Note

Electrostatic Gibbs free energy of solvation from gas chromatographic data

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(First received July 4th, 1983; revised manuscript received October 6th, 1983)

In partition chromatography the retention of the solute molecules is caused by their interaction with solvent molecules. A significant part of these intermolecular interactions has electrostatic character.

Our aim was to study the applicability of the reaction field theory referring to electrostatic interactions in order to interpret gas–liquid chromatographic (GLC) results. This method has been used successfully in the calculation of thermodynamic functions of transfer of *n*-nitroalkanes from *n*-octane to water at 298°K[1,2].

Model substances exhibiting strong electrostatic, but no electron donor–acceptor, interactions were chosen. Nitroalkanes and nitrobenzene having large dipole moments were used as solutes, while non-volatile liquids with different relative permittivities were applied as stationary phases (squalane, propylene carbonate, tricresyl phosphate).

Under isothermal conditions, the intermolecular interactions can be measured by the standard molar Gibbs free energy of the partition process. The electrostatic free energy was determined by GLC and also calculated by reaction field theory[3] applied to the $-C-NO_2$ group. The calculations gave results in reasonable agreement with the observations.

EXPERIMENTAL

A GCHF 18.3 (Chromatron, G.D.R.) gas chromatograph equipped with a thermal conductivity detector was used. Hydrogen was the carrier gas. The solid support was Chromosorb W HP (80–100 mesh) (Applied Science Labs.). The stationary phases were squalane (Carlo Erba), propylene carbonate (Merck-Schuchardt) and tricresyl phosphate (Schuchardt). A 2 m × 4 mm I.D. column with 10% liquid phase loading was used in each case. The solutes studied were commercially available compounds and were used without further purification.

Sample size was adjusted to keep all peaks on scale at the maximum sensitivity. Nitroalkane samples of 0.25–0.50 μl (3–5 components), gaseous hydrocarbons of 5–10 μl (3–4 components) and liquid hydrocarbons (each 0.05–0.1 μl) were injected by a Hamilton microsyringe. The dead volume was measured using air coinjected with the solutes. Retention times were corrected for column dead time.

RESULTS AND DISCUSSION

For the transfer of one mole of solute from a standard state in the gaseous phase (temperature T, concentration 1 mol dm^{-3}, perfect gas) to a standard state in the liquid phase (temperature T, concentration 1 mol dm^{-3}, ideal solution), the change in the standard molar Gibbs free energy is related to the specific retention volume, V_g (ref. 4).

$$\Delta G^\circ = -RT \ln (T\rho_1/273)V_g \tag{1}$$

where ρ_1 is the density of the liquid phase, T is the column temperature and R is the gas constant.

The standard molar Gibbs free energy is a sum of the energies of the inter-molecular interactions, and can be divided into a non-electrostatic, ΔG_n°, and an electrostatic, ΔG_e°, term

$$\Delta G^\circ = \Delta G_n^\circ + \Delta G_e^\circ \tag{2}$$

where the non-electrostatic term is the Gibbs free energy of a non-polar solute having the same size as the polar solute in question.

The electrostatic term can be obtained by using eqns. 1 and 2

$$\Delta G_e^\circ = RT \ln \frac{V_{gn}}{V_g} \tag{3}$$

where V_{gn} is the specific retention volume of a non-polar solute of the same size as the polar solute in question. Eqn. 3 is similar to that used in ref. 5, differing in the carbon numbers considered.

Using the same column at a constant flow-rate of carrier gas, temperature and pressure drop, eqn. 3 can be rewritten

$$\Delta G_e^\circ = RT \ln \frac{t'_{Rn}}{t'_R} \tag{4}$$

where t'_{Rn} and t'_R are the retention times of the non-polar and polar solutes, respectively, corrected for the column dead time.

Homomorphic hydrocarbons were used as the non-polar solutes. The observed electrostatic Gibbs free energies calculated by eqn. 4 are shown in Table I.

The electrostatic Gibbs free energies were also calculated by Böttcher's reaction field theory[3], which involves a polarizable dipole. In this case a new cavity radius belonging to the –C–NO$_2$ group was applied

$$\Delta G_e = -\frac{N_A}{a_2^3} \cdot \frac{\varepsilon_1 - 1}{2\varepsilon_1 + n_2^2} \cdot \frac{n_2^2 + 2}{3} \cdot \mu_{g2}^2 \tag{5}$$

where N_A is the Avogadro constant, ε is the relative permittivity, n the refractive index at sodium line, a_2 the radius of the –C–NO$_2$ group and μ_g is the permanent

TABLE I

OBSERVED AND CALCULATED ELECTROSTATIC GIBBS FREE ENERGIES, $-\Delta G_e$ (kJ mol^{-1})

Solute	Squalane								Tricresyl phosphate				Propylene carbonate,	
	22 ± 1°C		52 ± 1°C		79 ± 1°C		100 ± 2°C		25 ± 1°C		51 ± 1°C		22 ± 1°C	
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
Nitromethane	8.0	8.8	7.6	8.1	7.6	7.6	7.5	7.1	17.7	18.2	17.2	17.3	22.0	23.8
Nitroethane	7.6	8.8	7.3	8.1	7.0	7.6	6.9	7.1	16.7	18.2	16.2	17.3	20.6	23.8
1-Nitropropane	7.0	8.8	6.8	8.1	6.5	7.6	6.4	7.1	15.8	18.2	15.2	17.3	19.4	23.8
2-Nitropropane	7.2	8.8	7.0	8.1	6.7	7.6	6.5	7.1	15.5	18.2	15.0	17.3	18.8	23.8
1-Nitrobutane	6.8	8.8	6.6	8.1	6.3	7.6	6.3	7.1	15.5	18.2	14.9	17.3		
1-Nitropentane			6.6	8.1	6.3	7.6	6.2	7.1						
1-Nitrohexane			6.5	8.1	6.3	7.6	6.1	7.1						
Nitrobenzene			6.3	8.1	6.1	7.6	6.0	7.1						

TABLE II

RELATIVE PERMITTIVITIES OF THE STATIONARY LIQUID PHASES

Stationary phase	Temperature (°C)	Relative permittivity, ε
Squalane	20	2.11*
	52	2.07*
	79	2.04*
	100	2.01*
Tricresyl phosphate	25	6.7[10]
	40	6.9[10]
Propylene carbonate	25	64.4[11]

* Values calculated using the equation $\varepsilon = n^2$, where $n^{20°C} = 1.452$ (ref. 9) and $\partial n/\partial T$ is taken as $0.0004°K^{-1}$.

dipole moment of this group in the gas phase; the indices 1 and 2 refer to the stationary phase and the solute, respectively. The group radius (0.271 nm) is taken to be the sum of the N–O bond length (0.121 nm[6]) and the van der Waals radius of the oxygen atom (0.15 nm[7]). The temperature dependence of this radius is assumed to be the same as that of the Onsager radius[3]

$$\frac{\partial a_2^3}{\partial T} = \frac{3}{4\pi N_A} \frac{\partial V_2}{\partial T} \tag{6}$$

where V_2 is the molar volume of the nitro compound. This temperature dependence, the refractive index and its temperature dependence are taken as the average values of experimental data for 1-nitroalkanes[2] (up to 1-nitropropane[8]). Thus, $\partial a_2^3/\partial T = 3.9641 \cdot 10^{-26}$ cm^3 °K^{-1}, $\partial n_2^2/\partial T = -1.21 \cdot 10^{-3}$ °K^{-1} and $n_2 = 1.4025$. The relative permittivities of the solvents are collected in Table II.

The calculated electrostatic Gibbs free energies are given in Table I. The agreement with the observed values is quite reasonable, and supports the assumption that the electrostatic interaction depends mostly on the dipole moment and the size of the –C–NO$_2$ group and is nearly independent of the length of the alkyl chain in nitroalkanes.

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