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Phase Separation in Binary Mixtures Containing Linear Perfluoroalkanes

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Mixed systems containing fluorocarbons (FC) phase separate below certain temperatures. The liquid−liquid coexistence curves show upper critical solution temperatures (T_c) that depend on the nature of the components. In this work, we report the phase separation measurements of mixtures obtained from short-chain linear perfluoroalkanes (perfluorohexane, perfluoroheptane, and perfluorooctane) with some *n*-alkanes, cyclohexane, benzene, ethers, and chlorinated solvents. The results are discussed in terms of the chemical nature and polarizability of the components.

Introduction

Despite their similar formulas, fluorocarbons (FC) and hydrocarbons (HC) possess totally different structures and properties and express their reciprocal phobicity or incompatibility in a number of interesting phenomena.[1] The whole frame of the story depends basically on the intrinsic atomic properties of fluorine and carbon. Fluorine has the highest electronegativity in the periodic table, a large van der Waals radius (1.47 Å vs 1.20 Å for H), a high ionization potential, and a very low polarizability.[2] These parameters reduce the conformational freedom of fluorinated tails that therefore are bulky and rigid, arranged in a typical helical conformation (depending on temperature),[3,4] with a dense electron-rich coating that prevents chemical and biochemical attacks. This is the reason that FC possess very strong intramolecular (covalent) bonding and very weak intermolecular (van der Waals) interactions.[2] They are much more stable than their corresponding HCs, with low surface tensions, high fluidities and densities, low dielectric constants and refractive indexes, high vapor pressures, high compressibilities, and high gas solubilities.[5−8] Being chemically and biochemically inert, FC are useful in different fields, especially in some important biomedical applications. For example they can be used as oxygen carriers in blood sustitutes, in the aerobic conservation of transplant organs, or in cancer therapy (where an increased local concentration of O_2 is required), in ophthalmology, in diagnostic procedures, and in bone reconstruction.[6,7]

The mutual incompatibility between FC and HC generates a set of interesting phenomena in all states of matter. These are expressed in microphase separation, segregation, and self-assembly. Semifluorinated *n*-alkanes, $F(CF_2)_m(CH_2)_nH$, carry the two incompatible moieties linked by a covalent bond, and for this reason they form ordered smectogenic liquid crystals, adsorb at the air/hydrocarbon interface, produce gels in different organic liquids, and self-aggregate in selective solvents.[1,9−11]

Because of their chemical incompatibility, FC and HC phase separate and produce an upper consolute coexistence curve. At each temperature below the upper critical solution temperature (T_c), the system forms two coexisting liquid phases in equilibrium. Because of the density difference, the heavier bottom phase is richer in FC, and the upper phase contains mostly the hydrogenated component. The shape of the curve and the upper-point characteristic values x_c and T_c depend on the nature of the two components.[3]

In this article, we report the phase separation behavior of some FC + HC mixtures. In particular, by choosing different component pairs, we explore the effect of the fluorinated and hydrogenated chain lengths, a cyclic ring, aromaticity, the presence of branched CH_3 end groups, the substitution of a CH_2 with an ether moiety or the substitution of chlorine atoms in CCl_4, and the isotope effect ($CHCl_3$ and $CDCl_3$) on the phase separation of FC + HC binary mixtures. For brevity, by HC we mean all of the nonfluorinated counterparts in the binary mixtures, including chlorinated solvents.

Experimental Section

The fluorinated chemicals were obtained from Zentek (Milan, Italy). The mole fraction purities are those given by the suppliers: tetradecafluorohexane (perfluorohexane, C_6F_{14}, >98%), hexadecafluoroheptane (perfluoroheptane, C_7F_{16}, >97%), and octadecafluorooctane (perfluorooctane, C_8F_{18}, >98%). Hexane (n-C_6H_{14}, >99.5%), heptane (n-C_7H_{16}, >99%), octane (n-C_8H_{18}, >99.5%), 2,2,4-trimethylpentane (i-C_8H_{18}, >99.5%), decane (n-$C_{10}H_{22}$, >99.8%), benzene (C_6H_6, >99.5%), cyclohexane (C_6H_{12}, >99.8%), butyl methyl ether ($C_5H_{12}O$, >99.0%), butyl ethyl ether ($C_6H_{14}O$, >98.0%), carbon tetrachloride (CCl_4, >99.8%), trichloromethane ($CHCl_3$, >99.8%), deutero-chloroform ($CDCl_3$, >99.9 atom % D), and dichloromethane (CH_2Cl_2, >99.9%) were obtained from Sigma-Aldrich-Fluka (Milan, Italy). No further treatments were carried out to improve the purity of the perfluoroalkanes through the fractionation of isomers because it would not improve the quality of the thermodynamic data.[12] The mole fractions of mixtures were calculated from the known masses of the components (with the uncertainty of ±0.0001 g). The uncertainty in the mole fraction is better than 2×10^{-4}. All mixtures were prepared in sealed vials equipped with a small magnetic bar, and

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Table 1. Phase Separation Temperature (T) for Different Fluorocarbon + Hydrocarbon Mixtures at Different Mole Fractions (x)

C_6F_{14} + n-C_8H_{18}		C_6F_{14} + n-C_8H_{18}		C_6F_{14} + $C_{10}H_{22}$		C_6F_{14} + $C_{10}H_{22}$		C_6F_{14} + C_6H_{12}		C_6F_{14} + C_6H_{12}		C_6F_{14} + C_6H_6		C_6F_{14} + C_6H_6	
x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K
0.0503	282.3±0.2	0.4998	331.1±0.2	0.0499	296.6±0.4	0.4953	$366.1\pm0.2_5$	0.0500	311.8±0.3	0.4986	338.8±0.2	0.0499	339.1±0.3	0.4997	367.3±0.3
0.0999	$306.5\pm0.2_5$	0.5984	329.8±0.3	0.1008	326.0±0.3	0.5984	364.8±0.4	0.0997	330.4±0.3	0.5956	331.7±0.3	0.1004	$363.0\pm0.2_5$	0.5850	362.3±0.3
0.2003	$323.4\pm0.2_5$	0.6997	$325.3\pm0.2_5$	0.2000	345.1±0.3	0.6967	361.3±0.3	0.1986	$340.2\pm0.2_5$	0.6970	320.8±0.3	0.2005	370.0±0.3	0.6823	345.3±0.3
0.2979	329.4±0.2	0.7944	314.1±0.2	0.2998	359.3±0.3	0.7991	348.0±0.3	0.2964	$342.1\pm0.2_5$	0.8011	297.6±0.3	0.3011	371.0±0.3	0.7504	335.0±0.2
0.3991	331.3±0.2	0.8943	$293.9\pm0.2_5$	0.4004	365.6±0.3	0.8987	329.9±0.4	0.3976	$341.1\pm0.2_5$			0.4002	369.7±0.3	0.7935	326.2±0.3

C_6F_{14} + CCl_4		C_6F_{14} + CCl_4		C_6F_{14} + $CDCl_3$		C_6F_{14} + $CDCl_3$		C_6F_{14} + $CHCl_3$		C_6F_{14} + $CHCl_3$		C_6F_{14} + CH_2Cl_2		C_6F_{14} + CH_2Cl_2	
x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K
0.0503	295.1±0.2	0.3962	$321.3\pm0.2_5$	0.0333	303.3±0.2	0.3984	$339.3\pm0.2_5$	0.0503	$316.3\pm0.2_5$	0.4990	334.9±0.5	0.0333	$318.5\pm0.2_5$	0.3991	$356.0\pm0.2_5$
0.0711	$304.6\pm0.2_5$	0.4916	317.2±0.3	0.0498	$314.7\pm0.2_5$	0.4947	$333.7\pm0.2_5$	0.1011	335.3±0.3	0.5873	326.5±0.3	0.0501	$335.0\pm0.2_5$	0.4914	347.7±0.3
0.0999	313.2±0.3	0.5971	308.6±0.3	0.1000	333.4±0.3	0.6004	323.0±0.3	0.2016	342.8±0.3	0.7093	313.6±0.3	0.0999	357.5±0.2	0.5871	332.7±0.3
0.1370	318.4±0.3	0.6939	296.6±0.3	0.1330	338.1±0.3	0.6991	309.5±0.3	0.2982	$343.4\pm0.2_5$	0.8003	$294.7\pm0.2_5$	0.1333	$361.9\pm0.2_5$	0.6939	317.9±0.3
0.2002	$321.5\pm0.2_5$	0.7882	$283.1\pm0.2_5$	0.2007	$340.9\pm0.2_5$	0.7971	292.3±0.3	0.3946	$341.4\pm0.2_5$	0.8805	$279.1\pm0.2_5$	0.1981	363.0±0.2	0.7942	303.9±0.3
0.2999	322.4±0.3			0.2981	342.4±0.3	0.8750	276.3±0.3					0.2918	362.7±0.2	0.8944	287.9±0.3

C_7F_{16} + C_7H_{16}		C_7F_{16} + C_7H_{16}		C_7F_{16} + n-C_8H_{18}		C_7F_{16} + n-C_8H_{18}		C_7F_{16} + i-C_8H_{18}		C_7F_{16} + i-C_8H_{18}		C_7F_{16} + $C_{10}H_{22}$		C_7F_{16} + $C_{10}H_{22}$	
x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K
0.0390	286.8±0.2	0.4960	322.3±0.3	0.0505	292.0±0.3	0.4955	331.7±0.2	0.0805	276.0±0.2	0.4160	296.7±0.4	0.0502	307.5±0.3	0.4981	364.1±0.2
0.0620	$297.0\pm0.2_5$	0.5310	321.5±0.3	0.1008	313.4±0.3	0.5964	329.4±0.4	0.1111	282.9±0.2	0.5330	295.8±0.3	0.1005	333.8±0.3	0.5948	363.3±0.3
0.1350	$315.1\pm0.2_5$	0.6000	$318.8\pm0.2_5$	0.2007	326.7±0.3	0.6954	324.6±0.3	0.1550	289.9±0.2	0.6230	292.8±0.3	0.2009	352.9±0.3	0.6983	360.0±0.4
0.2130	321.5±0.3	0.7090	$309.5\pm0.2_5$	0.3001	331.5±0.2	0.7963	313.0±0.3	0.2320	295.2±0.3	0.7450	283.6±0.3	0.3020	360.4±0.3	0.7965	350.9±0.3
0.2930	322.9±0.3	0.7860	$300.3\pm0.2_5$	0.3950	332.0±0.2	0.9001	290.5±0.3	0.3230	296.6±0.2	0.8083	277.0±0.3	0.4014	363.0±0.3	0.8954	328.1±0.3
0.3910	323.0±0.3	0.8944	285.7±0.3												

C_7F_{16} + C_6H_{12}		C_7F_{16} + C_6H_{12}		C_7F_{16} + C_6H_6		C_7F_{16} + C_6H_6		C_7F_{16} + CCl_4		C_7F_{16} + CCl_4		C_7F_{16} + $CDCl_3$		C_7F_{16} + $CDCl_3$	
x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K
0.0250	305.8±0.2	0.4007	339.6±0.2	0.0251	310.0±0.3	0.5750	$352.9\pm0.2_5$	0.0457	306.4±0.3	0.3960	328.9±0.4	0.0501	$320.7\pm0.2_5$	0.4940	326.7±0.3
0.0502	317.7±0.3	0.5007	335.3±0.3	0.0515	342.6±0.3	0.6890	332.2±0.3	0.0972	326.3±0.3	0.5104	$322.1\pm0.3_5$	0.1000	336.1±0.3	0.5989	315.5±0.3
0.1002	$332.1\pm0.2_5$	0.5987	327.8±0.4	0.0999	366.1±0.3	0.7895	311.2±0.3	0.1511	330.6±0.3	0.6517	305.3±0.2	0.2005	340.1±0.2	0.6927	300.0±0.4
0.2015	338.8±0.3	0.6866	317.5±0.3	0.3896	370.4±0.3	0.8611	295.2±0.3	0.2210	$331.7\pm0.3_5$	0.8023	275.6±0.2	0.3005	338.1±0.2	0.7864	286.3±0.3
0.2980	341.0±0.2	0.7944	299.9±0.4	0.4900	364.5±0.4			0.3124	331.4±0.4			0.4004	333.5±0.3		

C_7F_{16} + $CHCl_3$		C_7F_{16} + $CHCl_3$		C_7F_{16} + CH_2Cl_2		C_7F_{16} + CH_2Cl_2		C_8F_{18} + C_6H_{14}		C_8F_{18} + C_6H_{14}		C_8F_{18} + C_7H_{16}		C_8F_{18} + C_7H_{16}	
x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K
0.0250	311.2±0.3	0.3580	347.8±0.4	0.0278	331.8±0.2	0.3967	351.2±0.3	0.0378	284.5±0.2	0.4671	309.8±0.3	0.0980	$307.1\pm0.2_5$	0.5985	329.9±0.3
0.0362	328.9±0.3	0.4553	342.1±0.4	0.0500	$346.0\pm0.2_5$	0.4807	340.3±0.4	0.0555	293.0±0.2	0.5669	301.6±0.3	0.1389	315.6±0.2	0.6972	326.0±0.2
0.0851	345.1±0.3	0.5950	329.1±0.3	0.1002	358.5±0.3	0.5995	324.4±0.4	0.0833	301.7±0.2	0.6953	287.5±0.3	0.1984	$324.5\pm0.2_5$	0.7965	316.6±0.3
0.1278	350.0±0.2	0.6917	314.1±0.3	0.2007	360.0±0.3	0.6902	311.1±0.3	0.1347	310.0±0.3	0.7754	274.0±0.3	0.2976	329.9±0.3	0.8444	308.0±0.2
0.1860	350.7±0.3	0.7758	$297.7\pm0.3_5$	0.3005	$358.2\pm0.2_5$	0.7908	294.3±0.3	0.2589	314.0±0.4	0.8694	259.5±0.2	0.3977	331.0±0.3	0.8991	$293.0\pm0.2_5$
0.2602	351.0±0.4	0.8639	276.8±0.3					0.3666	313.7±0.3			0.4973	331.1±0.3		

C_8F_{18} + C_8H_{18}		C_8F_{18} + C_8H_{18}		C_8F_{18} + i-C_8H_{18}		C_8F_{18} + i-C_8H_{18}		C_8F_{18} + $C_{10}H_{22}$		C_8F_{18} + $C_{10}H_{22}$		C_8F_{18} + C_6H_{12}		C_8F_{18} + C_6H_{12}	
x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K
0.0509	$315.3\pm0.2_5$	0.4907	348.2±0.4	0.0776	280.8±0.1	0.4214	299.8±0.2	0.0508	333.1±0.4	0.7928	362.9±0.4	0.0217	315.5±0.4	0.5563	340.5±0.3
0.0695	325.6±0.2	0.5901	344.6±0.3	0.0917	285±0.2	0.5014	298.5±0.1	0.1007	359.5±0.4	0.8911	336.1±0.3	0.0497	336.2±0.6	0.6120	334.7 ±0.2
0.0995	335.1±0.3	0.6942	337.4±0.3	0.1126	$289.8\pm0.1_5$	0.5993	295.0±0.1					0.0991	353.1±0.5	0.6407	329.5±0.5
0.1278	341.2±0.3	0.7610	328.9±0.3	0.1389	293.9±0.1	0.6500	292.5±0.2					0.1976	356.6±0.5	0.7220	315.8±0.4
0.1980	$346.4\pm0.2_5$	0.7968	322.3±0.4	0.1805	297.7±0.1	0.6971	289.7±0.2					0.2892	357.0±0.4	0.8017	299.5±0.6
0.3010	348.9±0.4	0.8417	311.0±0.3	0.2414	299.4±0.1	0.7472	284.9±0.2					0.4100	353.0±0.2	0.9013	273.0±0.3
0.3980	$349.2\pm0.2_5$	0.8990	295.1±0.3	0.2975	299.9±0.2	0.8054	277.4±0.3					0.4945	347.0±0.4		

C_8F_{18} + CCl_4		C_8F_{18} + CCl_4		C_8F_{18} + $CDCl_3$		C_8F_{18} + $CDCl_3$		C_8F_{18} + $CHCl_3$		C_8F_{18} + $CHCl_3$		C_8F_{18} + CH_2Cl_2		C_8F_{18} + CH_2Cl_2	
x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K
0.0375	314.0±0.4	0.3975	331.6±0.4	0.0190	334.0±0.2	0.4021	344.5±0.3	0.0530	340.8±0.3	0.2919	353.8±0.3	0.0311	348.7±0.3	0.3915	358.3±0.3
0.0504	320.6±0.5	0.4956	323.7±0.5	0.0506	346.9±0.3	0.4979	335.8±0.4	0.0700	348.3±0.3	0.4043	347.2±0.3	0.0502	356.5±0.4	0.5028	343.5±0.4
0.0686	326.8±0.4	0.5510	315.5±0.5	0.1006	352.4±0.3	0.5972	319.2±0.4	0.0985	354.1±0.3	0.5031	337.2±0.4	0.1289	361.0±0.4	0.6005	326.4±0.4
0.1010	332.9±0.4	0.5914	304.8±0.5	0.1997	$354.3\pm0.2_5$	0.6915	308.3±0.5	0.1450	355.8±0.2	0.5861	326.1±0.5	0.2290	362.6±0.4	0.6958	301.1±0.2
0.2000	336.2±0.4	0.6230	290.7±0.4	0.3001	$351.5\pm0.2_5$	0.8013	287.5±0.4	0.1909	$356.1\pm0.1_5$	0.6691	308.6±0.3	0.3070	$361.0\pm0.2_5$		
0.3024	335.1±0.3							0.2400	355.5±0.2	0.7461	288.1±0.3				

C_8F_{18} + $C_5H_{12}O$		C_8F_{18} + $C_5H_{12}O$		C_8F_{18} + $C_6H_{14}O$		C_8F_{18} + $C_6H_{14}O$	
x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K	x_1	$(T\pm\sigma)$/K
0.0639	297.2±0.2	0.4962	328.6±0.4	0.0986	314.8±0.2	0.6002	335.7±0.3
0.1004	308.4±0.2	0.6004	327.1±0.3	0.1417	324.0±0.2	0.6990	332.1±0.3
0.1361	316.5±0.3	0.6987	323.1±0.3	0.2013	331.4±0.2	0.8000	322.5±0.3
0.1986	322.7±0.3	0.7953	316.0±0.3	0.2999	336.2±0.3	0.8500	313.8±0.2
0.2985	327.0±0.3	0.8583	305.4±0.2	0.4004	336.9±0.3	0.8974	303.0±0.2
0.3918	328.3±0.3	0.8987	296.2±0.2	0.4992	336.9±0.4		

Table 2. Critical Mole Fraction ($x_c \pm 0.01$), Critical Volume Fraction ($\phi_c \pm 0.01$), Critical Temperature ($T_c \pm 0.1$)/K, Density (at T_c) ρ/g·mL^{-1}, and Molar Volume (at T_c) V/mL·mol^{-1} Values for the Different Mixtures and for Each Component

				T_c	$\rho_{FC}(T_c)$	$\rho_{HC}(T_c)$	$V_{FC}(T_c)$	$V_{HC}(T_c)$
FC	HC	x_c	ϕ_c	K	g·mL^{-1}	g·mL^{-1}	mL·mol^{-1}	mL·mol^{-1}
C_6F_{14}	C_8H_{18}	0.45	0.51	331.5	1.57466	0.67453	214.68	169.35
	$C_{10}H_{22}$	0.50	0.52	366.2	1.46813	0.67432	230.25	211.01
	C_6H_{12}	0.32	0.47	342.1	1.54211	0.73131	219.21	115.08
	C_6H_6	0.29	0.49	371.1	1.45308	0.79309	232.64	98.49
	CCl_4	0.29	0.46	322.5	1.60229	1.53477	210.98	100.22
	$CDCl_3$	0.27	0.49	342.5	1.54088	1.40495	219.38	85.68
	$CHCl_3$	0.27	0.49	344.0	1.53628	1.38854	220.04	85.97
	CH_2Cl_2	0.22	0.48	363.1	1.47764	1.19676	228.77	70.97
C_7F_{16}	C_7H_{16}	0.38	0.49	323.1	1.65296	0.65852	234.76	152.17
	C_8H_{18}	0.41	0.49	332.1	1.62686	0.67405	238.53	169.47
	i-C_8H_{18}	0.39	0.46	296.7	1.72952	0.68804	224.37	166.02
	$C_{10}H_{22}$	0.47	0.52	364.0	1.53435	0.67599	252.91	210.48
	C_6H_{12}	0.30	0.47	341.1	1.60076	0.73226	242.42	114.93
	C_6H_6	0.25	0.47	372.0	1.51115	0.79210	256.79	98.62
	CCl_4	0.26	0.45	332.0	1.62715	1.51606	238.49	101.46
	$CDCl_3$	0.23	0.46	340.5	1.60250	1.40883	242.15	85.45
	$CHCl_3$	0.24	0.47	351.0	1.57205	1.37496	246.84	86.82
	CH_2Cl_2	0.20	0.47	360.0	1.54595	1.20250	251.01	70.63
C_8F_{18}	C_6H_{14}	0.31	0.46	314.3	1.71453	0.63983	255.50	134.69
	C_7H_{16}	0.41	0.54	331.4	1.67024	0.65130	262.27	153.85
	C_8H_{18}	0.36	0.50	349.4	1.62362	0.66021	269.80	173.02
	i-C_8H_{18}	0.34	0.50	300.0	1.75157	0.68540	250.10	166.66
	C_6H_{12}	0.23	0.46	357.2	1.60342	0.71696	273.20	117.39
	CCl_4	0.22	0.44	336.2	1.65781	1.50779	264.24	102.02
	$CDCl_3$	0.19	0.46	354.4	1.61067	1.38186	271.97	87.12
	$CHCl_3$	0.19	0.46	356.3	1.60575	1.36468	272.81	87.47
	CH_2Cl_2	0.19	0.47	363.3	1.58762	1.19640	275.92	70.99
	$C_5H_{12}O$	0.45	0.57	328.8	1.67698	0.70740	261.22	124.61
	$C_6H_{14}O$	0.43	0.55	337.1	1.65548	0.71027	264.61	143.86

the demixing was observed visually through heating/cooling cycles in a thermostated bath (±0.1 K) under vigorous stirring. The demixing temperature was measured with an uncertainty of ±0.1 K. Each measurement of the demixing temperature is an average over at least five measurements.

Density measurements of fluorocarbons were carried out with an Anton Paar DMA 5000 instrument as a function of temperature.

Results and Discussion

Table 1 reports the full set of data for all of the mixtures investigated in this work. The phase separation temperature T is listed for different mole fraction values, with the standard deviation for each average value. Each mixture shows an upper critical solution temperature (T_c) that corresponds to a critical mole (or volume) fraction x_c (or ϕ_c). The critical values (x_c, ϕ_c, and T_c) obtained from the experimental coexistence curves are reported in Table 2. x_c has been determined by extrapolating the curve diameter up to T_c.

For the three series (C_6F_{14}, C_7F_{16}, and C_8F_{18}), the longer the FC and HC chains, the higher the T_c. The presence of a cyclic ring, and particularly an aromatic ring, largely increases the upper critical solution temperature (compare hexane, cyclohexane, and benzene). Instead, the presence of a branched alkyl chain as in 2,2,4-trimethylpentane consistently decreases T_c. In the case of chlorinated liquids, the most symmetric and apolar CCl_4 has the lowest T_c, and T_c increases up to dichloromethane. In particular, from CCl_4 to $CHCl_3$ the variation in T_c is very large, about 20 °C, whereas between $CHCl_3$ and CH_2Cl_2 it progressively decreases from C_6F_{14} to C_8F_{18}.

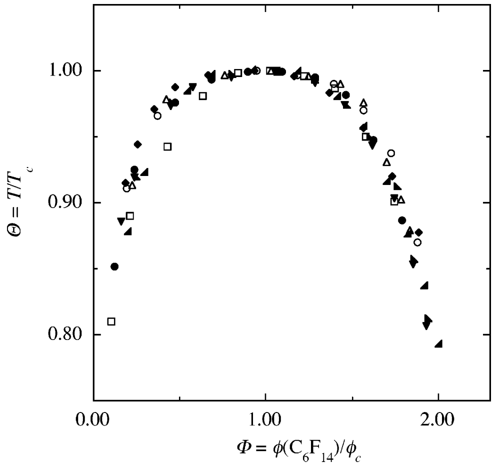

Figure 1. Liquid−liquid coexistence curves for binary mixtures containing perfluorohexane in reduced coordinates Θ/Φ. ●, C_6F_{14} + n-C_8H_{18}; □, C_6F_{14} + $C_{10}H_{22}$; ○, C_6F_{14} + C_6H_{12}; △, C_6F_{14} + C_6H_6; ◆, C_6F_{14} + CCl_4; ▼, C_6F_{14} + $CDCl_3$; solid, left-slanting triangle, C_6F_{14} + $CHCl_3$; solid, right-slanting triangle, C_6F_{14} + CH_2Cl_2.

The substitution of a $-CH_2-CH_2-CH_2-$ chain with a $-CH_2-O-CH_2-$ ether residue (hexane with butyl methyl ether or heptane with butyl ethyl ether) causes an increment in T_c.

The presence of deuterium in $CDCl_3$ slightly reduces T_c with respect to the value for $CHCl_3$. This lowering increases from C_6F_{14} (ΔT_c = 0.9 K) to C_7F_{16} (1.5 K) and to C_8F_{18} (1.9 K) and is consistent with the literature reports for similar systems (e.g., C_6F_{14} + C_6H_{12} and C_6F_{14} + C_6D_{12} mixtures, where a much stronger ΔT_c was detected[13]). Van Hook et al.[14] suggested that the exchange of hydrogen with deuterium leads to a strenghtening of the unlike molecule interactions that results in an increase in mutual solubility. This behavior (i.e., the variation of the upper critical consolute temperature of a demixing system due to the deuteration of the components) is inverted in water-based dispersions. For example, in D_2O + deuterated isobutyric acid[15] and in D_2O + dioctanoylphosphatidylcholine,[16] the cloud point temperature significantly rises when H_2O is replaced by D_2O because of a consistent modification of the hydrogen bonding network in the solvent that affect the interactions between the solvent and the surfactant. This effect also results in stronger effective lipid−lipid interactions.[16]

To highlight the similarities of the liquid−liquid coexistence curves, these can also be plotted in reduced coordinates: $\Theta = T/T_c$ versus $\Phi = \phi/\phi_c$. ϕ is calculated for each composition from the density values of the two components at the temperature of demixing: $\phi_i = x_iV_i/\sum_i x_iV_i$ and $V_i = M_i/\rho_i$, where ρ_i, M_i, and V_i are the density, molar mass, and molar volume for component i, respectively. This calculation of the volume fraction assumes ideal mixing behavior in FC + HC mixtures. A more realistic evaluation should consider the molar volume change due to nonideal mixing behavior. However, a rough estimation made from the experimental volume change for a volume ratio of 1 for the C_7F_{16} + C_7H_{16} system ($\Delta V_{mix} \approx 6$ cm^3·mol^{-1})[5] shows that ϕ_c should not differ more than 0.7% from the value calculated assuming ideal mixing. Figures 1, 2, and 3 report the Θ/Φ plots for C_6F_{14} + HC, C_7F_{16} + HC, and C_8F_{18} + HC systems, respectively. Most curves do fall on the same universal line, particularly in the critical central region of the graph. These results are in agreement with the findings reported by Munson[17] and Gilmour,[18] yet the universality of FC + HC binary mixtures is still debated.[12]

The density of each pure liquid has been measured directly as a function of temperature and is listed in Table 3.

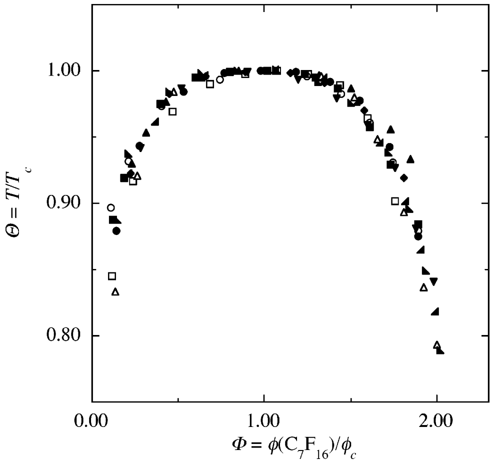

Figure 2. Liquid−liquid coexistence curves for binary mixtures containing perfluoroheptane in reduced coordinates Θ/Φ. ■, C_7F_{16} + C_7H_{16}; ●, C_7F_{16} + n-C_8H_{18}; ▲, C_7F_{16} + i-C_8H_{18}; □, C_7F_{16} + $C_{10}H_{22}$; ○, C_7F_{16} + C_6H_{12}; △, C_7F_{16} + C_6H_6; ◆, C_7F_{16} + CCl_4; ▼, C_7F_{16} + $CDCl_3$; solid, left-slanting triangle, C_7F_{16} + $CHCl_3$; solid, right-slanting triangle, C_7F_{16} + CH_2Cl_2.

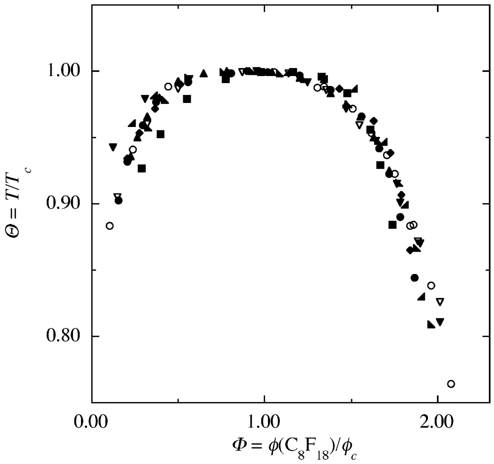

Figure 3. Liquid−liquid coexistence curves for binary mixtures containing perfluorooctane in reduced coordinates Θ/Φ. ▽, C_8F_{18} + C_6H_{14}; ■, C_8F_{18} + C_7H_{16}; ●, C_8F_{18} + n-C_8H_{18}; ▲, C_8F_{18} + i-C_8H_{18}; ○, C_8F_{18} + C_6H_{12}; ◆, C_8F_{18} + CCl_4; ▼, C_8F_{18} + $CDCl_3$; solid, left-slanting triangle, C_8F_{18} + $CHCl_3$; solid, right-slanting triangle, C_8F_{18} + CH_2Cl_2.

Table 3. Density of FC and HC as a Function of Temperature: $\rho = \rho_0 - aT$

	$(\rho_0 \pm \sigma)$/g·mL^{-1}	$(a \pm \sigma)$/g·K^{-1}·mL^{-1}	R^2
C_6F_{14}	$2.59236 \pm 5.09 \times 10^{-3}$	$0.00307 \pm 1.67 \times 10^{-5}$	.99974
C_7F_{16}	$2.58995 \pm 6.47 \times 10^{-3}$	$0.00290 \pm 2.03 \times 10^{-5}$	.99946
C_8F_{18}	$2.52857 \pm 9.19 \times 10^{-4}$	$0.00259 \pm 3.01 \times 10^{-7}$	1
CCl_4	$2.17010 \pm 1.14 \times 10^{-3}$	$0.00197 \pm 3.66 \times 10^{-6}$	.99984
$CDCl_3$	$2.06994 \pm 4.20 \times 10^{-4}$	$0.00194 \pm 1.37 \times 10^{-6}$	.99996
$CHCl_3$	$2.05590 \pm 1.73 \times 10^{-3}$	$0.00194 \pm 5.57 \times 10^{-6}$	.99986
CH_2Cl_2	$1.86850 \pm 2.38 \times 10^{-3}$	$0.00185 \pm 7.89 \times 10^{-6}$	.99985
C_6H_{14}	$0.92270 \pm 2.30 \times 10^{-4}$	$0.00090 \pm 1.00 \times 10^{-5}$	1
C_7H_{16}	$0.93962 \pm 2.53 \times 10^{-4}$	$0.00087 \pm 2.12 \times 10^{-5}$	.99988
C_8H_{18}	$0.93973 \pm 2.63 \times 10^{-4}$	$0.00080 \pm 3.12 \times 10^{-5}$	1
i-C_8H_{18}	$0.92540 \pm 1.83 \times 10^{-4}$	$0.00080 \pm 1.54 \times 10^{-5}$	1
$C_{10}H_{22}$	$0.99526 \pm 9.32 \times 10^{-5}$	$0.00076 \pm 3.05 \times 10^{-7}$	.99999
C_6H_{12}	$1.05630 \pm 1.67 \times 10^{-4}$	$0.00095 \pm 1.28 \times 10^{-5}$	1
C_6H_6	$1.20130 \pm 1.98 \times 10^{-3}$	$0.00110 \pm 2.71 \times 10^{-5}$	1
$C_5H_{12}O$	$1.05090 \pm 4.05 \times 10^{-4}$	$0.00104_5 \pm 1.28 \times 10^{-6}$	.99995
$C_6H_{14}O$	$1.04400 \pm 1.06 \times 10^{-3}$	$0.00099 \pm 3.35 \times 10^{-6}$	.99991

Table 4. Polarizability (α/Å^3) of HC

	α/Å^3
C_6H_{14}	11.81
C_7H_{16}	13.69
C_8H_{18}	15.50
i-C_8H_{18}	15.4
$C_{10}H_{22}$	19.22
C_6H_{12}	10.98
C_6H_6	10.51
CCl_4	10.47
$CHCl_3$	8.23
CH_2Cl_2	6.48
$C_5H_{12}O$	10.63[a]
$C_6H_{14}O$	12.47[a]

[a] Values calculated according to ref 21.

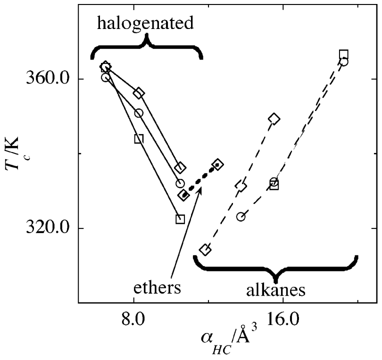

Figure 4. T_c/K vs α_{HC}/Å^3 (polarizability of the nonfluorinated component). □, C_6F_{14}; ○, C_7F_{16}; ◇, C_8F_{18}. Solid lines are for halogenated solvents, dotted lines are for alkanes, and the thick dotted line is for ethers.

Because the interactions that rule the phase separation behavior of this kind of mixture are mainly derived from dispersion forces that are dictated by polarizabilities and ionization potentials,[19] it is interesting to relate the experimental results to the polarizability (α/Å^3) of the components.

Table 4 lists the values of α for the different liquids that were obtained from the literature.[20−22]

Figure 4 reports T_c as a function of the polarizability of the hydrogenated solvent (α_{HC}/Å^3) for all FC. The plot shows that

(1) T_c depends almost linearly on α_{HC};

(2) for chlorinated solvents (solid lines), T_c decreases as polarizability increases; and

(3) for n-alkanes (dotted lines) and ethers (thick dotted line) the trend is inverted, with an increment of T_c as a function of the polarizability of HC.

This different behavior can be explained by considering the different interactions that are established between the components.

When mixed with other organic liquids, perfluoroalkanes mainly interact via dispersion (London) forces that directly depend on polarizabilities, α_i, and ionization potentials, I_i ($U_{\text{disp}} \propto -I_1I_2\alpha_1\alpha_2/(I_1 + I_2)r^6$). If the second component has a nonzero dipole moment μ_i, then FC can also establish dipole−induced dipole (Debye) interactions ($U_i = -\alpha_1\mu_2^2 + \alpha_2\mu_1^2/r^6$). However, FC do not participate in orientation or dipole−dipole (Keesom) interactions because these temperature-dependent forces require that both components be polar ($U_o \propto -\mu_1^2\mu_2^2/k_BTr^6$).

As for CO_2 + perfluoalkanes solutions,[23] in the case of fluorocarbon + alkane mixtures, the dominant interaction is of the dispersion kind because both components are almost completely apolar. The phase separation behavior will be mainly affected by the molecular size and geometry,[24] as indicated by the lowering of T_c when perfluorooctane is mixed with the branched 2,2,4-trimethylpentane and by the increment in T_c in cyclohexane-containing mixtures. In the case of mixtures containing ethers that possess a nonzero dipole moment, Debye interactions emerge. Moreover, perfluoroalkanes have some capacity to act as weak electron acceptors, and ethers behave as electrons donors.[19] Finally, chloroform and dichloromethane possess dipole moments (about 3.8×10^{-30} C·m and 5.2×10^{-30} C·m, respectively) and can establish orientation, induced, and electron acceptor−donor interactions.[19] It is evident that the mixing of a fluorocarbon with $CHCl_3$ or CH_2Cl_2 would progressively destroy the intermolecular orientation forces in the pure chlorinated components and substitute them with much weaker unlike molecular interactions. This effect is more pronounced in the case of CH_2Cl_2, and in fact, T_c increases for all fluorocarbons from carbon tetrachloride to chloroform to dichloromethane.

Conclusions

The phase separation in fluorocarbon + hydrocarbon mixtures reflects the nonideality of such systems and strongly depends on the chemical structure of the components. In the present work, we determined the coexistence curves of mixtures containing a linear perfluoroalkane (perfluorohexane, perfluoroheptane, or perfluorooctane) and a linear, branched, cyclic, aromatic, deuterated, oxygenated, or halogenated hydrocarbon. The results indicate that the presence of aromaticity and oxygen or chlorine atoms in the hydrogenated component significantly increments the upper consolute temperature (T_c) of the binary mixture.

The reduced plots (T/T_c versus ϕ/ϕ_c) for the different mixtures indicate a universal behavior of the liquid−liquid coexistence curves.

In general, more asymmetric and polarizable chemicals produce a decrement in mutual solubility with fluorocarbons, and mixing occurs only at higher temperatures. The presence of deuterium lowers the critical consolute temperature.

The dependence of the upper consolute solution temperature on the polarizability of the components reflects the specific dominant role played by dispersion forces in these systems. However, the real system is more complex, and ionization potential differences, real effective polarizabilities in the mixed systems, local dipole moments, and noncentral (surface) interactions seem to remain relevant factors in determining the anomalies of fluorinated mixtures.

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