Journal of Fluorine Chemistry, 5 (1975) 359 - 369

Received: November 5, 1974

FLUOROCOMPOUNDS AS ANTISOLVENTS IN HYDROCARBONS SEPARATION (+)

IRENEO KIKIC, PAOLO ALESSI

Istituto di Chimica Applicata, Università degli Studi di Trieste, Trieste (Italy)

SUMMARY

The behaviour of perfluorotributylamine (FC43) with respect to hydrocarbons is investigated, and a comparison is made with perfluorocyclic oxide. The results obtained suggest the use of these fluorocompounds, especially of FC75, as antisolvents, in conjunction with a polar solvent, in the liquid-liquid extraction of hydrocarbons, particularly for the separation of aromatics from cycloparaffins.

INTRODUCTION

Because of the ever increasing sophistication required in the separation processes, efforts are constantly being made to improve the efficiency of separation. It can so happen that separation by liquid-liquid extraction is no more sufficient and the addition of suitable antisolvents becomes necessary.

In general, antisolvents tend to increase the selectivity of pure polar solvent and consequently to decrease the solubility of the solutes in the same solvent. The selectivity of the mixture of the two solvents is intermediate between those of the two pure solvents. Water, for example, is a solvent employed as antisolvent: its high selectivity with regard to hydrocarbon compounds is depressed by the selectivity of the polar sol-

---

(+) Paper presented at the 5th European Symposium on Fluorine Chemistry, Aviemore. Scotland, 16-20 September 1974.

vent, which, on the other hand, provides a sufficient solubility. In these cases the selectivities of the solvent and of the antisolvent act in the same direction, i.e., towards the same solute.

When, viceversa, the selectivity of the antisolvent is "negative", or contrary to that of the polar solvent, in principle the total separation factor should be increased, thereby making the separation easier.

It is for this reason that we have studied fluorocarbons [1] containing heteroatoms (e.g. nitrogen or oxygen) in their molecules. Fluorocompounds are commonly used in industry as inert media for organic chemical reactions. Recently [2] [3], however, the particular property of having "negative" selectivity (in comparison with that of the polar solvents) was found in one of these compounds, perfluorocyclic oxide (FC75). This substance, immiscible with water and with polar solvents, completely miscible with pentane and pentene and only partially miscible with other hydrocarbons, always shows a selectivity for the "more" paraffinic of the hydrocarbons to be separated.

In this paper we have studied the behaviour of another of these fluorocompounds, perfluorotributylamine (FC43), to see whether their inertness is real or only apparent, in which case they might be suitable for use as antisolvents in the separation of hydrocarbons.

So we have determined the liquid-liquid equilibrium data of some ternary systems composed of FC43 and various hydrocarbon couples. From the correlation of these data and a comparison with those obtained with FC75 [4] it appears that these solvents might be employed, in conjuction with a polar solvent, for the extraction of aromatic from paraffinic hydrocarbons.

EXPERIMENTAL

The hydrocarbons examined were of purity higher than 99.9 mol % (Fluka). The perfluorotributylamine, FC43 (3M Minnesota), did not contain any detectable impurity.

Liquid-liquid equilibrium was established in test tubes (10 ml), kept at constant temperature (25°C), closed at the two ends by pierceable gaskets to allow the sampling of the two liq uid phases with a syringe for GLC analysis.

The mutual solubilities of the binary mixtures were determined both by GLC and by the cloud point method.

RESULTS AND DISCUSSION

Tables 1-8 report the equilibrium compositions at 25°C of the two liquid phases for the ternary systems n.hexane-1.hexene--FC43, n.heptane-1.heptene-FC43, n.hexane-cyclohexane-FC43, n.

TABLE 1

Equilibrium composition of the two liquid phases at 25°C for the system n.hexane-1.hexene-FC43

$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
-	0.1287	0.8713	-	0.9901	0.0099
0.0210	0.1195	0.8595	0.1410	0.8501	0.0099
0.0600	0.1050	0.8350	0.3520	0.6380	0.0100
0.1330	0.0750	0.7920	0.6260	0.3610	0.0130
0.2140	0.0220	0.7640	0.8945	0.0915	0.0140
0.2835	-	0.7165	0.9812	-	0.0188

TABLE 2

Equilibrium composition of the two liquid phases at 25°C for the system n.heptane-1.heptene-FC43

$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
-	0.0987	0.9013	-	0.9993	0.0007
0.0150	0.0940	0.8910	0.1410	0.8500	0.0090
0.0470	0.0830	0.8700	0.3500	0.6400	0.0100
0.0900	0.0570	0.8530	0.6270	0.3600	0.0130
0.1550	0.0174	0.8276	0.8950	0.0900	0.0150
0.1747	-	0.8253	0.9949	-	0.0051

.heptane-methylcyclohexane-FC43, n.hexane-benzene-FC43, n.heptane-toluene-FC43, cyclohexane-benzene-FC43 and methylcyclohexane-toluene-FC43.

The distribution isotherms and the tie lines for the system n.heptane-toluene-FC43 are reported as an example in Fig. 1.

TABLE 3

Equilibrium composition of the two liquid phases at 25°C for the system n.hexane-cyclohexane-FC43

$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
-	0.2205	0.7795	-	0.9985	0.0015
0.0491	0.1555	0.7954	0.2043	0.7893	0.0064
0.0831	0.1327	0.7842	0.3463	0.6439	0.0098
0.1216	0.1049	0.7735	0.5012	0.4841	0.0147
0.1562	0.0788	0.7650	0.6346	0.3496	0.0158
0.1940	0.0490	0.7570	0.7706	0.2114	0.0180
0.2835	-	0.7165	0.9812	-	0.0188

TABLE 4

Equilibrium composition of the two liquid phases at 25°C for the system n.heptane-methylcyclohexane-FC43

$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
-	0.1928	0.8072	-	0.9964	0.0036
0.0445	0.1475	0.8080	0.2068	0.7893	0.0049
0.0703	0.1244	0.8053	0.3506	0.6439	0.0055
0.1004	0.0970	0.8026	0.5099	0.4841	0.0060
0.1261	0.0690	0.8049	0.6453	0.3476	0.0071
0.1526	0.0425	0.8049	0.7847	0.2067	0.0086
0.1747	-	0.8253	0.9949	-	0.0051

For the eight systems studied the distribution isotherms are similar in that they all consist of two partially miscible pairs and one miscible pair. The experimental results have been correlated by means of the NRTL equation [5] (see Appendix), and the parameters obtained for all the binary systems are reported in Table 9. With these parameters we have also calculated the equilibrium compositions of the two liquid phases: the

TABLE 5

Equilibrium composition of the two liquid phases at 25°C for the system n.hexane-benzene-FC43

$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
-	0.1677	0.8323	-	0.9996	0.0004
0.0430	0.1620	0.7950	0.1553	0.8440	0.0007
0.0700	0.1470	0.7830	0.2846	0.7128	0.0026
0.0975	0.1280	0.7745	0.4280	0.5683	0.0037
0.1270	0.1100	0.7630	0.5734	0.4203	0.0063
0.1905	0.0910	0.7185	0.7463	0.2427	0.0100
0.2835	-	0.7165	0.9812	-	0.0188

TABLE 6

Equilibrium composition of the two liquid phases at 25°C for the system n.heptane-toluene-FC43

$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
-	0.1238	0.8762	-	0.9997	0.0003
0.0140	0.1190	0.8670	0.0483	0.9510	0.0007
0.0949	0.0761	0.8290	0.4813	0.5154	0.0033
0.1471	0.0363	0.8166	0.7940	0.1996	0.0064
0.1719	0.0119	0.8162	0.9316	0.0604	0.0080
0.1747	-	0.8253	0.9949	-	0.0051

differences between experimental and calculated values are less than 2%, on the average about 1%.

As concerns the systems hydrocarbon-FC43 it can be seen that the C_{Hy-FC} (C_{ij}) parameter is always greater that the cor-

TABLE 7

Equilibrium composition of the two liquid phases at 25°C for the system cyclohexane-benzene-FC43

$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
-	0.1677	0.8323	-	0.9996	0.0004
0.0150	0.1670	0.8180	0.0430	0.9568	0.0002
0.0440	0.1490	0.8070	0.1403	0.8593	0.0004
0.0775	0.1235	0.7990	0.3026	0.6968	0.0006
0.1070	0.1000	0.7930	0.4728	0.5262	0.0010
0.1435	0.0700	0.7865	0.7180	0.2808	0.0012
0.1730	0.0450	0.7820	0.8315	0.1672	0.0013
0.2000	0.0190	0.7810	0.9431	0.0556	0.0013
0.2205	-	0.7795	0.9985	-	0.0015

TABLE 8

Equilibrium composition of the two liquid phases at 25°C for the system methylcyclohexane-toluene-FC43

$x_1^{(1)}$	$x_2^{(1)}$	$x_3^{(1)}$	$x_1^{(2)}$	$x_2^{(2)}$	$x_3^{(2)}$
-	0.1238	0.8762	-	0.9997	0.0003
0.0101	0.1219	0.8680	0.0425	0.9568	0.0007
0.0315	0.1117	0.8568	0.1398	0.8593	0.0009
0.0631	0.0945	0.8424	0.3019	0.6968	0.0013
0.0930	0.0757	0.8313	0.4721	0.5262	0.0017
0.1344	0.0449	0.8207	0.7166	0.2808	0.0026
0.1742	0.0099	0.8159	0.9409	0.0556	0.0035
0.1928	-	0.8072	0.9964	-	0.0036

responding C_{FC-Hy} (C_{ji}) parameter, and that the C_{Hy-FC} parameters increase from the systems of FC43 with paraffins and olefins, through those with cycloparaffins and with aromatics; the last ones show the highest values. This results also reflects the great asymmetry of the mutual solubilities hydrocarbon-FC43; in effect, while the solubilities of hydrocarbons in

TABLE 9

Parameters of NRTL equation

System i	j	C_{ij}	C_{ji}	α_{ji}
n.hexane	-1.hexene	31.0	31.0	0.300
n.heptane	-1.heptene	25.0	20.0	0.300
n.hexane	-cyclohexane	- 473.0	636.0	0.200
n.heptane	-methylcyclohexane	- 250.0	370.0	0.200
n.hexane	-benzene	- 313.6	854.0	0.200
n.heptane	-toluene	- 177.0	511.4	0.200
cyclohexane	-benzene	- 76.0	413.8	0.200
methylcyclohexane	-toluene	- 45.0	280.0	0.200
n.hexane	-FC43	2000.0	100.0	0.200
1.hexene	-FC43	2800.0	250.0	0.200
n.heptane	-FC43	2695.9	110.0	0.200
1.heptene	-FC43	2582.4	372.2	0.200
benzene	-FC43	4840.0	250.0	0.200
toluene	-FC43	4044.2	358.1	0.200
cyclohexane	-FC43	3300.0	90.0	0.200
methylcyclohexane	-FC43	3187.4	94.8	0.200
n.hexane	-FC75	1450.0	305.0	0.205
1.hexene	-FC75	1363.0	400.0	0.204
n.heptane	-FC75	1575.0	320.0	0.206
1.heptene	-FC75	1410.0	420.0	0.205
benzene	-FC75	2556.0	371.8	0.200
toluene	-FC75	2475.0	520.0	0.206
cyclohexane	-FC75	2174.0	250.0	0.200
methylcyclohexane	-FC75	2156.6	314.0	0.200

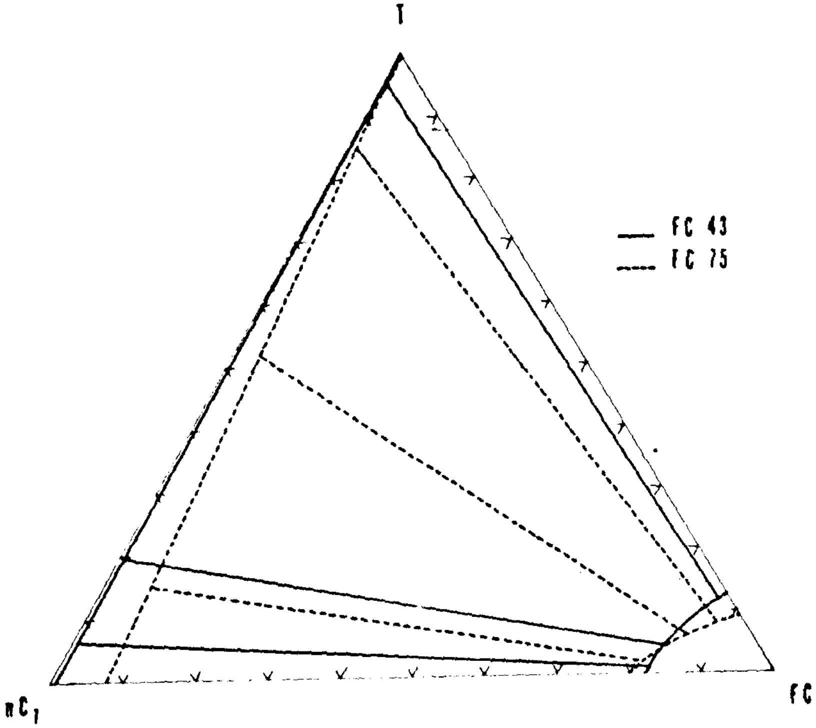

FIGURE 1 - Miscibility isotherms and experimental tie lines at 25°C for the systems n.heptane-toluene-FC43 and n.heptane-toluene-FC75.

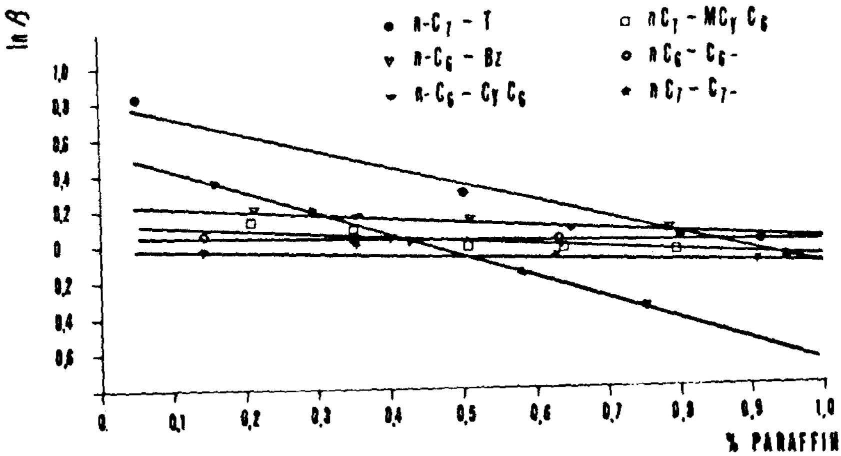

FIGURE 2 - Selectivity variation of FC43 with the concentration of the paraffin.

FC43 are considerably high (about 20% for benzene and toluene), those of the fluorocompound in hydrocarbons are very small.

In Fig. 2 the selectivity of FC43 calculated from the equilibrium composition data of the two liquid phases is reported as a function of the concentration of the paraffinic hydrocarbons expressed as

$$\frac{x_1^{(2)}}{x_1^{(2)} + x_2^{(2)}}$$

It can be observed that in the paraffin-olefin and paraffin-cycloparaffin systems the selectivity is almost independent of composition and close to unity, while in the paraffin-aromatic systems it is slightly greater and varies appreciably with composition. As an example, the selectivity values for a ratio hydrocarbon A/hydrocarbon B = 1 are reported in Table 10.

TABLE 10

Comparison between the selectivities of FC75 and FC43 (ratio hydrocarbon A/ hydrocarbon B = 1)

System		FC43		FC75	
		$\beta_{0.5}$	$\ln \beta_{0.5}$	$\beta_{0.5}$	$\ln \beta_{0.5}$
n.hexane	-1.hexene	1.03	0.030	1.02	0.120
n.heptane	-1.heptene	0.93	- 0.073	1.07	0.068
n.hexane	-cyclohexane	1.14	0.131	1.17	0.157
n.heptane	-methylcyclohexane	1.03	0.030	1.22	0.199
n.hexane	-benzene	0.93	- 0.073	1.41	0.344
n.heptane	-toluene	1.40	0.336	1.60	0.470
cyclohexane	-benzene	1.12	0.113	1.26	0.231
methylcyclohexane	-toluene	1.32	0.278	1.41	0.344

COMPARISON BETWEEN FC75 AND FC43

The presence of a heteroatom, namely N and O in FC43 and in FC75 respectively, and, above all, the cyclic structure of the latter compound make-the properties of the two fluorocompounds remarkably different.

Mutual solubility with hydrocarbons - Table 11 shows that the mutual solubilities of hydrocarbons with FC43 and FC75 are substantially different; consequently, the behaviour of the systems hydrocarbon A-hydrocarbon B-FC75 differs from that of the systems hydrocarbon A-hydrocarbon B-FC43.

As an example, we can consider the systems n.heptane-toluene-FC75 and n.heptane-toluene-FC43: while the solubilities of the hydrocarbons in FC43 and in FC75 are comparable, the solubilities of FC43 in the hydrocarbons are always lower than those of FC75 (Table 11); this is also clear from Fig. 1, where the branches representing the mixtures rich in the fluorocompound are also comparable, while those representing the mixtures rich in the hydrocarbons appear different.

NRTL parameters - The difference ($C_{Hy-FC}-C_{FC-Hy}$) is greater for the systems hydrocarbon-FC43 than for the systems hydrocarbon-FC75; in particular, all the C_{ij} parameters in FC43 are about 1.5 times as much as those in FC75.

TABLE 11

Mutual solubilities between hydrocarbons and fluorocompounds (FC43 and FC75)

	Solubility (mole %)			
	hydrocarbon in FC43	FC43 in hydrocarbon	hydrocarbon in FC75	FC75 in hydrocarbon
n.hexane	0.2835	0.0188	0.2580	0.1095
1.hexene	0.1287	0.0099	0.2630	0.0900
n.heptane	0.1747	0.0051	0.2007	0.0741
1.heptene	0.0987	0.0007	0.2115	0.0702
cyclohexane	0.2205	0.0015	0.1910	0.0196
methylcyclohexane	0.1928	0.0036	0.1830	0.0312
benzene	0.1677	0.0004	0.1080	0.0055
toluene	0.1238	0.0003	0.0867	0.0050
	temperature: 25°C		temperature: 23°C	

Selectivity of fluorocarbons - Table 10 presents the selectivities of FC75 and of FC43. The values relative to FC43 are always lower than those relative to FC75, so it can be stated that the properties of an inert material are more marked in FC43, whose selectivity is practically equal to unity with regard not only to paraffin-olefin couples (as was the case for FC75), but also to paraffin-cycloparaffin couples. Even in this case the selectivity is towards the more "paraffinic" hydrocarbon: paraffin in paraffin-olefin, paraffin-cycloparaffin and paraffin-aromatic systems, cycloparaffin in cycloparaffin-aromatic systems.

ACKNOWLEDGEMENTS

This work has been supported by the National Research Council (C.N.R.), Centro di Studi di Chimica Analitica Strumentale, Bari.

REFERENCES

1 I. Kikic, P. Alessi, Gazz. Chim. Ital., 103 (1973) 699.

2 I. Kikic, P. Alessi, Riv. Comb., 28 (1974) 11.

3 I. Kikic, P. Alessi, Proc. "International Solvent Extraction Conference" (Lyon 1974), Soc. of Chem. Ind. (London).

4 I. Kikic, P. Alessi, Riv. Comb., 28 (1974) 85.

5 H. Renon, L. Asselineau, G. Cohen, C. Raimbault, "Calcul sur ordinateur des équilibres liquide-vapeur et liquide-liquide", Technip, Paris 1971.