CHROM. 21 157

SOLVENT STRENGTH AND SELECTIVITY PROPERTIES OF SUPERCRITICAL CARBON DIOXIDE RELATIVE TO LIQUID HEXANE

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SUMMARY

Non-polar, non-polar chromatography (chromatography with non-polar solvents and a non-polar stationary phase) was used to study the solvent properties of supercritical carbon dioxide. Six substituted benzenes were chosen as chromatographic test probes on C_{18} reversed-phase columns to examine selectivity differences between hexane and supercritical carbon dioxide mobile phases. We have found that Lewis base properties of supercritical carbon dioxide give it selectivity properties not observed in hexane. Addition of 3.0% methanol modifier has only minor effects on the solvent strength and selectivity of supercritical carbon dioxide. Lewis acid–base interaction appears to be the primary mechanism for separation and elution order. By understanding Lewis acid–base pairing, hydrogen bonding and induced dipole interactions observed in non-polar, non-polar chromatography we can improve our understanding of chromatographic separations and industrial extractions using supercritical carbon dioxide.

INTRODUCTION

Supercritical carbon dioxide has unique properties as a non-toxic yet effective chromatographic mobile phase and extraction fluid. Applications in which supercritical carbon dioxide has been used include, the extraction of petroleum products, synthetic oils, foods, flavors, fragrances, drugs, biologically active compounds and the removal of toxic organics from environmental matrices[1–4]. Analytical separations utilizing supercritical carbon dioxide include packed, capillary and preparative-scale chromatography[5–7]. The addition of "modifiers" or "entrainers" to supercritical carbon dioxide has been used to improve its solubility and selectivity properties[8]. Although supercritical carbon dioxide has been used for a number of decades in the separation sciences, its selectivity properties and the mechanism of modifier action are not well understood. The field of supercritical fluid chromatography (SFC) is expanding rapidly and the increasing interest in supercritical fluid extraction (SFE) is

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out-pacing our understanding of supercritical fluid solubility and selectivity properties. This lack of knowledge prevents the accurate prediction of the optimal supercritical solvent systems for industrial and analytical applications.

The better our understanding is of the system we are studying the better our ability to predict the outcome of a given extraction or separation. By knowing the chemical composition of the matrix (stationary phase) and the chemical structure of the products (analytes) the appropriate supercritical solvent system may be chosen. In many cases carbon dioxide with appropriate modifiers can be used to achieve the desired separation. Pure supercritical carbon dioxide is a poor extractor of caffeine from coffee beans or nicotine from tobacco unless a small percentage of a polar modifier such as water or methanol is present. On the other hand the extraction of fatty acids from fish tissue, which is composed primarily of collagen, occurs rapidly with pure supercritical carbon dioxide.

Several researchers have compared the selectivity and solubility properties of supercritical carbon dioxide to hexane. Randall[9] used an experimental design similar to that described by Snyder to characterize the solvent properties of supercritical carbon dioxide. Randall[9] concluded that the solvent power of supercritical carbon dioxide was similar to hexane with some strong dipole selectivity tendencies. Mourier et al.[7] examined four different stationary phases using supercritical carbon dioxide with various polar modifiers. Mourier et al.[7] concluded that supercritical carbon dioxide was a non-polar solvent similar to hexane but its selectivity could be changed by modifier addition. Levy and Ritchey[12] investigated modifier effects on carbon dioxide when eluting polyaromatic hydrocarbons from C_8 and diol packed columns. The modifiers studied were methanol, 2-methoxyethanol, 1-propanol, tetrahydrofuran, dimethylsulfoxide, acetonitrile, sulfurhexafluoride and fluorotrichloromethane. They concluded that polar modifiers improved both the solvent strength and selectivity of supercritical carbon dioxide, however any selectivity changes observed were subtle[10]. Wright et al.[13] investigated the solvent strength and selectivity of supercritical carbon dioxide with and without 2.5% methanol modifier on a 5% phenyl poly(methylphenylsiloxane) capillary column. A polarity test mix was used to follow changes. Wright et al.[13] saw little effect on the solvent power or selectivity of the supercritical carbon dioxide with the addition of modifier. Deviation from previously mentioned packed column work was attributed to the low number of active sites on the capillary column. Recently, Morin et al.[14] reported both non-polar–non-polar partitioning and π–π interactions when comparing the separations of several substituted benzenes on a PRP-1 column. This paper will undertake a systematic investigation of the chromatographic separation of substituted benzenes on silica- and polystyrene–divinylbenzene (PSDVB)-based C_{18} columns. The elution order and chromatographic peak shape observed when using analytes with various functional groups will be used to improve our understanding of supercritical carbon dioxide solubility and selectivity properties relative to liquid hexane.

EXPERIMENTAL

Apparatus

The high-performance liquid chromatographic (HPLC) system consisted of two Waters 6000 dual piston pumps, a Wisp 7108 autosampler, a Waters 440 vari-

able, dual-wavelength UV absorbance detector and a Waters system controller/data module. One pump was used to supply hexane and the other supplied methanol. The chromatographic conditions are found in Table I.

The SFC system is a Hewlett Packard 1084 liquid chromatograph which has been modified at the factory for supercritical-fluid operation. The modifications included heat exchangers on the pump heads to maintain the carbon dioxide as a liquid for proper compression, a high-pressure UV cell, a thermostatted backpressure regulator, an inlet pressure gauge and an exit pressure gauge. Two single-piston diaphragm pumps are at the heart of the system and a variable, dual-wavelength UV detector is placed prior to the back pressure regulator. One pump is used to pump carbon dioxide from a diptube cylinder and the second is used to pump liquid methanol. During 100% carbon dioxide operation both pumps are used to pump the carbon dioxide to prevent leakage of trace amounts of methanol into the system. The chromatographic conditions can be found in Table I.

Chromatographic columns

Separate columns from the same lot were used for carbon dioxide and for hexane to eliminate any confusion which may arise due to permanent phase modification by either solvent. The silica-based, high-coverage C$_{18}$ columns were purchased from Analytical Sciences, (Santa Clara, CA, U.S.A.). The PSDVB-based ACT-1 C$_{18}$ columns were purchased from Interaction Chemicals (Mountain View, CA, U.S.A.).

Chemicals and reagents

Dip tibe, high purity (99.998%) carbon dioxide was purchased from Matheson (Seacaucus, NJ, U.S.A.). Hexane, methanol and benzene were all distilled-in-glass

TABLE I

CHROMATOGRAPHIC CONDITIONS

	HPLC	*SFC*
Mobile phase	Hexane	Supercritical CO$_2$
Modifier	Methanol	Methanol
Modifier concentration	3.0% (v/v)	3.0% (v/v)
Pressure	1000–2000 p.s.i.g.	2400 p.s.i.g.
Temperature	24°C	45°C
Flow-rate	1.5 ml/min	1.5 ml/min
Column A	ASI C$_{18}$	ASI C$_{18}$
Material	Silica	Silica
Dimensions	30 cm × 4.6 mm I.D.	30 cm × 4.6 mm I.D.
Particle size	5 μm d_p	5 μm d_p
Plates	7900	7850
Column B	ACT-1 C$_{18}$	ACT-1 C$_{18}$
Material	PSDVB	PSDVB
Dimensions	17.5 cm × 4.6 mm I.D.	17.5 cm × 4.6 mm I.D.
Particle size	10 μm	10 μm
Plates	6800	6700
Wavelength	254 nm	254 nm

high-purity-grade solvents purchased from Burdick & Jackson Labs. (Muskegon, MI, U.S.A.). The substituted benzenes were supplied by Aldrich (Milwaukee, WI, U.S.A.).

Experimental design

A set of eight experiments was chosen to limit the number of variables and to provide a solid base on which to build our understanding of supercritical carbon dioxide solvent properties. All researchers studying supercritical carbon dioxide have found it to be quite comparable to hexane. Since the solvent properties of hexane are well understood, hexane was used as a benchmark. Most matrices which are of interest for supercritical extraction are hydrocarbon based, therefore a C_{18} stationary phase was chosen for the test chromatographic column. Since C_{18}, hexane and supercritical carbon dioxide are all non-polar, subtle changes in solvent strength and selectivity will be more readily noticed. A PSDVB-based C_{18} column was also used to help distinguish the effects of partitioning from adsorption on silica-based columns.

Substituted benzenes were chosen as analyte test probes such that they would differ from each other only by their functional group. The following analytes were selected; toluene (non-polar hydrocarbon), aniline (base), benzoic acid (acid), phenol (hydrogen bonding), nitrobenzene (strong dipole), chlorobenzene (electrophilic) and benzene (non-substituted benchmark). To avoid solute interaction each analyte was run separately. Methanol was selected as the polar modifier, since its use has been referred to extensively in the literature[9,12]. Other workers have shown that the most dramatic changes in solvent power occur due to coverage of active sites on the chromatographic column at modifier concentrations up to 1%[8]. A modifier concentration of 3% was chosen to ensure that the coverage of active sites was complete and not a variable in these studies. Each test probe would be analyzed under eight different conditions, hexane mobile phase on a silica-based C_{18} column, hexane on PSDVB C_{18}, supercritical carbon dioxide on silica C_{18}, supercritical carbon dioxide on PSDVB C_{18}, hexane–3% methanol on silica C_{18}, hexane–3% methanol on PSDVB C_{18}, supercritical carbon dioxide–3% methanol on silica C_{18}, and supercritical carbon dioxide–3% methanol on PSDVB C_{18}.

Procedure

Both the SFC and the HPLC conditions were as identical as possible with the exception of the mobile phase being used (Table 7). Injections of each analyte were made in triplicate to determine accurate retention times. After retention times for all components had been determined for the single solvent systems, 3.0% methanol modifier was added to each mobile phase and the experiments repeated. This procedure was carried out on both the silica- and polymer-based C_{18} columns.

For each set of chromatographic conditions, peak shape was noted with respect to tailing, fronting and sharpness. Retention times to the closest hundreths-of-a-minute were recorded but were rounded down to tenths-of-a-minute after averaging the three runs. Once the average retention times were compiled for each component, capacity factors were calculated according to $k' = (t_R - t_0)/t_0$ where k' is the capacity factor, t_R the retention time of the component and t_0 the retention time of an unretained component.

The t_0 for HPLC was calculated by dividing the column volume by the mobile

phase flow-rate. For packed-column SFC, this calculation does not hold since the mobile phase density and therefore volume changes with temperature and pressure. Therefore, the t_0 was determined experimentally by injecting C$_4$, C$_3$, C$_2$ and C$_1$ hydrocarbons. The packed-column SFC system was fitted with a flame ionization detector for this set of experiments. The retention times of the C$_1$–C$_4$ hydrocarbons were then plotted against carbon number and the C$_0$ retention time was used as t_0.

RESULTS AND DISCUSSION

The t_0 capacity factor and peak shape results are summarized numerically in Table II. Peak shape and relative peak retention times are summarized graphically in Figs. 1 and 2. The figures are graphic representations of the peak shape of each component positioned on a time axis relative to the retention time of benzene. By plotting the retention time of substituted benzenes relative to benzene, the effect of each substituent can be clearly visualized. The retention of all analytes can be explained by Lewis acid–base pairing, hydrogen bonding, π electron interaction and induced dipoles. Table III lists the major forces affecting the retention of analytes in the chromatographic systems studies. The predominance of a particular force varies depending upon the chromatographic conditions. Lewis acid–base pairing can occur between solute and solvent, solute and modifier, solute and stationary phase, solvent and modifier, solute and stationary phase and modifier and stationary phase. The Lewis acid–base pair strength is primarily dependent on the electrostatic and covalent interactions between the acid and the base[15,16].

Solvent strength

The strength of a given solvent is related to its overall "polarity", P', which is often referred to as its chromatographic strength, solvent strength or solvating power. Snyder[10] has characterized the three major types of solvent–solute interactions in liquid chromatography as proton acceptor, proton donor and strong dipole. The overall polarity, P', of a solvent is approximately equal to the sum of these interactions and the proportion of these interactions determined the selectivity of the solvent:

$$P' = p' \text{ (proton acceptor)} + p' \text{ (proton donor)} + p' \text{ (strong dipole)}$$

The proton acceptor and proton donor interactions can be described more universally as electron pair donors and electron pair acceptors (Lewis bases and Lewis acids). Dipole interactions in non-polar, non-polar chromatography range in strength from weak induced dipoles and π electron interaction to stronger hydrogen bonding.

A way of comparing the relative solvent strength of two mobile phases is by comparing capacity factors (Table II). The greater the solvent strength of the mobile phase the smaller k' will be. When carbon dioxide is used as the mobile phase smaller k' values are obtained for most analytes. Thus carbon dioxide at 2400 p.s.i.g. and 45°C density ($d = 0.77$), has slightly greater solvent strength than liquid hexane. Unlike hexane, the solvent strength of supercritical carbon dioxide increases with density. This change is most dramatic near the critical point and is a parabolic function which passes through a maximum[17].

TABLE II

ANALYTE CAPACITY FACTORS (k') UNDER VARIOUS CONDITIONS

T = Tail; t = slight tail; B = broad; S = sharp.

| Compound	Silica C_{18}				PSDVB C_{18}			
	CO_2 (t_0 = 1.3 min)	CO_2 + methanol (t_0 = 1.3 min)	Hexane (t_0 = 1.2 min)	Hexane + methanol (t_0 = 1.2 min)	CO_2 (t_0 = 1.2 min)	CO_2 + methanol (t_0 = 1.2 min)	Hexane (t_0 = 1.1 min)	Hexane + methanol (t_0 = 1.1 min)
Aniline	17.85(T)	3.62(T)	3.83(t)	0.83(S)	2.92(S)	2.50(S)	3.55(S)	1.00(S)
Benzene	0.31(S)	0.69(S)	0.67(S)	1.33(S)	0.58(S)	0.50(S)	1.00(S)	2.27(S)
Benzoic acid	>29.77	3.46(t)	>32.33	2.00(T)	4.58(t)	4.17(S)	>35.36	3.91(T)
Chlorobenzene	0.38(S)	0.77(S)	0.67(S)	0.75(S)	1.42(S)	1.17(S)	1.18(S)	2.82(B)
Nitrobenzene	0.62(S)	0.92(S)	1.00(S)	0.75(S)	2.08(S)	2.08(S)	2.64(S)	3.64(S)
Phenol	6.15(S)	1.62(t)	9.50(BT)	0.75(S)	3.42(t)	3.25(S)	10.45(t)	3.18(S)
Toluene	0.38(S)	0.69(S)	0.58(S)	0.67(S)	1.10(S)	0.75(S)	0.91(S)	0.82(S)
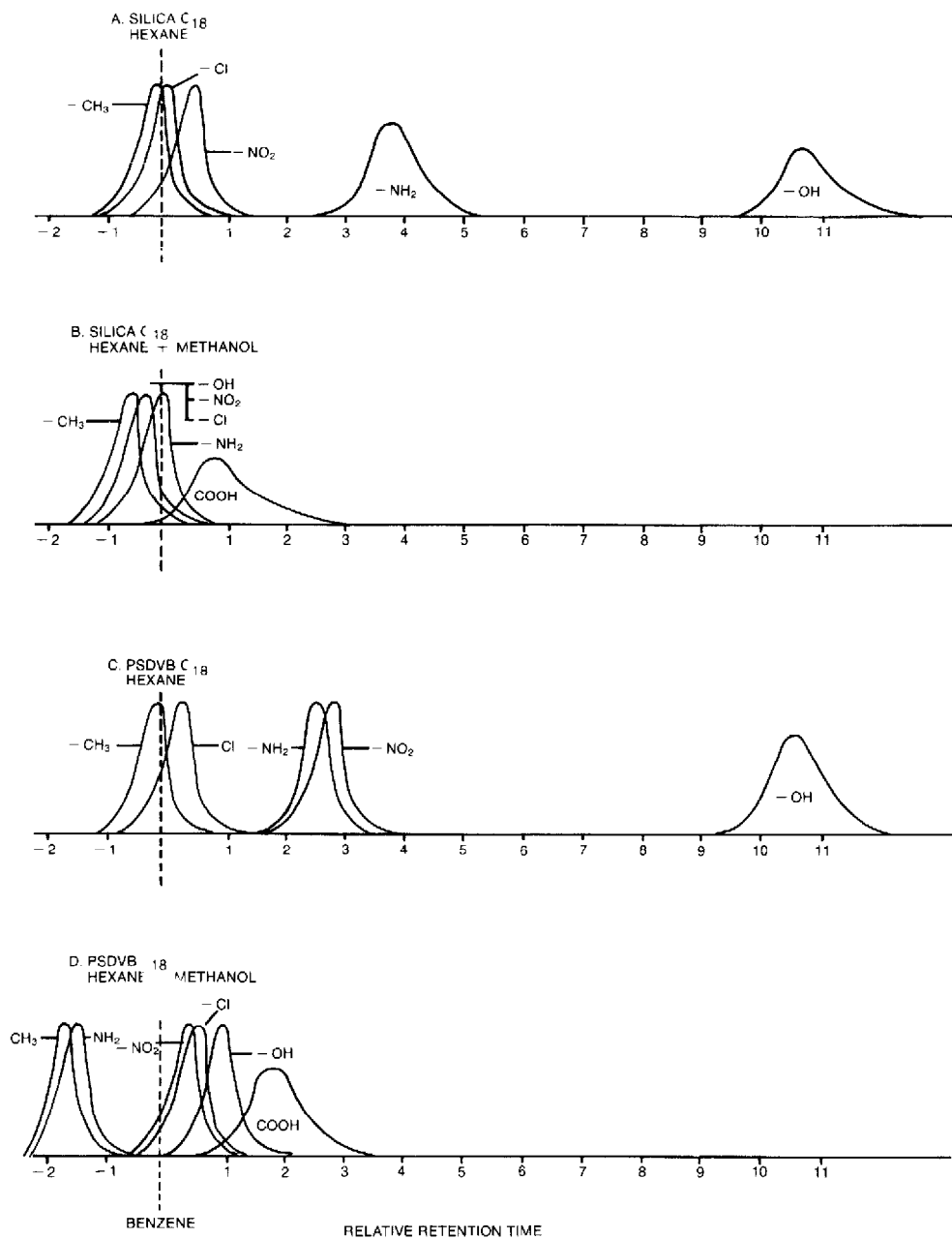
Fig. 1. Simulated chromatographic separation on various columns with a hexane-based mobile phase.
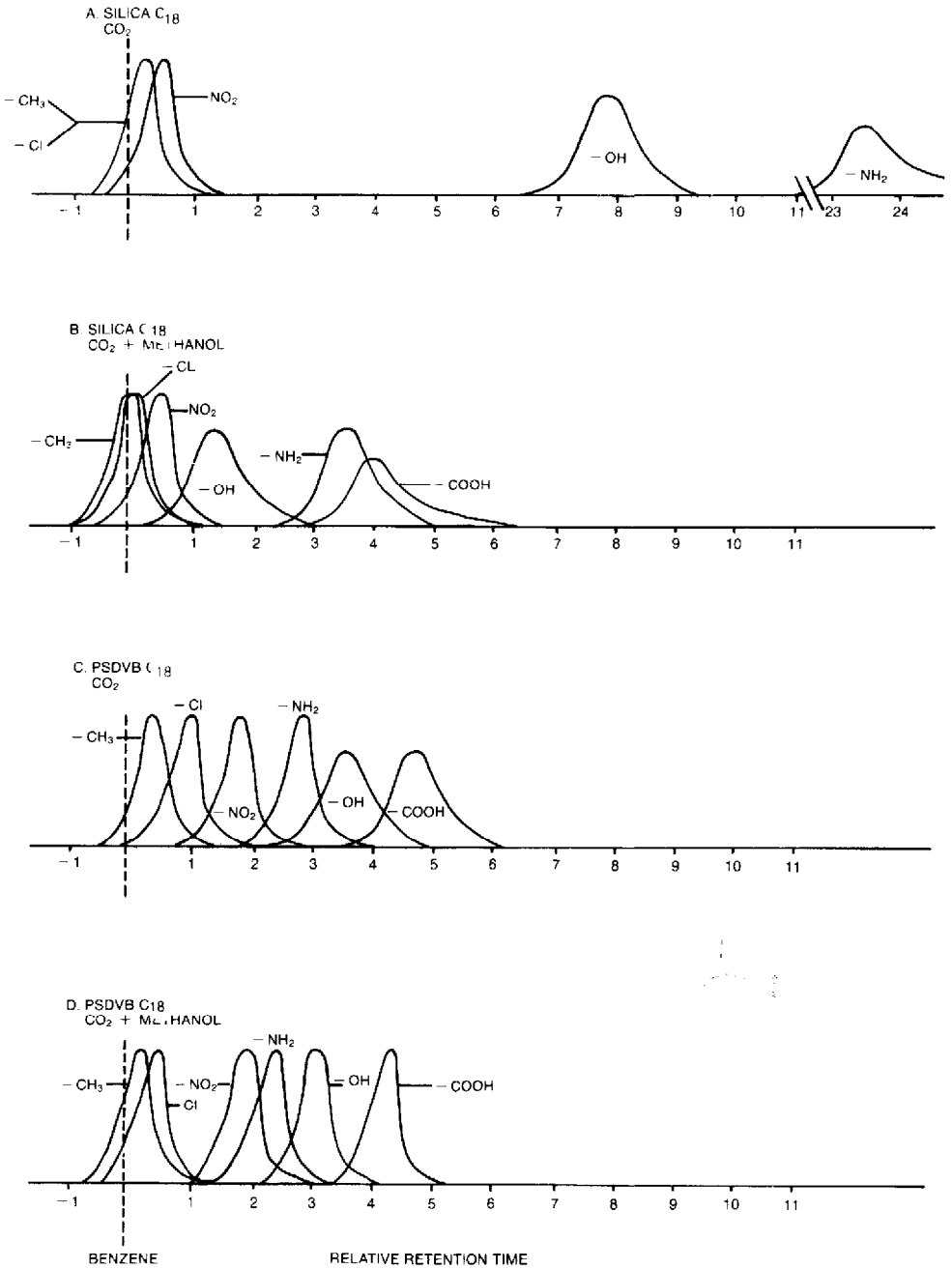
Fig. 2. Simulated chromatographic separation on various columns with a supercritical carbon dioxide-based mobile phase.

The addition of the polar methanol modifier increases the mobile phase solvent strength as can be seen by the decrease in k' values on the PSDVB-based column. The modifier effect is most pronounced with hexane and the effect of methanol modifier on supercritical carbon dioxide solvent strength appears to be minor. These results are in agreement with Wrights findings[13].

Unique properties of supercritical carbon dioxide

Carbon dioxide has been shown to have a solvent strength similar to hexane, with minor dipole selectivity properties[9]. The analyte with the strongest dipole is nitrobenzene. Out of all the experimental conditions, we would expect dipole–dipole interaction to be most noticeable between nitrobenzene and PSDVB. We find that nitrobenzene elutes slightly faster in carbon dioxide than hexane on the PSDVB-based column indicating that carbon dioxide has slightly greater dipole selectivity than hexane (Figs. 1C and 2C).

TABLE III

SUGGESTED INTERMOLECULAR FORCES AFFECTING SOLUTE RETENTION IN ORDER OF OBSERVED PREDOMINANCE

Species involved	Force involved
All mobile phases	
Benzoic acid + PSDVB	Lewis acid–base, π–π electron
Benzoic acid + silica	Lewis acid–base, hydrogen bonding
Benzoic acid + methanol	Lewis acid–base, hydrogen bonding
Phenol + PSDVB	Lewis acid–base, hydrogen bonding and π–π electron interaction
Supercritical CO$_2$ mobile phases	
Benzoic acid + CO$_2$	Lewis acid–base, hydrogen bonding
Phenol + CO$_2$	Lewis acid–base, hydrogen bonding
Silica + aniline	Lewis acid–base, hydrogen bonding
Phenol + silica	Lewis acid–base, hydrogen bonding
Methanol + CO$_2$	Lewis acid–base, hydrogen bonding
Methanol + silica	Lewis acid–base, hydrogen bonding
Methanol + PSDVB	Lewis acid–base
Phenol + methanol	Hydrogen bonding
Nitrobenzene + PSDVB	Induced dipole, π–π electron
Chlorobenzene + PSDVB	Induced dipole, π–π electron
Toluene + PSDVB	Induced dipole, π–π electron
Benzene + PSDVB	Induced dipole, π–π electron
Hexane mobile phases	
Methanol + aniline	Lewis acid–base, hydrogen bonding
Phenol + methanol	Lewis acid–base, hydrogen bonding
Phenol + silica	Lewis acid base, hydrogen bonding
Methanol + silica	Lewis acid–base, hydrogen bonding
Methanol + nitrobenzene	Lewis acid–base, hydrogen bonding
Phenol + PSDVB	Lewis acid–base, π–π electron
Methanol + PSDVB	Lewis acid–base, π–π electron
Nitrobenzene + PSDVB	Induced dipole, π–π electron
Aniline + PSDVB	Induced dipole, π–π electron
Chlorobenzene + PSDVB	Induced dipole

Although supercritical carbon dioxide is similar to hexane in respect to its polarity, it is significantly different from hexane in its ability to Lewis acid–base pair and hydrogen bond[18]. It is interesting to note that phenol tails quite badly on the silica column in hexane, but not in carbon dioxide (Fig. 2A). Since carbon dioxide is a Lewis base, it readily pairs with the Lewis acid phenol so that it is unavailable for hydrogen bonding with the silicon dioxide groups. On the other hand carbon dioxide does not pair with the aniline, except for some hydrogen bonding, therefore aniline is free to interact with the silica. Under every chromatographic condition studied, benzoic acid is the last compound to elute due to Lewis acid–base pairing, hydrogen bonding and π electron interactions with the various supports. Benzoic acid tails significantly in hexane but not in supercritical carbon dioxide. The decrease tailing in carbon dioxide is most likely due to Lewis acid–base pairing and hydrogen bonding between benzoic acid and carbon dioxide.

PSDVB-based C_{18} column

With the PSDVB-based C_{18} column, the presence of silicon dioxide and silicon hydroxide sites are eliminated and compounds are no longer retained, via the mechanism of hydrogen bonding. Although tailing is significantly reduced on the PSDVB column, species capable of hydrogen bonding on the silica-based column are also retained on PSDVB (Fig. 1C). This can be explained by the π electrons in the extensive aromatic ring structure of PSDVB. These electrons are easily polarizable causing induced dipoles and π electron interaction with solute electron orbitals[19]. We would expect the PSDVB-based column to retain all analytes which are not capable of hydrogen bonding longer than the silica-based column due to chemical similarity. The NH_2 functionality in aniline is a ring activator which increases the electron density of the ring making it a better candiate for π–π electron interactions with the PSDVB. Nitrobenzene, the strongest dipole, is retained somewhat by the PSDVB due to induced dipole interactions. The benzene rings in PSDVB with their high electron density can act as weak Lewis bases[20]. Supercritical carbon dioxide however is a slightly stronger Lewis base than PSDVB and successfully competes with the PSDVB for the Lewis acid analytes phenol and benzoic acid.

Modifier effects

It has been reported that small amounts of methanol modifier (less than 1.0%) added to non-polar solvents have a large effect on solute retention, especially when species capable of hydrogen bonding are involved[7,8,21]. Once the active sites have been covered, additional amounts of methanol modifier do not have the same dramatic effect on the retention time of these species. This dramatic change in retention for hydrogen bonding species was attributed primarily to the coverage of active sites on the silica support. We observed the same phenomenon for hydrogen bonding species on the silica-based C_{18} column with hexane as the mobile phase (Fig. 1A). Hydrogen bonding accounts for the increased retention of aniline, phenol and benzoic acid[21]. When methanol modifier is added, it acts as a Lewis acid, readily pairing with aniline, silicon dioxide groups and the PSDVB support. Lewis acid–base pairing and hydrogen bonding with methanol allow aniline, phenol and benzoic acid to elute from the column more rapidly (Fig. 18).

Methanol, like water, can act as either a Lewis acid or base and has hydrogen

bonding capabilities. As a Lewis acid, methanol readily pairs with aniline. The aniline–methanol complex is no longer a ring activator and therefore the aniline elutes close to toluene due to its similar partitioning characteristics. Since methanol is a slightly stronger Lewis base than benzene, it successfully competes with the PSDVB for phenol and benzoic acid[22]. Nitrobenzene, which is not retained on the PSDVB by a Lewis acid–base mechanism is not affected by the addition of methanol (Fig. 2).

A number of mechanisms have been proposed to account for the effects of polar modifiers in SFC: (1) interaction of polar modifiers with free silane active sites; (2) solute–modifier interaction forming a stable species which favors the mobile phase; (3) short-range clusters are formed between the modifier and the mobile phase; (4) the polar modifier acts as a surfactant causing a decrease in interfacial tension between the mobile phase and the stationary phase; (5) enhanced solubility and selectivity of certain analytes is caused by the formation of Lewis acid–base pairs between the modifier and the solute. At the 3.0% modifier concentration we cannot rule out mechanism 1. The coverage of active sites dramatically affects the retention of polar species in both hexane and supercritical carbon dioxide. Proposed mechanisms 2 and 5 are essentially the same. Although hydrogen bonding and induced dipole interactions should not be overlooked, Lewis acid–base pairing appears to be the most important force involved in solute–modifier interaction. Interaction between the modifier and the solute is only one type of interaction that can occur in chromatographic systems. Mechanism 3 focuses on another type of interaction. Short-range cluster formation may be very important, especially in the case of supercritical carbon dioxide with a Lewis acid modifier such as methanol. Mechanism 4 does not dominate because we do not observe a proportional decrease in the retention of all solutes with the addition of modifier.

CONCLUSION

Supercritical carbon dioxide is a Lewis base with proton acceptor selectivity properties. This selectivity may not have shown up in earlier studies due to dominant active-site interactions. Supercritical carbon dioxide has been shown to have hydrogen bonding capabilities and some dipole selectivity. The large effects caused by methanol on solute retention are due to the coverage of active sites on the stationary phase. The addition of methanol appears to give supercritical carbon dioxide slightly greater solvent strength but without changing its selectivity as far as solvent–solute interactions are concerned. We are only able to separate solvent–solute interactions from solvent–matrix and solute–matrix interactions in controlled experiments. Fortunately, the understanding of supercritical carbon dioxide solvent properties gained through such experiments can help us explain and predict its solvating power.

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