

Impact of fluorine on the phase behavior of bis-*p*-tolyl propane in supercritical CO₂, 1,1-difluoroethane, and 1,1,1,2-tetrafluoroethane

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ABSTRACT

Fluorine substitution on a solute can have a significant effect on solute solubility in a given solvent and fluorine substitution on a solvent can also have a significant effect on solvent quality. The effect of fluorine is demonstrated with the phase behavior data for bis(*p*-tolyl)propane (BTP) compared to bis(*p*-tolyl)hexafluoropropane (BTHFP) in supercritical carbon dioxide, 1,1-difluoroethane (F152a), and 1,1,1,2-tetrafluoroethane (F134a). Semifluorinated BTHFP is more soluble than non-fluorinated BTP in all three solvents, especially CO₂. The CO₂–BTP system exhibits solid solubility behavior while the CO₂–BTHFP system exhibits liquid–liquid–vapor (LLV) behavior near the critical point of CO₂. Although the two dipolar hydrofluorocarbons (HFC) are better solvents than CO₂ for these two aromatic solid compounds, F152a is the superior HFC solvent, especially for BTP, because F152a has a smaller molar volume and a larger effective dipole moment than F134a. LLV behavior is also observed for the F134a–BTP system near the critical point of F134a although the F134a–BTHFP, F152a–BTP, and F152a–BTHFP systems all appear to exhibit type-I phase behavior and no liquid–liquid immiscibility near the respective critical points.

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1. Introduction

The introduction of fluorine atoms into organic molecules has a significant impact on their physico-chemical properties [1], chemical reactivity [2,3] and biological activity [4] compared to the non-fluorinated analog compounds [5]. Fluorine, the most electronegative element of the periodic table, tightly binds its valence electrons, which results in both a low atomic polarizability and a fairly small van der Waals radius (1.47 Å [6]) [7]. C–F bonds are highly polar and very strong due to the electronegativity difference between carbon and fluorine (2.5 vs. 4.0) [8]. It is the strength of C–F bonds, which ranges as high as 130 kcal/mol [9], that makes fluorocarbons preferred for high temperature and/or corrosive environment applications. The steric effect of fluorine relative to other atoms or groups is an important, but, controversial issue [3]. Although the size of fluorine has been reported to be similar to that of hydrogen [3], it has also been suggested that the size of fluorine is more similar to hydroxyl or even methyl groups [10–13]. Interestingly, a trifluoromethyl group is claimed to have the steric effect of an isopropyl group [14,15]. In fact, Taft's E_s° [16–18] scale

suggests that the diameter of a trifluoromethyl group is approximately 40% larger than that of an isopropyl group and only ~15% smaller than that of a *tert-butyl* group [19]. All of these studies testify to the interesting, and sometimes perplexing, effect of fluorine when incorporated into a compound.

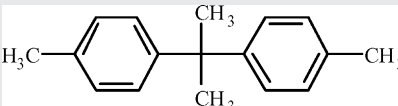
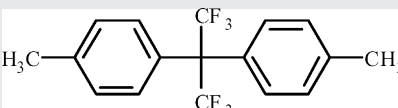
Numerous studies have shown that, compared to their hydrocarbon analogs, fluorinated perfluoroalkanes [20], perfluorinated alkylpolyethers [21], semifluorinated alcohols [22,23], and fluorinated metal chelates [24] have higher solubility in CO₂ [22,25–27]. The polarizability of CO₂ is small, near that of methane, but, it is easy to increase the density of CO₂ which increases the strength of nonpolar dispersion interactions [28]. CO₂ also has a quadrupole moment resulting from the strong electronegative character of oxygen relative to carbon. However, polar interactions decrease with increasing temperature [28] so at modest-to-high temperatures CO₂ behaves more as a weak nonpolar solvent than a polar solvent. There currently remains contradictory evidence on the existence of a specific interaction between CO₂ and a fluorinated molecule. Certain NMR studies suggest there is no specific interaction between fluorine and CO₂ [29,30] while other studies suggest just the opposite [31–33]. Molecular modeling studies also propose both possibilities [34–42]. For example, Stone et al. [42] demonstrate that CO₂ and perfluorocarbons do not exhibit any substantial specific interaction consistent with the results of other modeling [34–36,39,41] and phase behavior studies of fluorinated polymer–CO₂ mixtures [25,43]. Conversely, Fried and Hu [37] conclude that a favorable polar interaction exists between CO₂ and nonpolar CF₄ although they also conclude that a favorable interaction exists for CO₂ with

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Table 1
Select physical properties for 2,2-bis(*p*-tolyl)propane (BTP) and 2,2-bis(*p*-tolyl) hexafluoropropane (BTHFP)^a

		Molecular Weight (g mol ⁻¹)	Melting Temperature (°C)	Heat of Fusion (kJ mol ⁻¹)
2,2-Bis(<i>p</i> -tolyl)propane (BTP)		224.4	78.6	21.2
2,2-Bis(<i>p</i> -tolyl) hexafluoropropane (BTHFP)		332.3	84.1	22.3

^a Melting temperature and heat of fusion were measured with a TA Instruments model Q200 differential scanning calorimeter at 10 °C/min heating rate.

semifluorinated hydrocarbons, which, in our opinion, is more likely given that semifluorinated hydrocarbons possess a polar moment. Interestingly, one study [38] proposes that enhanced interactions between fluorine and CO₂ result from the increased solvent accessible surface of a fluorinated aromatic solute rather than from a specific CO₂–fluorine interaction. Several of the modeling studies [34,41,42] demonstrate that enhanced interactions, leading to improved solubility, are realized with semifluorinated materials having both Lewis acid and base sites configured in a manner to allow both sites to interact simultaneously.

In our previous study, we investigated the effect of fluorine on the phase behavior of bisphenol A (2,2-bis(4-hydroxyphenyl)propane) (BPA) and 2,2-bis(4-hydroxyphenyl) hexafluoropropane (bisphenol AF, BPAF) in supercritical CO₂, CH₃CHF₂ (F152a), and CH₂FCF₃ (F134a) [44]. The solubility of BPA is substantially increased in all three solvents when the methyl groups on isopropylidene are replaced with trifluoromethyl groups (BPAF). Note that both BPA and BPAF have hydroxyl groups which can inter- and intrahydrogen bond which is a much stronger interaction than polar or dispersion interactions. To eliminate the effect of hydrogen bonding on solubility, the present study compares the solubility of 2,2-bis(*p*-tolyl)propane (BTP) and 2,2-bis(*p*-tolyl)hexafluoropropane (BTHFP) in CO₂, F134a, and F152a. No attempt is made to determine detailed features of the complete phase diagrams for these binary mixtures. Rather, the objective is to ascertain the conditions needed to dissolve a certain amount of the solute in these SCF solvents of interest and to compare how these conditions change with the fluorine content of the solutes or the solvents.

Table 1, which lists the structure and physical properties of BTP and BTHFP, shows that both compounds have close to the same melting temperatures. Also, both compounds have almost equal heats of fusion although BTHFP has a much larger molecular weight. The heat of fusion of BTP is slightly lower than that of BTHFP which implies that the ideal mole fraction solubility of BTP is slightly greater than that of BTHFP. However, the ideal weight fraction solubilities for these two compounds are essentially equal after correcting for the differences in molecular weight. Therefore we do not expect the solubility behavior of these two compounds to be dominated by differences in the heats of fusion.

Table 2, which lists the physical properties of the SCF solvents used in this study, shows that both F134a and F152a have signifi-

Table 2
Physical properties of the solvents used in this study

	Molecular Weight (g/mol)	T _c (°C)	P _c (bar)	Polarizability (Å ³)	Dipole moment (D)
CO ₂	44.0	31.0	73.8	2.65	0
CH ₂ FCF ₃ (F134a)	102.0	101.1	40.6	4.38	2.1
CH ₃ CHF ₂ (F152a)	66.1	113.1	45.2	4.15	2.3

CO₂ has a quadrupole moment of 4.3 × 10⁻²⁶ erg^{1/2} cm^{5/2} [43].

cant dipole moments and have polarizabilities that are ~60% larger than that of CO₂. The larger number of fluorine atoms in F134a make it heavier than F152a and should give F134a a higher critical temperature. But, fluorine atoms have very weak self-interactions, which is the reason that the critical temperature of F134a is lower than that of F152a. It is important to recognize how the structure of these two freons impacts their solvent characteristics. Raveendran and Wallen note the importance of the charge separation and partial charges of the fluorine and hydrogen atoms which affects the strength of interactions even when these charges are weak [41]. In our earlier study we found F152a to be a much better solvent than F134a even though both F134a and F152a have essentially the same polarizability and dipole moment. We proposed that the difference in solvent strength is a consequence of the smaller molar volume of F152a which endows it with a higher effective polarity, $\mu^{\text{effective}} = \mu^2 / \sigma^3 kT$, where μ is the permanent dipole moment, σ is the collision diameter, k is Boltzmann's constant, and T is the absolute temperature [45]. We also speculated that the difference in solvent power between F134a and F152a is due to the separation of the hydrogen and fluorine atoms on each freon which fixes the electrostatic potential field surrounding each of these solvent molecules. Semi-empirical, quantum mechanics calculations [46] show that the isosurface with a potential of -0.03 a.u. for F134a is located within the van der Waals radius of the fluorine atoms, whereas, for F152a, a large portion of the two isosurfaces with potentials of +0.03 and -0.03 a.u. project slightly beyond the molecular dimension of the respective atoms [44]. These calculations suggest that F152a has stronger electrostatic interactions with other molecules over slightly greater separation distances than does F134a, which translates into stronger solvent power for F152a [44]. The experimental information generated in the present study with BTP and BTHFP in CO₂, F134a, and F152a will provide more insight into the interesting impact of fluorine on solubility.

2. Experimental

2.1. Phase transition

Described in detail elsewhere is the apparatus and techniques used to obtain SCF-solute phase behavior data [47]. A high-pressure, variable-volume cell (7.0 cm o.d. × 1.6 cm i.d., ~30 cm³ working vol-

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