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GAS CHROMATOGRAPHIC STUDY OF THE SOLUTION THERMODYNAMICS OF ORGANIC SOLUTES IN TETRAALKYLAMMONIUM ALKANESULFONATE AND PERFLUOROALKANESULFONATE SOLVENTS

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SUMMARY

The partial molar Gibbs free energy, enthalpy, and entropy of solution for a number of test solutes are determined in five pairs of tetraalkylammonium alkanesulfonate and perfluoroalkanesulfonate salts that are liquid at 121°C. The presence of fluorine is shown to reduce retention due to dispersive interactions, to have little influence on orientation and electron-donor interactions, and to have a large influence on proton–donor interactions. These properties are correlated with the weak dispersive interactions characteristic of highly fluorinated solvents and the inductive effect of fluorine which affects the electron density on the sulfonate group.

INTRODUCTION

Highly fluorinated stationary phases have been used in gas chromatography (GC) for the separation of chemically reactive compounds such as metal halides, interhalogen compounds, and the halides of hydrogen, sulphur, and phosphorus[1]. Fluorinated stationary phases also show unique selectivity for the separation of fluorocarbon homologues and freons. They have not been accepted, however, for general use in GC due to their poor support coating characteristics manifesting themselves in low column efficiencies and poor film stability at moderate to high temperatures. Fluorocarbon groups also exhibit weak support deactivating properties resulting in columns of high activity exhibiting poor peak shape for polar molecules. The film stability, column efficiency and support deactivating properties of highly fluorinated solvents can be dramatically enhanced by incorporating polar anchor groups into the solvent structure using poly(perfluoroalkyl ethers)[1-3], fluorocarbon surfactants containing polar functional groups[4,5] and tetraalkylammonium perfluoroalkanesulfonate salts[6]. The organic salt phases have low melting points, upper column operating temperature limits in the range 160–220°C, and acceptable chromatographic properties towards a wide range of polar solutes[6]. The alkanesulfonate analogues of the fluorinated salts are easily prepared and provide a convenient model system to study the influence of replacing alkane chains by perfluoroalkane chains on retention. In an earlier study it was shown that retention changes were significant and could be qualitatively explained by two types of behavior;

weak intermolecular interactions with the perfluorocarbon chain tending to diminish retention in a non-specific manner and selective retention of proton-donor solutes resulting from the high electronegativity of fluorine and its inductive effect[6]. In this paper a quantitative interpretation of solute–solvent interactions in the perfluoroalkanesulfonate salts is attempted to better explain the above observations using chemical thermodynamics.

EXPERIMENTAL

The synthesis, physical and spectroscopic properties of tetra-n-butylammonium methanesulfonate (QBA MS), tetra-n-butylammonium trifluoromethanesulfonate (QBA FMS), tetra-n-butylammonium butanesulfonate (QBA BuS), tetra-n-butylammonium perfluorobutanesulfonate (QBA FBuS), tetra-n-butylammonium octanesulfonate (QBA OS), tetra-n-butylammonium perfluorooctanesulfonate (QBA FOS), tri-n-butylmethylammonium butanesulfonate (TBMA BuS), tri-n-butylmethylammonium perfluorobutane sulfonate (TBMA FBuS), tri-n-butylmethylammonium octanesulfonate (TBMA OS), and tri-n-butylmethylammonium perfluorooctanesulfonate (TBMA FOS) are described elsewhere[6]. Chromosorb W AW (40–60 mesh) and Gas Chrom Q (60–80 mesh) were purchased from Anspec Co. (Ann Arbor, MI, U.S.A.). All other chemicals and reagents were analytical or reagent grade in the highest purity available.

For column evaluation a Varian 3700 gas chromatograph (Walnut Creek, CA, U.S.A.) was used and modified to permit the measurement of the inlet pressure with a mercury manometer (± 1 mmHg) and the average column temperature with a National Bureau of Standards certified thermometer ($\pm 0.2°C$). Nitrogen was used as the carrier gas at an accurately known flow-rate of approximately 20 ml/min determined with a thermostated soap-film bubble meter. Column packings were prepared by the rotary evaporator technique using standard procedures[6,7]. Accurate phase loadings were determined by exhaustive Soxhlet extraction, 20–30 h, with acetonitrile[6,8]. Samples were injected as headspace vapors to approximate the conditions for infinite dilution/zero surface coverage. All sample peaks were symmetrical and retention volumes were independent of sample size in the measurement region.

The net retention volume was determined using eqn. 1

$$V_N = 3/2[(P^2 - 1)/(P^3 - 1)][(t_R - t_m)F_a][T_c/T_a][1 - (P_W/P_a)] \tag{1}$$

where P is P_i/P_a, P_i the column inlet pressure, P_a the column outlet pressure, t_R the retention time, t_m the gas holdup 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 temperature (K), T_a the ambient temperature, and P_W the vapor pressure of water at T_a. Since retention was known to occur by a combination of gas–liquid partitioning and interfacial adsorption[6], the gas–liquid partition coefficients independent of interfacial adsorption were determined from plots of V_N^*/V_L vs. $1/V_L$ using eqn. 2[9–13]

$$V_N^*/V_L = K_L + (A_{GL}K_{GL} + A_{LS}K_{GLS})(1/V_L) \tag{2}$$

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_{GL} the gas–liquid interfacial area, K_{GL} the coefficient for adsorption at the gas-liquid interface, A_{LS} the gas–support interfacial area, and K_{GLS} the coefficient for adsorption at the support surface. The K_L value for each test solute at a fixed temperature were obtained by linear extrapolation of the data for four columns with phase loadings between 7 and 18% (w/w). The gas–liquid partition coefficients were determined at five temperatures in the range 110–140°C and the data fitted to eqn. 3[12]

$$\log K_L = A - B(T_c) \tag{3}$$

where A and B are constants determined by linear regression and T_c is the column temperature (K). The correlation coefficients, r^2, were generally better than 0.998 except for butylbenzene (0.991), nitropentane (0.997), nitrobenzene (0.997), 2-methyl-2-pentanol (0.997), nonanone (0.995), dihexyl ether (0.996), and benzodioxane (0.983) on QBA BuS; tetradecane (0.996), butylbenzene (0.990), nitropentane (0.988), nitrobenzene (0.995), nonanone (0.994), and dihexyl ether (0.993) on QBA FBuS; dodecyne (0.997), butylbenzene (0.996) on QBA FOS; dodecyne (0.990) on TBMA FBuS; and butylbenzene (0.993), nitropentane (0.996), and 2-methyl-2-pentanol (0.987) on TBMA FOS.

The liquid organic salt densities used to convert phase loadings into V_L values were taken from ref. 6.

The polarity of the liquid organic salts was determined by the solvent strength parameter (the partial molar Gibbs free energy of solution for a methylene group per unit solvent volume) using eqn. 4[14–16]

$$SSP = \Delta G_k^\circ(CH_2)/\rho_c \tag{4}$$

where $\Delta G_k^\circ(CH_2)$ is the partial molar Gibbs free energy of solution for a methylene group and ρ_c the stationary phase density at the column temperature, Table I. The

TABLE I

SOLVENT STRENGTH PARAMETERS FOR TETRAALKYLAMMONIUM ALKANESULFO-NATE AND PERFLUOROALKANESULFONATE SALTS AT 121°C

Phase	$\Delta G_k^\circ(CH_2)$ (cal/mol)	SSP (eqn. 4)
QBA MS	−384	−403
QBA FMS	−371	−358
QBA BuS	−403	−432
QBA FBuS	−374	−337
QBA OS	−446	−469
QBA FOS	−385	−293
TBMA Bus	−374	−395
TBMA FBuS	−360	−300
TBMA OS	−426	−459
TBMA FOS	−371	−278

partial molar Gibbs free energy of solution for each test solute was calculated according to eqn. 5[17-20]:

$$\Delta G_k^\circ(X) = -2.3 \, RT_c \log K_L^X \tag{5}$$

The partial molar enthalpy of solution for solute X was calculated according to eqn. 6[20]

$$\Delta H_k^\circ(X) = 2.3 \, RT_c^2 B \tag{6}$$

where $\Delta H_k^\circ(X)$ is the partial molar enthalpy of solution for solute X and B the regression coefficient defined in eqn. 3. The partial molar entropy of solution for solute X, $\Delta S_k^\circ(X)$, was calculated by difference according to eqn. 7:

$$\Delta S_k^\circ(X) = [\Delta H_k^\circ(X) - \Delta G_k^\circ(X)]/T_c \tag{7}$$

RESULTS AND DISCUSSION

An established property of fluorocarbon solvents is the large positive deviations from Raoult's law for their mixtures with alkane solvents that in some cases are so large as to cause limited miscibility[21]. It is also well known that derivatives formed with fluorocarbon-containing reagents are less retained on most non-fluorinated stationary phases than their hydrocarbon analogues when retention occurs exclusively by gas–liquid partitioning and selective interactions are absent[22,23].

In support of the above arguments the solubility of n-alkanes in the tetraalkyl-ammonium alkanesulfonate salts is more favorable than for the perfluoroalkane-sulfonate salts. The partial molar Gibbs free energy of solution for a methylene group is in all cases more positive for the fluoroalkanesulfonate salts than for their alkanesulfonate analogues, Table I. Likewise, the partial molar Gibbs free energy of solution for tetradecane in the tetraalkylammonium salts, Table II, is more positive for the fluoroalkanesulfonate salts than their analogous alkanesulfonate salts. These differences in properties are due to enthalpy differences as demonstrated by Fig. 1. From the figure it can be seen that entropy changes accompanying solution of the n-alkanes are adequately accounted for by the changes in freedom of migration associated with the differences in strength of the solute–solvent enthalpic interactions (enthalpy–entropy compensation). The differences in slope for QBA BuS and QBA FOS compared to the other salts indicates that the capacity of the salts for solute–solvent interactions may also depend on solvent structure. There is no thorough knowledge of the structure of liquid organic salts but most studies indicate that the salts are at least partially ordered and held together by the strong Coulombic fields between ions, and in some cases, by additional ion–ion molecular interactions to form ion aggregates[12,24-26]. For QBA BuS and QBA FOS we might infer that differences in the melt structure exist compared to the other salts which influence the solubility of the n-alkanes but since the n-alkanes can only interact by dispersive and inductive forces there is no change in the selectivity of these interactions due to changes in solvent structure. Confirmation of this observation comes from plotting either the enthalpy or Gibbs free energy of solution for tetradecane in the fluoroalkanesulfonate salts against

TABLE II

SOLUTION THERMODYNAMICS OF TEST SOLUTES IN THE TETRAALKYLAMMONIUM SULFONATE SALTS AT 121°C

Stationary phase	Test solute	$-\Delta G_k^\circ$ (kcal/mol)	$-\Delta H_k^\circ$ (kcal/mol)	$-\Delta S_k^\circ$ (cal/mol·K)
QBA MS	Tetradecane	4.24 ± 0.03	12.7 ± 0.3	21.4 ± 0.8
QBA FMS		4.18 ± 0.03	11.5 ± 0.3	18.6 ± 0.8
QBA BuS		4.50 ± 0.03	13.2 ± 0.7	22.1 ± 1.8
QBA FBus		4.28 ± 0.05	10.8 ± 0.7	16.7 ± 2.0
QBA OS		5.08 ± 0.04	12.5 ± 0.4	18.9 ± 0.9
QBA FOS		4.50 ± 0.03	11.7 ± 0.2	18.3 ± 0.4
TBMA Bus		4.60 ± 0.03	12.4 ± 0.3	19.7 ± 0.8
TBMA FBuS		4.44 ± 0.03	10.5 ± 0.2	15.4 ± 0.4
TBMA OS		4.89 ± 0.03	11.8 ± 0.2	17.5 ± 0.4
TBMA FOS		4.29 ± 0.03	11.1 ± 0.2	17.2 ± 0.5
QBA MS	n-Butylbenzene	4.04 ± 0.04	10.4 ± 0.3	16.2 ± 0.7
QBA FMS		4.08 ± 0.03	9.9 ± 0.4	14.8 ± 0.9
QBA BuS		4.02 ± 0.03	11.7 ± 0.5	19.4 ± 1.0
QBA FBuS		3.85 ± 0.05	9.4 ± 1.2	14.0 ± 2.0
QBA OS		4.35 ± 0.02	9.7 ± 0.2	13.5 ± 0.5
QBA FOS		3.93 ± 0.03	10.9 ± 0.5	17.6 ± 1.2
TBMA BuS		4.17 ± 0.03	9.9 ± 0.2	14.6 ± 0.5
TBMA FBuS		4.21 ± 0.03	9.9 ± 0.7	14.4 ± 1.8
TBMA OS		4.22 ± 0.06	9.6 ± 0.3	13.7 ± 0.8
TBMA FOS		3.71 ± 0.03	9.5 ± 0.8	14.6 ± 2.0
QBA MS	1-Nitropentane	4.87 ± 0.03	10.7 ± 0.1	14.7 ± 0.3
QBA FMS		4.76 ± 0.03	9.7 ± 0.2	12.5 ± 0.5
QBA BuS		4.79 ± 0.02	11.6 ± 0.6	17.2 ± 1.5
QBA FBuS		4.51 ± 0.03	7.2 ± 0.1	6.7 ± 0.1
QBA OS		5.13 ± 0.10	10.0 ± 2	12.0 ± 6
QBA FOS		4.42 ± 0.02	9.6 ± 0.1	13.2 ± 0.3
TBMA BuS		4.94 ± 0.03	10.5 ± 0.5	14.2 ± 1.2
TBMA FBuS		4.89 ± 0.03	8.8 ± 0.2	10.0 ± 0.4
TBMA OS		4.71 ± 0.03	9.4 ± 0.2	11.8 ± 0.4
TBMA FOS		4.35 ± 0.03	8.5 ± 0.5	10.6 ± 1.3
QBA MS	Nitrobenzene	6.06 ± 0.03	12.0 ± 0.1	15.1 ± 0.3
QBA FMS		5.78 ± 0.03	10.7 ± 0.4	12.6 ± 1.0
QBA BuS		6.19 ± 0.03	12.7 ± 0.7	16.5 ± 1.7
QBA FBuS		5.44 ± 0.03	9.3 ± 0.7	9.8 ± 1.7
QBA OS		5.94 ± 0.04	10.9 ± 0.4	12.6 ± 0.9
QBA FOS		5.27 ± 0.03	9.9 ± 0.3	11.8 ± 0.6
TBMA BuS		6.11 ± 0.03	11.9 ± 0.5	14.7 ± 1.3
TBMA FBuS		5.76 ± 0.03	9.5 ± 0.2	9.6 ± 0.4
TBMA OS		5.80 ± 0.03	10.5 ± 0.2	12.0 ± 0.4
TBMA FOS		5.16 ± 0.03	9.8 ± 0.3	11.7 ± 0.8
QBA MS	2-Methyl-2-pentanol	4.27 ± 0.03	12.2 ± 0.1	20.1 ± 0.1
QBA FMS		3.45 ± 0.03	9.8 ± 0.1	16.1 ± 0.2
QBA BuS		4.26 ± 0.07	13.2 ± 0.7	22.7 ± 1.8
QBA FBuS		3.33 ± 0.02	9.9 ± 0.4	16.8 ± 1.0
QBA OS		4.36 ± 0.05	11.7 ± 0.3	18.7 ± 0.7
QBA FOS		3.22 ± 0.02	10.5 ± 0.4	18.4 ± 0.9
TBMA BuS		4.54 ± 0.03	12.3 ± 0.4	19.6 ± 1.0

TABLE II (continued)

Stationary phase	Test solute	$-\Delta G_k^\circ$ (kcal/mol)	$-\Delta H_k^\circ$ (kcal/mol)	$-\Delta S_k^\circ$ (cal/mol·K)
TBMA FBuS		3.63 ± 0.03	8.7 ± 0.4	12.7 ± 1.1
TBMA OS		4.23 ± 0.03	10.8 ± 0.2	16.6 ± 0.6
TBMA FOS		3.19 ± 0.04	10.8 ± 1.2	19.2 ± 3.2
QBA MS	Nonanone	4.57 ± 0.03	11.2 ± 0.1	16.9 ± 0.2
QBA FMS		4.71 ± 0.03	10.7 ± 0.3	15.1 ± 0.7
QBA BuS		4.57 ± 0.03	12.4 ± 0.9	20.0 ± 2.3
QBA FBuS		4.56 ± 0.01	9.8 ± 0.8	13.4 ± 2.0
QBA OS		4.81 ± 0.04	10.8 ± 0.4	15.2 ± 0.9
QBA FOS		4.64 ± 0.03	10.8 ± 0.4	15.6 ± 1.0
TBMA BuS		4.68 ± 0.02	11.2 ± 0.5	16.5 ± 1.3
TBMA FBuS		4.98 ± 0.03	9.7 ± 0.1	11.9 ± 0.3
TBMA OS		4.65 ± 0.03	10.1 ± 0.2	13.9 ± 0.4
TBMA FOS		4.48 ± 0.04	10.2 ± 0.2	14.4 ± 0.6
QBA MS	Dihexyl ether	4.03 ± 0.03	11.7 ± 0.2	19.6 ± 0.5
QBA FMS		4.07 ± 0.04	10.9 ± 0.3	17.3 ± 0.7
QBA BuS		4.50 ± 0.01	11.4 ± 0.1	17.5 ± 0.2
QBA FBuS		4.08 ± 0.04	10.6 ± 0.9	16.6 ± 2.3
QBA OS		4.67 ± 0.03	11.8 ± 0.3	18.2 ± 1.0
QBA FOS		4.24 ± 0.04	11.2 ± 0.3	17.8 ± 0.8
TBMA BuS		4.22 ± 0.03	11.2 ± 0.4	18.9 ± 1.1
TBMA FBuS		4.33 ± 0.02	10.1 ± 0.2	14.7 ± 0.4
TBMA OS	·	4.53 ± 0.03	11.0 ± 0.4	16.5 ± 1.1
TBMA FOS		4.04 ± 0.03	10.5 ± 0.2	16.5 ± 0.7
QBA MS	Benzodioxane	6.02 ± 0.03	12.6 ± 0.1	16.7 ± 0.2
QBA FMS		5.76 ± 0.03	11.3 ± 0.3	14.1 ± 0.8
QBA BuS		5.84 ± 0.02	16.0 ± 2.1	25.8 ± 5
QBA FBuS		5.40 ± 0.03	10.0 ± 0.1	11.7 ± 0.3
QBA OS		5.96 ± 0.01	11.5 ± 0.1	14.0 ± 0.4
QBA FOS		5.21 ± 0.03	10.5 ± 0.2	13.4 ± 0.6
TBMA BuS		5.69 ± 0.03	11.9 ± 0.7	15.8 ± 1.8
TBMA FBuS		5.74 ± 0.03	10.4 ± 0.4	11.8 ± 1.0
TBMA OS		5.83 ± 0.03	11.0 ± 0.1	13.2 ± 0.3
TBMA FOS		5.12 ± 0.03	10.6 ± 0.3	13.9 ± 0.7

the analogous alkanesulfonate salts which line up into two groups with parallel slopes that depend only on the identity of the cation (QBA or TBMA).

The solvent strength parameter (SSP) has been suggested as a single parameter to evaluate solvent polarity[14,16]. It is equivalent to the partial molar Gibbs free energy of solution for a methylene group per unit solvent volume and, unlike the free energy itself, has been demonstrated to show linear relationships with changes in solvent composition for homologous solvents. For the salts studied in Table I the SSP parameter shows a linear correlation for both series of salts with increasing number of methylene groups or carbon difluoride groups in the alkane- and perfluoroalkane-sulfonate anions. With increasing chain length the SSP value decreases by approximately 23 cal · cm³/g.mol for each carbon unit when a carbon difluoride group replaces a methylene group in the alkanesulfonate chain. This value encompasses two trends. An increase in the magnitude of the SSP value for the alkanesulfonate anion with
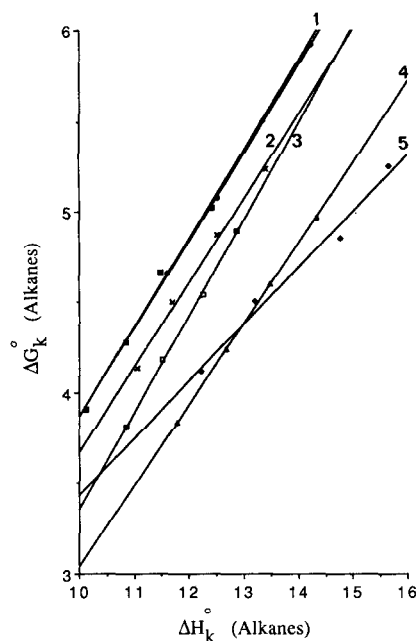
Fig. 1. A plot of ΔG_k° against ΔH_k° for the C_{13}–C_{16} n-alkanes on the tetra-n-butylammonium sulfonate salts. Identification: 1, QBA FBuS and QBA OS; 2, QBA FOS; 3, QBA FMS; 4, QBA MS; 5, QBA BuS. Numerical values for axes are negative.

increasing chain length and a decrease in magnitude of the SSP value for the perfluoroalkanesulfonate anion with increasing chain length.

The aromatic test solute n-butylbenzene and dodecyne, Table III, were selected as examples of non-polar test solutes that are readily polarized and might be expected to show different solution behavior to the n-alkanes due to the presence of strong Coulombic fields in the liquid organic salts. Dodecane and dodecyne have similar boiling points (difference is 1.2°C at atmospheric pressure) and have similar molecular sizes. They should, therefore, have similar cavity terms and differences in their solution properties must be due largely to selective interactions of a dipolar nature. Differences in the free energy of solution for dodecane and dodecyne in the analogous alkanesulfonate and fluoroalkanesulfonate salts are substantial being greatest for the methanesulfonates (1.11 kcal/mol) and least for the octanesulfonates. If the dispersive interactions of dodecane and dodecyne are assumed to be of similar magnitude then there is a small but significant difference between the free energy of solution for the solutes in analogous alkane- and fluoroalkanesulfonate salts. The selective interaction for dodecyne, then, is primarily due to the presence of strong Coulombic fields between ions which are modified to a small extent by the inductive effect of fluorine which lowers the electron density on the sulfonate group compared to the analogous alkanesulfonate anion. Similar behavior is seen for n-butylbenzene except that compared to dodecyne the differences in free energy and enthalpy of solution for the alkanesulfonate and perfluoroalkanesulfonate salts are much smaller.

1-Nitropentane and nitrobenzene, were selected as test solutes expected to have

TABLE III

SOLUTION THERMODYNAMICS FOR DODECANE AND DODECYNE IN TETRAALKYL-
AMMONIUM ALKANESULFONATES AND PERFLUOROALKANESULFONATES AT 121°C

Average uncertainty in ΔG_k° is 0.03 kcal/mol, ΔH_k° 0.35 kcal/mol, and ΔS_k° 0.7 cal/mol·K.

Stationary phase	Dodecane			Dodecyne		
	$-\Delta G_k^\circ$ (kcal/mol)	$-\Delta H_k^\circ$ (kcal/mol)	$-\Delta S_k^\circ$ (cal/mol·K)	$-\Delta G_k^\circ$ (kcal/mol)	$-\Delta H_k^\circ$ (kcal/mol)	$-\Delta S_k^\circ$ (cal/mol·K)
QBA MS	3.43	11.0	19.2	4.54	12.9	21.2
QBA FMS	3.32	10.2	17.5	4.30	11.5	18.1
QBA BuS	3.72	11.0	18.5	4.51	16.3	29.9
QBA FBuS	3.49	9.3	14.8	4.09	11.7	19.2
QBA OS	4.15	10.8	16.8	4.97	12.5	19.2
QBA FOS	3.73	10.2	16.4	4.24	11.5	18.4
TBMA BuS	3.55	10.9	18.5	4.70	12.6	20.1
TBMA OS	3.93	10.2	15.8	4.83	11.7	17.5
TBMA FOS	3.61	9.4	18.6	4.07	11.0	17.5

a large contribution from orientation interactions to their retention (dipole moments
3.52 and 3.97 respectively[14]). In all cases the free energy and enthalpy of solution are
less for the fluoroalkanesulfonate than for the analogous alkanesulfonate salts. From
a plot of ΔG_k° vs. ΔH_k°, shown for nitrobenzene in Fig. 2, there is a reasonable grouping
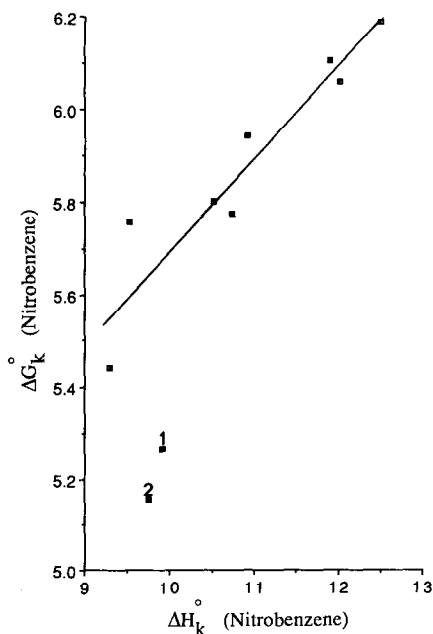of points around a central line for all salts except those containing a perfluoro-

Fig. 2. Plot of ΔG_k° against ΔH_k° for nitrobenzene in the sulfonate salts illustrating the anomolous behavior
of the perfluorooctanesulfonate salts. Identification: 1, tri-n-butylmethylammonium and 2, tetra-n-butyl-
ammonium perfluorooctanesulfonates. Numerical values for axes are negative.

octanesulfonate group (this behavior is typical of 1-nitropentane as well). The octanesulfonate chain is fairly flexible and can be packed into the ordered structure of the liquid organic salts. The covalent radius of fluorine (0.67 Å) is somewhat larger than that of hydrogen (0.37 Å) reducing the flexibility of the perfluorooctane chain which does not pack as easily into the salt structure. The Coulombic fields between ions is changed to accommodate the stiffer perfluorooctanesulfonate anions compared to the octanesulfonate anions which in turn influences the strength of orientation interactions. The difference in solution enthalpy and entropy between the alkanesulfonate and fluoroalkanesulfonate salts is significantly greater for the methanesulfonates and butanesulfonates than for the octanesulfonate salts suggesting an increase in enthalpy (and decrease in entropy) associated with solution of the dipolar solutes in the perfluorooctanesulfonate salts.

2-Methyl-2-pentanol, dihexyl ether, nonanone, and benzodioxane were selected as test solutes to evaluate proton donor–acceptor interactions. The sulfonate group is the most likely proton-acceptor center in the sulfonate salts and 2-methyl-2-pentanol should be the most sensitive test solute for observing changes resulting from the inductive effect of fluorine on the electron density on the sulfonate group. In all cases the free energy and enthalpy of solution are less favorable for solution of 2-methyl-2-pentanol in the fluoroalkanesulfonate salts than for the analogous alkanesulfonate salts. The differences in free energy and enthalpy of solution for the alcohol in the alkanesulfonate and fluoroalkanesulfonate salts are large by comparison to the other test solutes. This difference is largest for the methanesulfonate salts and then increases only shallowly as the length of the alkyl chain is increased. The differences in solution
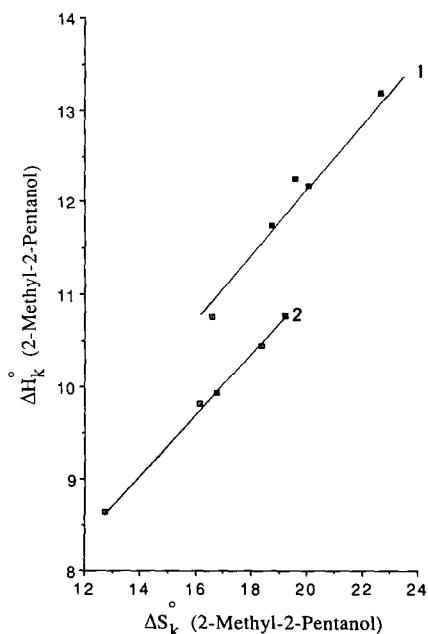

Fig. 3. Plot of ΔH_k° against ΔS_k° for 2-methyl-2-pentanol in the sulfonate salts indicating the difference in behavior for 1, alkanesulfonates and 2, perfluoroalkanesulfonates. Numerical values for axes are negative.

enthalpy increase from the methanesulfonates to the butanesulfonates and then decline significantly to the octanesulfonates. A plot of ΔH_k° against ΔS_k° for 2-methyl-2-pentanol in the sulfonate salts, Fig. 3, divides the salts into two essentially linear groups depending upon whether the anion contains fluorine or not. Enthalpy–entropy compensation is similar for both groups (slope of the line) indicating that the difference between the two groups depends primarily on enthalpy differences. The fluoroalkanesulfonate salts exhibit lower enthalpic interactions compared to their alkanesulfonate analogues due to the inductive effect of fluorine which reduces the electron density on the sulfonate group and is reinforced by weaker dispersive interactions for the perfluorocarbon chains compared to the analogous hydrocarbon chains. It is well established that in aqueous solution the perfluoroalkanesulfonic acids are very strong acids, much stronger than the alkanesulfonic acids, which has been explained in terms of the inductive effect of fluorine[27]. The first carbon difluoride group adjacent to the sulfonic acid moiety is most responsible for the acid strength and the addition of further carbon difluoride groups has only a small effect. This picture is entirely consistent with the interpretation of the thermodynamic solution data for 2-methyl-2-pentanol in the alkanesulfonate and fluoroalkanesulfonate salts.

For nonanone and dihexyl ether the differences in free energy and enthalpy of solution between the alkanesulphonates and fluoroalkanesulphonates are generally small indicating a specific interaction between the electron-donor solutes and the fluoroalkanesulfonate salts that must occur in opposition to the general reduction in dispersive interactions. In a few cases, particularly for the methanesulfonates, the free energy of solution for the test solutes is more favorable for the fluoroalkanesulfonates than the alkanesulfonates. Either the sulfonate group or the carbon backbone of the fluoroalkanesulfonate group could act as electron-donor acceptor sites as their electron density are both influenced by the inductive influence of fluorine. The magnitude of the observed differences is not so large as to suggest that electron-donor interactions for fluoroalkanesulfonate salts are strong selective interactions, particularly when compared to the differences observed for proton-donor solutes. There are of course two possible explanations for this. Either the observed interactions are not very selective compared to those for the alcohols or dihexyl ether, nonanone, and benzodioxane are much weaker electron-donor test solutes than the alcohols are examples of proton-donor test solutes. This question cannot be answered adequately at present but there is reasonable evidence to suggest that the conventional selection of ethers and ketones as electron-donor solutes in schemes designed to evaluate stationary phase selectivity in GC may have to be revised[14,16,18].

The model solvent systems studied here permit a quantitative evaluation of the influence of replacing the alkyl chains by perfluoroalkyl chains in sulfonate anions on the solvent properties of tetraalkylammonium alkanesulfonate solvents used as stationary phases for GC. The general influence of fluorine is to diminish dispersive interactions and to selectively reduce proton-donor interactions through the inductive removal of electron density from the sulfonate group. The inductive effect of fluorine does not seem to have a large influence on the strength of the Coulombic fields between ions which dominate orientation interactions. The stiffness of the perfluorooctane chain may influence orientation interactions compared to the analogous alkanesulfonate salts by changing the ion separation distances in the ordered structure of the liquid salts. The Coulombic fields also influence the solubility of easily polarizable molecules

such as aromatic and unsaturated alkanes which are retained much longer than their saturated analogues of similar volatility.

REFERENCES

1   R. M. Pomaville and C. F. Poole, *Anal. Chim. Acta*, 200 (1987) 151.
2   S. C. Dhanesar and C. F. Poole, *J. Chromatogr.*, 267 (1983) 388.
3   S. C. Dhanesar and C. F. Poole, *Anal. Chem.*, 55 (1983) 1462.
4   W. W. Blaser and W. R. Kracht, *J. Chromatogr. Sci.*, 16 (1978) 111.
5   S. C. Dhanesar and C. F. Poole, *Anal. Chem.*, 55 (1983) 2148.
6   R. M. Pomaville and C. F. Poole, *J. Chromatogr.*, 468 (1989) 261.
7   C. F. Poole and S. A. Schuette, *Contemporary Practice of Chromatography*, Elsevier, Amsterdam, 1984, p. 60.
8   E. F. Sanchez, J. A. G. Dominguez, J. G. Munoz and M. J. Molera, *J. Chromatogr.*, 299 (1984) 151.
9   C. F. Poole, K. G. Furton, R. M. Pomaville, S. K. Poole and B. R. Kersten, in G. Lovering and R. D. Gale (Editors), *Molten Salt Techniques*, Vol. 4, Plenum, New York, 1989, in press.
10   B. R. Kersten and C. F. Poole, *J. Chromatogr.*, 399 (1987) 1.
11   R. M. Pomaville and C. F. Poole, *Anal. Chem.*, 60 (1988) 1103.
12   S. K. Poole, P. H. Shetty and C. F. Poole, *Anal. Chim. Acta*, 218 (1989) 241.
13   C. F. Poole and S. K. Poole, *Chem. Rev.*, 89 (1989) 377.
14   B. R. Kersten, S. K. Poole and C. F. Poole, *J. Chromatogr.*, 468 (1989) 235.
15   C. F. Poole, R. M. Pomaville and T. A. Dean, *Anal. Chim. Acta*, (1989) in press.
16   S. K. Poole and C. F. Poole, *J. Chromatogr.*, 500 (1990) 329.
17   S. K. Poole, B. R. Kersten and C. F. Poole, *J. Chromatogr.*, 471 (1989) 91.
18   B. R. Kersten and C. F. Poole, *J. Chromatogr.*, 452 (1988) 191.
19   B. R. Kersten, C. F. Poole and K. G. Furton, *J. Chromatogr.*, 411 (1987) 43.
20   R. C. Castells, *J. Chromatogr.*, 350 (1985) 339.
21   C. R. Patrick, in R. E. Banks (Editor), *Preparation, Properties, and Industrial Applications of Organofluorine Compounds*, Ellis Horwood, Chichester, 1982, p. 323.
22   S. H. Langer, R. J. Sheehan and J.-C. Huang, *J. Phys. Chem.*, 86 (1982) 4605.
23   C. F. Poole and S. K. Poole, *J. Chromatogr. Sci.*, 25 (1987) 434.
24   C. F. Poole, K. G. Furton and B. R. Kersten, *J. Chromatogr. Sci.*, 24 (1986) 400.
25   C. L. Hussey, *Adv. Molten Salt Chem.*, 5 (1983) 185.
26   J. E. Lind, *Adv. Molten Salt Chem.*, 2 (1973) 1.
27   G. A. Olah, G. K. Surya Prakash and J. Sommer, *Superacids*, Wiley, New York, 1985, p. 36.