ANALYSIS OF POLAR COMPOUNDS ON POLYETHYLENE GLYCOL GLASS CAPILLARY COLUMNS

THE INFLUENCE OF KF AND Na_3PO_4 ON THE CHANGE IN PARTIAL MOLAR FREE ENERGY

R. V. GOLOVNYA* and A. L. SAMUSENKO
Institute of Organo-Element Compounds of the USSR Academy of Sciences, ul. Vavilova 28, Moscow (U.S.S.R.)

SUMMARY

The effect of treating the glass column surface in capillary chromatography with KF and Na_3PO_4 on the retention of polar and non-polar compounds has been investigated. Aliphatic hydrocarbons, benzene, toluene, nitrobenzene, pyridine and polar derivatives of octane with such functional groups as $-NH_2$, $-OH$, $-SH$, $-Br$ and $=C=O$ have been analyzed using PEG-40M, PEG-40M + KF and PEG-40M + Na_3PO_4 glass capillary columns. The energy contributions of functional groups to partial molar free energy of sorption of octane derivatives on these three columns were calculated. The increase of the energy contributions of proton donor functional groups $-NH_2$, $=NH$, $-OH$ for the PEG + KF system was observed and explained by hydrogen bonding with KF taking part as a base in the chromatographic separation.

INTRODUCTION

Glass capillary columns are widely used in gas chromatographic (GC) separation of complex mixtures of organic compounds. With polar substances such as alcohols, amines, etc., difficulties are encountered owing to adsorption on active sites of the glass surface. To reduce this, glass surfaces have been treated with various compounds including inorganic salts, *e.g.*, $BaCO_3$ (ref. 1), Na_3PO_4, K_2CO_3 (ref. 2), KF (ref. 3). The effect of such salts is of a complicated nature[3,4]. For example, there are reasons for believing that the specific effect of Na_3PO_4 in GC analysis of amines is due to its capability for donor–acceptor interaction with the sample or the stationary phase[5,6]. It has also been observed that the treatment of glass capillary columns with KF affects the GC separation of nitrogen-containing organic bases[3].

The present work deals with the effect of KF and Na_3PO_4 on the retention of polar and non-polar compounds by polyethylene glycol (PEG) as stationary phase under the conditions of capillary chromatography.

EXPERIMENTAL

Glass capillaries were drawn from borosilicate glass by a standard procedure[7]. Columns were treated with 5 ml of 1 % aqueous HF solution under nitrogen at 5 atm. The acid was displaced with nitrogen and the columns were washed in sequence with 3 ml distilled water, 5 ml of 1 % potassium hydroxide–methanol solution, and 2 ml methanol. Next, a "hexane plug"[2] was used to coat the inner surface of columns with a KF (column 2) or a Na_3PO_4 (column 3, see Table I) layer from 0.5 % methanolic solutions of these salts. For the reference column (column 1, see Table I) this step was omitted. The liquid phase (PEG-40M) was applied on the walls of the columns by a high-pressure static method with the help of a special unit[3], temperatures being 400°C in the evaporator and 200°C in the thermostat.

TABLE I

CHARACTERISTICS OF GLASS CAPILLARY COLUMNS WITH PEG-40M

Characteristic	Column		
	1 (neutral)	2 (with KF)	3 (with Na_3PO_4)
Length (m)	24.7	24.9	25.3
Internal diameter (mm)	0.30	0.25	0.25
Volume (ml)	1.74	1.19	1.24
Phase mass (g)	0.0044	0.0030	0.0031
Flow-rate of carrier gas during analysis (ml/min)	0.68	0.34	0.33

The columns were conditioned at 250°C under a stream of dry nitrogen for 3 h. Analyses were conducted on a Biochrom-1 chromatograph with a flame ionization detector; nitrogen was used as carrier gas. The temperature in all three columns was 110°C and the column inlet splitting ratio was 150:1. The columns are characterized in Table I. Standard mixtures were prepared by dissolving 20 μl of each compound in 1 ml pentane. The sample size for analysis was 0.2 μl.

Retention times of compounds were determined as averages from 5–7 measurements. The specific retention volume at the analysis temperature, V_g^T, was calculated[8] from

$$V_g^T = t'_R w j^{3/2}/m_p$$

where t'_R is the corrected retention time (min) of a substance, w is the volumetric flow-rate (ml/min) of carrier gas, m_p is the mass (g) of liquid phase in the column and $j^{3/2}$ is the pressure drop factor in the column

$$j^{3/2} = \frac{3}{2} \cdot \frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1}$$

where p_i is the column inlet pressure (mmHg) and p_0 is the column outlet pressure (mmHg) equal to atmospheric pressure.

The V_g^T values given in Table II were used to calculate the contribution of the functional group of the substance analysed to the differential molar free energy of sorption

$$\delta(\Delta G)_{X,Y} = -2.3 \, RT \log \left[(V_g^T)_X / (V_g^T)_Y \right] \tag{1}$$

where T is the analysis temperature ($^\circ$K), and $(V_g^T)_X$ and $(V_g^T)_Y$ are the specific retention volumes of compound X and of octane or benzene, depending on the group of substances compared. The neutral column with PEG-40M applied on the surface of a glass capillary previously deactivated with alkali–methanol solution was taken as reference (column 1, Table I).

TABLE II

SPECIFIC RETENTION VOLUMES, V_g^T, (ml/g), OF COMPOUNDS ON GLASS CAPILLARY COLUMNS WITH PEG-40M AT 110°C

No.	Compound X	Column		
		1 (neutral)	2 (with KF)	3 (with Na₃PO₄)
1	Benzene	34.7	16.3	27.6
2	Toluene	61.2	29.1	49.1
3	Nitrobenzene	2231.9	940.3	1760.3
4	Pyridine	141.6	73.0	118.5
5	2-Octanone	240.4	96.1	189.0
6	1-Octanol	1065.4	630.2	804.3
7	Octylamine	279.8	159.1	238.2
8	Dibutylamine	80.2	44.9	66.6
9	Dipropylethylamine	23.3	11.2	17.8
10	Octyl bromide	338.0	135.8	265.6
11	Octyl mercaptan	356.6	132.5	255.0
12	Octane	12.3	5.6	9.8
13	Tetradecane	412.4	211.3	319.1
14	Pentadecane	713.2	369.3	554.6

RESULTS AND DISCUSSION

KF and Na₃PO₄ were chosen for the study of the ability of polyethylene glycol to dissolve various organic substances in the presence of inorganic salts. Potassium fluoride in non-aqueous media behaves as a base, therefore the formation of $KF^{\delta-} \cdots A^{\delta+}$ complexes cannot be excluded. Trisodium phosphate can form donor–acceptor bonds of two types[6], $\equiv P = O^{\delta-} \cdots A^{\delta+}$ and $\equiv P^{\delta+} \cdots B^{\delta-}$, with the substances under study. Also, in analysis on packed columns with PEG + LiCl, it was noted[9] that electrostatic interaction with the metal cation of the salt is probable. This possibility cannot be ruled out in our case either.

Theoretical analysis shows that the partial molar free energy of solution is the sum of the energies of the intermolecular interactions: non-specific (due to physical forces) and specific electron donor–acceptor interactions of chemical nature. Physical forces acting between the molecules of a substance and a stationary phase are associated with dispersive, inductive and orientative interactions. When a polar substance is analysed on a polar stationary phase, the total partial molar free energy of solution comprises the energies of dispersive, inductive, orientative and donor–acceptor interactions. In our case, the ability of PEG, PEG + KF and PEG + Na_3PO_4 to participate in dispersive interaction was evaluated on the basis of values of the partial molar free energy of solution of an n-alkane methylene group, ΔG^{CH_2}, obtained from V_g^T values for pentadecane and tetradecane on each of the columns. The almost identical ΔG^{CH_2} values for all the columns (Table III) demonstrate that the ability of PEG to participate in dispersive interaction with hydrocarbons does not change after treatment of the column with KF or Na_3PO_4. In other words, after the introduction of these salts into the chromatographic system, the "dispersive polarity"[10] of polyethylene glycol remains unchanged, *i.e.*, in all the three columns, PEG possesses the same ability to dissolve n-alkanes.

TABLE III

PARTIAL MOLAR FREE ENERGY OF SOLUTION OF METHYLENE GROUP (ΔG^{CH_2}) CALCULATED FOR n-TETRADECANE AND n-PENTADECANE BY EQN. 1 USING V_g^T VALUES AT 110°C

Column	Stationary phase	$-\Delta G^{CH_2}$ (cal/mole)
1	PEG-40M	425
2	PEG-40M + KF	420
3	PEG-40M + Na_3PO_4	423

Benzene has been used as a test substance for evaluating the ability of a phase to participate in dispersive interaction and π complex formation[11]. For this reason we determined the specific retention volumes and calculated the difference in sorption free energies, $\delta(\Delta G)_{X,Y}$, for toluene, nitrobenzene and pyridine with respect to benzene on the three columns (Fig. 1). As seen in Table IV, all columns give very similar $\delta(\Delta G)_{X,Y}$ values for the toluene–benzene pair which are close to the ΔG^{CH_2} values (Table III). Thus, in this case the ability of PEG to dissolve benzene and toluene does not change after the addition of salts. For the nitrobenzene–benzene pair, the $\delta(\Delta G)_{X,Y}$ value is lower on the PEG + KF column than on columns with PEG and PEG + Na_3PO_4. This may be due to a higher contribution of orientative interaction energy from nitrobenzene, dipole moment 3.98 D[12], on the neutral column and on the column with Na_3PO_4 than in the case of KF. Apparently, the ability of PEG + KF to participate in orientative interactions is lower than that of the neutral column with pure PEG. A similar picture is found for 2-octanone.

The behaviour of pyridine is of special interest. Unlike benzene, its interaction energy is greater on columns treated with salts, being slightly higher on KF than on Na_3PO_4. Since pyridine is a donor of electrons, it can be assumed that there is an
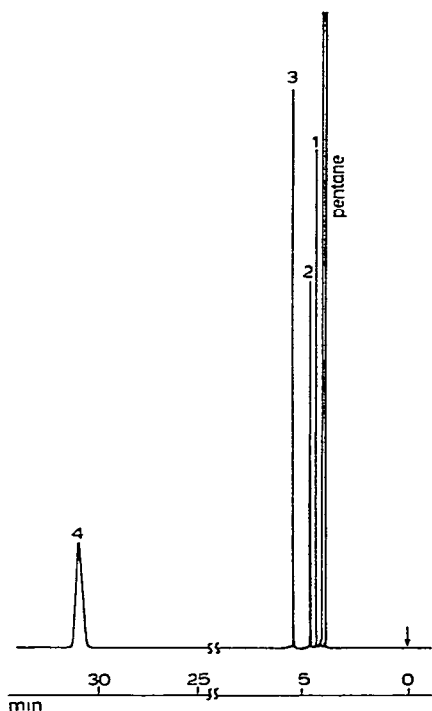
Fig. 1. Chromatogram of benzene and related compounds on a glass capillary column with PEG + Na$_3$PO$_4$ (column 3, Table I). Analysis temperature: 110°C. Column inlet pressure: 0.25 atm. Peaks: 1 = benzene; 2 = toluene; 3 = pyridine; 4 = nitrobenzene.

TABLE IV

CONTRIBUTION OF FUNCTIONAL GROUPS OF COMPOUNDS X TO PARTIAL MOLAR FREE ENERGY OF SORPTION, $-\delta(\Delta G)_{X,Y}$ (cal/mole), ON GLASS CAPILLARY COLUMNS WITH PEG-40M AT 110°C

Y is a reference: benzene for compounds 1–4, n-octane for compounds 5–12.

No.	Compound X	Column		
		1 (neutral)	2 (with KF)	3 (with Na$_3$PO$_4$)
1	Benzene	0	0	0
2	Toluene	432	439	439
3	Nitrobenzene	3170	3087	3163
4	Pyridine	1071	1141	1109
5	Octane	0	0	0
6	1-Octanol	3397	3596	3356
7	Octylamine	2379	2548	2429
8	Dibutylamine	1427	1585	1459
9	Dipropylethylamine	486	529	454
10	Octyl bromide	2523	2427	2512
11	2-Octanone	2263	2165	2253
12	Octyl mercaptan	2563	2408	2481

extra energy contribution due to the electrostatic interaction with metal ions of the salts:

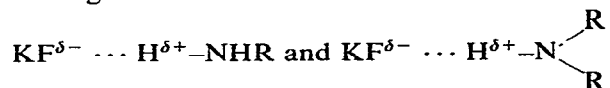$$\langle\!\!\!\bigcirc\!\!\!\rangle N^{\delta-}K^+ \,(Na^+)$$
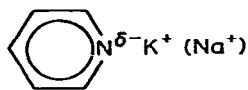
The same type of interaction can also occur for the tertiary amine dipropylethyl-amine, whose $\delta(\Delta G)_{X,Y}$ is slightly higher on the column with KF than on the neutral column:

$$\begin{array}{c} R \\ \diagdown \\ N^{\delta-}:K^+ \\ R \diagup \quad | \\ R' \end{array}$$
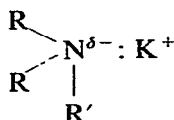
   To discriminate between columns 1, 2 and 3 with respect to orientative, inductive and donor–acceptor interactions, we compared the partial molar free energies of sorption of 1-octanol, octyl mercaptan, octyl bromide, 2-octanone, octylamine, dibutylamine and dipropylethylamine with that of n-octane on each of the columns (Fig. 2). This made it possible to determine the energy contribution of each functional group to the total sorption energy and to compare the corresponding values for columns with or without salt (Table IV). The columns were found to differ in their ability to participate in intermolecular interaction with octane derivatives. The energy contribution in the cases of alcohol and primary or secondary amine groups is highest on the column with PEG + KF, the maximum value being specific for the OH group in 1-octanol. Indeed, while on the neutral column with PEG, $\delta(\Delta G)_{X,Y} = -3397$ cal/mole, in the presence of KF the corresponding value approaches -3596 cal/mole. Thus, with KF in PEG, the energy contribution of the OH group rises by 199 cal/mole. The most probable explanation of this is based on the formation of a weak hydrogen bond of the following type:

$$KF^{\delta-} \cdots H^{\delta+}\!\!-\!O\!-\!C_8H_{17}$$
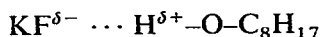
For octylamine and dibutylamine, which are also capable of being hydrogen donors, the energy contribution of the $-NH_2$ and $=NH$ groups on the column with KF increases by 169 and 158 cal/mole, respectively. This extra energy is apparently due to the following interactions:

$$KF^{\delta-} \cdots H^{\delta+}\!\!-\!NHR \quad \text{and} \quad KF^{\delta-} \cdots H^{\delta+}\!\!-\!N\!\!\begin{array}{c} \diagup R \\ \diagdown R \end{array}$$

   It is of interest that for octyl mercaptan, which is incapable of hydrogen bonding with polyethylene glycols[13], the energy contribution of the $-SH$ group is lower in columns containing salts than in column 1, probably because of a decrease in the total sorption capacity of columns 2 and 3.
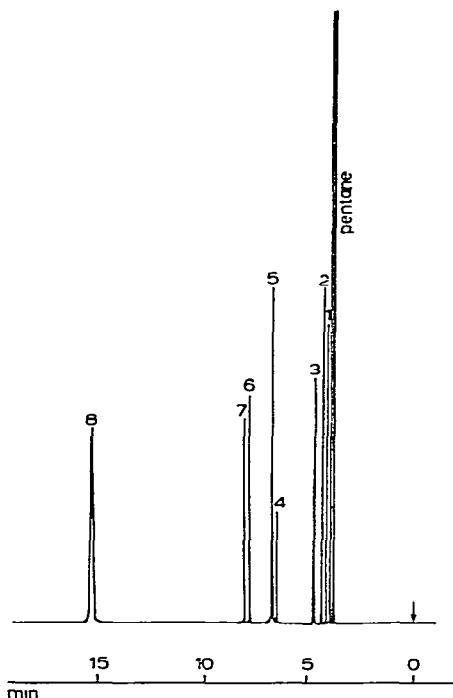   Thus, the analyses on columns with polyethylene glycol containing salts reveal

Fig. 2. Chromatogram of octane and related compounds on a glass capillary column with PEG + Na_3PO_4 (column 3, Table I). Analysis temperature; 110°C. Column inlet pressure: 0.25 atm. Peaks: 1 = octane; 2 = dipropylethylamine; 3 = dibutylamine; 4 = 2-octanone; 5 = octylamine; 6 = octyl mercaptan; 7 = octyl bromide; 8 = 1-octanol.

a complex sorption process. On the one hand, the interaction intensity of the functional groups of some substances increases in the presence of KF and Na_3PO_4. On the other hand, the total free energy of sorption of each of the substances decreases, probably because of the reduction in sorption capacity of the columns after treatment of their inner surfaces with salts. From the comparison of V_g^T values (Table II), the highest partial molar free energies of sorption of each of the fourteen compounds studied are found on the neutral column. For example, V_q^T values for n-alkanes decrease in the series of columns 1, 3, 2, while ΔH^{CH_2} remains unchanged (Table III).

Our data on the energy contributions of functional groups, viz., –OH, –NH$_2$, –SH, =C=O and –Br, and of benzene, toluene, nitrobenzene and pyridine in pure polyethylene glycol and in the presence of salts (KF and Na_3PO_4), demonstrate the participation of the salts in the chromatographic separation process of polar substances, and the ability of potassium fluoride to act as a base in analyses of hydrogen donor substances.

CONCLUSIONS

(1) The observed increase in energy contributions of hydrogen donor functional groups in analyses on polyethylene glycol in the presence of KF can be ac-

counted for in terms of hydrogen bond formation, with the salt acting as a base in the chromatographic separation process.

(2) The electrostatic interactions with metal ions of the salts seem to be a component of the sorption energy of pyridine as well as of tertiary amines.

(3) In analyses of n-alkanes on PEG, the partial molar free energy of solution per methylene group, ΔG^{CH_2}, is not affected by the presence of KF and Na_3PO_4.

REFERENCES

1 K. Grob and G. Grob, *J. Chromatogr.*, 125 (1976) 471.
2 E. A. Mistryukov, A. L. Samusenko and R. V. Golovnya, *J. Chromatogr.*, 169 (1979) 391.
3 R. V. Golovnya, A. L. Samusenko and E. A. Mistryukov, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 2 (1979) 609.
4 K. Grob, Jr., G. Grob and K. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 1 (1978) 149.
5 R. V. Golovnya and I. L. Zhuravleva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2 (1973) 482.
6 R. V. Golovnya, I. L. Zhuravleva, S. V. Zenin, V. A. Polyakov and G. B. Sergeev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 11 (1973) 2595.
7 E. A. Mistryukov, R. V. Golovnya and A. L. Samusenko, *J. Chromatogr.*, 148 (1978) 490.
8 D. H. Desty and W. T. Swanton, *J. Phys. Chem.*, 65 (1961) 766.
9 A. Betti, F. Dondi, G. Lodi and C. Bighi, *J. Chromatogr.*, 68 (1972) 59.
10 R. V. Golovnya and T. A. Misharina, *Usp. Khim.*, 1 (1980) 171.
11 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
12 O. A. Osipov and V. I. Minkin, *Spravochnic po dipolnym momentam*, "*Vyzshaya shcola*", Moscow, 1965.
13 R. V. Golovnya and T. A. Misharina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 8 (1977) 1794.