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GAS CHROMATOGRAPHY ON SOME SELF-ASSOCIATING OCTADECANE DERIVATIVES

L. PREMRU AND M. KREMSER

Chemical Institute Borisa Kidriča, Hajdrihova 19, Ljubljana (Yugoslavia)

SUMMARY

The specific retention volumes of simple monofunctional organic compounds and lower alkanes were measured on different stationary phases. Octadecane derivatives were mainly used as stationary phases, but some other polar and nonpolar liquids were also used in order to obtain more information about the dependence of the specific retention values on the solute and the solvent structure. The purpose of this study was the determination of the influence of hydrogen bonding on the retention volumes and the determination of thermodynamic properties reflecting this influence. Systems showing an appreciable solvent self-association were of particular interest.

INTRODUCTION

GLC has been used in several instances as a convenient tool in the study of specific interactions in various systems[1-3]. The main advantage of the method is its simplicity and the speed with which results can be obtained if the phase is not appreciably self-associating. If the latter phenomenon cannot be negligible the method loses a great deal of its simplicity. However, there is still one possible approach to overcome this problem, that is by using several columns with different amounts of the polar stationary phase and proceeding with calculations neglecting the self-association. The results have to be extrapolated to a value for zero concentration. This method is accompanied by considerable experimental errors which obscure the results. In our work a rather different approach was used. We chose a model which can be described by certain equations, then compared the measured results with those predicted from the model.

METHOD

The following model was selected as a basis for the study of associating systems. Let us consider the system: nonpolar solvent–nonpolar and polar solute and polar solvent–nonpolar and polar solute. The nonpolar solvent is the reference one. Four specific retention volumes can be determined in this system:

$\overline{V}_g{}^{0d} .. V_g{}^{0d}$ specific retention volume of nonpolar and polar solute in a polar solvent,

$\overline{V}_g{}^{0r} .. V_g{}^{0r}$ specific retention volume of the same pair of solutes in a nonpolar reference solvent.

From this system we got our model after some restrictions. These restrictions are required by some of the calculations. In our work we used the approach of LANGER and co-workers which was discussed by MARTIRE[2].

They obtained the following equation:

$$\frac{\bar{\gamma}_2{}^r}{\bar{\gamma}_2{}^d} = \frac{e^{[Z \cdot N \cdot \varepsilon_{11}{}^r]\,(2RT)^{-1}}}{e^{[Z \cdot N \cdot \varepsilon_{11}{}^d]\,(2RT)^{-1}}} \tag{1}$$

where

N = Avogadro's number;

$\varepsilon_{11}{}^d$ and $\varepsilon_{11}{}^r$ = solvent–solvent pairwise potential energy of interaction in the reference solvent and in the polar one;

$\bar{\gamma}_2{}^d$ and $\bar{\gamma}_2{}^r$ = activity coefficients of nonpolar solute in the same pair of solvents.

Here we can see that for each nonpolar solute or for each solute which can interact only by the dispersion forces the ratio of the activity coefficients in two solvents of the same molecular shape and polarizability depends only on solvent–solvent pairwise potential energy and is independent of the solute. Because of this we can assume the above expression to be valid for an uncomplexed solute as well. This is true if all orientational effects are included in the complexation term and if all dipole-induced dipole interactions are small. For nonpolar solutes eqn. 1 holds in every case. This result was obtained by calculations made by MARTIRE[2] and serves as our model. For this model we require that:

the polarizabilities of the reference solvent and the polar solvent must be the same;

the molar volumes of the same pair of solvents must be the same;

the dipole-induced dipole interactions must be small;

only a 1:1 adduct is formed.

These requirements do not all hold for systems which were actually measured. In the case of octadecane derivatives not only a 1:1 adduct is formed since appreciable self-association occurs. Nevertheless, we can consider these systems in the same way as our model because all the equilibria which occur due to the association of solute–solvent and self-association are reversible. So the same probability can be given for each molecule of the solvent to be attached to the solute. It makes no difference whether the site of solute attachment is at the end or in the middele of the chain. But because of the solvent self-association the polarizability of the stationary phase changes and our model is not valid any more. For the other systems polarizabilities of reference and polar solvent differ so much that we certainly cannot expect eqn. 1 to be valid even if solvent self-association is not present.

In our work we also used the equations derived for the model for these systems. The differences between the results obtained and those predicted by the model should reveal the role played by the specific forces.

If the polarizabilities of two solvents are not the same then we can get eqn. 3 from eqn. 1 and from expression 2.

$$\varepsilon_{12} = \frac{3}{2} \cdot \frac{h}{a^6} \cdot \frac{\nu_1 \cdot \nu_2}{\nu_1 + \nu_2} \cdot \alpha_1 \cdot \alpha_2 \tag{2}$$

$$\frac{\bar{\gamma}_2{}^r}{\bar{\gamma}_2{}^d} = e^{\dfrac{Z \cdot N \cdot (1/2\varepsilon_{11}{}^r - \varepsilon_{12}{}^r + 1/2\varepsilon_{11}{}^d + \varepsilon_{12}{}^d)}{RT}} \tag{3}$$

where

a = distance between molecular centers;

α_1, α_2 = polarizabilities;

ν_1, ν_2 = frequencies of the electronic vibrators;

$\varepsilon_1, \varepsilon_2$ = solute–solvent pairwise potential energy of interaction.

From 1 and 3, if we write:

$$\varepsilon_{12} = c \cdot \alpha_1 \cdot \alpha_2 \tag{4}$$

$$\left(c = \frac{3}{2} \cdot \frac{h}{a^6} \cdot \frac{\nu_1 \cdot \nu_2}{\nu_1 + \nu_2} \right)$$

we get:

$$\frac{\bar{\gamma}_2{}^r}{\bar{\gamma}_2{}^d} = c_1 \cdot e^{\dfrac{Z \cdot N \cdot c \cdot \alpha_2 (\alpha_1{}^d - \alpha_1{}^r)}{RT}} \tag{5}$$

where:

$$c_1 = e^{\dfrac{Z \cdot N \cdot (1/2\varepsilon_{1,1}{}^r - 1/2\varepsilon_{1,1}{}^d)}{RT}}$$

In this case the activity coefficient ratio is not independent of the solute. It depends on the polarizabilities of the solvents. Thus it cannot be the same for all nonpolar solutes and of course it cannot be the same for all uncomplexed solutes. This result will be discussed later. Now we can proceed with the calculations for our model. If an adduct between an electron-donor D and a proton-donor H is formed according to the next expression:

$$H + D \rightleftharpoons HD \tag{6}$$

we can write the equilibrium constant as follows:

$$K = \frac{a_{HD}}{a_D \cdot a_H} \tag{7}$$

where

a_H = activity of the proton-donor;

a_D = activity of the electron-donor;

a_{HD} = activity of the adduct.

Because we are dealing with infinitely dilute solutions and because the activity of the solvent does not change when the adduct HD is formed, we have:

$$K \cdot a_D = K' = \frac{c_{HD}}{c_H} \tag{8}$$

From eqns. 1 and 8 we get:

$$K' + 1 = \frac{V_g{}^{0d} \cdot \overline{V}_g{}^{0r}}{V_g{}^{0r} \cdot \overline{V}_g{}^{0d}} \tag{9}$$

Thus the constant K' can be obtained by measuring four V_g values. K' is connected with the equilibrium constant K as follows:

$$K' = K \cdot \gamma \cdot c_D \tag{10}$$

DISCUSSION AND RESULTS

Our measurements were made in the temperature range 50–80° C. Lower aliphatic alcohols and alkanes were used as solvents. Stationary phases, in addition to the octadecane derivatives, were other liquids such as triethanolamine and squalane. The measure of how much a particular stationary phase is in agreement with the model regarding the reference solvent octadecane for the octadecane derivatives and squalane for the other phases is the ratio

$$\frac{\overline{V}_g{}^{0r}}{\overline{V}_g{}^{0d}} \text{ and } \frac{V_g{}^{0d}}{V_g{}^{0r}}$$

When $\alpha_1{}^r = \alpha_1{}^d$ then:

$$\frac{\overline{V}_g{}^{0r}}{\overline{V}_g{}^{0d}} = \frac{\bar{\gamma}_2{}^d}{\bar{\gamma}_2{}^r} C'' = c_1 \cdot C'' = \text{constant} \tag{11}$$

In the case when $\alpha_1{}^r \neq \alpha_1{}^d$, then $V_g{}^{0r}/V_g{}^{0d}$ is not independent of the solute and it is not constant for all nonpolar solutes. For the systems measured we get the values given below:

Stationary phase	Solvent		
	Hexane	Heptane	Octane
Octadecylamine	1.32	1.32	1.34
Octadecanol	1.39	1.80	1.88
Octadecyl cyanide	1.36	1.40	1.44
Triethanolamine	10.60	21.90	32.90
Diethylene glycol succinate	3.50	15.30	29.30
		$T = 70°$ C	
Octadecylamine	1.56	1.61	1.67
Octadecyl cyanide	1.37	1.45	1.57
		$T = 60°$ C	

Octadecane derivatives are compared with octadecane. If solvent self-association does not occur then the polarizability of each derivative is practically the same as for the reference solvent. When self-association occurs then the differences become notable. Octadecanol shows the strongest self-association and consequently the differences are here the largest. The other two derivatives show weaker association and thus the ratio is nearly constant. It is interesting to note that at 60° C this ratio is not constant any more.

With lower temperatures the association becomes stronger and the results for $V_g{}^{0r}/V_g{}^{0d}$ show this. This is reflected in Fig. 1.

Triethanolamine is a different case altogether. Here we have both effects: strong self-association and quite different polarizability between triethanolamine and the reference solvent squalane. As a result of this fact the differences in the ratio $V_g{}^{0r}/V_g{}^{0d}$ between homologs are very large.

Diethylene glycol succinate also has very different polarizability and the differences are large, although this solvent shows no self-association.
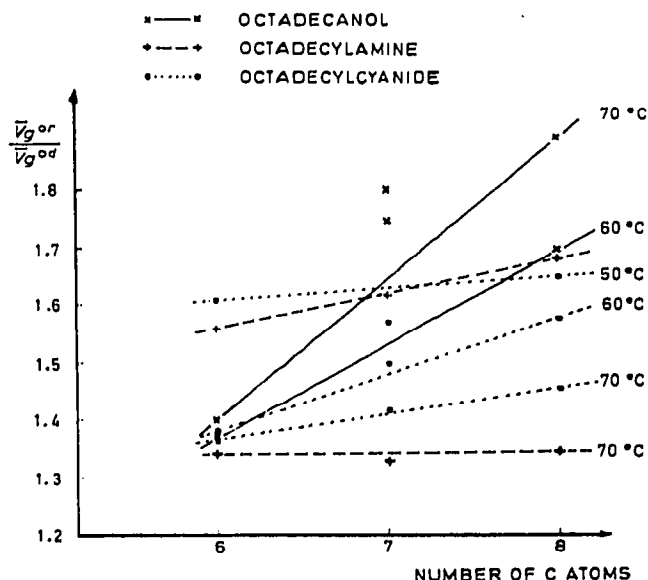

Fig. 1. The specific retention volume ratio as a function of C atom number.

In the case where $\alpha_1{}^r = \alpha_1{}^d$ we can write:

$$\frac{V_g{}^{0d}}{V_g{}^{0r}} = \frac{(K' + 1) \cdot \gamma_2{}^r \cdot M_r}{\gamma_2{}^d \cdot M_d} = \frac{\gamma_2{}^r}{\gamma_2{}^d} (K' + 1)C' = (K' + 1) \cdot \text{constant}. \qquad (12)$$

This ratio is dependent on K' only, i.e. on K. So it measures the specific interactions of the polar solute with the polar solvent. But when $\alpha_1{}^r \neq \alpha_1{}^d$ then the K' term in eqn. 12 is not constant and the difference between the polarizabilities of two solvents and the polarizability of the solute affects the results. If these dispersion forces are small we can expect that the relative order of these ratios will be in accordance with the general principles of acidity. For triethanolamine we get:

	Methanol	Ethanol	1-Propanol	1-Butanol	1-Pentanol
$\dot{V}_g{}^{0d}/V_g{}^{0r}$	4.13	3.98	3.26	2.45	1.74
K'	92.3	89.0	72.6	54.9	38.8

The values decrease with the decreasing acidity of the alcohol. In this case the hydrogen bonds are very strong and dispersion forces have no effect on the relative order of the values for $V_g{}^{0d}/V_g{}^{0r}$.

For octadecanol we get:

	Methanol	Ethanol	Propanol	Butanol
$V_g{}^{0d}/V_g{}^{0r}$	2.57	5.04	5.48	5.82
K'	3.03	6.91	7.61	8.15

TABLE I

SPECIFIC RETENTION VOLUMES OF LOWER ALIPHATIC ALCOHOLS AND ALKANES ON DIFFERENT STATIONARY PHASES

	$T(°C)$	V_g^0 (ml/g)							
		Pentane	Hexane	Heptane	Octane	Methanol	Ethanol	Propanol	Butanol
Octadecane	50	105.85	263.45	634.40	1742.00	33.67	42.24	87.76	232.47
	60	68.33	167.40	423.22	1110.90	28.06	28.65	62.23	157.20
	70	55.46	130.42	303.33	733.80	24.00	22.40	44.98	105.60
Octadecanol	60	51.84	123.66	242.25	556.51	93.02	165.04	401.02	1046.80
	70	45.02	93.64	168.61	390.01	61.61	112.84	246.43	614.78
	80	37.17	72.04	120.51	262.65	44.50	74.04	157.44	369.50
Octadecylamine	60	47.88	107.73	263.34	664.16	99.18	167.04	444.60	1320.12
	70	42.38	98.12	229.83	549.31	64.00	113.10	255.80	678.40
	80	37.56	80.12	169.02	391.25	45.21	75.34	157.46	446.02
Octadecyl cyanide	50	69.06	164.01	405.70	1066.05	71.21	125.16	315.07	850.25
	60	58.91	122.03	290.35	709.05	50.50	88.37	227.23	547.04
	70	48.84	95.65	216.10	508.75	42.73	69.19	156.70	358.51
Triethanolamine	50	—	9.80	12.60	17.64	208.61	273.80	505.04	992.12
	60	—	6.96	8.35	11.13	141.45	172.20	301.84	564.57
	70	—	5.62	6.37	10.25	99.15	114.49	192.44	332.76
Diethylhexylsebacate	50	—	107.38	215.97	567.14	45.89	75.25	193.02	531.65
	60	—	91.53	139.43	342.20	33.64	49.41	117.91	304.92
	70	—	67.50	108.81	247.94	28.19	38.19	87.90	215.20
Diethylene glycol succinate	50	—	17.32	12.78	17.94	77.62	97.10	179.90	351.89
	60	—	17.32	9.74	14.31	61.79	73.06	128.76	243.52
	70	—	16.94	9.13	11.26	44.75	52.05	86.75	151.89
Squalane	50	—	100.76	259.04	687.94	33.67	51.68	112.69	294.06
	60	—	74.86	184.89	455.26	28.06	35.66	79.24	198.09
	70	—	59.72	139.04	329.65	24.00	28.93	59.17	135.76

TABLE II

V_g^{or}/V_g^{od} RATIOS FOR LOWER ALKANES ON DIFFERENT STATIONARY PHASES

	T (°C)	$\overline{V}_g^{or}/\overline{V}_g^{od}$			
		Pentane	Hexane	Heptane	Octane
Octadecanol	60	1.318	1.354	1.747	1.691
	70	1.216	1.393	1.799	1.881
Octadecylamine	60	1.427	1.555	1.607	1.672
	70	1.308	1.329	1.320	1.336
Octadecyl cyanide	50	1.533	1.606	1.563	1.634
	60	1.159	1.372	1.488	1.566
	70	1.135	1.363	1.403	1.443
Triethanolamine	50	—	10.976	20.704	39.370
	60	—	10.526	24.119	49.100
	70	—	19.352	21.527	32.165

TABLE III

V_g^{od}/V_g^{or} RATIOS FOR LOWER ALIPHATIC ALCOHOLS ON DIFFERENT STATIONARY PHASES

	T (°C)	$\overline{V}_g^{od}/\overline{V}_g^{or}$			
		Methanol	Ethanol	Propanol	Butanol
Octadecanol	60	3.315	5.760	6.444	6.659
	70	2.567	5.037	5.478	5.821
Octadecylamine	60	3.534	5.830	7.144	8.397
	70	2.666	5.049	5.680	6.424
Octadecyl cyanide	50	2.963	2.963	3.590	3.657
	60	2.695	3.084	3.651	3.479
	70	2.529	3.088	3.483	3.395
Triethanolamine	50	6.659	5.154	4.543	3.110
	60	5.115	4.295	3.641	2.168
	70	4.133	3.277	3.149	2.612

TABLE IV

K' VALUES FOR LOWER ALIPHATIC ALCOHOLS ON OCTADECANE DERIVATIVES

	T (°C)	K'			
		Methanol	Ethanol	Propanol	Butanol
Octadecanol	60	4.062	7.801	8.846	9.174
	70	3.032	6.918	7.611	8.150
Octadecylamine	60	4.513	8.094	10.180	12.142
	70	2.524	5.674	6.508	7.498
Octadecyl cyanide	50	3.612	3.693	4.686	4.792
	60	2.762	3.305	4.096	3.856
	70	2.377	3.124	3.652	3.534

In the case of octadecanol the influence of the dispersion forces and of the other effects is so large that it completely changes the relative order. It is obvious that in this case the values calculated from the expression derived for the described model are far from the quantities like the equilibrium constant and others. Data are listed in Tables I–IV. For some system it would perhaps be possible to find some relationship between the values thus calculated and the true quantities.

EXPERIMENTAL

For this study, high accuracy in measuring specific retention volumes is required. In our work a Varian 1800 gas chromatograph with a flame ionization detector was used. Commercially available instruments of this kind keep the column temperature constant at best within $\pm 0.5°$ C or worse. For this reason most of our measurements were made in a home-made oil thermostat incorporated in the original chromatograph. The heaters for the original air thermostat were used to heat the oil bath and consequently a longer time is needed for the stabilization. Nevertheless quite good results were obtained. Temperature was constant within $\pm 0.02°$ C. Stainless steel columns 5 ft. $\times$ 1/8 in. I.D. were used. The detector signal was recorded on a Speedomax G, 1 mV, recorder. The temperatures of the detector and the injector block were the same as that of the column. Columns were prepared in the usual manner. Embacel 60–100 mesh was used as support and argon as the carrier gas. Reagents from Fluka AG were used without further purification. A 20 % loading was used in all cases.

The exact amount of liquid phase was determined by the combustion method. The solute sample sizes were between 0.02 and 0.1 μl. In this range the amount of solute has no effect on the retention time found. Peaks were symmetrical in most cases, exceptions being some polar solutes but the deformation was never large. For the determination of V_g^0 known methods were adopted[1,4].

Specific retention volumes were calculated from the expression given below:

$$V_g^0 = \frac{L \cdot F \cdot 273.2 \cdot [p_o - p_{H_2O}] \cdot \left[\left(\frac{p_i}{p_o}\right)^2 - 1\right] \cdot 3}{V \cdot W \cdot T_m \cdot p_o \cdot \left[\left(\frac{p_i}{p_o}\right)^3 - 1\right] \cdot 2} \qquad (13)$$

where

L = distance between solute peak maximum and starting point (cm);
V = recorder chart speed (cm/min);
F = carrier gas flow rate (ml/min);
W = amount of liquid phase (g);
T_m = flowmeter temperature (°K);
p_i = inlet pressure (mm Hg);
p_o = outlet (atmospheric) pressure (mm Hg).

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