Fraction		Benzene, Mole Fraction	
Temp., ° C.	Liquid	Vapor	Liquid	Vapor
104.2	0.72	0.05	0.02	0.12
102.0	0.71	0.04	0.04	0.20
. . .	0.69	0.06	0.04	0.21
101.1	0.70	0.04	0.05	0.25
. . .	0.70	0.06	0.05	0.25
. . .	0.71	0.03	0.07	0.33
97.0	0.70	0.02	0.11	0.48
96.5	0.71	0.03	0.12	0.51
93.5	0.70	0.03	0.16	0.59
92.7	0.71	0.03	0.17	0.64
90.2	0.70	0.03	0.20	0.70
90.6	0.71	0.04	0.21	0.71
89.5	0.70	0.04	0.22	0.76
89.1	0.70	0.04	0.23	0.76
87.8	0.71	0.04	0.23	0.80
86.7	0.70	0.05	0.26	0.84
86.0	0.70	0.03	0.25	0.87
84.7	0.71	0.03	0.28	0.92

RESULTS

Activity coefficients for the binary system benzene–2,3-dimethylpentane were calculated from the temperature-composition data by means of Equation 3.

$$\gamma_i = \frac{y_i \pi}{x_i p_i^0} \qquad (3)$$

In using Equation 3 one makes the usual assumption that fugacities may be replaced by pressures. These activity coefficients are plotted *vs.* composition in Figure 5 along

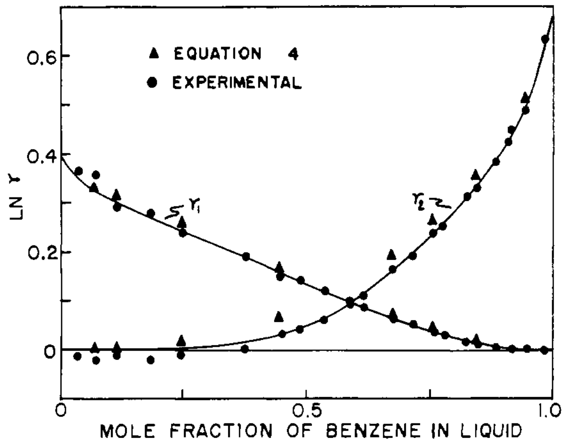

Figure 5. Activity coefficients in the system: benzene–2,3-dimethylpentane

with activity coefficients calculated by the Scatchard-Hildebrand equations

$$RT \ln \gamma_1 = V_1(\delta_1 - \delta_2)^2 \phi_2^2$$
$$RT \ln \gamma_2 = V_2(\delta_1 - \delta_2)^2 \phi_1^2 \qquad (4)$$

Activity coefficients calculated from Equations 4 show a maximum deviation of only 10% from activity coefficients calculated from the experimental data thus indicating that the system can be classified as regular. The physical data necessary for use of Equations 4 are listed in Table V.

Table V. Physical Data for Use in Equations 2 and 4

Compound	Solubility Parameter, $(\text{Cal./Cc.})^{1/2}$	Molar Volume, Cc.
Benzene	8.34[a]	96[c]
2,3-Dimethylpentane	6.45[a]	157[d]
Perfluorotributylamine	5.89[b]	386[e]

[a] Calculated enthalpy of vaporization and density at normal boiling point using data of (*1*).

[b] Calculated from molar volume at 90° C. and enthalpy of vaporization, evaluated from vapor pressure data in temperature range 60° to 120° C. (*11*).

[c] (*1*).

[d] Extrapolation of data from (*1*).

[e] (*11*).

The relative volatility of benzene over 2,3-dimethylpentane calculated from the ternary vapor-liquid equilibrium data was found to vary from 1.98 to 1.36 with an average value of 1.56. Using physical data listed in Table V, Equation 2 predicts a value of γ_1'/γ_2' equal to 1.47 for a ternary mixture containing 70 mole % of perfluorotributylamine. At a temperature of 90° C., the vapor pressure ratio is 1.33, which results in a predicted relative volatility of 1.94. Although the fluorocarbon was not as good a solvent as expected, its performance was qualitatively predicted by Equation 2. This is probably the most to be expected of Equation 2 in view of the assumptions involved in its derivation.

It is interesting to note in Figure 2 that the relative volatility curves for the binary and ternary systems coincide in the region of 0. to 50 mole % of benzene, thus indicating that the added fluorocarbon solvent has little effect in solutions rich in 2,3-dimethylpentane. However, the binary azeotrope was destroyed by the addition of the solvent showing the solvent to be effective in benzene-rich solutions. The extremely low boiling temperatures of the ternary mixtures rich in benzene are indicative of the very large deviations from Raoult's law exhibited by this system.

NOMENCLATURE

p^0 = vapor pressure
R = gas law constant
T = absolute temperature
V = molar volume of the liquid
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase
α_{12}' = relative volatility of component 1 to component 2 in the presence of a solvent, component 3
δ = solubility parameter. δ^2 is defined as the energy of vaporization divided by the molar volume of the liquid, all at the same temperature.
γ = activity coefficient
ϕ = volume fraction
π = total pressure

Subscripts

1 = more volatile component
2 = the next most volatile component
3 = the solvent

Superscript. Primed quantities refer to ternary mixtures.

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