CHANGES IN RETENTION AND POLARITY ACCOMPANYING THE REPLACEMENT OF HYDROGEN BY FLUORINE IN TETRAALKYLAMMONIUM ALKYL- AND ARYLSULFONATE SALTS USED AS STATIONARY PHASES IN GAS CHROMATOGRAPHY

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SUMMARY

Fourteen tetraalkylammonium alkanesulfonate, perfluoroalkanesulfonate, and benzene- and pentafluorobenzenesulfonate salts possessing useful chromatographic properties were synthesized. All salts had wide liquid temperature ranges with an upper column operating temperature limit in the range 160–220°C and yielded efficient column packings. The substitution of fluorine for hydrogen in the alkanesulfonate chain resulted in a general reduction in solute non-specific and proton donor interactions accompanied by an increase in solute electron donor interactions. These findings are rationalized in terms of the weak dispersive interactions for solutes with the perfluoroalkane side chains and the ability of fluorine to effect changes in the electron density of the sulfonate group through its inductive effect. On over half the salts studied retention is shown to depend on both gas–liquid partitioning and interfacial adsorption for a wide range of solutes but the relative importance and magnitude of the adsorption contribution to retention is not simply related to the structure of the salts or the incorporation of fluorine into the anion.

INTRODUCTION

The small size and large electronegativity of fluorine, the low degree of polarizability of the carbon–fluorine bond, and the weak intermolecular forces operative in perfluorocarbon solvents are dominant features of the unique chemistry of organofluorine compounds[1]. Fluorocarbons are much more volatile than hydrocarbons of similar molecular weight, they have a higher density and compressibility than hydrocarbons, lower critical temperatures and pressures, and extremely low surface tensions. These unique properties are exploited in numerous industrial processes particularly in the production of synthetic oils and lubricants, plastics and polymers, and pharmaceutical and agricultural chemicals[2].

Numerous attempts have been made to exploit the unique physical and chemical properties of perfluorocarbon solvents in chromatography. Perfluorocarbon stationary phases in gas chromatography (GC) have been used to separate substances of high chemical reactivity such as metal fluorides, halogens, halides of sulfur and phos-

phorus, etc.[3]. Perfluorocarbon phases show unique selectivity for the separation of fluorocarbon isomers and Freons. However, their use in GC is far from common place since perfluorocarbon phases yield unstable films on diatomaceous supports or glass capillary column walls resulting in columns of low efficiency and low temperature stability. For the above applications it was the unique chemical stability or the selectivity for fluorocarbon isomers that was important and the otherwise poor chromatographic characteristics had to be tolerated. A number of polar group derivatizing reagents for GC contain perfluorocarbon substituents as these reagents generally yield derivatives with retention times less than their hydrocarbon analogues and have a favorable response to the sensitive electron-capture detector. This is probably the most successful application of perfluorocarbon compounds in GC[4,5]. Bonded phase packings containing perfluorocarbon chains have been used in reversed-phase liquid chromatography to selectively separate fluorocarbon compounds and to diminish the retention of solutes compared to their hydrocarbon analogues, a role in which they have only been partially successful, and this combined with poor hydrolytic stability of the packings has diminished interest in their general use[6-10].

Highly-fluorinated polymers have been investigated as a means of extending the molecular weight range of samples that could be analyzed by GC and/or to permit the analysis of thermally labile substances at lower temperatures than is possible with conventional phases. This possibility has been adequately demonstrated using column packings prepared from poly(perfluoroalkyl ethers)[11,12]. However, this approach was limited by two familiar problems associated with perfluorocarbon solvents. Film instability limited the upper column temperature limit to about 250°C and the perfluorocarbon chains provided little masking of support activity which frequently led to poor peak shapes for polar compounds. Taking a different approach we decided to evaluate the use of highly-fluorinated liquid organic salts as stationary phases. The liquid organic salts have good film building properties and are excellent column deactivating agents[13,14]. The alkyl- and arylsulfonate salts have been the most widely studied since these salts frequently have low melting points and wide liquid ranges[15-20]. They also provide a well defined model system to study the influence of the perfluorocarbon group on retention and solvent selectivity in a quantitative manner. Studies of this kind have been lacking in the past[3], and given the problems of coating and immobilizing perfluorocarbon solvents, provide some insight into the properties that could be anticipated for partially fluorinated solvents that would be much easier to synthesize and work with as stationary phases compatible with modern column technology.

EXPERIMENTAL

Tetra-n-butylammonium hydroxide [40% (w/w) in water], butanesulfonyl chloride, barium salt of pentafluorobenzenesulfonic acid, benzenesulfonic acid, and the sodium salt of hexanesulfonic acid were obtained from Aldrich (Milwaukee, WI, U.S.A.). Tributylmethylammonium hydroxide [40% (w/w) in water], tetra-n-butyl-ammonium methanesulfonate and trifluoromethanesulfonate were obtained from Fluka (Ronkonkoma, NY, U.S.A.), octanesulfonyl chloride from Alfa Products (Danvers, MA, U.S.A.), perfluorooctanesulfonic acid [50% (w/w) solution in water]

from Crescent (Hauppauge, NY, U.S.A.), and perfluorobutanesulfonyl fluoride from SCM (Gainesville, FL, U.S.A.). Chromosorb W-AW (40–60 mesh), HPLC-grade solvents and chemical standards were obtained from Anspec (Ann Arbor, MI, U.S.A.).

Tetra-n-butylammonium benzenesulfonate (QBA BS), pentafluorobenzene-sulfonate (QBA FBS), butanesulfonate (QBA BuS), octanesulfonate (QBA OS), perfluorooctanesulfonate (QBA FOS), hexanesulfonate (QBA HS), tri-n-butylmethyl-ammonium butanesulfonate (TBMA BuS), perfluorobutanesulfonate (TBMA FBuS), octanesulfonate (TBMA OS), perfluorooctanesulfonate, (TBMA FOS), and hexane-sulfonate (TBMA HS) were prepared by a neutralization technique. The sulfonyl chlorides or fluorides were first partially hydrolyzed by adding an excess of water which was then removed under vacuum on a rotary evaporator. Sodium salts were converted to the barium salts by precipitation with excess barium hydroxide solution. The barium salts were converted to the acid by addition of an equimolar amount of dilute sulfuric acid followed by removal of barium sulfate by filtration and excess water on a rotary evaporator. For the hydrocarbon salts, the sulfonic acid was added in equimolar amounts to an aqueous solution of the tetraalkylammonium hydroxide. The water was removed on a rotary evaporator and the product dissolved in acetonitrile, treated with decolorizing charcoal (previously cleaned by Soxhlet extraction with methylene chloride), and filtered through a bed of celite. The solvent was removed on a rotary evaporator and the product dried under high vacuum (< 0.2 mm Hg). The perfluorocarbon salts were prepared in a similar manner, however, after the neutralization reaction the product precipitated out of the aqueous solution. It was filtered off, washed three times with cold water, and dried under vacuum (< 0.2 mm Hg). The identity as well as the purity of the salts was confirmed by IR and NMR spectroscopy, Table I. IR spectra were obtained as a smear on a sodium chloride plate using a Nicolet 20DX Fourier transform infrared spectrometer (Madison, WI, U.S.A.) at 1 cm^{-1} resolution. ^{1}H (300 MHz) and ^{13}C (75.5 MHz) NMR spectra were recorded on a General Electric QE-300 (Freemont, CA, U.S.A.) spectrometer with the salts dissolved in deuterated chloroform.

Liquid densities as a function of temperature for the tetraalkylammonium salts were determined using a modified Lipkin bicapillary pycnometer[16]. Density relation-ships were fitted to the equation

$$\rho_t = A - B(T) \tag{1}$$

where ρ_t is the density of the organic salt at temperature T (°C) and A and B are constants determined by linear regression (Table II).

Column packings containing 5–20% (w/w) of salt on Chromosorb W-AW were prepared using the rotary evaporator technique with acetonitrile as the slurry solvent. After coating the packings were dried in a fluidized-bed drier and packed into glass columns (2–3.5 m × 2 mm I.D.) with the aid of suction and gentle vibration. Individual phase loadings were determined by exhaustive Soxhlet extraction, 20–30 h, of the column packing materials with acetonitrile[21].

For column evaluation a Varian 3700 gas chromatograph (Palo Alto, CA, U.S.A.) with heated on-column injectors and a flame-ionization detector was used. The column temperature was stabilized at 121°C (±0.2°C). Nitrogen was used as the

TABLE I

SPECTRAL FEATURES FOR TETRAALKYLAMMONIUM SULFONATE SALTS

Salt	Principal IR bands (cm^{-1})	NMR chemical shifts	
		^1H Spectra[a]	^{13}C Spectra
QBA BuS	2971, 2884, 1470 1350, 1264, 1211 1131, 1052, 1005 872, 799, 732	cation: 0.94 (12), 1.34 (8) 1.64 (8), 3.13 (8) anion: 0.80 (3), 1.38 (2) 1.73 (2), 2.78 (2)	cation: 58.86, 29.08, 19.75, 13.68 anion: 51.79, 26.96, 22.00, 13.76
QBA FBuS	2964, 2877, 1470 1384, 1198, 1032 886, 746	cation: 0.94 (12), 1.38 (8) 1.58 (8), 3.24 (8)	cation: 58.31, 23.26, 19.24, 12.68
QBA HS	2957, 2931, 2877 1470, 1384, 1191 1038, 885, 746	cation: 1.03 (12), 1.49 (8) 1.66 (8), 3.32 (8) anion: 0.88 (3), 1.29 (4) 1.87 (4), 2.80 (2)	cation: 58.95, 24.18, 19.84 13.77 anion: 52.36, 31.77, 28.91 25.59, 22.59, 14.15
QBA OS	2969, 2866, 1682 1476, 1270, 1160 1098, 884, 742	cation: 1.01 (12), 1.43 (8) 1.64 (8), 3.22 (8) anion: 0.86 (3), 1.34 (10) 1.58 (2), 2.57 (2)	cation: 58.81, 24.02, 19.69 13.61 anion: 61.97, 52.12, 31.77, 29.31, 29.09, 25.15, 22.57
QBA FOS	2964, 2877, 1642 1516, 1483, 1383 1244, 1098, 1044 985, 885, 793	cation: 1.00 (12), 1.45 (8) 1.65 (8), 3.30 (8)	cation: 58.45, 23.39, 19.34 12.73
QBA BS	2964, 2878, 1483 1244, 885, 793 633	cation: 0.98 (12), 1.38 (8) 1.59 (8), 3.24 (8) anion: 7.89 (2), 7.29 (3)	cation: 58.71, 23.95, 19.62, 13.35 anion: 147.63, 128.65, 127.63 126.12
QBA FBS	2964, 2878, 1470 1384, 1350, 1271 1125, 1052, 1005 886, 799, 733	cation: 0.94 (12), 1.39 (8) 1.58 (8), 3.09 (8)	cation: 58.70, 23.00, 19.50 13.50
TBMA BuS	2969, 2879, 1772 1489, 1200, 1059 883, 748	cation: 0.96 (9), 1.34 (6) 1.58 (6), 3.09 (3) 3.30 (6) anion: 0.79 (3), 1.38 (2) 1.73 (2), 2.78 (2)	cation: 58.86, 24.08, 19.75, 13.68 anion: 51.79, 26.96 22.01, 13.76
TBMA FBuS	2964, 2877, 1470 1384, 1198, 1032 886, 746	cation: 0.96 (9), 1.38 (6) 1.58 (6), 3.24 (6) 3.10 (3)	cation: 61.38, 23.65, 19.23, 12.68
TBMA HS	2964, 2931, 2878 1470, 1384, 1191 1038, 892, 779 739, 713	cation: 1.02 (9), 1.43 (6) 1.65 (6), 3.24 (3) 3.37 (6) anion: 0.86 (3), 1.28 (4) 1.81 (2), 2.77 (2)	cation: 61.38, 48.83, 24.42 19.79, 13.77 anion: 52.32, 31.74, 28.84 25.54, 22.59, 14.12

TABLE I (*continued*)

Salt	Principal IR bands (cm^{-1})	NMR chemical shifts	
		^1H Spectra^a	^{13}C Spectra
TBMA OS	2964, 2932, 2871 1630, 1470, 1377 1191, 1038, 892 779, 739	cation: 1.01 (9), 1.45 (6) 1.65 (6), 3.37 (6) 3.24 (3) anion: 0.83 (3), 1.81 (2) 2.78 (2), 3.37 (2) 1.25 (8)	cation: 61.18, 24.15, 19.56 13.53 anion: 52.09, 48.71, 31.71 29.27, 29.04, 28.96 25.33, 22.49
TBMA FOS	2970, 2885, 1696 1484, 1264, 1211 1151, 1058, 965 912, 766, 746	cation: 1.01 (9), 1.44 (6) 1.60 (6), 3.28 (6) 3.10 (3)	cation: 61.62, 24.31, 19.64 13.53

^{a} Number in parentheses denotes the number of protons integrated at the chemical shift.

carrier gas at an accurately known flow-rate of approximately 20 ml/min determined with a thermostated soap-film bubble meter. The column pressure drop was determined with a mercury manometer (± 1 mmHg). Samples were injected as headspace vapors to approximate the infinite dilution condition in the linear portion of the sorption isotherm as indicated by the independence of retention volume on sample size.

The net retention volume was determined using eqn. 2

$$V_N = \frac{3}{2} \frac{(P^2 - 1)}{(P^3 - 1)} (t_R - t_m) F_a \left(\frac{T_c}{T_a} \right) \left(1 - \frac{P_W}{P_a} \right) \tag{2}$$

TABLE II

DENSITY AS A FUNCTION OF TEMPERATURE FOR TETRAALKYLAMMONIUM SULFONATE SALTS

Salt	Temperature range of measurements (°C)	Coefficients		S.D. in the intercept
		A	$10^4 B$	
QBA MS	100–134	1.0421	7.321	0.0003
QBA FMS	120–142	1.1332	8.092	0.0006
QBA BuS	70–130	1.0119	7.396	0.0012
QBA FBuS	65–120	1.2487	11.538	0.0054
QBA HS	70–125	1.0586	7.250	0.0013
QBA OS	75–130	1.0537	8.509	0.0014
QBA FOS	85–140	1.4813	13.911	0.0060
QBA BS	105–145	1.1278	9.466	0.0036
QBA FBS	75–120	1.2368	8.914	0.0021
TBMA BuS	95–130	1.0318	7.003	0.0015
TBMA FBuS	95–125	1.4203	18.239	0.0068
TBMA HS	90–125	1.0395	7.690	0.0023
TBMA OS	95–130	1.0270	8.133	0.0024
TBMA FOS	105–130	1.4746	11.461	0.0034

where P is P_i/P_a (P_i being the column inlet pressure and P_a the column outlet pressure), t_R the retention time, t_m the gas hold-up time (assumed to be equal to the retention time of methane at T_c), F_a the column flow-rate measured at P_a and T_a, T_c the column operating temperature (K), T_a the ambient temperature, and P_W the vapor pressure of water at T_a. Gas–liquid partition coefficients were calculated by linear extrapolation of plots of V_N^*/V_L vs. $1/V_L$ to infinite phase volume based on eqn. 3[14,20,22,23]

$$\frac{V_N^*}{V_L} = K_L + (A_{LS}K_{LS} + A_{GS}K_{GS})\frac{1}{V_L} \qquad (3)$$

where V_N^* is the net retention volume per gram of packing, V_L the volume of liquid phase per gram of packing, K_L the gas–liquid partition coefficient, A_{LS} the surface area of the liquid phase, K_{LS} the coefficient for adsorption at the gas–liquid interface, A_{GS} the available surface area of the support surface, and K_{GS} the coefficient for adsorption at the gas support interface. Values for the gas–liquid partition coefficients of test solutes are given in Table III together with the uncertainty in their determination. The partition coefficients for the n-alkanes, 2-alkanones, and fatty acid methyl esters were fitted to eqn. 4

$$\log K_L = C + D(n) \qquad (4)$$

where C and D are coefficients fitted by linear regression and n is the number of carbon

TABLE III

GAS–LIQUID PARTITION COEFFICIENTS FOR McREYNOLDS TEST SOLUTES ON TETRAALKYL-AMMONIUM SULFONATE SALTS AT 121°C

Salt	Test solute						
	Benzene	Butanol	2-Pentanone	Nitropropane	2-Methyl-2-pentanol	2-Octyne	Dioxane
QBA MS	28.5(0.5)[a]	408.8(11.0)	42.0(0.2)	196.5(4.0)	226.1(5.6)	32.0(0.5)	48.7(0.9)
QBA FMS	25.4(1.9)	97.8(0.2)	48.3(0.4)	149.0(3.2)	70.4(0.8)	16.5(1.0)	50.0(0.2)
QBA BuS	24.2(1.4)	183.9(6.4)	31.5(2.0)	122.8(2.9)	183.9(6.4)	25.8(0.5)	33.4(1.0)
QBA FBuS	19.1(1.2)	82.7(5.5)	40.8(0.1)	128.8(5.0)	65.0(1.0)	25.9(0.6)	35.7(0.2)
QBA HS	29.2(1.3)	432.9(8.4)	44.6(0.9)	187.9(4.0)	259.8(5.4)	45.9(1.0)	47.0(0.9)
QBA OS	27.6(0.4)	408.0(20.0)	41.1(1.0)	155.4(1.1)	210.2(2.3)	46.9(1.0)	38.8(0.9)
QBA FOS	19.7(0.5)	67.3(2.1)	44.6(5.6)	106.0(1.5)	63.0(1.9)	32.3(0.9)	46.6(2.0)
QBA BS	23.9(1.1)	230.0(8.8)	37.1(1.0)	159.4(2.8)	126.3(4.5)	26.5(1.1)	44.8(1.7)
QBA FBS	23.1(0.7)	102.6(5.0)	40.8(0.8)	156.5(24.4)	65.8(2.0)	27.0(0.8)	41.2(2.1)
TBMA BuS	31.6(0.6)	687.4(20.0)	50.2(0.7)	211.2(2.2)	331.6(14.2)	38.3(0.8)	58.6(0.7)
TBMA FBuS	24.9(0.3)	96.4(1.2)	54.4(1.0)	160.8(10.8)	76.2(0.1)	28.3(0.7)	46.5(0.8)
TBMA HS	23.4(0.5)	333.6(8.3)	33.8(0.4)	132.3(2.8)	195.7(4.1)	34.5(0.5)	38.0(0.9)
TBMA OS	24.7(0.6)	383.1(9.2)	34.3(0.7)	138.5(5.0)	218.2(2.8)	38.7(1.3)	38.2(0.4)
TBMA FOS	16.8(1.2)	83.3(0.01)	47.5(0.6)	117.4(6.1)	71.9(0.5)	27.5(0.8)	39.8(3.3)
Squalane	32.1(0.9)	18.1(0.9)	26.4(0.3)	31.3(0.7)	39.1(0.6)	114.8(1.7)	31.4(0.4)

[a] Number in parentheses denotes the standard deviation.

atoms for the *n*-alkanes and the number of carbon atoms minus 2 for the 2-alkanones and fatty acid methyl esters. Coefficients obtained by linear regression are summarized in Table IV.

TABLE IV

COEFFICIENTS FOR EQN. 4

Salt	Homologous series	Regression coefficients			Range (n)
		C	D	r^2	
QBA MS	Alkanes	−0.6120	0.2094	1.00	13–16
	2-Alkanones	0.9881	0.2173	1.00	4–6
	FAME	1.0770	0..2124	1.00	5–8
QBA FMS	Alkanes	−0.6091	0.2040	1.00	13–15
	2-Alkanones	1.1192	0.2078	1.00	5–7
	FAME	1.0674	0.2113	1.00	4–7
QBA BuS	Alkanes	−0.4768	0.2114	1.00	13–16
	2-Alkanones	1.0339	0.2256	1.00	5–8
	FAME	1.1229	0.2211	1.00	5–7
QBA FBuS	Alkanes	−0.5548	0.2075	1.00	13–16
	2-Alkanones	0.9912	0.2180	1.00	4–7
	FAME	1.0863	0.2211	1.00	5–8
QBA HS	Alkanes	−0.4644	0.2257	1.00	13–17
	2-Alkanones	1.1005	0.2319	1.00	5–9
	FAME	0.9506	0.2416	1.00	4–7
QBA OS	Alkanes	−0.4987	0.2331	1.00	13–16
	2-Alkanones	0.8609	0.2491	1.00	5–7
	FAME	1.0017	0.2451	1.00	5–8
QBA FOS	Alkanes	−0.3860	0.2045	1.00	13–16
	2-Alkanones	1.0490	0.2144	1.00	5–7
	FAME	0.9242	0.2217	1.00	5–8
QBA BS	Alkanes	−0.6431	0.2031	1.00	13–16
	2-Alkanones	0.9347	0.2139	1.00	4–7
	FAME	0.7899	0.2097	1.00	5–8
QBA FBS	Alkanes	−0.6726	0.2170	1.00	13–16
	2-Alkanones	0.9469	0.2297	1.00	4–7
	FAME	0.8234	0.2241	1.00	5–8
TBMA BuS	Alkanes	−0.5238	0.2077	1.00	13–16
	2-Alkanones	1.0750	0.2132	1.00	4–7
	FAME	1.1740	0.2071	1.00	6–9
TBMA FBuS	Alkanes	−0.4372	0.1952	1.00	13–16
	2-Alkanones	1.1390	0.2042	1.00	5–7
	FAME	1.2070	0.1992	1.00	6–8
TBMA HS	Alkanes	−0.5735	0.2202	1.00	13–17
	2-Alkanones	0.8440	0.2340	1.00	4–7
	FAME	0.9945	0.2265	1.00	5–9
TBMA OS	Alkanes	−0.5886	0.2305	1.00	13–16
	2-Alkanones	0.8242	0.2449	1.00	4–6
	FAME	1.0156	0.2336	1.00	6–9
TBMA FOS	Alkanes	−0.4900	0.2079	1.00	13–16
	2-Alkanones	0.9188	0.2329	1.00	6–8
	FAME	1.1760	0.2040	1.00	6–9

The partial molar Gibbs free energy of solution for a methylene group was calculated according to eqn. 5

$$\Delta G_K^0 (CH_2)^P = -2.3RT_c D_P \tag{5}$$

where $\Delta G_K^0 (CH_2)^P$ is the partial molar Gibbs free energy of solution for a methylene group on phase P, R the universal gas constant (1.987 cal mol^{-1} K^{-1}), and D_P the regression coefficient for phase P defined in eqn. 4. In a similar way the partial molar Gibbs free energy of solution was calculated according to eqn. 6

$$(\Delta G_K^0 X)^P = -2.3RT_c \, log \, K_L^X \tag{6}$$

where $(\Delta G_K^0 X)^P$ is the partial molar Gibbs free energy of solution for solute X on phase P with a gas–liquid partition coefficient K_L^X. The difference in free energies for solute X on two compared phases, one of which is the non-polar reference phase squalane, is given by eqn. 7

$$\delta(\Delta G_K^0 X)_{SQ}^P = (\Delta G_K^0 X)^P - (\Delta G_K^0 X)^{SQ} \tag{7}$$

where $\delta(\Delta G_K^0 X)_{SQ}^P$ is the difference in partial molar Gibbs free energy of solution for solute X on stationary phase P and squalane, SQ[23–26].

The activity coefficients at infinite dilution for the test solutes in the tetraalkylammonium sulfonate salts were calculated from eqn. 8

$$Y^0 = \frac{62\,370\rho T_c}{MP^0 K_L} \tag{8}$$

where Y^0 is the approximate infinite dilution activity coefficient uncorrected for solute fugacity and gas phase non-ideality, ρ the solvent density at the column temperature T_c, M the molecular weight of the salt, and P^0 is the solute saturation vapor pressure at T_c obtained from tables in ref. 27.

RESULTS AND DISCUSSION

The tetraalkylammonium sulfonate salts are easy to prepare in high yield for the perfluoroalkanesulfonate salts (ca. 90%) and moderate yield for the alkanesulfonate salts (ca. 40%). Both series of salts are air stable compounds although the alkanesulfonates are hygroscopic, a property not shared by the perfluoroalkanesulfonate salts. The salts have favorable liquid ranges for GC, exceeding 100°C in all cases, with upper column temperature limits in the range 160–220°C (Table V). The greater density (Table II), higher melting points and greater thermal stability of perfluoroalkane compounds over their alkane analogues is a general characteristic feature of perfluorocarbon compounds[28]. All salts exhibited good column efficiencies with average values similar to those of conventional non-ionic phases prepared from the same batch of support. A typical test chromatogram for a mixture of 2-alkanones and acetophenone on QBA BuS and QBA FBuS is shown in Fig. 1.

TABLE V

USEFUL TEMPERATURE OPERATING RANGE FOR THE TETRAALKYLAMMONIUM SULFONATE SALTS

Salt	Melting point (°C)	Column temperature limit (°C)[a]	Liquid range (°C)[b]
QBA MS	78.5–79.5	180	101
QBA FMS	111.5–112.5	240	128
QBA BuS	34.5–35.5	160	130
QBA FBuS	44.5–45.5	220	175
QBA HS	Gel	170	(150)
QBA OS	Liquid	180	(160)
QBA FOS	Liquid	220	(200)
QBA BS	77.5–78.5	210	132
QBA FBS	51.5–52.5	210	158
TBMA BuS	44.5–45.5	160	115
TBMA FBuS	71.5–72.5	200	128
TBMA HS	49.5–50.5	170	120
TBMA OS	Gel	200	(180)
TBMA FOS	92.5–93.5	210	−117

[a] Defined as the highest temperature that the column could be maintained at for 24 h without change in retention or peak shape in a test chromatogram obtained at a lower temperature before and after the conditioning period.

[b] Values in parentheses assume a minimum operating temperature of room temperature (20°C) although these salts remain useable below room temperature.

The introduction of fluorine into the alkanesulfonate anion can influence retention in two ways. By the difference in interaction between solutes and the alkane and perfluoroalkane chains and by differences in the electron density on the sulfonate group resulting from the differences in inductive effects of the perfluoroalkane and alkane chains. These affects may not work in concert and should influence retention in a solute specific manner. For example, for alkanes that are retained largely by dispersive and inductive interactions there is a substantial reduction in retention on the QBA FOS salt compared to the QBA OS salt (Fig. 2). Assuming a partition model this must reflect a reduction in the dispersive interactions between n-alkanes and perfluoroalkanesulfonate salts compared to the analogous alkanesulfonate salts. Polar and hydrogen bond donor–acceptor solutes are influenced by changes in dispersive interactions and changes in specific solute–solvent interactions which should be more significantly influenced by the inductive effect of fluorine. For example, there are substantial changes in retention for a polar mixture on similar columns of QBA BuS and QBA FBuS (Fig. 3). An understanding of the above changes in terms of solute solvent interactions requires a more quantitative mechanistic treatment than is possible by comparing relative retention times of solutes on similar columns prepared with different salts.

The mechanism by which solutes are retained in gas–liquid chromatography can be either exclusively partitioning, exclusively adsorption or a mechanism in which both processes operate concurrently[22,25,26]. The gas–liquid partition coefficient, indepen-
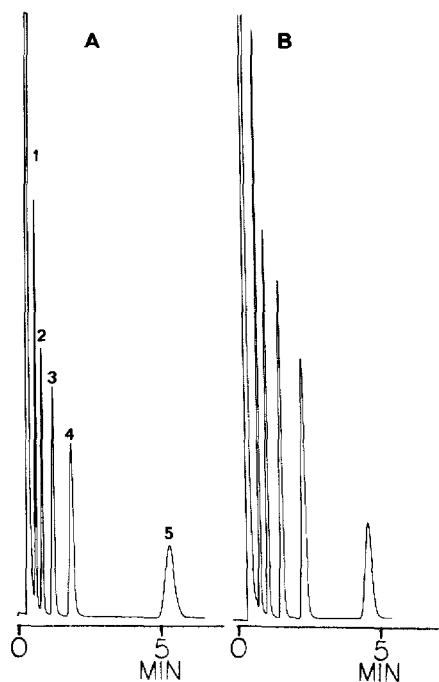
Fig. 1. Separation of a test mixture of ketones on 3.5 m × 2 mm I.D. columns of QBA BuS (A) and QBA FBuS (B) with 6% (w/w) loading of salt on Chromosorb W-AW (40–60 mesh) at 121°C with a nitrogen carrier gas flow-rate of 11.0 ml/min. Peak identification: 1 = hexan-2-one; 2 = heptan-2-one; 3 = octan-2-one; 4 = nonan-2-one; 5 = acetophenone.
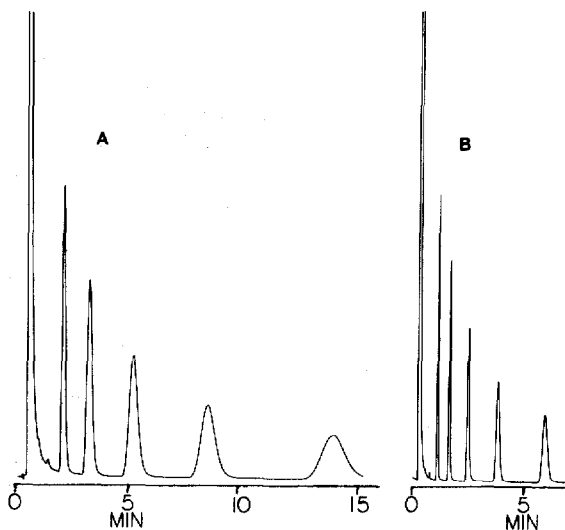

Fig. 2. Separation of a test mixture of n-alkanes (C_{13}–C_{17}) on matched columns of (A) QBA OS and (B) QBA FOS. Column 3.5 m × 2 mm I.D. with 8.0% (w/w) salt on Chromosorb W-AW (40–60 mesh) at 121°C with a nitrogen carrier gas flow-rate of 17.0 ml/min.

Fig. 3. Separation of a polar test mixture on matched columns of (A) QBA BuS and (B) QBA FBuS. Column 3.5 m × 2 mm I.D. with 6.0% (w/w) salt on Chromosorb W-AW (40–60 mesh) at 131°C with a nitrogen carrier gas flow-rate of 11.0 ml/min. Peak identification: 1 = n-butylbenzene; 2 = dihexyl ether; 3 = 2-methyl-2-pentanol; 4 = 1-nitropentane; 5 = benzonitrile; 6 = naphthalene; 7 = benzodioxane.

dent of contributions to retention arising from interfacial adsorption, can be obtained from plots of V_N^*/V_L vs. $1/V_L$ according to eqn. 3 and a qualitative estimate of the importance of interfacial adsorption obtained from the slopes. Of the alkanesulfonate and perfluoroalkanesulfonate salts selected for study only QBA MS, QBA FMS, QBA HS, TBMA BuS, and TBMA FBuS retained a wide range of different solutes exclusively by gas–liquid partitioning. In all other cases retention occurs by a combination of partitioning and interfacial adsorption. The relative importance of interfacial adsorption as a retention mechanism depends on properties of both the solute and the salt and is not related in any manner to the incorporation of fluorine into the alkanesulfonate group. Interfacial adsorption seems to be more important for the arylsulfonate salts (Fig. 4) than for the alkanesulfonate salts for which the data for QBA BuS and QBA FBuS (Fig. 5) are fairly representative. Since experimental data for the interfacial areas required to evaluate the adsorption coefficients in eqn. 3 are unavailable and just about impossible to measure reliably[14,22,23], a quantitative indication of the importance of interfacial adsorption as a retention mechanism can be obtained by comparing the experimental specific retention volume with the specific retention volume calculated from the gas–liquid partition coefficient. The difference between these two values is the contribution made to retention attributable to interfacial adsorption. These data are collected in Table VI at two phase loadings corresponding to $1/V_L = 3$ [ca. 5% (w/w) salt] and $1/V_L = 8$ [ca. 15% (w/w)]. For an
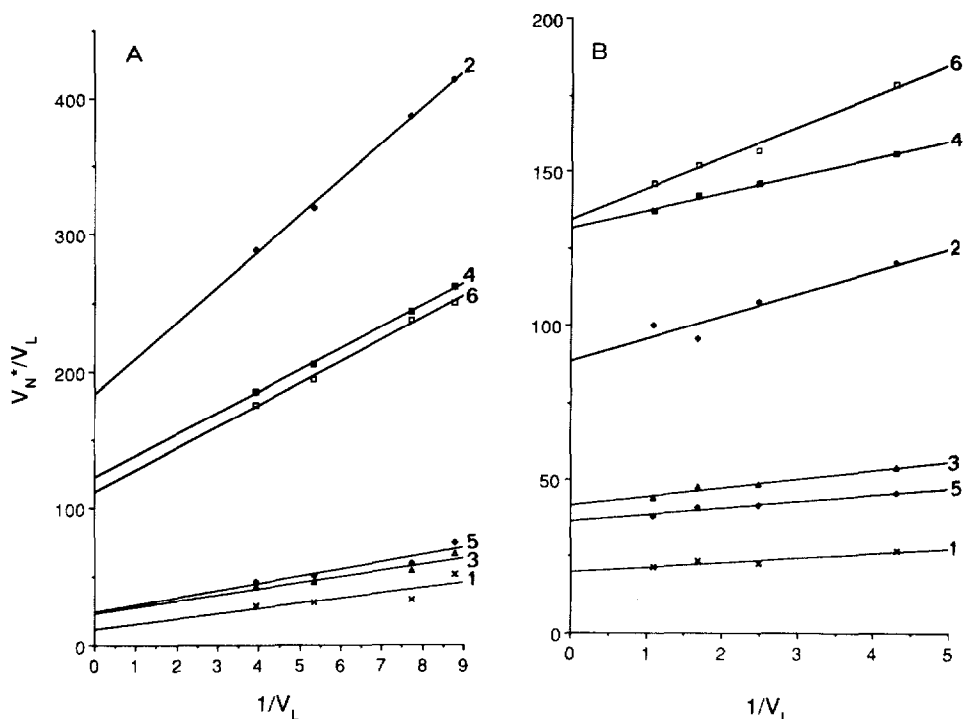
Fig. 4. Plot of V_N^*/V_L vs. $1/V_L$ for a series of test solutes on QBA BS (A) and QBA FBS (B). Solute identification: 1 = benzene; 2 = butanol; 3 = 2-pentanone; 4 = 1-nitropropane; 5 = dioxane; 6 = tridecane.

exclusively gas–liquid partitioning mechanism the specific retention volume is independent of the volume of liquid phase but this is not the case when interfacial adsorption also contributes to retention. Interfacial adsorption should be less important at high phase loadings when retention occurs by a mixed mechanism since the ratio of the phase volume to surface area is higher and the liquid surface area, which does not change linearly with V_L, declines due to preferential filling of the micropores of the support ahead of the macropores[23]. This behavior is clearly seen in the data in Table VI. The contribution made by interfacial adsorption is very variable but in several cases is clearly significant, accounting for the greater part of the observed experimental specific retention volume. There is no general trend, however, attributable to the incorporation of fluorine into the alkanesulfonate anion as far as the relative importance of partitioning and interfacial adsorption are concerned. In most cases though the observed retention $[V_g(Ex)]$ and that portion of the observed experimental retention that is attributable to gas–liquid partitioning $[V_g(K_L)]$ is smaller for the perfluoroalkanesulfonate anions than their alkanesulfonate analogues.

The influence of anion chain length on the partitioning component of the retention volume can be discerned from plots of K_L as a function of the carbon number of the anion. When the test solutes are n-alkanes (Fig. 6) there is a linear relationship between K_L and the number of carbon atoms substituted with hydrogen or fluorine in the anion. Both homologous series of anions show a positive slope with the slope for
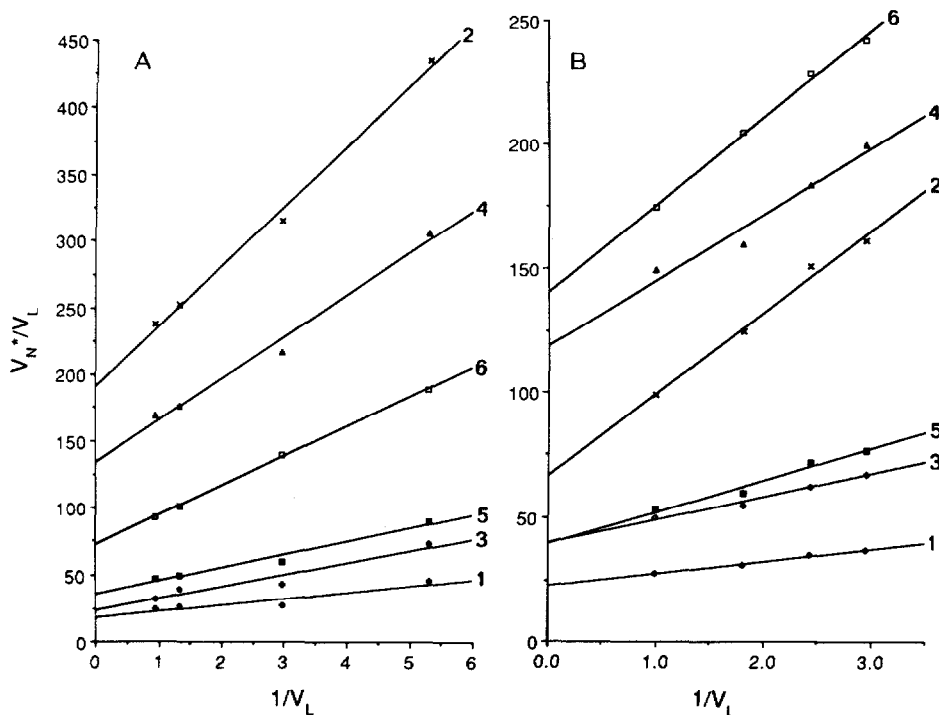
Fig. 5. Plot of V_N^*/V_L vs. $1/V_L$ for a series of test solutes on QBA BuS (A) and QBA FBuS (B). Solutes are identified in Fig. 4.

the perfluoroalkanesulfonates being significantly smaller than that of the alkane-sulfonates. Retention increases with increasing chain length and the lowest retention of the n-alkanes is observed for the methanesulfonate and trifluoromethanesulfonate anions. The difference in the partial molar Gibbs free energy of solution per methylene group, Table VII, for transfer between a tetrabutylammonium alkanesulfonate and perfluoroalkanesulfonate corresponds to 12, 20, and 59 cal/mol for the C_1, C_4, and C_8 anion sidechains, respectively. This is in good agreement with the values for the tributylmethylammonium salts of 18 and 59 cal/mol for a C_4 and C_8 sidechain, respectively.

For polar test solutes the change in K_L as a function of anion chain length is less well defined. The alkanesulfonates show either little change or a great deal of scatter around what seems to be a mean value. The perfluoroalkanesulfonate salts show similar behavior or a decrease in the value of K_L with increasing chain length. This difference in behavior of the n-alkanes and polar test solutes is most likely due to differences in the importance of selective solute–solvent interactions which are influenced by the inductive effect of fluorine as well as by its influence on non-specific solute–solvent interactions. The behavior of the n-alkane standards can not be used as a reliable measure of the behavior of polar test solutes or to predict the general trends concerning the importance of chain length on retention.

Differences in selectivity accompanying the replacement of hydrogen by fluorine in the alkanesulfonate anions are discernible from differences in the values for

TABLE VI

CONTRIBUTION OF INTERFACIAL ADSORPTION TO RETENTION

$V_g(K_L)$ = Specific retention volume calculated from the gas–liquid partition coefficient. $V_g(Ex)$ = Experimentally determined value of the specific retention volume at a specific value of V_L. $\Delta\% = \{[V_g(Ex) - V_g(K_L)]/V_g(K_L)\} \cdot 100\%$.

Salt	$1/V_L$	Tridecane			Ethylbenzene			2-Methyl-2-pentanol		
		$V_g(K_L)$	$V_g(Ex)$	$\Delta\%$	$V_g(K_L)$	$V_g(Ex)$	$\Delta\%$	$V_g(K_L)$	$V_g(Ex)$	$\Delta\%$
QBA BuS	3	151.7	151.7	0	41.6	51.2	23		194.4	42
	8					67.1	61	136.6	291.4	113
QBA FBuS	3	86.7	100.6	16	32.0	39.7	24	40.6	48.5	19
	8		124.0	43		51.0	59		61.7	52
QBA OS	3	247.5	247.5	0	59.5	59.5	0	153.2	189.7	24
	8								252.9	65
QBA FOS	3	98.8	98.8	0	29.1	29.7	2	33.2	33.2	0
	8					33.0	13		41.4	25
QBA BS	3	67.8	67.8	0		43.7	9	86.4	99.9	16
	8				40.2	48.0	19		125.8	46
QBA FBS	3	86.1	151.3	76	37.9	60.9	61	40.4	76.0	88
	8		259.9	202		99.3	162		135.5	235
TBMA OS	3	191.0	226.7	19	53.1	58.9	11	162.8	177.9	9
	8		281.6	47		68.9	30		202.3	24
TBMA FOS	3	84.8	87.3	3	30.5	30.6	0	37.3	37.7	1
	8		91.7	8		30.8	0		38.6	3

Salt	$1/V_L$	Octanone			Nitropropane			Dioxane		
		$V_g(K_L)$	$V_g(Ex)$	$\Delta\%$	$V_g(K_L)$	$V_g(Ex)$	$\Delta\%$	$V_g(K_L)$	$V_g(Ex)$	$\Delta\%$
QBA BuS	3			0	91.2	126.1	38	24.8	30.5	23
	8	181.4	181.4			184.7	103		49.5	100
QBA FBuS	3	125.2	145.1	16	80.0	87.0	8	22.3	26.8	20
	8		176.6	41		100.2	24		34.0	52
QBA OS	3	166.2	187.6	13	113.3	126.0	11	28.3	35.2	24
	8		218.5	31		147.9	31		46.8	65
QBA FOS	3	114.4	114.4	0	55.9	55.9	0	24.6	24.6	0
	8									
QBA BS	3	113.3	132.7	17	109.0	132.1	21	30.7	36.1	18
	8		169.3	49		172.8	59		46.6	52
QBA FBS	3	131.0	211.9	62	96.1	96.1	0	25.3	47.2	87
	8		346.6	165					83.8	231
TBMA OS	3	146.8	164.3	12	103.4	103.4	0	28.5	33.2	16
	8		193.3	32					41.3	45
TBMA FOS	3	107.2	110.5	3	60.9	60.9	0	20.6	20.6	0
	8		116.2	8						

$\delta(\Delta G_K^0 X)_{SQ}^P$ where X represents different test solutes selected to express specific molecular interactions (the McReynolds test solutes)[22–26,29]. The values of $\delta(\Delta G_K^0 X)_{SQ}^P$ for benzene and 2-octyne are all positive indicating greater solubility in the non-selective reference phase, squalane, than in any of the salts. In agreement with the previous discussion these solutes show stronger interactions with the alkanesulfonate
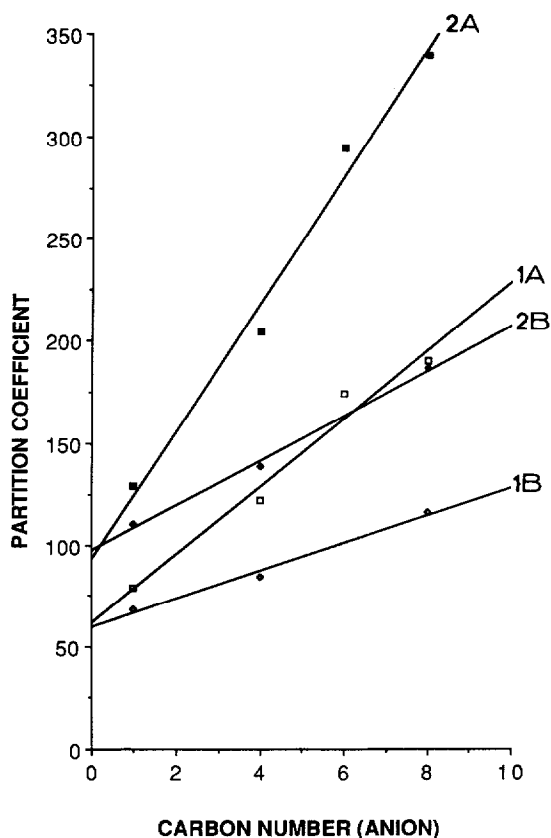
Fig. 6. Plots of the gas–liquid partition coefficient as a function of the number of carbon atoms in the anion chain for dodecane (1) and tridecane (2) on the tetrabutylammonium alkanesulfonates (A) and perfluoroalkanesulfonates (B) at 121.2°C.

salts than with the perfluoroalkanesulfonate analogues. The proton donor solutes butanol and 2-methyl-2-pentanol are strongly retained by all salts; more strongly by the alkanesulfonates than the perfluoroalkanesulfonate analogues. The differences in the $\delta(\Delta G_R^0 X)_{SO}^P$ values in this case are quite large, generally greater than 1 kcal/mol, and it seems reasonable to speculate that this must result in large part from a reduction in the electron density on the sulfonate group caused by the inductive effect of the perfluoroalkane group. Substantial differences in the retention of alcohols on alkanesulfonates and perfluoroalkanesulfonates will occur, therefore, on matched columns with the alcohols showing diminished retention on the perfluoroalkane-sulfonate salts. In the case of the electron donor solutes, 2-pentanone and dioxane, an increase in retention on the perfluoroalkanesulfonates compared to their alkane-sulfonate analogues was observed. These differences are generally not very great but must occur in opposition to any reduction in the magnitude of non-specific interactions. Since the salts contain no proton donor groups it can be assumed that 2-pentanone and dioxane are selectively retained on the perfluoroalkanesulfonates by electron donation to the electron deficient group or carbon backbone of the

TABLE VII

CHANGES IN SOLVENT STRENGTH AND SELECTIVITY ACCOMPANYING THE INTRODUCTION OF PERFLUOROCARBON GROUPS INTO TETRAALKYLAMMONIUM SULFONATE SALTS

Salt	$\Delta G_K^0(CH_2)$	$\delta(\Delta G_K^0 X)_{SQ}^P$						
		Benzene	Butanol	2-Pentanone	1-Nitropropane	2-Methyl-2-pentanol	2-Octyne	Dioxane
QBA MS	-486	0.092	-2.443	-0.363	-1.440	-1.376	1.000	-0.344
QBA FMS	-474	0.182	-1.322	-0.473	-1.223	-0.461	1.150	-0.365
QBA BuS	-505	0.219	-1.817	-0.138	-1.071	-1.214	1.170	-0.048
QBA FBuS	-485	0.405	-1.191	-0.340	-1.109	-0.399	1.167	-0.101
QBA HS	-412	0.073	-2.488	-0.410	-1.405	-1.263	0.942	-0.316
QBA OS	-541	0.120	-2.442	-0.346	-1.256	-1.319	0.701	-0.166
QBA FOS	-482	0.383	-1.030	-0.410	-0.956	-0.374	0.994	-0.309
QBA BS	-467	0.229	-1.993	-0.265	-1.276	-0.919	1.150	-0.279
QBA FBS	-499	0.257	-1.360	-0.341	-1.262	-0.408	1.135	-0.212
TBMA BuS	-469	0.012	-2.850	-0.502	-1.497	-1.676	0.861	-0.489
TBMA FBuS	-451	0.198	-1.310	-0.565	-1.283	-0.523	1.097	-0.308
TBMA OS	-525	0.204	-2.392	-0.205	-1.166	-1.348	0.852	-0.155
TBMA FOS	-466	0.509	-1.196	-0.469	-1.036	-0.478	1.119	-0.185
TBMA HS	-402	0.073	-2.284	-0.192	-1.130	-1.485	0.942	-0.150

perfluoroalkanesulfonate anions resulting from the inductive effect of fluorine. For the dipole probe 1-nitropropane the $\delta(\varDelta G_K^0 X)_{SQ}^P$ values are generally more favorable for the alkanesulfonates but differences between the alkanesulfonates and perfluoroalkanesulfonates are generally quite small. The inductive effect of fluorine does not have a large influence on orientation interactions which are, presumably, mainly dominated by the Coulombic fields between ions.

Activity coefficients for the test solutes in the alkanesulfonate and perfluoroalkanesulfonate salts are summarized in Table VIII. These are uncorrected for solute fugacity and non-ideality of the gas phase and should only be considered as approximate. However, they are sufficiently accurate to illustrate some interesting differences in the solution characteristics of the different anion types. Dodecane shows a large deviation from regular solution behavior but this is due mainly to its low vapor pressure at the measurement temperature. In general, the solution of non-polar solutes in the perfluoroalkanesulfonate salts shows a greater deviation from ideality than the dissolution of the same solute in the alkanesulfonate salt. This is in general agreement with the fact that n-alkane and perfluoroalkane solvents are only partially miscible and although not differing greatly in polarity they do not form ideal solutions[28]. When the solute becomes polarizable, in the case of benzene, solution in the perfluoroalkanesulfonates is more ideal than in the case of the alkanesulfonates. Butanol shows similar behavior with the differences in activity coefficients between the alkanesulfonate and perfluoroalkanesulfonates being much larger. The opposite general behavior is seen for the electron donor solutes confirming that deviations from ideal solution behavior result from specific solute–solvent interactions, to a large extent, and these are influenced primarily by the inductive effect of fluorine.

In conclusion, the tetraalkylammonium sulfonate salts are useful stationary phases possessing wide liquid ranges and good thermal stability. The introduction of fluorine into the alkanesulfonate anion has a significant influence on the selectivity of

TABLE VIII

APPROXIMATE ACTIVITY COEFFICIENTS AT 121.2°C FOR DIFFERENT TEST SOLUTES IN THE ALKANESULFONATE AND PERFLUOROALKANESULFONATE SALTS

Salt	Test solute					
	Dodecane	Benzene	Butanol	2-Pentanone	1-Nitropropane	Dioxane
QBA MS	19.88	0.86	0.20	1.26	0.63	1.07
QBA FMS	21.45	0.90	0.77	1.03	0.78	0.97
QBA BuS	11.20	0.88	0.38	1.46	0.88	1.48
QBA FBuS	13.48	0.91	0.70	0.94	0.70	1.05
QBA OS	6.38	0.69	0.15	1.00	0.62	1.03
QBA FOS	8.45	0.78	0.75	0.75	0.74	0.70
QBA BS	23.00	0.92	0.31	1.29	0.70	1.04
QBA FBS	15.11	0.86	0.64	1.06	0.65	1.03
TBMA BuS	18.05	0.69	0.12	1.05	0.58	0.88
TBMA FBuS	17.12	0.84	0.71	0.83	0.66	0.95
TBMA OS	8.82	0.83	0.18	1.29	0.75	1.14
TBMA FOS	10.40	0.99	0.59	0.76	0.72	0.88

the salts as well as acting to reduce the importance of non-specific interactions. The inductive effect of fluorine acts to reduce the retention of proton donor solutes such as alcohols and to increase the retention of electron donor solutes such as ketones and ethers. These competing factors must be considered when attempting to explain the observed retention of solutes on alkane- and perfluoroalkanesulfonate salts. The contribution to retention from interfacial adsorption cannot be ignored as a retention mechanism for some salts. Interfacial adsorption is not a characteristic property of a particular anion type, alkane- or perfluoroalkanesulfonate, and its relative importance cannot simply be estimated from a knowledge of anion structure.

ACKNOWLEDGEMENT

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