Kamlet−Taft Thermosolvatochromic Parameters of Hydrofluoroethers and Hydrofluoroether Azeotropic Mixtures

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The electronic transition maxima of three solvatochromic probes were measured at temperatures between (−13.5 and 70 °C) in five liquid hydrofluoroether (HFE) solvents. The electronic transition maxima were used to calculate thermosolvatochromic Kamlet−Taft parameters. The solubilities of naphthalene and benzoic acid were measured in the HFE solvents, and a linear solvation energy relationship (LSER) was calculated to model the solubility data using the measured Kamlet−Taft thermosolvatochromic parameters. Differences between the Kamlet−Taft values of the pure hydrofluoroethers and azeotropic mixtures of the hydrofluoroethers are discussed, along with the LSER results.

Introduction

Several hydrofluoroether (HFE) solvents and HFE azeotropic mixtures have gained popularity for use as replacement solvents for chlorofluorocarbon (CFC) solvents. Methoxynonafluorobutane (MNB) and ethoxynonafluorobutane (ENB), as well as azeotropic mixtures containing these two HFEs, are being commercially produced. The HFEs are non-ozone-depleting and have short atmospheric lifetimes (4.1 years for MNB and 0.8 years for ENB**)**. They have low toxicity and are thermally and hydrolytically stable, allowing their recirculation in cleaning systems without degredation. Chemically, the presence of the ether oxygen combined with the spatial separation of alkyl and perfluoroalkyl groups in the molecule gives rise to some interesting solvent capabilities.

The HFEs are being used for removal of light hydrocarbon oils, halogenated oils, greases, and particulates. The higher densities (1.52 g mL^{-1} at 25 °C for MNB and 1.43 g mL^{-1} at 25 °C for ENB**),** low evaporative losses (26.9 kPa at 25 °C for MNB and 14.5 kPa at 25 °C for ENB), and low surface tension (1.4×10^{-4} N m^{-1} at 25 °C for MNB and ENB) of these HFE solvents permits cleaning, rinsing, and drying in a single application. Furthermore, their compatibility with a wide range of metals, plastics, and elastomers permits direct solvent replacement in existing equipment. Azeotropic mixtures of HFEs with alcohols and organic solvents can be used for more demanding cleaning applications. The addition of other solvents to the HFE results in a dramatic increase in the solvent strength and permits cleaning of medium weight oils, silicone oils, flux residues, and low melting point waxes. HFE solvents and azeotropic mixtures have found use in the removal of fluxes from circuit boards and in the cleaning of medical components and aircraft bearings.

Prediction of thermodynamic and kinetic data associated with solution processes is important in evaluating the cleaning ability of HFEs. Likewise, other applications for HFEs require thermophysical data for assessment of potential replacement advantages. Solvatochromic interaction parameters (solvent scales) have successfully modeled thermodynamic and kinetic data. One of the most comprehensive solvent scales to date is the Kamlet−Taft solvent scale. The parameters of the Kamlet−Taft solvent scale quantify the solvent's hydrogen bond donor ability α, hydrogen bond acceptor ability β, and dipolarity/polarizability π^*.[1−3] The Kamlet−Taft values numerically quantify solvent−solute interactions that are representative in all types of solution equilibria by measuring a specific interaction that is local to the solvation shell about a dissolved solvatochromic solute. The parameters have been used extensively in linear solvation energy relationships (LSERs) to predict solution equilibria.[4−8] We envision that the Kamlet−Taft parameters for the HFEs reported herein can be used to develop LSERs to provide insight into the important molecular interactions in cleaning applications and can be used as a guide for future modifications of HFE molecular structures.

Table 1. Composition and Components of HFE Solvents Studied

mass %	components	solvent designation
100.0	methoxynonafluorobutane	MNB
100.0	ethoxynonafluorobutane	ENB
52.7	methoxynonafluorobutane	A1
44.6	*trans*-1,2-dichloroethylene	
2.7	ethyl alcohol	
50.0	methoxynonafluorobutane	A2
50.0	*trans*-1,2-dichloroethylene	
93.3	methoxynonafluorobutane	A3
6.7	isopropyl alcohol	

Experimental Section

Chemicals. The solvatochromic probe molecules 4-nitroanisole (**1**), 4-nitrophenol (**2**), and 2,6-diphenyl-4-[2,4,6-triphenylpyridinio]phenolate inner salt (Reichardt's Dye) (**3**) and the solutes naphthalene and benzoic acid were obtained from commercial suppliers in the highest purities available and were used as received. The hydrofluoroether solvents listed in Table 1 were obtained from a commercial supplier and used as received. The stated purities of all hydrofluorether solvents and solvent mixtures were greater than 99%.

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10.1021/je010201y

Measurement of Solution Spectra. The spectra of the solvatochromic probes were measured in matched 1 cm quartz cuvettes on a dual-beam, high-resolution, ultraviolet−visible spectrophotometer. The cuvette holder was a black-anodized aluminum block that was thermostated (±0.1 °C) by a circulating ethylene glycol and water bath. A second thermostated cuvette holder was fabricated to be used with a 10 cm quartz cuvette. This longer path length cuvette was necessary to measure a suitable visible spectrum of **3** because of the lower solubility of **3** in the HFE solvents and because of the lower extinction coefficient of **3**. Each solvatochromic probe was dissolved directly in the liquid HFE in a quartz cuvette and the concentration adjusted to 0.4 and 0.8 absorbance units at peak maximum. A reference cuvette containing the pure HFE was used in all measurements. The spectra of the solvatochromic probes in the HFEs were measured in triplicate at a resolution of 0.05 nm per data point.

Measurement of Naphthalene and Benzoic Acid Solubility. The solubilities of naphthalene and benzoic acid were measured by supersaturating the HFE solvents with a given solute and measuring the amount of dissolved solute by UV absorbance spectroscopy. Calibration curves of naphthalene and benzoic acid in acetonitrile were recorded at 25 °C using 1 cm thermostated quartz cuvettes. Crystals of the solute were added to a test tube containing the HFE solvent suspended in a circulating water bath to form a supersaturated solution. An aliquot of the solution was pipetted into a volumetric flask and the flask filled to the fiducial mark with acetonitrile. This solution was further diluted until the absorbance value (at 275 nm for naphthalene or 272 nm for benzoic acid) was within the linear range of the calibration curve.

Results

Solvatochromic Parameter Calculations. In the calculation of the solvatochromic interaction parameters, we have chosen to replace the solvatochromic equations for π^* and β of Kamlet and Taft[2,3,9] with the temperature-dependent solvatochromic equations of Laurence and Nicolet.[10,11] In eqs 1−7, the electronic transition frequency (ν) of any solvatochromic probe is expressed in units of 10^3 cm^{-1}. The π^* value of a solvent is calculated using the transition frequency maximum of a non-hydrogen-bonding solvatochromic probe in the solvent (ν), relative to the frequencies of the probe in cyclohexane (ν) and dimethyl sulfoxide (ν)

$$\pi^* = \frac{\nu(\text{solvent}) - \nu(\text{cyclohexane})}{\nu(\text{DMSO}) - \nu(\text{cyclohexane})} \tag{1}$$

The respective expression to calculate π^* values using the non-hydrogen-bonding probe **1** is then

$$\pi^*(\mathbf{1}) = \frac{\nu(\mathbf{1})^{\text{obs}} - 34.12}{-2.40} \tag{2}$$

In reevaluating numerous β scales, Laurence selected specific non-hydrogen bond acceptor solvents for the reference line to minimize errors in the solvatochromic values for slightly polar bases and highly polar bases and recommended solvatochromic probe pair **1** and **2** (for OH donors) to calculate β values.[10] The pertinent equation for the reference line is

$$\nu(\mathbf{2})^{\text{calc}} = 1.0434\nu(\mathbf{1})^{\text{obs}} - 0.57 \tag{3}$$

The β value of a solvent is proportional to its displacement from the reference line for a solvatochromic probe pair. The magnitude of the displacement from the reference line is the difference between the observed electronic transition and the reference line value from eq 3. Using eq 3, the deviation from the reference line, $-\Delta\Delta\nu(\mathbf{2}-\mathbf{1})$, is calculated from

$$-\Delta\Delta\nu(\mathbf{2}-\mathbf{1}) = \nu(\mathbf{2})^{\text{calc}} - \nu(\mathbf{2})^{\text{obs}} = 1.0434\nu(\mathbf{1})^{\text{obs}} - 0.57 - \nu(\mathbf{2})^{\text{obs}} \tag{4}$$

In the Kamlet−Taft methodology, to organize $-\Delta\Delta\nu(\mathbf{2}-\mathbf{1})$ values into a usable solvatochromic scale, the deviation from the reference line for a strong base (hexamethylphosphoramide) is assigned a β value of 1.00. This is typically done for the solvatochromic probe pair *p*-nitroaniline (**4**) and *p*-nitro-*N*,*N*-dimethylaniline (**5**). Next, values of $-\Delta\Delta\nu(\mathbf{2}-\mathbf{1})$ are plotted against $-\Delta\Delta\nu(\mathbf{4}-\mathbf{5})$ to generate an expression for the β value using **1** and **2** as a homologue. Laurence has shown that the class dependence of $-\Delta\Delta\nu(\mathbf{2}-\mathbf{1})$ against $-\Delta\Delta\nu(\mathbf{4}-\mathbf{5})$ is severe and thus it is perhaps best to assign a value of 1.00 to hexamethylphosphoramide (HMPA) for a given solvatochromic homologue.[10] Thus, it is the ratio of the deviation in a given solvent to the deviation of HMPA that is used to calculate a β value. For the **1** and **2** homologue,

$$\beta = \frac{-\Delta\Delta\nu(\mathbf{2}-\mathbf{1})_{\text{solvent}}}{-\Delta\Delta\nu(\mathbf{2}-\mathbf{1})_{\text{HMPA}}} = \frac{-\Delta\Delta\nu(\mathbf{2}-\mathbf{1})_{\text{solvent}}}{2.000} \tag{5}$$

A nonthermochromic reference line and equation for α values were established by Kamlet and Taft using probes **1** and **3**.[1] The pertinent equation is

$$-\Delta\Delta\nu(\mathbf{3}-\mathbf{1}) = \nu(\mathbf{3})^{\text{calc}} - \nu(\mathbf{3})^{\text{obs}} = 1.873\nu(\mathbf{1})^{\text{obs}} - 74.58 + \nu(\mathbf{3})^{\text{obs}} \tag{6}$$

The α scale is normalized to methanol ($\alpha = 1.00$) by use of

$$\alpha = \frac{-\Delta\Delta\nu(\mathbf{4}-\mathbf{1})_{\text{solvent}}}{-\Delta\Delta\nu(\mathbf{4}-\mathbf{1})_{\text{methanol}}} = \frac{-\Delta\Delta\nu(\mathbf{4}-\mathbf{1})_{\text{solvent}}}{6.24} \tag{7}$$

The temperature-dependent frequency maxima of the solvatochromic probes in the HFE solvents and their calculated Kamlet−Taft values are presented in Table 2. The average uncertainty in the frequency maximum is ±6 cm^{-1}, and the average uncertainty in the calculated Kamlet−Taft values is ±0.005 units. All reported uncertainties have been multiplied by a coverage factor of 2.0.[12]

Results for the measured solubilities of naphthalene and benzoic acid are given in Table 3. The average relative uncertainty in the reported mole fraction solubility was ±6%.

Discussion

The results of Table 2 indicate that the HFE solvents are stronger hydrogen bond donor solvents than the fluorinated alkane solvents studied previously.[13−15] For solvatochromic probes **1** and **2**, a hypsochromic shift occurs with increasing temperature, while for **3** a bathochromic shift occurs with increasing temperature, because of the nature of the ground- and excited-state energy stabilization. It is difficult to predict the magnitudes of the solvatochromic shifts of hydrogen bond donor and hydrogen bond acceptor probes with temperature. This is due to the competing effects of both the hydrogen bond formation equilibrium between the probe and the solvent, and the autoassociation equilibrium. Another complicating factor

Table 2. Frequency Maxima of Solvatochromic Probe Molecules and Calculated Kamlet–Taft Values for the HFE Solvents

t °C	$10^{-3}\nu(\mathbf{1})$ cm^{-1}	$10^{-3}\nu(\mathbf{2})$ cm^{-1}	$10^{-3}\nu(\mathbf{3})$ cm^{-1}	α	β	π^*
			MNB			
−13.5	33.365	34.021	16.903	0.771	0.111	0.334
−5.0	33.437	34.178	16.595	0.744	0.070	0.304
10.0	33.536	34.392	15.962	0.672	0.015	0.263
25.0	33.660	34.558	15.287	0.602	−0.003	0.211
40.1	33.742	34.708	14.626	0.520	−0.036	0.177
55.0	33.860	34.884	13.954	0.448	−0.062	0.129
			ENB			
−13.5	33.422	34.168	16.512	0.726	0.067	0.310
−5.0	33.452	34.241	16.335	0.707	0.047	0.298
10.0	33.612	34.485	15.752	0.661	0.008	0.232
25.1	33.666	34.612	15.252	0.598	−0.027	0.209
40.1	33.765	34.730	14.660	0.532	−0.035	0.168
55.0	33.879	34.868	13.983	0.458	−0.044	0.121
70.0	34.008	35.034	13.352	0.396	−0.060	0.067
			A1			
−13.5	32.868	31.879	16.376	0.538	0.922	0.540
−5.1	32.947	31.962	16.110	0.519	0.922	0.507
10.0	33.061	32.108	15.685	0.485	0.909	0.460
25.0	33.160	32.265	15.341	0.460	0.882	0.419
35.1	33.224	32.387	15.099	0.440	0.855	0.392
			A2			
−13.5	32.712	32.355	14.505	0.191	0.603	0.605
−5.0	32.765	32.436	14.250	0.167	0.590	0.583
10.0	32.834	32.547	13.892	0.130	0.571	0.554
25.0	32.916	32.669	13.474	0.088	0.553	0.520
35.1	32.963	32.781	13.150	0.050	0.521	0.501
			A3			
−13.5	33.241	32.108	16.583	0.726	1.003	0.385
−5.0	33.272	32.158	16.705	0.712	0.994	0.372
10.0	33.631	32.261	16.379	0.686	0.989	0.335
25.0	33.439	32.386	16.139	0.672	0.967	0.303
40.0	33.510	32.515	15.844	0.646	0.940	0.274
50.0	33.581	32.616	15.606	0.629	0.926	0.244

in the thermosolvatochromic approach is that the relative intensities of vibrational bands that are superimposed under the absorption band can skew the measured maximum in the absorption band.[11]

In the original design of their solvatochromic scales, Kamlet and Taft suggested that a number of different values be determined for β using different solvatochromic probes and that an average value of β be reported. They calculated β values using the **1**−**2** homologue using

$$\beta = \frac{-\Delta\Delta\nu(\mathbf{2}-\mathbf{1})_{\text{solvent}}}{-\Delta\Delta\nu(\mathbf{2}-\mathbf{1})_{\text{HMPA}}} = \frac{-\Delta\Delta\nu(\mathbf{2}-\mathbf{1})_{\text{solvent}}}{2.80(0.825)} \tag{8}$$

This equation was derived by comparison of the **1**−**2** homologue with the **4**−**5** homologue. Our calculated values using eq 5 are similar (±0.05) to those calculated from eq 8 for most of the HFE solvents studied, with the notable exception of **A1** and **A3,** which contain alcohol cosolvents. The discrepancy is most probably attributable to the solvent-class dependence of the **1**−**2** homologue.

The hydrogen-bonding values, α and β, decreased for all solvents with increasing solvent temperature. This is expected, as hydrogen bond energy is expected to decrease with temperature. What is interesting to note is the very large values of α and β for **A1** and **A3** with only a small mass fraction of alcohol cosolvent. It is expected that the self-association of alcohols in nonpolar solvents will have a dramatic effect on the solvent structure and compete with the interaction of the solvatochromic probe with free alcohol. This is manifested in the slopes of the α, β, and π^* values with temperature as shown in Figures 1−3, respectively. For MNB and ENB**,** the α values exhibit a distinctly different temperature dependence than the α values for the azeotropic mixtures containing alcohol. It would appear from the measurements that the solvatochromism of the probe-alcohol pair is the predominant hydrogen-bonding interaction being measured.

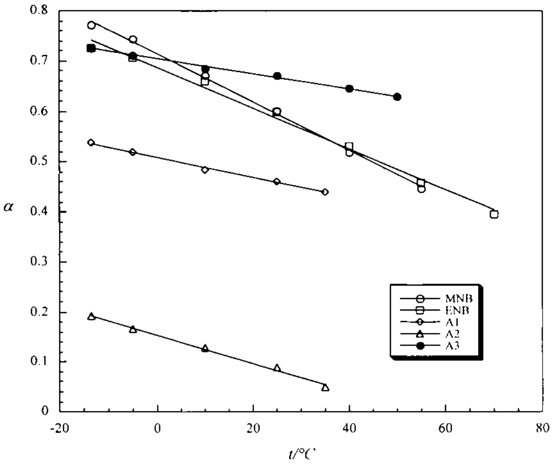

Figure 1. Temperature dependence of α for HFE solvents.

Table 3. Mole Fraction Solubility of Naphthalene and Benzoic Acid in the HFE Solvents

t/°C	x(naphthalene)	x(benzoic acid)
	MNB	
−13.5	1.79×10^{-3}	1.38×10^{-4}
−5.0	2.64×10^{-3}	1.72×10^{-4}
10.0	6.78×10^{-3}	2.72×10^{-4}
25.0	1.07×10^{-2}	5.60×10^{-4}
40.1	1.33×10^{-2}	1.10×10^{-3}
55.0	3.20×10^{-2}	2.35×10^{-3}
	ENB	
−13.5	3.74×10^{-3}	2.82×10^{-4}
−5.0	5.00×10^{-3}	2.97×10^{-4}
10.0	7.63×10^{-3}	4.59×10^{-4}
25.1	1.37×10^{-2}	8.57×10^{-4}
40.1	2.16×10^{-2}	1.33×10^{-3}
55.0	2.07×10^{-1}	2.42×10^{-3}
70.0	2.61×10^{-1}	4.63×10^{-3}
	A1	
−13.5	3.05×10^{-3}	1.61×10^{-2}
−5.1	3.51×10^{-2}	2.03×10^{-2}
10.0	6.52×10^{-2}	2.72×10^{-2}
25.0	1.06×10^{-1}	3.32×10^{-2}
35.1	1.54×10^{-1}	3.72×10^{-2}
	A2	
−13.5	3.26×10^{-2}	5.28×10^{-3}
−5.0	3.90×10^{-2}	7.56×10^{-3}
10.0	5.51×10^{-2}	1.14×10^{-2}
25.0	7.85×10^{-2}	1.62×10^{-2}
35.1	9.35×10^{-2}	1.90×10^{-2}
	A3	
−13.5	5.08×10^{-3}	6.15×10^{-3}
−5.0	5.11×10^{-3}	7.05×10^{-3}
10.0	8.42×10^{-3}	1.08×10^{-2}
25.0	1.43×10^{-2}	1.38×10^{-2}
40.0	3.20×10^{-2}	1.63×10^{-2}
50.0	4.32×10^{-2}	1.89×10^{-2}

The β values for the **A2** azeotrope are unusually large. The addition of *trans*-1,2-dichloroethylene (α = 0.00, β = 0.00, π^* = 0.44)[16] would not be expected to increase β so significantly because it does not possess a hydrogen bond acceptor ability. Attenuated total reflectance−Fourier transform infrared spectroscopy (ATR-FTIR) measurements

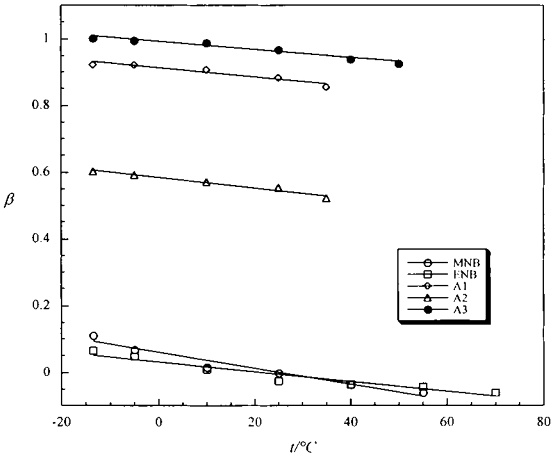

Figure 2. Temperature dependence of β for HFE solvents.

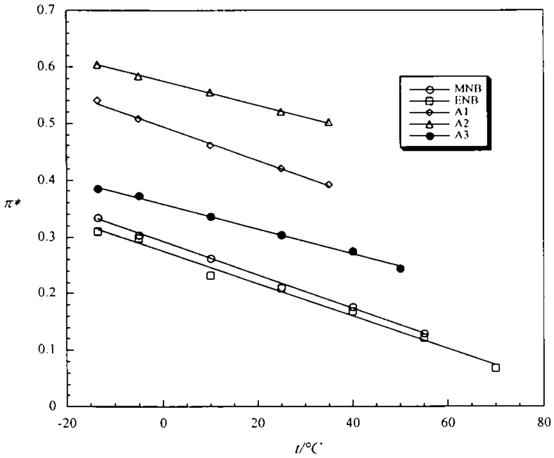

Figure 3. Temperature dependence of π^* for HFE solvents.

were made on MNB and **A2** to try to rationalize the β value of **A2**. The only spectral difference between the two solvents and that of pure *trans*-1,2-dichloroethylene was in the C−O asymmetric stretching frequency. A significant decrease in the peak doublet at 1222 cm^{-1} was observed in **A2**, and the other peak of the doublet was shifted from 1240 cm^{-1} in MNB to 1250 cm^{-1} in **A2**. This same spectral characteristic is also present in **A1**, which also contains 2.7% ethanol. These observations suggest that the ether oxygen of MNB is associating to some extent with *trans*-1,2-dichloroethylene to increase the hydrogen bond acceptor ability of the solution. There is not a simple explanation to the experimental observations because if the ether oxygen of MNB is involved in a complex with *trans*-1,2-dichloroethylene, then MNB will be less available for external complexation with a hydrogen-bonding acid and not more available as experimentally observed.

Table 3 reports the measured solubilities of naphthalene and benzoic acid. In all HFE solvents, the solubility of naphthalene is greater than the solubility of benzoic acid. The solubilities of Table 3 were next used as the dependent variable in a LSER that incorporated the measured Kamlet−Taft values of Table 2. For benzoic acid ($\alpha = 0.59$, $\beta = 0.40$, $\pi^* = 0.90$),[4] the mole fraction solubility, x, is expressed using the measured Kamlet−Taft parameters of the HFE solvents using the following calculated LSER equation,

$$\ln x = -2.62\ (\pm\ 0.38) - [5.63\ (\pm\ 0.43)]\alpha + [4.93\ (\pm\ 0.23)]\beta - [6.19\ (\pm\ 0.77)]\pi^*$$

$$r = 0.98, \quad n = 29, \quad \mathrm{sd} = 0.36 \qquad (9)$$

For naphthalene ($\alpha = 0.00$, $\beta = 0.20$, $\pi^* = 0.92$),[4] the calculated LSER is

$$\ln x = -1.70\ (\pm\ 0.66) - [7.14\ (\pm\ 0.74)]\alpha + [1.83\ (\pm\ 0.39)]\beta - [8.11\ (\pm\ 1.31)]\pi^*$$

$$r = 0.89, \quad n = 29, \quad \mathrm{sd} = 0.57 \qquad (10)$$

The correlation coefficient r shows that the predictive ability of the LSER for benzoic acid is better than that of the LSER for naphthalene. This is perhaps because three of the HFE solvents studied are azeotropes that strongly depend on the interactions of the minor alcohol cosolvent, which may be the primary species interacting with the more polar molecule of benzoic acid. Since the measured Kamlet−Taft parameters appear to be strongly influenced by the alcohol component of the azeotrope, the measured Kamlet−Taft parameters for the mixture would be valid descriptors of an interaction primarily between benzoic acid and the alcohol component. The nonpolar naphthalene molecule in solution may be interacting with the less polar HFE component of the azeotrope. The limited predictive ability of the naphthalene LSER can therefore be attributed to the strong dependence of the Kamlet−Taft parameters on the alcohol cosolvent.

Conclusions

The thermosolvatochromic Kamlet−Taft values of five HFE solvents were measured as well as the solubilities of naphthalene and benzoic acid in the HFE solvents. LSERs were established to model the solubility data using the measured Kamlet−Taft values. It is evident that the Kamlet−Taft values of the azeotropic mixtures of the hydrofluoroethers strongly depend on the cosolvent, and this is reflected in the ability of the LSERs to accurately model the measured solubility data.

Acknowledgment

The 3M Corporation is gratefully acknowledged for providing the HFE solvents used in this work.

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Received for review July 16, 2001. Accepted September 20, 2001.

JE010201Y