Estimation of hydrocarbon solubilities in hydrofluorocarbons

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Abstract

A new solubility parameter, SP, for hydrofluorocarbons (HFCs) has been developed ($SP = 1.175$ $\ln(np) + 0.025H - 0.063F - 0.028\alpha - 0.018\beta$ where np depends on the molar volume and the molar refractivity; H and F are the number of hydrogens and fluorines, respectively, in the molecule; and α and β are the respective numbers of $H-C-F$ and $H-C-C-F$ connections). Values of SP have been used to predict if an HFC would be a good solvent for various hydrocarbons at 25 °C. Within an isomeric HFC family, the individual HFCs having the greatest solvency for hydrocarbons were those having the maximum separation of fluorines from hydrogens. Hildebrand solubility parameters, δ, are compared with the semi-empirical SP values.

Syntheses for 10 new compounds are given: 3,3,4,4,5,5,6,6,7,7-decafluorononane, 1,1,1,2-tetrafluoro-2-(trifluoromethyl)-3-methylbutane, 1,1,1,2,2-pentafluoro-3-methylbutane, 1,1,1,2,2,3,3,4,4-nonafluoro-5-methylhexane, 1,1,1,2,2,3,3,4,4-nonafluoroheptane, 1,1,1,2-tetrafluoro-2-(trifluoromethyl)butane, 1,1,1-trifluoro-3-(trifluoromethyl)butane, 1,1,1,2,2,3,3,5-octafluorohexane, 1,1,1,2,2-pentahydroperfluorooctane and 1,1,1,2,2-pentahydroperfluorodecane.

Introduction

Chlorocarbons, chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) are widely used in a variety of cleaning applications. For this purpose, they possess two highly desirable properties, namely, non-flammability and the ability to dissolve a variety of soils. Since these materials must be replaced because of environmental concerns, the industry has examined perfluorocarbons (F-alkanes† or FCs) and especially HFCs as potential alternatives. Although nonflammability is assured for HFCs with high enough fluorine content, it is far less certain that nonflammable HFCs or F-alkanes will possess adequate solvency for typical cleaning applications.

In this paper, we examine the solvency of a variety of F-alkanes and HFCs, using alkanes as model "soils". In theory, it should be possible to use differences in solubility parameters to make qualitative miscibility predictions [1]. However, mixtures of F-alkanes and alkanes display marked deviations from ideality [2]. Although liquid F-alkanes, like alkanes, are non-polar, the old adage, "like dissolves like" does not always hold for FC–alkane mixtures. Consequently, predictions based on differences in solubility parameters can be

misleading [3]*. Scott [5] evaluated various theories to explain the anomalous behavior of these solutions, but concluded that no single theory could adequately explain all the experimental observations. In view of this, it is important and timely to develop more suitable solubility parameters to predict HFC–hydrocarbon miscibility.

Experimental

Hydrocarbons used in the solubility tests were dry, reagent grade (at least 99% n-isomer) materials. Mineral oil refers to light paraffinic oil purchased from Fisher (maximum Saybolt viscosity 158). Commercial F-alkanes were generally 85% n-isomer.

Solubilities were determined by adding the solute via a syringe in 0.02 ml or greater increments to 1–5 ml of solvent held at 25 °C.

Commercial compounds (Table 1 numbering) **15, 24, 27, 28, 31, 34** and **35** were used as received. Compound **22** was a gift from S. Ferguson and compound **14** from H. Magid. Other HFCs were synthesized and purified to a minimum of 95% (GC) purity for solubility determinations. HFCs prepared by literature methods were **6** [6], **7** [7], **12** [8], **25** [9] and **32** [10]. The synthesis of compounds **18, 21, 30, 33** and **36–39** will be reported separately.

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†For the sake of brevity, the term F-alkane will be used in place of perfluoroalkane.

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*This problem is not limited to FC–alkane pairs. For a recent example, see ref. 4.

TABLE 1. Solubility data for hydrocarbons (vol.%)[a] in HFCs and FCs at 25 °C

Solvent	Solute						
	Mineral oil	$C_{16}H_{34}$	$C_{12}H_{26}$	$C_{10}H_{22}$	C_8H_{18}	C_7H_{16}	C_6H_{14}
1 $CF_3CF_2(CH_2)_3CH_3$	M[b]						
2 $(CH_3CH_2CF_2CF_2)_2CF_2$	13	M					
3 $(CF_3)_2CFCH(CH_3)_2$	6						
4 $CF_3CF_2CH(CH_3)_2$	15						
5 $CF_3(CF_2)_2CH(CH_3)_2$	6	M					
6 $CH_3CF_2CF_2CH_2CH_3$	M						
7 $CF_3CF_2CF_2CH_2CH_2CH_3$	7	M					
8 $CF_3(CF_2)_3CH(CH_3)_2$	2						
9 $CF_3(CF_2)_3CH_2CH_2CH_3$	4						
10 $(CF_3)_2CFCH_2CH_3$	Insol[c]	M					
11 $CF_3CF_2CF_2CH_2CH_3$	Insol	33[d]	M				
12 $CH_3CF_2CH_2CF_2CH_3$	Insol	9	M				
13 $CF_3(CF_2)_3CH_2CH_3$		11	M				
14 1,1,2,2-Tetrafluorocyclobutane		9	M				
15 $FCH_2CH_2CH_2F$		20	M	M			
16 $CF_3(CH_3)CHCH_2CF_3$	Insol	15	M				
17 $CF_3(CF_2)_2CH_2CHFCH_3$		6	19				
18 $CH_3CF_2CF_2CF_2CH_3$		7	M				
19 $CF_3(CF_2)_5CH_2CH_3$		4	17	M			
20 $CF_3(CF_2)_7CH_2CH_3$				17	M		
21 $HCF_2CF_2CF_2CF_2CH_3$				18	M		
22 $CF_3CH_2CF_2CH_3$			9	13			
23 $CF_3CH_2CH_2CF_3$			9	29			
24 *F*-Dimethylcyclobutane					15	M	
25 CH_2FCH_2F					13	19	30
26 $HCF_2CF_2CF_2CF_2CH_2F$					12	22	
27 *F*-Methylcyclohexane					14	32	M
28 *F*-Dimethylcyclohexane					10	17	M
29 $CF_3CH_2CH(CF_3)_2$				11	M		
30 HCF_2CHFCF_2H					7		21
31 *F*-Pentane					12	22	
32 $CF_3CH_2CF_2CH_2CF_3$			2	4	10		
33 $CF_3(CF_2)_4CF_2H$					17	M	
34 *F*-hexane					9	17	M
35 *F*-Octane					5	11	23
36 c-1,2-Dihydrohexafluorocyclobutane			2	9			
37 t-1,2-Dihydrohexafluorocyclobutane			7	25			
38 c-1,2-Dihydrooctafluorocyclopentane				6			
39 t-1,2-Dihydrooctafluorocyclopentane				27	M		

[a]Vol.% = vol. solute/(vol. solvent + vol. solute).
[b]M = miscible (at least 50 vol.%).
[c]Insol = <2 vol.%.
[d]Miscible at 27 °C.

^{1}H NMR spectra were recorded in $CDCl_3$ and ^{19}F NMR spectra [upfield (negative values) from internal $CFCl_3$] in the same solvent using a Varian EM-390 spectrometer.

1,1,1,2,2-Pentafluorohexane $CF_3CF_2CH_2CH_2CH_2CH_3$ (1)

To a solution of methyl pentafluoropropionate (75 g, 0.42 mol) in anhydrous ether (400 ml) at 0 °C was added propyl magnesium bromide (1.05 mol in 900 ml ether) and the solution stirred for 1 h. The reaction was quenched with 10% H_2SO_4 (300 ml), washed twice with ether (100 nml), dried ($MgSO_4$) and distilled to give 54 g (67% yield) of 1,1,1,2,2-pentafluorohexan-3-ol, b.p. 108–111 °C. ^{1}H NMR δ: 3.8–4.2 (m, 1H); 1.3–1.8 (m, 4H); 0.8–1.2 (m, 3H) ppm. ^{19}F NMR δ: −82.8 (d, 3F); −129 (dq, 2F) ppm.

A mixture of the above alcohol (54 g, 0.28 mol) and 50 g (0.35 mol) of P_2O_5 was heated to 200 °C for 3 h. The product (1,1,1,2,2-pentafluorohex-3-ene, 30 g, 61% yield) was recovered by vacuum evaporation into a dry-ice trap, and was used without further purification in the next step. The olefin (29 g, 0.167 mol) was hydrogenated at 25 °C under 100 atm H_2 for 18 h using

0.7 g Rh/C catalyst. The catalyst was filtered through Celite and the filtrate distilled, affording 17.6 g (61% yield) of compound 1, b.p. 61–62 °C. ^{1}H NMR δ: 1.2–2.4 (m, 6H); 0.9–1.2 (3H) ppm. ^{19}F NMR δ: −86 (s, 3F); −119 (t, 2F) ppm.

3,3,4,4,5,5,6,6,7,7-Decafluorononane $C_2H_5(CF_2)_5C_2H_5$ (2)

A solution of perfluoroglutaric acid (24 g, 0.10 mol) in 60 ml of anhydrous ether was added to ethyl magnesium bromide (200 ml of a 3 M solution in ether, 0.9 mol) at a rate sufficient to sustain vigorous reflux. After the addition was complete, the reaction was stirred for 0.5 h, and poured onto 700 g ice containing 150 ml HCl. The aqueous layer was extracted with 3×100 ml portions of ether, and the combined organic layers were washed with saturated NaHCO$_3$ (2×100 ml) and 100 ml saturated NaCl, and dried (MgSO$_4$). After removal of the solvent, the residue was distilled, yielding 18.6 g (70% yield) of 4,4,5,5,6,6-hexafluorononane-3,7-dione, b.p. 108–110 °C/6 mmHg. ^{1}H NMR δ: 1.13 (t, 6H); 2.80 (q, 4H) ppm. ^{19}F NMR δ: −121.5 (s, 4F); −125.4 (s, 2F) ppm.

A 600 ml autoclave containing 4,4,5,5,6,6-hexafluorononane-3,7-dione (31.5 g, 0.119 mol) and 120 ml of CH$_2$Cl$_2$ .was cooled to −40 °C and charged with 12 g (0.6 mol) of HF and 64 g (0.6 mol) of SF$_4$. The contents were stirred for 18 h at 60 °C, cooled to 25 °C and vented through a KOH scrubber. The contents were poured into 100 g ice and water, and the organic layer separated. After washing with water (100 ml), 2×100 ml 10% NaOH and drying (MgSO$_4$), the solvent was removed by rotary evaporation. Distillation of the residue gave 7.5 g of 2, b.p. 45–46 °C/5 mmHg. ^{1}H NMR δ: 1.08 (t, 6H, $J=7$ Hz); 2.1 (m, 4H) ppm.

1,1,1,2-Tetrafluoro-2-(trifluoromethyl)-3-methylbutane $(CF_3)_2CFCH(CH_3)_2$ (3)

A 100 ml flask was charged with 7.5 ml of 96% H$_2$SO$_4$ and 26.2 g (0.122 mol) of perfluoroisobutyric acid [11]. To the stirred slurry was added 8.5 ml (0.145 mol) of ethanol over 1 h while the temperature rose to 50 °C. The mixture was stirred and heated at 95 °C for 16 h. The volatile product (ethyl 2-(trifluoromethyl)tetrafluoropropionate, 19.8 g) was collected in a cold trap upon applying vacuum (30–40 mmHg) at 50 °C. ^{1}H NMR δ: 1.5 (t, 3H); 4.5 (q, 2H) ppm. ^{19}F NMR δ: −75.5 (6F); −183 (1F) ppm.

The Grignard reagent prepared from 5.13 g of Mg and 31.5 g of CH$_3$I in 90 ml ether was cooled to 0 °C, and 20.3 g of ethyl perfluoroisobutyrate (prepared above) in 20 ml of ether added over 2 h. The mixture was allowed to warm to room temperature and quenched with dilute H$_2$SO$_4$ at 0 °C. The aqueous phase was extracted with 6×75 ml of ether, and the combined

ether extracts washed with 3% aqueous NaHCO$_3$, dried (MgSO$_4$) and distilled to give 3,4,4,4-tetrafluoro-2-methyl-3-(trifluoromethyl)butan-2-ol contaminated with about 25% ether. The above alcohol–ether mixture was subjected to dehydration with H$_2$SO$_4$ [12] giving 2-(heptafluoroisopropyl)propene. ^{1}H NMR δ: 2.0 (s, 3H); 5.6 (s, 2H) ppm. Hydrogenation of 10 g of the olefin (5% Rh/C, 100 atm H$_2$, 25 °C, 65 h) gave 7.89 g of crude product. Two distillations afforded 98% of pure compound 3 (3.4 g), b.p. 61.5–62 °C. ^{1}H NMR δ: 1.2 (d, 6H); 2.5 (m, 1H) ppm. ^{19}F NMR δ: −74 (d, 6F); −178 (m, 1F) ppm.

1,1,1,2,2-Pentafluoro-3-methylbutane $C_2F_5CH(CH_3)_2$ (4)

2-Methyl-3,3,4,4,4-pentafluorobut-1-ene was prepared in 83% yield by conc. H$_2$SO$_4$ dehydration [12] of 2-methyl-3,3,4,4,4-pentafluorobutan-2-ol, which, in turn, was prepared in 64% yield by the action of methyl Grignard on methyl pentafluoropropionate as described by McBee et al. [13]. Compound 4 (b.p. 36–37 °C) was prepared by hydrogenation of the above olefin (64% yield) at 100 atm H$_2$ using Rh/C as the catalyst. ^{1}H NMR δ: 1.2 (d, $J=6$ Hz); 2.35 (m) ppm. ^{19}F NMR δ: −83 (s); −124 (d) ppm.

1,1,1,2,2,3,3-Heptafluoro-4-methylpentane $C_3F_7CH(CH_3)_2$ (5)

The addition of methyl heptafluorobutyrate to 2 equiv. of methyl Grignard gave 1,1,1,2,2,3,3-heptafluoro-4-methylpentan-4-ol (b.p. 108 °C) which was dehydrated with H$_2$SO$_4$ to give 2-methyl-3,3,4,4,5,5,5-heptafluoropent-1-ene (b.p. 55 °C). The olefin was hydrogenated as described for compound 4 to give compound 5, b.p. 59–61 °C. ^{1}H NMR δ: 1.2 (d); 2.45 (m) ppm.

1,1,1,2,2,3,3,4,4-Nonafluoro-5-methylhexane $C_4F_9CH(CH_3)_2$ (8)

To a solution of 2.3 ml (0.013 mol) perfluorobutyl iodide in 150 ml anhydrous ether at −78 °C was added ethyl magnesium bromide (5 ml of a 3 M solution; 0.015 mol) dropwise while keeping the temperature below −60 °C. After stirring for 0.5 h, acetone (1.1 ml, 0.015 mol) was added at a rate to keep the temperature below −65 °C. The mixture was stirred for 1 h at −78 °C, 1 h at room temperature and quenched with 10% HCl. The organic layer was washed with water, dried (MgSO$_4$) and distilled to give 2.7 g (71% yield) of 2-methyl-3,3,4,4,5,5,6,6,6-nonafluorohexan-2-ol, b.p. 125–127 °C. ^{19}F NMR δ: −83, −122, −124 and −128 ppm. This alcohol (15 g, 0.054 mol) and 17 ml of sulfuric acid were combined and heated to 120 °C while distilling off the volatile product. The distillate was washed twice with saturated NaHCO$_3$ and dried (MgSO$_4$) to give 8.12 g (57% yield) of 2-methyl-

3,3,4,4,5,5,6,6,6-nonafluorohex-1-ene. ^{1}H NMR δ: 5.5 (d, 2H); 1.9 (s, 3H) ppm. ^{19}F NMR δ: −83, −117, −125 and −128 ppm.

The above olefin was hydrogenated over 5% Rh/C (100 atm H$_2$, room temperature, 18 h), to give, after filtration of the catalyst through Celite, 9.9 g of compound **8**, b.p. 86–88 °C. ^{1}H NMR δ: 2.0–2.7 (m, 1H); 1.1 (s, 3H); 0.95 (s, 3H) ppm. ^{19}F NMR δ: −82, −121, −123 and −127 ppm.

1,1,1,2,2,3,3,4,4-Nonafluoroheptane $C_4F_9C_3H_7$ (9)

Perfluorobutyliodide (99.7 g, 0.288 mol), 65 g (1.02 mol) of activated copper and 340 ml of DMSO were stirred at 110 °C for 2 h, 25 °C for 2 h and allowed to stand unstirred for 4 h. The dark green supernatant liquid was decanted into a flask and 41 ml (57.3 g, 0.47 mol) of allyl bromide added. An immediate exothermic reaction took place. The mixture was stirred overnight and the volatile components distilled under reduced pressure. The distillate was washed with water and three equal volumes of aqueous NaOCl, and finally dried (MgSO$_4$) to give 23.7 g of 74% pure (GC) product. The crude product was hydrogenated at 100 atm H$_2$ (5% Rh/C, 25 °C) for 60 h. The catalyst was filtered and the product distilled repeatedly until 98% purity was obtained (b.p. 87 °C). ^{1}H NMR δ: 1.0 (t, 3H); 1.5–2.4 (4H) ppm. ^{19}F NMR δ: −83 (3F), −116 (2F), −126 (2F) and −128 (2F) ppm.

1,1,1,2-Tetrafluoro-2-(trifluoromethyl)butane $(CF_3)_2CFCH_2CH_3$ (10)

A 500 ml flask fitted with a mechanical stirrer, distillation column and take-off head was charged with 15 g (0.046 mol) of 4-iodo-2-trifluoromethyl-1,1,1,2-tetrafluorobutane, 28.5 g (0.45 mol) of Zn dust and 230 ml of 10% HCl. As the mixture was stirred and heated to 50 °C, 7.4 g (80% yield) of compound **10** (b.p. 37–39 °C) was collected. ^{1}H NMR δ: 2.1 (m, 2H); 1.2 (t, 3H) ppm.

1,1,1,2,2,3,3-Heptafluoropentane $C_3F_7C_2H_5$ (11)

An autoclave was charged with 25 g of 3,3,4,4,5,5,5-heptafluoropentene, 2.2 g of 0.5% Pd/Al$_2$O$_3$ and pressurized with H$_2$ to 6.8 atm. The autoclave was re-pressurized periodically to 6.8 atm until the H$_2$ uptake was complete. After filtering the catalyst, the liquid was distilled to give 15 g (63% yield) of compound **11**, b.p. 41 °C (99.8% purity). ^{1}H NMR δ: 2.1 (m), 1.1 (t) ppm. ^{19}F NMR δ: −92, −118, and −129 ppm.

1,1,1,2,2,3,3,4,4-Nonafluorohexane $C_4F_9C_2H_5$ (13)

A 600 ml autoclave was charged with 25.7 g (0.074 mol) of perfluorobutyl iodide and heated to 200 °C. Ethylene was added in three 3.4 atm increments, each followed by a moderate exotherm of 15–30 °C. The

total amount of ethylene added was 10.4 g (0.371 mol). After cooling and venting the reactor, 24 g of a pale brown material was collected. This was washed with aqueous Na$_2$S$_2$O$_3$ and NaHCO$_3$, and dried (MgSO$_4$). The resulting material was combined with 21 g from a previous run and unreacted perfluorobutyl iodide (20.8 g) was removed by distillation. The pot residue was identified as the desired CF$_3$CF$_2$CF$_2$CF$_2$CH$_2$CH$_2$I (57% yield, 97% purity) and was used in the next step without further purification. ^{19}F NMR δ: −82 (3F); −116 (2F); −125 (2F); −127 (2F) ppm.

A mixture of the above iodide (20.4 g, 0.055 mol), 36.6 g of Zn dust (0.56 mol) and 250 ml of 10% HCl was stirred mechanically and heated to 70 °C. Compound **13** (9.5 g, 70% yield) distilled out of the flask as it was formed (head temperature 60–65 °C, lit. value [14], b.p. 67 °C). ^{1}H NMR δ: 1.1 (t); 1.6–2.5 (m) ppm. ^{19}F NMR δ: −82, −118, −126 and −127 ppm.

1,1,1-Trifluoro-3-(trifluoromethyl)butane $CF_3CH_2CH(CF_3)CH_3$ (16)

3-Trifluoromethylbutanoic acid (25 g, 0.16 mol) and SF$_4$ (60 g, 0.566 mol) were allowed to react in an autoclave at 130 °C for 6 h. The autoclave was vented through a KOH scrubber and into a 0 °C cold trap to give 13.6 g (47% yield) of compound **16** (97% pure by GC, b.p. 42–43 °C). ^{1}H NMR δ: 1.07 (d, 3H, $J=6$ Hz); 1.5–2.6 (m, 3H) ppm. ^{19}F NMR δ: −66.5 (t, $J=8$ Hz); −77 (d, $J=9$ Hz) ppm.

1,1,1,2,2,3,3,5-Octafluorohexane $C_3F_7CH_2CHFCH_3$ (17)

A 600 ml autoclave was charged with 22.7 g (0.1 mol) of CF$_3$CF$_2$CF$_2$CHOHCH$_2$CH$_3$ (prepared by the same method as compound **7**) and 17 g (0.157 mol) of SF$_4$ at −78 °C. On warming to 50 °C, an exotherm occurred (to 70 °C) during the first 0.5 h, and another (to 168 °C) during the second 0.5 h. After cooling (ice bath) the mixture was stirred overnight and vented. The autoclave residue was poured into 100 ml ice–water, washed with cold dilute NaOH and dried (MgSO$_4$) to give 16 g of liquid. Distillation afforded 1.0 g [b.p. 79–80 °C (87% pure)] and 5.9 g [b.p. 80–81 °C (95.3% pure)] for a total of 6.9 g (30%). The NMR spectra were not consistent with CF$_3$CF$_2$CF$_2$CHFCH$_2$CH$_3$, but rather with the rearranged product CF$_3$CF$_2$CF$_2$CH$_2$CHFCH$_3$. The presence of a −CHFCH$_3$ moiety was indicated by the 25 Hz F−C−CH_3 coupling in the proton spectrum [δ 1.47 (dd, CH$_3$, $J=7$, 25 Hz); 2.4 (m, CH$_2$); 5.1 (d of multiplets, CHF) ppm]. In the fluorine spectrum, the CHF fluorine was observed at −173.5 ppm, which is in good agreement with the calculated [15] value of −167.7 ppm for CF$_3$CF$_2$CF$_2$CH$_2$CHFCH$_3$, but considerably different

from the calculated value for the CHF fluorine in $CF_3CF_2CF_2CHFCH_2CH_3$ (-192.5 ppm).

1,1,1,2,2-Pentahydroperfluorooctane $C_6F_{13}C_2H_5$ (19)

1,1,2-H-Perfluorooctene (25.4 g) was hydrogenated over 3.5 g of 0.5% Pd/Al_2O_3 for 1 h in a Parr hydrogenator at an initial H_2 pressure of 1.7 atm. After filtering the catalyst, 17.6 g of a clear colorless liquid (99.6% by GC) was obtained, b.p. 112–114 °C. ^1H NMR δ: 2.1 (m); 1.1 (t) ppm.

1,1,1,2,2-Pentahydroperfluorodecane $C_8F_{17}C_2H_5$ (20)

1H,1H,2H-Perfluorodecene was hydrogenated in a manner similar to that described for compound 19 to give compound 20, b.p. 150 °C. ^1H NMR δ: 1.1 (t, $J=6$ Hz); 2.1 (m) ppm.

1,1,1,4,4,4-Hexafluorobutane $CF_3CH_2CH_2CF_3$ (23)

Hexafluoro-2-butyne was hydrogenated in the gas phase at atmospheric pressure using a water jacketed column containing 15 cm^3 of 0.5% Pd on Al_2O_3 pellets to give compound 23 in 75% distilled yield, b.p. 25 °C (lit. value [16], 25 °C). ^1H NMR δ: 2.38 (m) ppm. ^{19}F NMR δ: -68.3 ppm.

1,1,2,2,3,3,4,4,5-Nonafluoropentane $H(CF_2)_4CH_2F$ (26)

A mixture consisting of 104 g of $H(CF_2)_4CH_2OH$, 88 g of tosyl chloride and 150 ml of water was stirred mechanically and heated to 50 °C. A solution of 20 g of NaOH in 80 ml water was added over 0.5 h, keeping the temperature below 65 °C. Stirring and heating were continued until the pH was neutral. The mixture was cooled and extracted with CH_2Cl_2. The organic layer was washed with 50 ml of aqueous ammonia, water and dried ($MgSO_4$). Distillation gave 115 g of 2,2,3,3,4,4,5,5-octafluoropentyl p-toluenesulfonate, b.p. 110–115 °C/0.08 mmHg (66%). The above tosylate (301.5 g), 600 ml of NMP and 100 g KF were heated together (in a flask fitted with a distillation column and takeoff head) at 195 °C for 6 h to give 114.2 g of compound 26 (96% purity) which distilled out of the flask as the reaction progressed. Re-distillation provided 98% pure 26, b.p. 82–83.5 °C. ^1H NMR δ: 5.97 (tt, 1H); 4.67 (dt, 2H) ppm.

1,1,1,4,4,4-Hexafluoro-2-(trifluoromethyl)butane $(CF_3)_2CHCH_2CF_3$ (29)

A 300 ml autoclave was charged with 21.0 g (0.1 mol) 4,4,4-trifluoro-3-(trifluoromethyl)butyric acid (prepared by hydrogenation and hydrolysis of commercially available ethyl 4,4,4-trifluoro-3-(trifluoromethyl)crotonate), 25 ml of cyclohexane and 38 g (0.35 mol) of SF_4. The contents were heated to 65–70 °C for 3 d, vented through a KOH scrubber and poured into a separatory funnel containing 40 ml of water.

The aqueous layer was extracted with 2×25 ml portions of cyclohexane, and the combined organic layers distilled. An azeotrope of the desired product and cyclohexane was obtained (b.p. 41–42 °C) which contained about 20% cyclohexane. The desired HFC was obtained in 23% yield following extraction with light mineral oil and distillation. A second distillation provided material of 99% purity, b.p. 43–44 °C. ^1H NMR δ: 3.25 (m, 1H); 2.63 (dq, 2H) ppm. ^{19}F NMR δ: -67.3 (3F); -69.5 (6F) ppm.

Results and discussion

Inadequacy of current solubility parameter models

Solubility parameters for perfluorocarbons range from about 5.5 to 6.0 Hildebrand units. Bryce [17] estimates that Hildebrand δ values [in (cal cm^{-3})$^{1/2}$] increase from 5.5 for F-pentane to 5.6 for F-hexane and 5.7 for F-heptane, F-octane and F-nonane. Scott's estimates [5] agree with this trend (F-pentane, 5.7; F-hexane, 5.8; and F-heptane, 5.9). Thus, it is expected that F-alkanes, with δ values of 5.7–6.1 will not be miscible with organic liquids having δ values >8.6, since according to solubility parameter theory, there is a greater likelihood of miscibility for two liquids when the difference in solubility parameters is small. For a given hydrocarbon, e.g. octane, an increase in solubilities should be observed in the order F-heptane$>F$-hexane$>F$-pentane. Using Small's [18] molar attraction constants, the calculated values for the same F-alkanes are very similar and a clear trend is not apparent (F-pentane, 5.77; F-hexane, 5.72; F-heptane, 5.75). We have determined that, at 25 °C, the approximate solubility of heptane (vol.%=vol. heptane/total solution volume) in F-pentane, F-hexane and F-octane is 22, 17 and 11 vol.%, respectively (the same order is observed on a mole fraction basis). Octane shows a similar trend (5% in F-octane, 9% in F-hexane and 12% in F-pentane). Although these differences are small, they clearly contradict predictions based on the δ values. However, for a given F-alkane solvent, the expected relative alkane solubilities are observed: octane solubility is 5% in F-octane; heptane 11%; and hexane 23%; similarly, in F-hexane, octane solubility is 9 vol.%; heptane 17%; while hexane is miscible.

The δ value for a given organic substance can be estimated by determining its solubility in a series of solvents of varying solubility parameter values. A maximum in solubility should occur when the δ values of the solute and solvent are closest. For unavailable HFCs, estimation methods are necessary. Group attraction constants (such as those for $-CF_2-$ and $-CF_3$ groups in F-alkanes as determined by Small) cannot distinguish geometrical isomers, such as $CH_3CF_2CH_2CF_2CH_3$

(Table 1, entry **12**, b.p. 75 °C) and $CH_3CF_2CF_2CH_2CH_3$ (entry **6**, b.p. 47 °C). The former is miscible with hydrocarbons up to dodecane, while the latter is miscible with hydrocarbons up to and including light mineral oil. These isomeric pentane HFCs clearly have different cohesive energy densities, as seen from their boiling points and solubility data. In order to predict the relative solvency of isomeric materials such as these, three-dimensional solubility parameters (such as those developed by Hansen [19], incorporating the contributions of non-polar and hydrogen-bonding effects) are needed. However, the required group contributions for HFCs, particularly the polar contributions to the solubility parameter are not, in general, available. For the same reason, the hydrogen-bonding component to three-dimensional solubility parameters for HFCs cannot be estimated. Assuming a negligible hydrogen-bonding component [20a], available group contributions allow three-dimensional solubility parameters to be estimated only for HFCs having a single fluorine attached to carbon [20b]. One such compound is 1,3-difluoropropane (est. $\delta_{total} = 7.75$ using the known molar volume; compare pentane, $\delta = 7.1$), for which the fractional polar contribution is <2%. However, dodecane ($\delta = 7.8$) is miscible with 1,3-difluoropropane (**15**), but the solubility of hexadecane ($\delta = 8.0$ [21]) is only about 20 vol.%. Thus, the solubility data conflict with expectation (miscibility with both hydrocarbons) based on the difference in δ values, even for this HFC with relatively low fluorine content. For highly fluorinated HFCs, abnormal solution behavior with alkanes can be expected simply because FCs exhibit abnormal behavior.

Approach

Because of the failure of the Hildebrand solubility parameters to adequately predict miscibilities of hydrocarbons in either FCs or HFCs, we have developed a semi-empirical solubility parameter (*SP*) for HFCs and FCs which is specific to their interactions with hydrocarbons. Our approach was driven by an urgent need to develop a pragmatic method for screening and evaluating a large number of HFCs as potential CFC replacements.

Owing to the synthetic effort required, methods for determining hydrocarbon solubilities were adopted to minimize the amount of sample needed. A series of hydrocarbons consisting of hexane, heptane, octane, decane, dodecane, hexadecane and light mineral oil was used. Whenever possible, for each HFC, the highest molecular weight hydrocarbon in the series which formed a homogeneous 1:1 (v/v) solution at 25 °C was determined. Solubility data for the HFC–HC combinations are shown in Table 1.

Molecular forces which determine boiling points are essentially the same as those which control sol-

vent–solute interactions, i.e. London dispersion forces, dipole–dipole interactions, dipole–induced dipole interactions and hydrogen bonding. For mixtures of HFCs and alkanes, attractive intermolecular interactions between non-identical molecules should be limited to dispersion forces and dipole–induced dipole interactions. Polar effects may be represented by a polar index, similar to that used in correlations involving molecular connectivity analyses. This index identifies the polar functionalities in an HFC such as $-CHF-$, $-CF_2H$, $-CH_2F$ and $-CH_2CF_2-$ groups which have significant bond dipole moments. The sum of α $(H-C-F)$ and β $(H-C-C-F)$ groupings was used as the polar index in this study.

For the non-polar effect (dispersion forces), the term $R_m V^{-1/3}$ can be used, where R_m is the molar refractivity and V the molar volume. This term has recently been shown to correlate the boiling point of a variety of non-polar compounds, including alkanes and perfluoroalkanes [22]. It was assumed that this term also reflects the non-polar contribution in polar HFCs. Thus, the values ('np') calculated for HFCs by this method reflect the contribution to the boiling point, and therefore the solubility parameter, made by dispersion forces.

Numerical values were assigned as follows. First, it was assumed that the solubility parameters could be related to a linear function of non-polar and polar effects [e.g. $SP = a(\text{non-polar}) + b(\text{polar}) + c$]. Second, the scale was arbitrarily fixed with F-methylcyclohexane at ~ 6.0 and pentane at ~ 7.0 (the δ values for these compounds are similar, allowing the magnitude of the difference between δ and SP for other compounds to be ascertained). Third, hydrocarbon solubilities were determined for a sample set of FCs and HFCs. This set was then ranked; the highest ranking was given to compounds miscible with higher molecular weight hydrocarbons, or which dissolved the same amount of hydrocarbon at a lower temperature. The coefficients a, b and c were then adjusted to give the best fit to reproduce the observed ranking.

For n-alkanes, SP values are approximately the same as δ values using the relation $SP = 1.175 \ln(np) + 0.025H$ where H is the number of hydrogens in the molecule, and np is the value calculated by the boiling point estimation method*. For F-alkanes, the equation $SP = 1.175 \ln(np) - 0.063F$ (F is the number of fluorines in the molecule) reproduces the observed ranking for F-alkanes. Table 2 compares the literature δ values with SP values for some alkanes and F-alkanes. SP Values are dimensionless and should not be interpreted

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*A sample calculation for hydrocarbons and perfluorocarbons is given in ref. 22. Values for S_c and S_b in HFCs are: $S_c = 0.95$ for cyclopentane and cyclohexane HFCs (for all others $S_c = 1.00$); $S_b = 1.03$ for branched HFCs.

TABLE 2. Comparison of δ and SP values for alkanes and F-alkanes

Compound	δ	SP
Butane	6.8–6.9	6.859
Pentane	7.0–7.1	7.041
Hexane	7.3	7.204
Heptane	7.4–7.5	7.351
Methylcyclohexane	7.8	7.304
F-Pentane	5.5	5.942
F-Hexane	5.6	5.926
F-Heptane	5.7–5.9	5.896
F-Octane	5.7	5.855
F-Methylcyclohexane	6.0–6.1	6.001

as cohesive energy densities (as are δ values). The relative δ and SP values for the alkanes are the same except for methylcyclohexane, which has an SP value nearly that for heptane on the SP scale.

The SP values for F-alkanes vary little, but there is a consistent trend for the linear compounds. Unlike the δ scale, the SP values for F-methylcyclohexane and F-pentane are very similar; the slightly higher value for F-methylcyclohexane requires very slightly higher solubilities (vol.%) for alkanes as solutes than F-pentane, in accord with observations.

For HFCs, a polar contribution, P, was added, calculated as -0.028 for each α and -0.018 for each β interaction [eqn. (1)]. The values were determined by ranking HFCs with respect to their solvencies, as was done for F-alkanes. Ranking was not always clear cut, however. For example, $C_8F_{17}C_2H_5$ (20) was ranked above $CF_3CH_2CF_2CH_3$ (22) because the solubility of decane at 25 °C was 17 vol.% in the former solvent but only 13 vol.% in the latter. However, decane was miscible with $CF_3CH_2CF_2CH_3$ at 32 °C, but only 23% soluble in $C_8F_{17}C_2H_5$ at 34 °C.

$$SP = 1.175 \ln(np) + 0.025H - 0.063F - 0.028\alpha - 0.018\beta$$

$$(1)$$

The polar term always makes a negative contribution to the SP value. This is because the ranking for the small data set is based on observed solubilities and therefore takes into account interactions between the two liquids. Three-dimensional Hildebrand solubility values are for *pure* liquids. The non-polar, polar and hydrogen-bonding contributions to the total, δ_T, are necessarily positive $(\delta_T^2 = \delta_{np}^2 + \delta_p^2 + \delta_H^2)$.

Effects of structure on solvency
Branching effects

In HFCs, branching has a small effect on alkane solubilities, as suggested by their SP values and supported by solubility data. Hexadecane, for example, has essentially the same solubility in the isomeric pentane

HFCs $(CF_3)_2CFCH_2CH_3$ (10, $SP = 6.336$) and $CF_3CF_2CF_2CH_2CH_3$ (11, $SP = 6.326$). Mineral oil has practically the same solubility in the isomeric hexane HFCs $CF_3CF_2CF_2CH(CH_3)_2$ (5), $(CF_3)_2CFCH(CH_3)_2$ (3) and $CF_3CF_2CF_2CH_2CH_2CH_3$ (7), for which the range of SP values is < 0.03 units. The solubilities of decane and octane in $CF_3CH_2CH(CF_3)_2$, however, were somewhat higher than expected based on its SP value of 5.96.

In contrast, a large decrease in δ results from branching in alkanes [21] (compare pentane, δ 7.1 with isopentane, δ 6.7 and octane, δ 7.6 with 2,2,4-trimethylpentane δ 7.0), while branching in FCs has a small positive effect on δ (compare F-n-pentane, δ 5.77 with F-isopentane, δ 5.86 [23]) and no effect on SP. Experimentally, octane and heptane solubilities in n-F-hexane (9 and 17 vol.%, respectively) and in F-2-methylpentane (10 and 18 vol.%) were nearly identical.

Ring effects

Hildebrand solubility parameters, δ, for cyclic hydrocarbons are generally larger by 0.2–0.3 units than the values for acyclic ones with the same number of carbons. Judging from the difference in δ values between F-heptane and F-methylcyclohexane (Table 2), which is comparable in magnitude to the difference between heptane and methylcyclohexane, one might expect this trend to hold for HFCs as well. If that were so, the solvency of cyclic HFCs would be expected to be substantially better than their acyclic counterparts. The SP scale predicts that F-methylcyclohexane ($SP = 6.001$) will have a greater solvency with respect to hydrocarbons than F-heptane ($SP = 5.896$), as observed, but that heptane ($SP = 7.351$) as a solute will be less soluble in an F-alkane solvent than would methylcyclohexane ($SP = 7.304$), since the difference in SP values will be greater for the heptane–perfluoroalkane pair. However, the solubility of methylcyclohexane in F-hexane was 12 vol.% compared to 17 vol.% for heptane in F-hexane, contrary to expectation based on SP values. We interpret this as a measure of the precision that can be expected from the SP scale. In other cases, the SP scale appears to predict the solvencies of cyclic compounds fairly well. Compound 13, $CF_3(CF_2)_3CH_2CH_3$ ($SP = 6.309$) and 1,1,2,2-tetrafluorocyclobutane (14, $SP = 6.303$) have essentially the same SP value and similar solvency. Dodecane is miscible with both, while hexadecane is 11 vol.% soluble in the former, and 9% in the latter.

Polar effects

In HFCs, polar C–F, C–C and C–H bonds give rise to overall dipole moments. The magnitude of the polar effect on hydrocarbon solubilities can overshadow the effect due to the percentage fluorine in the molecule (compare $CF_3CF_2CF_2CH_2CH_3$ (entry 11, 67% F,

$\mu = 1.95$) with $CH_3CF_2CH_2CF_2CH_3$ (entry 12, 53% F, $\mu = 4.12$). Some HFCs, with substantial hydrogen content, dissolve less hydrocarbon solutes than perfluorocarbons (compare HCF_2CHFCF_2H (30) and $CF_3CH_2CF_2CH_2CF_3$ (32) with F-pentane or F-methylcyclohexane).

Use of the terms α and β (eqn. (1)) assumes that individual bond dipoles influence solvency, in addition to the overall dipole moment. Entry 23, $CF_3CH_2CH_2CF_3$, has a substantial polar contribution to SP ($12\beta = -0.216$) even though the overall dipole moment should be quite small due to molecular symmetry.

Because overall dipole moments are not considered in eqn. (1), it cannot distinguish between regio- or stereo-isomers. In such cases, although the SP values are identical, hydrocarbons will have the lowest solubility in the isomer with the largest dipole moment. This effect is clearly demonstrated with the solubility data for cis- and trans-1,2-dihydroperfluorocyclopentane (38 and 39) and the corresponding cyclobutanes (36 and 37). The solubility of decane is approximately three-to four-times greater in the less polar trans isomer than in the more polar cis isomer.

Utility of SP values

Once a means of assigning solubility parameter (SP) values to HFCs was found, the relationship of this quantity to the solubility of a given solute could be determined. This is normally done by plotting non-polar versus polar (and hydrogen-bonding, if appropriate) contributions to define the region of solubility for a given solute in a number of solvents. Figure 1 displays the solubility of hexadecane in various HFCs. The soluble region was arbitrarily defined by homogeneous systems at 25 °C with solute/solvent ratios of $\geqslant 1{:}10$ ($\geqslant 9$ vol.%). The non-polar contribution to SP ($1.175 \ln(np) + 0.025H - 0.063F$) is plotted against the
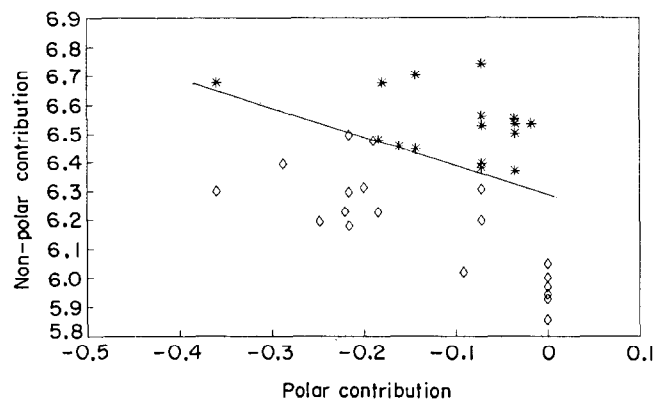

Fig. 1. Hexadecane solubility in HFCs. Non-polar contribution to SP ($1.175 \ln(np) + 0.025H - 0.063F$) versus the polar contribution $= \Sigma[\alpha + \beta]$. Soluble ($*$ soluble; $\diamond$ not soluble) is defined as a homogeneous solution with a solute/solvent volume ratio $\geqslant 0.10$.

polar contribution ($P = \Sigma[\alpha + \beta]$). The SP values for the FCs and HFCs used in Fig. 1 are listed in Table 3. From Fig. 1, it appears that this solubility condition holds when SP_{total} is $\geqslant 6.29$. Similar two-dimensional plots can be made for other solutes, for other definitions of solubility or for miscibility. Thus, using the data of Table 1, the minimum SP values needed for miscibility at 25 °C are about 6.0 for heptane, 6.2 for decane, 6.3_3 for hexadecane and 6.5 for light mineral oil as solutes. These are approximate guidelines for predicting the extent of solubility of hydrocarbons in an HFC. Light mineral oil, for example, may or may not be completely miscible in HFCs with SP values near 6.5, but some solubility (i.e. ~ 5 vol.% or more) should be observed.

Values of SP also provide useful guidelines for the separation of HFC–HFC or HFC–hydrocarbon mixtures by extraction with a suitable hydrocarbon. For example, $(CF_3)_2CHCH_2CF_3$ (29, $SP = 5.96$), which formed an azeotrope with cyclohexane ($SP = 7.18$), was purified by extraction of the cyclohexane with light mineral oil.

One of the most powerful applications of eqn. (1) is its use as a screening tool. In eqn. (1) the polar contributions are always negative, and hence maximum SP values can be calculated for families of HFCs. For example, the maximum SP value for the $C_6H_4F_{10}$ family is calculated by zeroing the polar contribution, so that $SP_{max} = 6.20$. This implies that no HFC with the molecular formula $C_6H_4F_{10}$ will be miscible with dodecane at 25 °C, although miscibility with decane is possible. It is also possible to conclude that for pentane HFCs, SP_{max} values of $\geqslant 6.5$ are possible only for the $C_5H_7F_5$, $C_5H_8F_4$, $C_5H_9F_3$, $C_5H_{10}F_2$ and $C_5H_{11}F$ families.

Conclusions

A new solubility parameter scale for HFCs has been developed from semi-quantitative data. Although the SP scale is semi-empirical, it has substantial practical utility. The dominant dispersion and polar forces for HFC–hydrocarbon pairs are represented in eqn. (1). Increasing the amount of fluorine in an HFC can increase or diminish hydrocarbon solubility depending both on the location and extent of fluorine substitution.

For an isomeric HFC family, those HFCs having the greatest solvency toward hydrocarbons are the least polar, and have structures (e.g. R_fR) which minimize the scrambling of the fluorines in the molecule and consequently the polar contribution.

Plots of non-polar versus polar contributions, similar to Fig. 1, could be used for other solutes, both polar and non-polar, to identify areas of solubility. This may be the best approach available for HFC solvents, given the present limitations of normal solution theory.

TABLE 3. SP values for FCs and HFCs used in Fig. 1

Compound	SP_{total}	$SP_{non-polar}$	SP_{polar}
1 $CF_3CF_2CH_2CH_2CH_2CH_3$	6.670	6.742	−0.072
2 $(CH_3CH_2CF_2CF_2)_2CF_2$	6.557	6.701	−0.144
3 $(CF_3)_2CFCH(CH_3)_2$	6.516	6.534	−0.018
4 $CF_3CF_2CH(CH_3)_2$	6.516	6.552	−0.036
5 $CF_3CF_2CF_2CH(CH_3)_2$	6.498	6.534	−0.036
6 $CH_3CF_2CF_2CH_2CH_3$	6.496	6.676	−0.180
7 $CF_3CF_2CF_2CH_2CH_2CH_3$	6.489	6.561	−0.072
8 $CF_3(CF_2)_3CH(CH_3)_2$	6.466	6.502	−0.036
9 $CF_3(CF_2)_3CH_2CH_2CH_3$	6.457	6.529	−0.072
10 $(CF_3)_2CFCH_2CH_3$	6.336	6.371	−0.036
11 $CF_3CF_2CF_2CH_2CH_3$	6.326	6.398	−0.072
12 $CH_3CF_2CH_2CF_2CH_3$	6.316	6.676	−0.360
13 $CF_3(CF_2)_3CH_2CH_3$	6.309	6.381	−0.072
14 1,1,2,2-Tetrafluorocyclobutane	6.303	6.447	−0.144
15 $FCH_2CH_2CH_2F$	6.296	6.481	−0.184
16 $CF_3(CH_3)CHCH_2CF_3$	6.293	6.455	−0.162
17 $CF_3CF_2CF_2CH_2CHFCH_3$	6.285	6.475	−0.190
18 $CH_3CF_2CF_2CF_2CH_3$	6.279	6.495	−0.216
19 $CF_3(CF_2)_5CH_2CH_3$	6.235	6.307	−0.072
20 $CF_3(CF_2)_7CH_2CH_3$	6.126	6.198	−0.072
21 $HCF_2CF_2CF_2CF_2CH_3$	6.113	6.313	−0.200
22 $CF_3CH_2CF_2CH_3$	6.107	6.395	−0.288
23 $CF_3CH_2CH_2CF_3$	6.081	6.297	−0.216
24 F-Dimethylcyclobutane	6.048	6.048	0.0
25 FCH_2CH_2F	6.042	6.226	−0.184
26 $HCF_2CF_2CF_2CF_2CH_2F$	6.008	6.228	−0.220
27 F-Methylcyclohexane	6.001	6.001	0.0
28 F-Dimethylcyclohexane	5.967	5.967	0.0
29 $CF_3CH_2CH(CF_3)_2$	5.963	6.179	−0.216
30 HCF_2CFHCF_2H	5.946	6.194	−0.248
31 F-Pentane	5.942	5.942	0.0
32 $CF_3CH_2CF_2CH_2CF_3$	5.941	6.301	−0.360
33 $CF_3(CF_2)_4CF_2H$	5.928	6.020	−0.092
34 F-Hexane	5.926	5.926	0.0
35 F-Octane	5.855	5.855	0.0

Equation (1) has allowed maximum SP values to be determined for families of HFCs. It has been our general observation that for HFCs, a minimum of about 67 wt.% fluorine is required for nonflammability. This observation, together with maximum SP values and the relationship between SP and hydrocarbon solubility, indicates that HFCs do not have the same potential for degreasing and dewaxing as CFCs and nonflammable HCFCs with similar boiling points. Thus, the use of nonflammable HFCs as cleaning solvents will likely require modifications in cleaning methodology, such as two-stage cleaning [24]. Nevertheless, nonflammable HFCs have substantial potential as solvents for polar solutes.

Acknowledgment

References

1 A.F.M. Barton, *Handbook of Solubility Parameters and Other Cohesion Parameters*, 2nd edn., CRC Press, Boca Raton, FL, 1991.
2 J.H. Hildebrand and R.L. Scott, *Solubility of Nonelectrolytes*, Reinhold, New York, 1950.
3 J.H. Hildebrand, B.B. Fisher and H.A. Benesi, *J. Am. Chem. Soc.*, *72* (1950) 4348.
4 N. Sivaraman, R. Dhamodran, I. Kaliappan, T.G. Srinivasan, P.R. Vasudeva Rao and C.K. Mathews, *J. Org. Chem.*, *57* (1992) 6077.
5 R.L. Scott, *J. Phys. Chem.*, *62* (1958) 136.
6 A.I. Burmakov, I.V. Stepanov, B.V. Kunshenko, L.N. Sedova, L.A. Alekseeva and L.M. Yagupol'skii, *J. Org. Chem. USSR (Engl. Trans.)*, *18* (1982) 1009.
7 R.H. Groth, *J. Org. Chem.*, *24* (1959) 1709.
8 I.V. Stepanov, A.I. Burmakov, B.V. Kunshenko, L.A. Alekseeva and L.M. Yagupo'skii, *J. Org. Chem. USSR (Engl. Trans.)*, *19* (1983) 244.
9 W.F. Edgell and L. Parts, *J. Am. Chem. Soc.*, *77* (1955) 4899.

10 F.A. Bloshchitsa, A.I. Burmakov, B.V. Kunshenko, L.A. Alekseeva and L.M. Yagupol'skii, *J. Org. Chem. USSR (Engl. Trans.), 21* (1985) 1286.

11 D.P. Graham and W.B. McCormack, *J. Org. Chem., 31* (1965) 955.

12 E.T. McBee, O.R. Pierce and M.C. Chen, *J. Am. Chem. Soc., 75* (1953) 2324.

13 E.T. McBee, J.F. Higgins and O.R. Pierce, *J. Am. Chem. Soc., 74* (1952) 1387.

14 Y.K. Kim, A.G. Smith and O.R. Pierce, *J. Org. Chem., 38* (1973) 1615.

15 A. Battais, G. Baudin, B. Boutevin and Y. Pietrasanta, *J. Fluorine Chem., 31* (1986) 197.

16 R.N. Haszeldine, *J. Chem. Soc.,* (1952) 2504.

17 H.G. Bryce, in J.H. Simons (ed.), *Fluorine Chemistry,* Academic Press, New York, 1964, Vol. 5, p. 315.

18 P.A. Small, *J. Appl. Chem., 3* (1953) 71.

19 C.M. Hansen, *J. Paint Technol., 39* (1967) 104. See also ref. 1, Chap. 9, and references cited therein.

20 A.F.M. Barton, *Handbook of Solubility Parameters and Other Cohesion Parameters,* 2nd edn., CRC Press, Boca Raton, FL, 1991, (a) Table 14, p. 86; (b) Table 13, p. 85.

21 C. Hansen and A. Beerbower, in *Kirk-Othmer Encyclopedia of Chemical Technology,* 2nd edn., Interscience, New York, 1971, Suppl. Vol., p. 889.

22 M. Van Der Puy, *J. Fluorine Chem., 63* (1993) 165.

23 E.J. Barber and G.H. Cady, *J. Phys. Chem., 60* (1956) 504.

24 R.M. Sluga, R.H. Watkins, J.D. Fisher, D.C. Berry and M. Eldridge, *US Pat. 5 106 425* (1992); [*Chem. Abs. 117* (1992) 194 550g].