Some Ternary Liquid Systems Containing Fluorocarbons

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TIE LINE DATA have been determined for three ternary liquid systems containing fluorocarbons: I. perfluoroheptane (C_7F_{16})–perfluorocyclic oxide ($C_8F_{16}O$)–carbon tetrachloride; II. perfluoroheptane–perfluorocyclic oxide–*n*-heptane; III. toluene–methylcyclohexane–methyl perfluoro-octanoate ($C_7F_{15}COOCH_3$). For systems I and II the Scatchard-Hildebrand equations using "effective" solubility parameters determined from binary systems successfully predicted solvent selectivities.

To date only one ternary liquid-liquid system containing a fluorochemical has been reported (*7*). Vreeland and Dunlap determined solubility boundaries in the system isooctane–nitroethane–perfluorotributylamine at several temperatures, but reported no extensive tie line data.

The present investigation was undertaken to determine whether fluorocarbon compounds could be separated by solvent extraction and whether fluorine-containing compounds could be used as solvents for the separation of hydrocarbon mixtures.

A mixture of perfluoroheptane and perfluorocyclic oxide was selected as a typical fluorocarbon mixture and various types of organic compounds were tested as possible solvents. Preliminary tests indicated that carbon tetrachloride and *n*-heptane were the most promising solvents; hence tie line data were obtained for the ternary systems perfluoroheptane–perfluorocyclic oxide–carbon tetrachloride and perfluoroheptane–perfluorocyclic oxide–*n*-heptane.

From examination of binary solubility data (*4*) it was believed that the compound methyl perfluoro-octanoate might be a selective solvent for a mixture of toluene and methylcyclohexane. Tie line data were also determined for the system toluene–methylcyclohexane–methyl perfluoro-octanoate.

EXPERIMENTAL

The physical properties and methods of purification of the compounds used in this work have been reported (*4*). Perfluorocyclic oxide was the major constituent in Fluorochemical 0-75 (Minnesota Mining and Manufacturing Co.) and is considered to be a five- or six-membered oxygen-containing ring with side chains.

The preliminary solvent evaluation tests were performed by vigorously shaking an approximately equimolar mixture of the two fluorocarbons with the prospective solvent and using a Perkin-Elmer Vapor Fractometer to analyze the two coexisting liquid phases. The criterion of a promising solvent was taken to be the difference in fluorocarbon peak height fractions in the two phases. A variety of organic compounds were tested in this manner, including paraffinic, naphthenic, and aromatic hydrocarbons, alcohols, aldehydes, ketones, esters, ethers, and chlorinated and nitrated hydrocarbons.

The isothermal, ternary liquid phase diagrams were determined from chromatographic analysis of the two coexisting liquid phases. The liquid mixture was contained in a screw-cap vial and was vigorously shaken by an air-driven mechanism while immersed in a water bath.

After being shaken for some time, samples of each phase were withdrawn for analysis by a hypodermic syringe and the mixture was again shaken. Two or three successive samples were taken with shaking between sampling. The hypodermic syringe was warmed to approximately 10° C. above the temperature of the mixture prior to sampling in order to prevent any concentration changes due to cooling of the saturated phases. The sample was injected into the chromatograph immediately after sampling, so as to prevent formation of a second phase in the syringe upon cooling. The agreement between the analyses for successive samples was taken as the criterion of equilibrium.

The ternary analyses were determined from calibration curves of peak height fraction *vs.* weight fraction for binary systems. A ternary mixture could be analyzed from calibration data for two of the three possible binary mixtures.

Table I. Tie Line Data

Light Phase			Heavy Phase		
W_1	W_2	W_3	W_1'	W_2'	W_3'
$\underset{1}{C_8F_{16}O}$–$\underset{2}{C_7F_{16}}$–$\underset{3}{CCl_4}$ System at 30° C.					
0.128	...	0.872	0.777	...	0.223
...	0.084	0.916	...	0.800	0.200
...	0.084	0.916	...	0.836	0.164
0.118	0.008	0.874	0.724	0.056	0.220
0.106	0.018	0.876	0.655	0.128	0.217
0.100	0.025	0.875	0.615	0.182	0.203
0.078	0.057	0.864	0.514	0.276	0.210
0.076	0.031	0.893	0.514	0.276	0.210
0.062	0.047	0.891	0.414	0.389	0.197
0.018	0.082	0.900	0.123	0.398	0.180
0.025	0.053	0.922	0.232	0.575	0.193
0.032	0.074	0.894	0.213	0.586	0.183
0.045	0.058	0.897	0.336	0.477	0.187
0.045	0.058	0.897	0.321	0.472	0.206
0.010	0.091	0.900	0.073	0.769	0.157
0.010	0.091	0.900	0.071	0.753	0.180
0.018	0.088	0.893	0.132	0.710	0.159
0.018	0.088	0.893	0.131	0.700	0.170
0.024	0.077	0.900	0.175	0.645	0.182
0.024	0.077	0.900	0.182	0.648	0.168
$\underset{1}{C_8F_{16}O}$–$\underset{2}{C_7F_{16}}$–$\underset{3}{n\text{-}C_7H_{16}}$ System at 30° C.					
...	0.245	0.755	...	0.930	0.070
0.297	...	0.703	0.925	...	0.075
0.142	0.179	0.679	0.395	0.530	0.075
0.119	0.200	0.681	0.333	0.593	0.074
0.080	0.236	0.683	0.227	0.700	0.073
0.046	0.262	0.692	0.140	0.784	0.076
0.280	0.043	0.677	0.775	0.146	0.079
0.220	0.096	0.684	0.619	0.304	0.077
0.142	0.176	0.682	0.400	0.528	0.072
$\underset{1}{C_6H_5CH_3}$–$\underset{2}{C_6H_{11}CH_3}$–$\underset{3}{C_7F_{15}COOCH_3}$ System at 25° C.					
...	0.782	0.218	...	0.096	0.904
0.025	0.727	0.248	0.005	0.111	0.883
0.052	0.685	0.263	0.010	0.116	0.875
0.081	0.619	0.300	0.019	0.118	0.864
0.106	0.551	0.343	0.031	0.131	0.838
0.146	0.427	0.427	0.060	0.162	0.778
$\underset{1}{C_6H_5CH_3}$–$\underset{2}{C_6H_{11}CH_3}$–$\underset{3}{C_7F_{15}COOCH_3}$ System at 10° C.					
...	0.950	0.050	...	0.055	0.945
0.286	0.534	0.180	0.053	0.077	0.870
0.371	0.346	0.283	0.128	0.092	0.780
0.401	0.235	0.364	0.196	0.094	0.710
0.415	0.233	0.352	0.192	0.091	0.717
0.242	0.606	0.152	0.024	0.076	0.900
0.131	0.755	0.112	0.017	0.077	0.906
0.242	0.596	0.162	0.040	0.082	0.878
0.402	0.218	0.374	0.266	0.101	0.673

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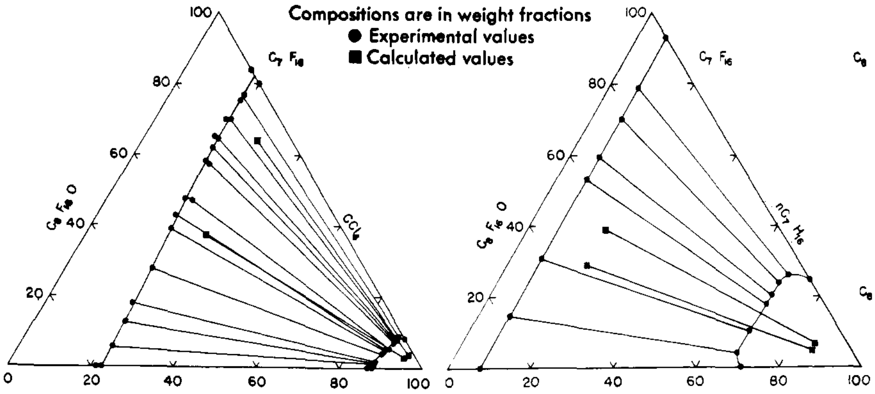

Figure 1. Phase diagrams at 30° C.

Left: $C_7F_{16} - C_8F_{16}O - CCl_4$
Right: $C_7F_{16} - C_8F_{16}O - n\text{-}C_7H_{16}$

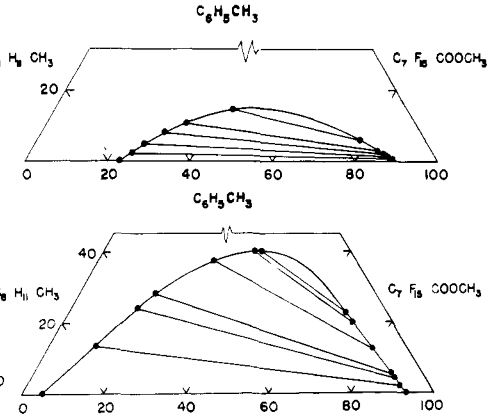

Figure 2. Phase diagrams

Bottom: $C_6H_5CH_4$–$C_6H_{11}CH_3$–$C_7F_{15}COOCH_3$ at 10° C.
Top: $C_6H_5CH_3$–$C_6H_{11}CH_3$–$C_7F_{15}COOCH_3$ at 25° C.

A column containing the ethylester of a Kel-F acid $[Cl(CF_2CFCl)_3CF_2COOC_2H_5]$ (5) as the partitioning liquid was used for analyses in the sytems containing perfluoroheptane and perfluorocyclic oxide. A mixture of Dow Corning Silicone DC550 and stearic acid was used as a partitioning liquid for the analyses in the system containing methyl perfluoro-octanoate.

RESULTS

The tie line data are tabulated in Table I and plotted on triangular coordinates (Figures 1 and 2). The data were also used to calculate the solvent selectivity, β, as defined below.

$$\beta = \frac{W_1}{W_1'} \times \frac{W_2'}{W_2} = \frac{x_1}{x_1'} \times \frac{x_2'}{x_2} = \frac{\gamma_1'}{\gamma_1} \times \frac{\gamma_2}{\gamma_2'} \qquad (1)$$

This term was first introduced by Varteressian and Fenske (6) and is analogous to the relative volatility used in distillation. It is a measure of the ease with which a binary mixture can be separated by solvent extraction with a given solvent. Values of the selectivity in the systems reported here varied only slightly with composition and therefore only the average values are listed in Table II.

From Table II it is obvious that neither carbon tetrachloride nor n-heptane is a very good selective solvent for the fluorocarbon mixture. The fact that methyl perfluoro-octanoate shows poor selectivity for the hydrocarbon mixture is surprising, because this compound was found to be completely miscible with toluene down to 6° C. while forming two liquid phases with methylcyclohexane up to 45° C. (4).

Calculation of Activities in Ternary Systems. In the Scatchard-Hildebrand theory of solutions (2) the activity coefficients in a binary mixture are given as

$$\begin{aligned} RT \ln \gamma_1 &= V_1(\delta_1 - \delta_2)^2 \Phi_2^2 \\ RT \ln \gamma_2 &= V_2(\delta_1 - \delta_2)^2 \Phi_1^2 \end{aligned} \qquad (2)$$

The theory has been extended to ternary mixtures and yields the following expressions for activity coefficients:

$$\begin{aligned} RT \ln \gamma_1 &= V_1[(\delta_1 - \delta_2)\,\Phi_2 + (\delta_1 - \delta_3)\,\Phi_3]^2 \\ RT \ln \gamma_2 &= V_2[(\delta_2 - \delta_1)\,\Phi_1 + (\delta_2 - \delta_3)\,\Phi_3]^2 \\ RT \ln \gamma_3 &= V_3[(\delta_3 - \delta_1)\,\Phi_1 + (\delta_3 - \delta_2)\,\Phi_2]^2 \end{aligned} \qquad (3)$$

Equations 3 can be used to calculate activity coefficients in the two conjugate phases from the tie line data. If these calculated activity coefficients are correct, they must satisfy the equilibrium conditions that the activity of each component be equal in both phases.

$$\begin{aligned} x_1\gamma_1 &= x_1'\gamma_1' \\ x_2\gamma_2 &= x_2'\gamma_2' \\ x_3\gamma_3 &= x_3'\gamma_3' \end{aligned} \qquad (4)$$

Activities in the conjugate phases were calculated for the two systems containing perfluoroheptane and perfluorocyclic oxide by means of Equations 3 using the experimental tie line data and molar volumes and solubility parameters evaluated at 30° C. Conjugate activities calculated in this manner did not satisfy the conditions of Equations 4. However, when effective solubility parameters were employed in Equations 3 along with the experimental tie line data, the calculated conjugate activities satisfied the conditions of Equations 4. A tabulation of conjugate activities calculated from Equations 3 using effective solubility parameters is presented in Table III.

Table II. Solvent Selectivities

System[a]	Temp., ° C.	Av. β
$C_8F_{16}O$-C_7F_{16}-CCl_4	30	1.20
$C_8F_{16}O$-C_7F_{16}-n-C_7H_{16}	30	1.09
$C_6H_5CH_3$-$C_6H_{11}CH_3$-$C_7F_{15}COOCH_5$	25	1.16
$C_6H_5CH_3$-$C_6H_{11}CH_3$-$C_7F_{15}COOCH_3$	10	1.16

[a] First listed component is identified as component one. Third listed component is the solvent.

Table III. Conjugate Activities Calculated From Equations 3 With Effective δ ' s

a_1	a_1'	a_2	a_2'	a_3	a_3'
$C_8F_{16}O$-C_7F_{16}-CCl_4 System at 30° C. 1 2 3					
0.19	0.16	0.58	0.57	0.97	0.96
0.36	0.32	0.40	0.36	0.97	0.96
0.62	0.57	0.13	0.13	0.97	0.99
0.58	0.53	0.17	0.18	0.97	0.96
0.48	0.44	0.24	0.27	0.97	0.98
0.39	0.35	0.35	0.37	0.97	0.97
0.28	0.27	0.43	0.45	0.97	0.98
$C_8F_{16}O$-C_7F_{16}-n-C_7H_{16} System at 30° C. 1 2 3					
0.39	0.33	0.55	0.50	0.94	0.95
0.33	0.28	0.61	0.55	0.94	0.94
0.22	0.19	0.72	0.64	0.94	0.95
0.12	0.12	0.81	0.71	0.94	0.96
0.73	0.68	0.14	0.14	0.94	0.97
0.63	0.53	0.31	0.29	0.94	0.96
0.39	0.34	0.55	0.54	0.94	0.95

Effective solubility parameters were evaluated from reported binary solubility data (*4*) by substituting Equations 2 in Equations 4. Two empirical values of $(\delta_1 - \delta_2)$ are obtained for each binary system by this procedure. The difference between these two $(\delta_1 - \delta_2)$ terms was found to be small; therefore average values were used for substitution in Equations 3. The solubility parameter difference terms for two binary systems are sufficient for the evaluation of all difference terms required in Equations 3 because of the following relation:

$$(\delta_1 - \delta_3) - (\delta_2 - \delta_3) = (\delta_1 - \delta_2) \tag{5}$$

A comparison of effective $(\delta_1 - \delta_2)$ values with those calculated from pure component physical properties is shown in Table IV.

Table IV. Comparison of δ Difference at 30° C.

	δ Difference	
System	Pure compounds	Solubility
C_7F_{16} – *n*-C_7H_{16}	1.46	2.87
$C_8F_{16}O$ – *n*-C_7H_{16}	1.23	2.78
C_7F_{16} – CCl_4	2.53	3.10
$C_8F_{16}O$ – CCl_4	2.30	2.94

Estimation of Solvent Selectivity. The conditions specified by Equations 4 are not sufficient to prove the validity of the activity coefficients calculated from Equations 3, because there is an infinite number of pairs of activity coefficients which will satisfy these equations. A further test of these equations would involve a comparison of experimental tie line data with tie line data calculated by means of Equations 3 with effective solubility parameters. Two such calculated tie lines were determined for both of the systems containing perfluoroheptane and perfluorocyclic oxide using a calculation procedure described by Black (*1*). These tie lines are shown in Figure 1. Although only fair agreement was obtained between the calculated and experimental tie lines, solvent selectivities evaluated from the calculated tie line data were in excellent agreement with experimental values. A comparison of these solvent selectivities is given in Table V. Tie lines were not calculated for the system toluene-methylcyclohexane–methyl perfluoro-octanoate, because complete binary solubility data were not available.

Table V. Comparison of Calculated and Experimental Solvent Selectivities

	Solvent Selectivity	
System	Exptl.	Calcd.
C_7F_{16}– $C_8F_{16}O$ – CCl_4	1.20	1.19 1.22
C_7F_{16} – $C_8F_{16}O$ – *n*-C_7H_{16}	1.09	1.04 1.05

A possible explanation of the fact that calculated solvent selectivities are correct, while calculated tie lines are incorrect, follows from an examination of Equation 1. The solvent selectivity can be expressed as a ratio of activity coefficients with the result that while individual activity coefficients are incorrect their ratio can have the correct value. Satisfaction of Equations 4 only verifies the activity coefficient ratios.

In taking the ratio of activity coefficients it is possible that errors in the expressions for individual activity coefficients will cancel. To illustrate this possibility, consider the alteration of Equations 3 to account for the effect of a disparity in molar volumes upon the entropy of mixing.

$$RT \ln \gamma_1 = V_1[(\delta_1 - \delta_2)\Phi_2 + (\delta_1 - \delta_3)\Phi_3]^2 + RT\left[\Phi_2\left(1 - \frac{V_1}{V_2}\right) + \Phi_3\left(1 - \frac{V_1}{V_3}\right) + \ln \frac{\Phi_1}{x_1}\right]$$

$$RT \ln \gamma_2 = V_2[(\delta_2 - \delta_1)\Phi_1 + (\delta_2 - \delta_3)\Phi_3]^2 + RT\left[\Phi_1\left(1 - \frac{V_2}{V_1}\right) + \Phi_3\left(1 - \frac{V_2}{V_3}\right) + \ln \frac{\Phi_2}{x_2}\right]$$

$$RT \ln \gamma_3 = V_3[(\delta_3 - \delta_1)\Phi_1 + (\delta_3 - \delta_2)\Phi_2]^2 + RT\left[\Phi_1\left(1 - \frac{V_3}{V_1}\right) + \Phi_2\left(1 - \frac{V_3}{V_2}\right) + \ln \frac{\Phi_3}{x_3}\right] \tag{3a}$$

In each of the above equations the second bracketed term represents the entropy correction for molar volume disparity as given by Hildebrand and Scott (*3*). Substitution of either Equations 3 or Equations 3a in Equation 1 written in logarithmic form results in exactly the same expression. Although Equations 3 and 3a would yield different values for individual activity coefficients, they would predict identical values for solvent selectivity.

DISCUSSION

Van Laar equations are similar in form to the Scatchard-Hildebrand equations and may be considered empirical versions of these theoretical expressions. The use of effective solubility parameters is equivalent to empirically determining one constant for each binary system and results in semitheoretical expressions. These expressions retain the volume fraction as the composition variable and are not equivalent to the completely empirical Van Laar equations which involve the determination of two empirical constants for each binary system.

The solvent selectivity provides a good criterion for evaluation of extraction solvents and appears to be relatively insensitive to the inadequacies of activity coefficient equations. For these reasons the solvent selectivity should be employed when ternary liquid solubility relations are to be predicted from binary data.

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NOMENCLATURE

a = activity
V = molar volume of liquid
W = weight fraction
x = mole fraction
β = solvent selectivity
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, neglecting volume change on mixing
Superscripts refer to phases
Subscripts refer to components

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