EFFECT OF VAPOUR-PHASE ELUENT ON RETENTION AND SEPARATION OF SUBSTANCES IN GAS CHROMATOGRAPHY

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SUMMARY

Contributions to changes in retention time on replacing nitrogen with a vapour-phase eluent, resulting from the use of a non-ideal gas phase, modification of the solid carrier and absorption of water by the stationary phase, have been studied.

INTRODUCTION

The reduction in retention volume in chromatography when using a vapour as the mobile phase is usually explained by the effect of using a non-ideal gas phase, adsorption of water on the surface of the solid carrier and dissolution of water in the film of the stationary phase (absorption)[1–5]. The determination of the relative influence of each of these factors on the retention of different types of sorbates is described in this paper. Experiments were carried out using the unit described by Nonaka[1].

EFFECT OF A NON-IDEAL GAS PHASE

The effect of a non-ideal gas phase on the retention volume was estimated by using flows of nitrogen and water vapour in a column packed with Polychrom 1 polytetrafluoroethylene (PTFE) support coated with 16.7% (w/w) silicone elastomer E-301 non-polar hydrophobic stationary phase. Sorption of water by this sorbent was assumed to be negligible and all of the changes in retention volumes to be due to the non-ideal gas phase.

The relative changes in retention volume, ΔV_1, when nitrogen was replaced with water vapour were as follows (at 120°): propanol, −3.8; butanol, −6.4; benzene, −2.7; toluene, −4.4; and heptane, −3.5%. In each instance a reduction in retention volume was found, the differences being less than 7%. The reductions were probably related not only to the use of a non-ideal gas phase, but also to partial adsorption of water on the sorbent and in the connecting lines, as shown by some enhancement of the asymmetry coefficient, A, determined as the ratio of the front and back peak half-widths. When water vapour was used instead of nitrogen, A changed from 0.51 to 0.68 for butanol, and from 0.70 to 0.78 for benzene. Thus, the values of ΔV_1 should be considered as high estimates of the probable influence of a

non-ideal gas phase on the retention volume. Therefore, it was interesting to calculate ΔV_1 by using the equation[3]

$$\ln V_R = \ln V_{R0} - \frac{B_{12} - V_\infty}{RT}$$

where V_R and V_{R0} are the retention volumes using a non-ideal and an ideal gas as mobile phase, respectively, B_{12} is the second mixed virial coefficient and V_∞ is the partial molar volume of the sorbate at infinite dilution.

The virial coefficients are related to the constants of the Van der Waals equation:

$$B = b - \frac{a}{RT}$$

The constants a_{12} and b_{12}, required for calculations of B_{12}, were found from the equations[4]

$$a_{12} = \sqrt{a_1 a_2}$$

and

$$b_{12} = \tfrac{1}{2}(b_1^{1/3} + b_2^{1/3})$$

while the constants a_1, a_2, b_1 and b_2 for different substances were taken from ref. 6. As can be seen from the calculated values of ΔV_1, the contribution of a non-ideal gas phase to the changes in the retention volume for substances with a low molecular weight is not more than 2–3%. Values of the parameters concerned are given in Table I.

TABLE I

INFLUENCE OF NON-IDEALITY OF GAS PHASE ON RETENTION VOLUME

Substance	$a \cdot 10^6$ $(cm^6/atm \cdot mole)$	b $(cm^3/mole)$	$-B_1$	$-B_{12}$	$\Delta V_1 (\%)$
Water	5.46	30.53	138.9	—	—
Benzene	18.00	115.44	442.79	243.69	1.9
Heptane	31.51	265.62	711.47	298.00	2.65
Propanol	14.34	101.27	361.74	221.10	1.6
Butanol	17.03	114.38	413.65	235.65	1.7

EFFECT OF MODIFICATION OF THE SOLID CARRIER

To estimate the influence of modification of a solid carrier, produced by water vapour, the same stationary phase E-301, coated to the extent of 16.7% on the more adsorption-active solid carrier Chromosorb W, was used. The relative changes in retention volume on this sorbent when nitrogen was replaced with water vapour at 120° were as follows: propanol, −8.7; benzene, −8.1; and heptane, −3.4.

Even for polar propanol this change is less than 9% and if ΔV_1 is subtracted from these values, the values obtained, ΔV_2 (−4.9% for propanol, −5.4% for benzene and 0.1% for heptane), characterize the influence of modification of the solid carrier on retention, and are about 5% for substances capable of specific interaction and close to zero for alkanes, which are incapable of such interactions. ΔV_2 must depend to a considerable extent on the nature of the stationary phase and on the amount of it on the solid support, and also on the quality of the solid support. When 5% of E-301 was applied on the same support (Chromosorb W), the values of ΔV_2 were 30% for propanol, 9.1% for benzene and 1.2% for heptane, i.e., they were particularly increased for polar compounds. With a small amount of the stationary phase, replacing nitrogen with water vapour considerably improves the peak symmetry and causes a decrease in the HETP value for polar compounds (Table II). With 16.7% Apiezon L on firebrick, the ΔV_2 values even for non-polar octane and decane were 13.3 and 12.8%, respectively, while for benzene and toluene the peak symmetry was considerably improved when water vapour was used.

TABLE II

COEFFICIENTS OF SYMMETRY (A) AND HETPs (H) FOR DIFFERENT SORBENTS

1 = E-301 on Chromosorb W; 2 = PEGA on firebrick; 3 = PEGA on Chromosorb W.

Substance	A						H (mm)					
	Nitrogen			Water vapour			Nitrogen			Water vapour		
	1	2	3	1	2	3	1	2	3	1	2	3
Ethanol	0.25	0.56	0.60	0.82	0.9	0.87	4.48	2.4	2.0	2.27	1.8	1.3
Propanol	0.29	0.60	0.75	0.60	0.85	0.86	3.25	2.2	1.3	2.41	1.6	1.2
Butanol	0.36	0.75	0.82	0.80	0.92	0.90	4.25	1.8	1.2	2.21	1.3	1.1
Benzene	0.43	0.75	0.8	0.79	0.89	0.84	1.82	1.9	1.4	2.03	1.8	1.3
Heptane	0.80	0.71	0.78	0.83	0.92	0.90	1.70	3.6	3.1	2.05	3.9	3.5

EFFECT OF ABSORPTION OF WATER BY THE STATIONARY PHASE

To estimate the influence of absorption of water by the stationary phase on retention, polyethylene glycol adipate (PEGA) on Polychrom was studied, adsorption of water at the solid–liquid interface being neglected. The stationary phase PEGA dissolves water well: at 120° there is more than 0.03 g, (3%, w/w) of water per gram of the stationary phase. The temperature dependences of the relative changes in retention volume, given in Fig. 1, show that absorption of water by PEGA has different effects on the retentions of sorbates belonging to different classes of compounds. Whereas for alkanes and aromatic compounds absorption of water causes a reduction in retention volume, for alcohols it causes an enhancement. Such regularities are easily explained by an increase in the polarity of the stationary phase and its being rendered capable of formation of hydrogen bonds after absorption of water. At 120° the quantities ΔV_{13} and ΔV_3 ($\Delta V_3 = \Delta V_{13} - \Delta V_1$) have the following values: ethanol, +28 and +33; benzene, −13 and −10; and nonane, −24 and −20, respectively. The values of ΔV_3 are much larger than ΔV_1 and ΔV_2, except for aromatic compounds, for which all three quantities are approximately the same.
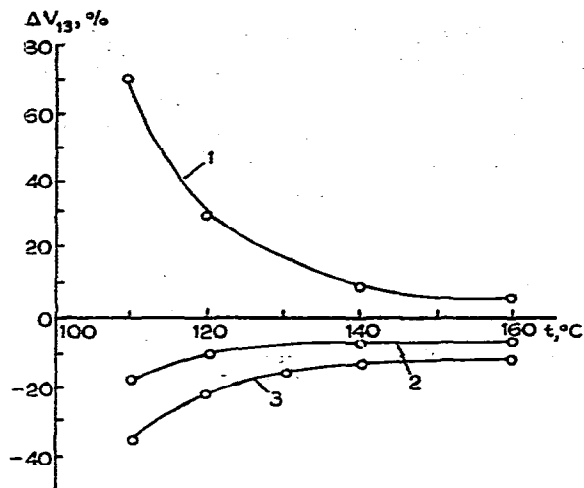
Fig. 1. Effect of dissolution of water in PEGA on retention of sorbates. 1 = Ethanol; 2 = benzene; 3 = nonane.

OVERALL EFFECT OF A VAPOUR-PHASE ELUENT ON RETENTION

To estimate the overall effect of a vapour phase as the mobile phase on retention, the systems PEGA–Chromosorb and PEGA–firebrick were studied. The relative changes in retention volumes when nitrogen was replaced with water vapour are shown in Fig. 2. Because for alcohols absorption of water and its adsorption by the solid-support have opposite influences on the retention volume, ΔV_0 decreases in the order Polychrom > Chromosorb > firebrick, corresponding to increasing adsorption activity of the supports. For hydrocarbons both effects have the same influence on the retention volume and therefore the value of ΔV_0 increases in the above order.

At high temperatures the sign of ΔV_0 is changed for alcohols, becoming negative. Obviously water adsorbed on the active support is retained more strongly than
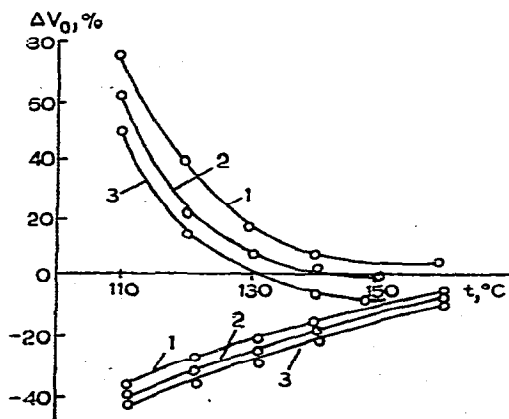

Fig. 2. Overall effect of change in retention volume when nitrogen is replaced with water vapour. Upper lines, Propanol; lower lines, decane. 1 = PEGA–Polychrom; 2 = PEGA–Chromosorb; 3 = PEGA–firebrick.

that absorbed by the stationary phase and is removed more slowly with increasing temperature.

An improvement in the peak shape was observed for all of the sorbate–sorbent systems studied when nitrogen was replaced with water vapour, and with the latter the symmetry coefficients obtained were virtually the same for all supports (Table II). Therefore, for chromatography using water vapour the quality of the support is not so important and in many instances relatively inexpensive supports can be used, which is particularly important in preparative gas chromatography.

As absorption of water by the stationary phase led to an increase in its polarity, it was interesting to estimate the variation in selectivity when nitrogen was replaced with water vapour. The binary mixtures nonane–undecane, benzene–toluene and ethanol–propanol have practically the same values of the separation factor, α. For substances belonging to different homologous series and differing in their capacities for specific interactions, the use of water vapour sharply changed α (Fig. 3). Thus, for the binary mixtures toluene–propanol and benzene–ethanol a sharp increase in α was observed when water vapour was used owing to the strong retention of alcohols, and a decrease in the retention times of aromatic compounds. Inversion of the order of elution of alcohols and aromatic compounds is related to the following. With increasing temperature, induction interactions and hydrogen bonds, which are characteristic of alcohols, are weakened to a greater extent than those caused by π-bonds of aromatic compounds. Such an inversion with the vapour-phase eluent occurs at a higher temperature. The mixture propanol–undecane remains practically unseparated on nitrogen and propanol is eluted first ($\alpha < 1$), and naturally there cannot be any inversion of the order of elution. When water vapour is used, α for
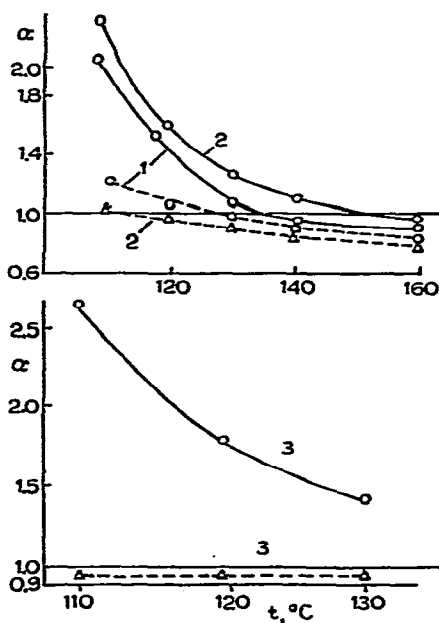

Fig. 3. Dependence of the relative retention volume on temperature using nitrogen (broken lines) and water vapour (solid lines). 1 = Benzene–ethanol; 2 = toluene–propanol; 3 = undecane–propanol.

this mixture is sharply increased. In this instance inversion of the order of elution is not observed with increasing temperature, probably owing to the weak retention of undecane on the polar stationary phase. Smaller changes are observed for the binary mixtures undecane–benzene and undecane–toluene. Hence, the use of water vapour for the separation of substances, belonging to different homologous series permits a greatly improved separation or an inversion of their order of elution to be achieved in a number of instances. The latter effect can be useful in the analysis of impurities when it is desirable for the impurities to be eluted before the major component.

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