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EFFECT OF TEMPERATURE AND MODIFIER CONCENTRATION ON RETENTION IN SUPERCRITICAL FLUID CHROMATOGRAPHY

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SUMMARY

Use of binary modifiers in supercritical fluid chromatography (SFC) enhances the solvating capabilities of the supercritical mobile phase, allowing the mobile phase to be chemically tailored to a specific separation. The effects of temperature, density and modifier mole fraction on the retention process in capillary SFC was studied. Selectivity, as well as the enthalpy of solute transfer, were seen to be dependent on modifier concentration. Specific molecular interactions between the binary fluid and the solutes as well as enhanced solvation of the bonded stationary phase are suggested by the experimental data.

INTRODUCTION

The dependence of retention as a function of temperature in supercritical fluid chromatography (SFC) with pure fluid systems has been described theoretically[1] and experimentally[2–5]. The effect of temperature at constant density on retention in SFC has been studied recently for pure fluids[6,7]. Lauer *et al.*[6] have reported average values for the enthalpy of transfer between phases of −6 kcal/mole for selected solutes with supercritical carbon dioxide and nitrous oxide at a constant density of 0.80 g/ml with a PRP-1 (styrene–divinylbenzene copolymer) micro-particle packed column, while Yonker and Smith[7] reported enthalpy values of −5.9 to −8.4 kcal/mole and −3.9 to −8.6 kcal/mole for selected probe molecules on OV-17 and SE-54 capillary columns, respectively, for carbon dioxide densities between 0.20 and 0.50 g/ml.

Binary mobile phases are attracting attention in SFC due to the ability to chemically tailor the mobile phase through judicious selection of solvent modifier. Depending on the choice of modifier, one can increase the fluid's dielectric constant, introduce hydrogen-bonding capabilities, or alter mass transfer characteristics and solvent viscosity. This allows control of the mobile phase-solute interactions that impact retention or selectivity. Reported work with binary fluids entailing constant modifier composition[8–11] and modifier gradient studies[12–14] has demonstrated the flex-

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ibility of binary fluid mobile phases. However, due to the complexity of the phase equilibria and the effect of both pressure and temperature upon fluid density, the role of these variables upon SFC retention processes with binary fluids has remained confused. In this work, we have explored the effect of a binary modifier on solute retention as a function of temperature and modifier concentration over a range of fluid density.

EXPERIMENTAL

Retention of 9-phenanthrol, chrysene, 6-aminochrysene and myristophenone (Aldrich) was studied over a wide range of densities, mole fraction and temperature. The organic solvent modifier chosen for use in this study was 2-propanol, due to its specific (hydrogen bonding) interactions with many of the polar solute molecules and the available vapor–liquid equilibrium data for carbon dioxide–2-propanol mixtures at various pressures and temperatures[15]. The 2-propanol was obtained from Burdick and Jackson and SFC grade carbon dioxide was obtained from Scott Specialty Gases (Plumsteadville, PA, U.S.A.). Various mixtures of 2-propanol in carbon dioxide were made by weighing a known amount of 2-propanol into a clean lecture bottle. The lecture bottle was then cooled, loaded with carbon dioxide and reweighed. The mole fraction of 2-propanol in the carbon dioxide could then be determined. The resulting mixture was then transferred to a high pressure syringe pump. Another technique for making standard mixtures of 2-propanol in carbon dioxide involved the direct introduction of a measured volume of 2-propanol into the syringe pump, followed by the addition of a known weight of carbon dioxide from a lecture bottle. The contents of the syringe pump were mixed with a recirculating pump (Micropump, Concord, CA, U.S.A.) for 12 h at the experimental pressure. These solvent mixtures were studied chromatographically with the solute probes and retention monitored as a function of temperature and fluid density. The density of the binary solution was calculated using a two parameter cubic equation of state, the Peng–Robinson equation[16], which gave a relative deviation of $<4\%$ from densimeter measurements (Mettler/Paar DMA60)[17]. The experimental conditions were adjusted accordingly to give the desired fluid density.

Solute detection of the polynuclear aromatic hydrocarbons was accomplished using a fluorescence detector (Kratos Analytical Instruments) in which the 50-μm I.D. analytical column was sleeved by a length of 250 μm I.D. fused silica in which a cell window had been made by removal of the polyimide coating. The column was positioned at the base of the cell window and the entire assembly was located in the UV light path of the fluorescence detector. Myristophenone was detected using a variable-wavelength UV detector in a second chromatographic system, where a section of the polyimide coating had been removed from the column and positioned in the light path.

The computer controlled Varian 8500 syringe pump was calibrated using a Heiss high-pressure gauge (0–5000 p.s.i., $\pm$ 1 p.s.i.). The capillary columns were coated with a 5% methylphenylpolysiloxane polymer phase (SE-54) and *in situ* cross-linked. Benzene was used to determine the capillary void volume. The capacity factors (k') of the solutes were calculated from the retention time of the analyte (t_R) and the elution time of the benzene peak (t_0) using $k' = (t_R - t_0)/t_0$. Further details on the experimental system have been reported by Wright and co-workers[18,19].

RESULTS AND DISCUSSION

The binary fluid system of carbon dioxide–2-propanol was chosen because of the expected specific molecular interactions and the availability of vapor–liquid equilibrium data reported by Radosz[15]. The vapor–liquid equilibrium data facilitated the estimation of the critical parameters for binary mixtures of carbon dioxide–2-propanol. Over the limited 2-propanol mole fraction (χ_{IPA}) range studied ($\chi_{IPA} < 0.2$), this system was well behaved, having a continuous critical loci. Experimental conditions of pressure and temperature could then be determined which assured operation in a single supercritical fluid-phase region for the binary solvent.

The density of the binary fluids was calculated from a two parameter, cubic equation of state described by Peng and Robinson[16], which is similar to the van der Waals equation of state. The binary interaction parameters used for the calculation of the binary fluid density with this equation were determined from the vapor–liquid equilibrium data. Retention data for the polynuclear aromatic hydrocarbons is contained in Table I. Fig. 1 gives the plots of ln k' *versus* density for 9-phenanthrol at 127.0°C for 0, 0.018, 0.040 and 0.081 mole fraction of 2-propanol in carbon dioxide. The data in Fig. 1 shows two major trends: (1) a decrease in retention (k') with increasing density, and (2) a decrease in retention (k') with increasing mole fraction of the organic modifier at constant density. The first trend is a general observation seen in SFC with pure mobile phases; decreased solute retention is attributed to the enhanced solvating power of the fluid as density increases[20–23]. The decrease in solute retention as the mole fraction of solvent modifier increases at constant density reflects the qualitative change in the solute–solvent intermolecular interactions as the modifier concentration changes. The polar modifier, 2-propanol, can interact effectively with 9-phenanthrol due to its polar substituent. Thus, these results show two con-

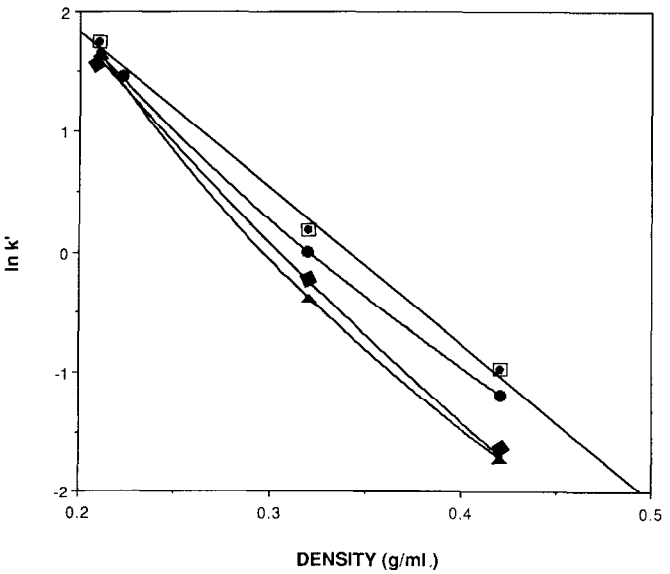

Fig. 1. Plots of ln k' *versus* density for 9-phenanthrol at 127°C for the mole fractions of 2-propanol of (⊡) 0.0, (●) 0.018, (◆) 0.040 and (▲) 0.081 2-propanol in carbon dioxide.

TABLE I

RETENTION DATA AS A FUNCTION OF DENSITY, TEMPERATURE AND 2-PROPANOL CONCENTRATION FOR SELECTED SOLUTES

Density (g/ml)	*Temp. (°C)*	*Mole fraction*	*k'*		
			Phenanthrol	*Chrysene*	*6-Aminochrysene*
0.21	107.2	0	15.61	26.42	–
0.21	117.3	0	7.97	14.76	–
0.21	127.4	0	5.74	10.82	15.89
0.21	96.7	0.018	17.60	–	–
0.21	106.6	0.018	11.83	18.95	–
0.21	116.8	0.018	7.79	12.90	–
0.21	126.6	0.018	5.20	8.97	27.65
0.21	96.7	0.040	–	–	–
0.21	106.5	0.040	13.91	17.88	–
0.21	116.4	0.040	7.73	11.47	–
0.21	126.4	0.040	4.99	8.05	23.60
0.21	107.2	0.081	–	–	–
0.21	117.3	0.081	9.81	10.89	–
0.21	127.4	0.081	5.26	7.08	–
0.32	96.6	0	3.75	5.40	–
0.32	107.2	0	2.75	4.39	–
0.32	117.3	0	1.69	2.71	7.06
0.32	127.4	0	1.20	1.81	4.72
0.32	96.7	0.018	2.22	3.27	8.29
0.32	106.6	0.018	1.76	2.63	6.46
0.32	116.8	0.018	1.37	2.05	5.00
0.32	126.6	0.018	1.00	1.49	3.51
0.32	96.8	0.040	1.71	2.42	5.57
0.32	106.5	0.040	1.40	2.06	4.66
0.32	116.4	0.040	1.00	1.55	3.39
0.32	126.3	0.040	0.78	1.21	2.62
0.32	97.3	0.081	1.90	2.21	4.43
0.32	107.2	0.081	1.19	1.61	3.18
0.32	117.3	0.081	0.85	1.22	2.38
0.32	127.4	0.081	0.68	1.02	1.96
0.42	96.6	0	0.92	1.19	2.92
0.42	106.6	0	0.66	0.86	2.54
0.42	117.3	0	0.48	0.66	1.48
0.42	127.4	0	0.38	0.51	1.21
0.42	96.7	0.018	0.50	0.69	1.48
0.42	106.6	0.018	0.43	0.61	1.25
0.42	116.8	0.018	0.33	0.49	1.02
0.42	126.6	0.018	0.31	0.43	0.84
0.42	96.9	0.040	0.39	0.58	1.10
0.42	106.5	0.040	0.32	0.50	0.93
0.42	116.4	0.040	0.27	0.41	0.76
0.42	126.5	0.040	0.19	0.31	0.57
0.42	97.2	0.081	0.27	0.41	0.70
0.42	107.2	0.081	0.24	0.37	0.62
0.42	117.3	0.081	0.20	0.30	0.51
0.42	127.4	0.081	0.18	0.26	0.46

tributions to the changes in solvent environment due to (a) the density and (b) the nature of the solute–solvent interactions which lead to reduced retention upon addition of a fluid modifier. These general trends are seen for retention of all the solutes investigated.

The selectivity of the column for one solute molecule compared to another is a sensitive probe of the separation process. Fig. 2 shows the change in selectivity *versus* mole fraction of 2-propanol in carbon dioxide at a constant density of 0.42 g/ml for chrysene and 6-aminochrysene at two different temperatures, 127.0°C and 107.0°C. For this case the selectivity is defined as the ratio of k' (6-aminochrysene)/k'(chrysene). Therefore, the selectivity of the system reflects the retention difference due to the polar amine substituent on the 6-aminochrysene. As the mole fraction of 2-propanol in carbon dioxide was increased, holding the overall density constant, the selectivity of the separation was observed to change substantially as a function of mole fraction 2-propanol. The selectivity values with pure carbon dioxide reflect vapor pressure differences between the two solutes at the two temperatures (polycyclic aromatic compound retention index for 6-aminochrysene is greater than chrysene's with a column comparable to SE-54[24]). The changes in selectivity for larger mole fractions of 2-propanol in the fluid mobile phase may be attributed to specific solute–solvent interactions with 2-propanol in the fluid phase or possible solvation of the stationary phase by the 2-propanol[25,26].

The change in selectivity for non-polar substituents would be expected to be independent of the mole fraction of 2-propanol. The selectivity of myristophenone referenced to laurophenone, which differs only by an ethyl group is plotted in Fig. 3. Indeed, as shown in Fig. 3, the selectivity remains relatively constant with mole

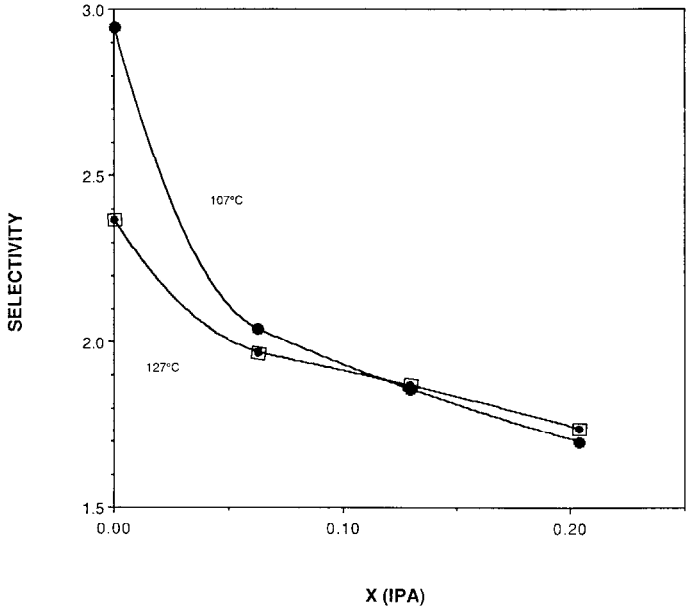

Fig. 2. Plots of selectivity of 6-aminochrysene–chrysene *versus* mole fraction of 2-propanol (χ_{IPA}) at a density of 0.42 g/ml for 127°C and 107°C.

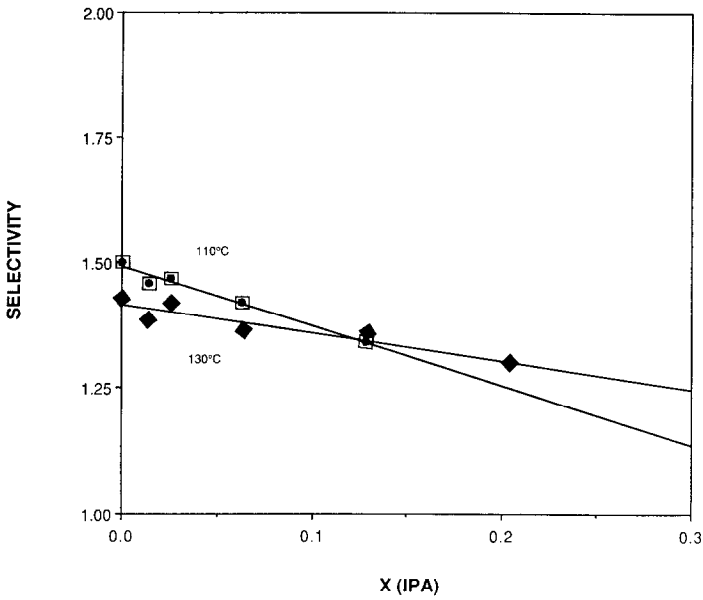

Fig. 3. Plots of selectivity of myristophenone–laurophenone *versus* mole fraction of 2-propanol (χ_{IPA}) at a density of 0.38 g/ml for 130°C and 110°C.

fraction at constant density for the temperatures of 110°C and 130°C. The concentration of 2-propanol has little effect on selectivity for the ethyl group as compared to the effect seen with an amino substituent. These facts suggest a selective interaction or solvation of the polar amino group by 2-propanol as compared to the ethyl group. The extent of hydrogen-bonding interaction between the basic amine and the weakly acidic proton on 2-propanol in the fluid remains to be studied.

The retention studies of Lauer *et al.*[6] with a packed column at constant density provide an interesting comparison to the study of Yonker and Smith[7] with capillary columns. Both groups investigated pure fluid mobile phases in SFC. At constant density, the logarithm of solute retention plotted against reciprocal temperature yields a linear plot with the slope related to the enthalpy of transfer (ΔH) of the solute from the mobile to the stationary phase. Fig. 4 shows representative data for ln k' *versus* 1/temperature at a 2-propanol mole fraction of 0.081, and a density of 0.42 g/ml using an SE-54 capillary column stationary phase. Modifier mole fractions of 0.00, 0.018, 0.040 and 0.081 were studied with the solute molecules of 9-phenanthrol, chrysene and 6-aminochrysene. Densities of 0.21, 0.32 and 0.42 g/ml were investigated over a temperature range of 96.6 to 127.4°C. Fig. 4 demonstrates that a linear relationship at constant density between ln k' and reciprocal temperature is also obtained with a binary fluid. The ΔH values calculated for these solutes using a binary fluid are listed in Table II. These ΔH values range from -4.85 to -19.2 kcal/mole and are consistent with values reported previously[6,7]. Fig. 5 presents representative ln k' data for myristophenone at 0.39 g/ml over a temperature range of 90 to 140°C. Table III contains the calculated ΔH values for myristophenone with

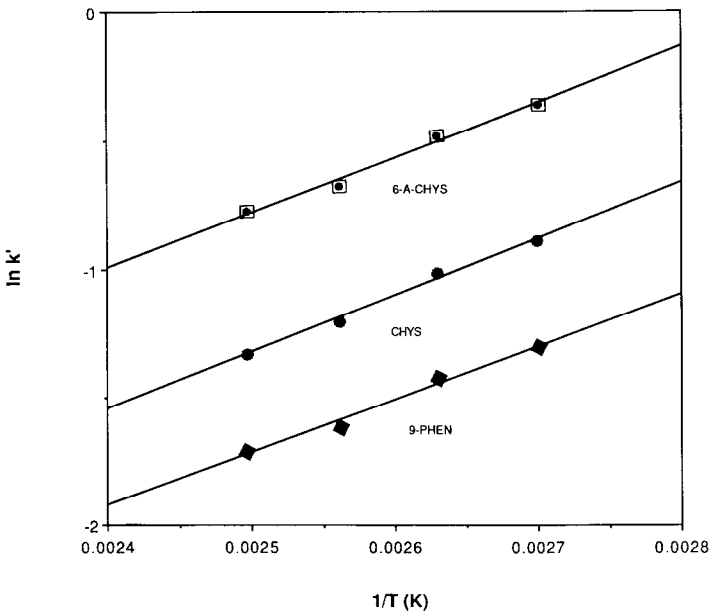

Fig. 4. Plots of ln k' *versus* reciprocal temperature for 9-phenanthrol (9-PHEN), chrysene (CHYS) and 6-aminochrysene (6-A-CHYS) at a density of 0.42 g/ml and a mole fraction of 2-propanol of 0.081.

SE-54 at densities of 0.39 and 0.44 g/ml for a range of mole fractions of IPA in carbon dioxide. Once again, the reported ΔH values for myristophenone are consistent with previously reported values for SFC as well as those for liquid and gas chromatography[27–31].

A change in mole fraction of the organic modifier in the binary fluid can be expected to impact the intermolecular interactions between the solute and fluid mo-

TABLE II

ENTHALPY OF SOLUTE TRANSFER WITH BINARY CARBON DIOXIDE–2-PROPANOL FLUID MIXTURES

Density (g/ml)	*Mole fraction 2-propanol*	*ΔH (kcal/mole)*		
		9-Phenanthrol	*Chrysene*	*6-Aminochrysene*
0.21	0.0	−15.0	−13.4	–
0.21	0.018	−11.9	−11.3	–
0.21	0.040	−15.6	−12.1	–
0.21	0.081	−19.2	−13.3	–
0.32	0.0	−11.2	−10.7	−12.4
0.32	0.018	−7.81	−7.63	− 8.33
0.32	0.040	−8.03	−7.07	− 7.69
0.32	0.081	−10.0	−7.63	− 8.07
0.42	0.0	−8.64	−8.01	− 9.10
0.42	0.018	−5.07	−4.85	− 5.58
0.42	0.040	−7.15	−6.34	− 6.46

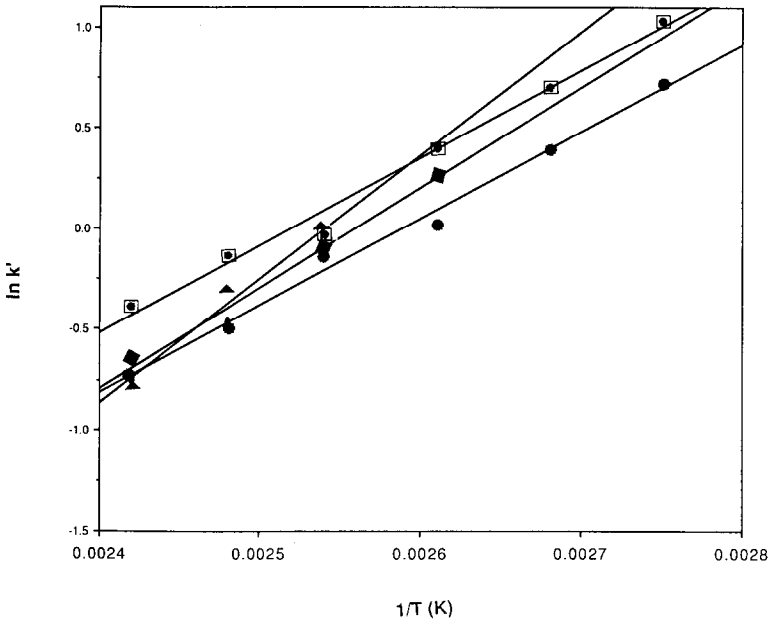

Fig. 5. Plots of ln *k' versus* reciprocal temperature for myristophenone at a density of 0.39 g/ml and a mole fraction of 2-propanol of (□) 0.00, (●) 0.063, ◆) 0.129 and (▲) 0.204.

bile phase and, hence, the retention process. The fluid modifier may also be selectively extracted into the organic stationary phase, thereby changing the composition of the stationary phase affecting retention and ΔH.

Both these processes suggest the possibility of chemically tailored binary fluid mobile phases for enhanced separations or altered selectivity, once their effects on

TABLE III

ENTHALPY OF SOLUTE TRANSFER WITH THE BINARY CARBON DIOXIDE–2-PROPANOL FLUID MIXTURES

Density (g/ml)	*Mole fraction 2-propanol*	*Myristophenone ΔH (kcal/mole)*
0.39	0.000	−8.62
0.39	0.014	−7.21
0.39	0.026	−7.28
0.39	0.063	−8.57
0.39	0.129	−9.90
0.39	0.204	−12.2
0.44	0.000	−8.12
0.44	0.014	−6.67
0.44	0.026	−6.10
0.44	0.063	−7.13
0.44	0.129	—
0.44	0.204	−11.8

retention are understood. Enhanced solvation of bonded stationary phase by an organic modifier has been studied in reversed-phase liquid chromatography. The work of Yonker *et al.*[32,33], Scott and Kucera[34] and Kikta and Grushka[35] supports a model having a stationary phase composed of the bonded hydrocarbon moiety and associated solvent molecules. In recent years, the distribution of aqueous and non-aqueous modifiers between the mobile phase and the bonded hydrocarbon moiety in reversed-phase liquid chromatography has been measured. Tilly-Melin *et al.*[36] and Westerlund and Theodorsen[37] reported preliminary results on the distribution of methanol and acetonitrile on an RP-8 bonded phase. Karger and McCormick[38] and Slaats *et al.*[39] have measured the distribution isotherms for methanol, acetonitrile and tetrahydrofuran between RP-8/RP-2 and RP-8/RP-18 bonded phases, respectively. That work supports the existence of a stationary phase composed of the bonded hydrocarbon and an associated layer of organic solvent modifier molecules. These data on bonded phase solvation by the organic modifier in liquid chromatography, coupled with reported bonded phase solvation by pure fluids[25,26], corroborate the premise of enhanced solvation of the bonded phase in SFC by the binary fluid organic modifier.

The competing phenomena of mobile phase interactions and solvated stationary phase have an impact on the enthalpy of transfer of the solute between the fluid mobile phase and the solvated stationary phase. The four plots shown in Fig. 6 depict the effect of 2-propanol mole fraction in carbon dioxide on the measured enthalpy for 9-phenanthrol, chrysene, 6-aminochrysene and myristophenone. In all cases a

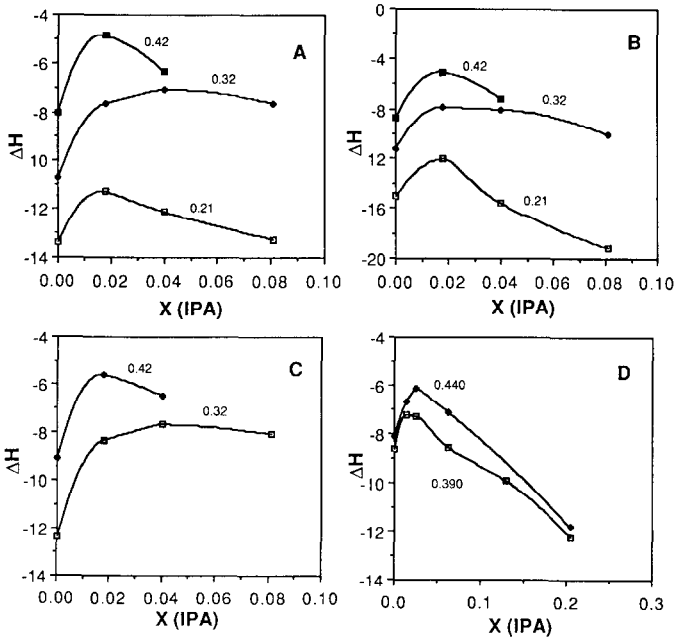

Fig. 6. Plots of ΔH (enthalpy in kcal/mole) *versus* mole fraction 2-propanol (χ_{IPA}) at the densities 0.21, 0.32 and 0.42 g/ml for (A) chrysene, (B) 9-phenanthrol, (C) 6-aminochrysene and (D) at the densities of 0.39 and 0.44 g/ml for myristophenone.

maximum is observed for the enthalpy at a mole fraction of 2-propanol between 0.00 and 0.04 for the SE-54 stationary phase. This may be due to solvation of the stationary phase as the mobile phase fraction of 2-propanol increases from 0.0 to 0.04. Similar behavior is seen for myristophenone over a wider range of 2-propanol concentration in carbon dioxide. Again, the maximum in the enthalpy of solute transfer for myristophenone is located between 0.0–0.04 mole fraction of 2-propanol in carbon dioxide. The change in enthalpy at higher 2-propanol concentrations is likely due to dynamic processes involving selective solvation of the organic stationary phase by 2-propanol and increased solvation of the solute in the mobile phase.

It is interesting to compare the k' data in Table I with the ΔH data presented in Fig. 6. One might postulate that k' could increase if the stationary phase is solvated by the 2-propanol modifier. The enthalpy of solute transfer shows a maximum as a function of mole fraction 2-propanol, but k' under similar density and temperature conditions undergoes a monotonic decrease. A plausible explanation for this phenomena could be that the mole fraction of the organic modifier in the stationary phase is greater than zero but still less than the mole fraction of 2-propanol in the mobile phase. Therefore, the stationary phase is solvated by the 2-propanol, but its relative solvent strength compared to that of the mobile phase is less. Thus, k' will decrease as a function of mole fraction 2-propanol, but ΔH would reflect the change in the solvent environment of the stationary phase on solvation by 2-propanol.

In order to further characterize the retention process, spectroscopic studies on the complexation of solute molecules in the binary fluid mobile phase as a function of mole fraction[22,23], as well as determinations of the extent of stationary phase solvation by the organic fluid modifier as a function of mole fraction, are in progress. Both processes impact on the retention mechanism for SFC and are reflected in the change in the enthalpy of solute transfer from the mobile to the stationary phase.

CONCLUSIONS

Binary modifiers have been shown to impact solute retention in SFC. As the mole fraction of a polar organic modifier (2-propanol) was increased at constant density, solute retention decreased. The selectivity of the column for compounds with a polar substituent, such as an amino group, was dramatically altered with the addition of a polar fluid modifier. By contrast, the selectivity for a non-polar substituent was minimally affected by the presence of 2-propanol. This can be explained by selective interactions of the polar substituent with the polar organic modifier. The impact of the binary fluid modifier on the retention mechanism in SFC can be seen in the change of the enthalpy for solute transfer between the mobile and stationary phases as a function of mole fraction of 2-propanol. Use of organic modifiers provides the capability of chemically tailoring the solvent to enhance the separation or extraction process, or alter selectivity. As a practical matter the addition of a less volatile solvent modified at a constant temperature and pressure has the additional effect of increasing the critical temperature of the mobile phase and thus the density or solvating power of the fluid.

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