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GAS CHROMATOGRAPHY WITH A VAPOUR MOBILE PHASE AT THE FINITE CONCENTRATION OF SORBATE

II. TEMPERATURE EFFECTS AND THE CHARACTERISTICS OF PREPARATIVE SEPARATIONS

Yu. A. SULTANOVICH, S. A. VOLKOV and K. I. SAKODYNSKII*

Karpov Institute of Physical Chemistry, Ul Obukha 10, 170120 Moscow B-120 (U.S.S.R.)

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SUMMARY

Temperature variations caused by the passage of the chromatographic band through the sorbent have been measured with water vapour as the carrier gas. With unsorbed and weakly sorbed substances, the passage of the band results in cooling of the packing owing to water desorption; the heating of the packing during elution of readily sorbed substances is not as large as in the case of conventional elution chromatography.

INTRODUCTION

The process of gas chromatography is usually regarded as taking place under isothermal conditions. However, when the sample concentration in the column is sufficiently high, the isotherm is disturbed because of the evolution and absorption of sorption heat ("temperature effect"). A detailed analysis of this phenomenon and its influence on band formation in conventional elution chromatography has been made by Scott¹.

In the case of vapour mobile phase chromatography (VPC), the displacement of the band of a sorbate over a given section of the sorbent decreases the water content in the gaseous phase above this section and disturbs the sorption equilibrium with regard to water: a certain amount of water is desorbed from the stationary phase, with absorption of heat. The reverse occurs at the rear edge of the band: water is absorbed in the stationary phase, and the heat of absorption is evolved. The above processes must have a substantial influence on the temperature effect.

THEORETICAL

According to Scott¹, the amount of heat evolved upon sorption of a substance (or absorbed upon its desorption) on a theoretical plate is equal to

$$Q_1 = K_1 h_1 (\partial x / \partial v) \partial v$$

where h_1 is the heat of sorption, K_1 is the distribution coefficient, x is the concentration of substance in the gaseous phase and v is the gas volume expressed in terms of the theoretical plate capacity

$$v = w\tau/(v_g + v_1K_1)$$

where w is the flow-rate of carrier gas, τ is the time and v_g , v_1 are the volumes of the gaseous and the liquid phase on the theoretical plate.

If x is replaced by the mole fraction, N , the thermal effect associated with water desorption caused by the change in the water content in the gaseous phase will be expressed by

$$Q_2 = -K_2h_2 (\partial N/\partial v) \partial v$$

and the overall effect of heat evolution (absorption) will be

$$Q = (K_1h_1 - K_2h_2) (\partial x/\partial v) \partial v$$

where indices 1 and 2 refer to the sorbate and the vapour eluent.

The equation of thermal balance for the theoretical plate can be written as

$$(v_1\rho_1c_1 + v_s\rho_sc_s) \partial\theta = (K_1h_1 - K_2h_2) (\partial x/\partial v) \partial v - (AZ/w) (v_g + K_1v_1) \theta \quad (1)$$

where A is the plate surface area, Z is the thermal conductivity of the packing, v , ρ , c are the volume, density and heat capacity of the packing, θ is the excess temperature and indices 1 and s stand for the stationary phase and the support. Denoting the coefficient of $d\theta$ by a we get Scott's equation

$$\frac{\partial\theta}{\partial v} + \beta\theta = a \frac{\partial x}{\partial v} \quad (2)$$

where $\beta = AZ(v_g + K_1v_1)/aw$ characterizes the loss of heat to the environment and $a(K_1h_1 - K_2h_2)/a$ is the thermal effect resulting from the sorption and desorption of the substance and the water.

Under adiabatic conditions, $\beta = 0$, and the solution of eqn. 2 has the form

$$\theta = \alpha x_0 e^{-\mu^2/2n} / \sqrt{2\pi n}$$

where n is the number of theoretical plates and μ is the band dispersion. In this case the shape of the temperature curve and that of the chromatographic peak are the same.

Although the obtained equations are only applicable to the case of a linear isotherm, they can be used for a qualitative discussion of the experimental data. Three important conclusions follow from the analysis of these expressions.

(1) The introduction of an unsorbed substance into the vapour eluent flow must result in cooling of the packing in the region of this substance's band. In this case we have $K_1h_1 = 0$ and $\alpha = -K_2h_2/a < 0$.

(2) The sign and the magnitude of the temperature signal resulting from the introduction of a sorbed component into the vapour eluent flow will be determined by the relationship between K_1h_1 and K_2h_2 .

(3) Even for well-sorbed components, when $K_1h_1 > K_2h_2$, the temperature signal in nitrogen must be greater than in water vapour.

RESULTS AND DISCUSSION

The experiments were conducted on a Tsvet-I chromatograph with an attachment to create the vapour eluent flow². Six openings were made in the wall of the column (850 × 18 mm), at different distances from the column inlet. Copper-constantan thermocouples on porcelain insulation were inserted into the openings which were then sealed with epoxide cement. Twelve thermocouples were used, connected in pairs in a differential circuit: one thermocouple was placed inside the packing on the column axis, and the second was fixed with epoxide cement on the column wall adjacent to the point of entry of the first thermocouple. All the six pairs of thermocouples were connected through a switch to an EZ-9 recording potentiometer. The distances from the column inlet to the thermocouples were 20, 120, 220, 370, 570 and 770 mm. The column was filled with Chromatone NAW DMCS with 15% of Carbowax 6000 which is a good sorbent for water.

In accordance with the theoretical analysis, when an unsorbed substance is introduced into the water vapour flow a negative temperature signal is observed which indicates that water is desorbed from the stationary phase. It is to be noted that the higher is the dose of unsorbed substance the greater is this effect. The dependence of θ for the first thermocouple on the dose of the unsorbed substance is linear, passing through the origin with a slope of 0.3°C/ml. When the water vapour flow passes through a column operated in the frontal chromatography mode, it was found that $\theta = +6.0^\circ\text{C}$. From a comparison of these values, it can be concluded that the presence of 10 ml of the unsorbed substance in the zone of thermocouple 1 results in the desorption of half the water dissolved in the stationary phase.

Results of the measurement of thermal effects for sorbed substances in a flow of nitrogen and water vapour are given in Fig. 1. In nitrogen all the six thermocouples recorded a positive temperature signal on passage of the sorbate band, and in water vapour a negative signal was recorded for ethanol and propanol. In the case of butanol the signal is approximately zero; for this compound, probably, $K_1h_1 \approx K_2h_2$. When hexanol is eluted the signal is positive but is much (2–3 times) smaller than in the nitrogen flow.

The above trends are clearly seen in Fig. 2 where the magnitude of the temperature signal for the first thermocouple is presented as a function of the number of carbon atoms, n_c , in the alcohol molecule. When nitrogen is used as the carrier gas the dependence of the magnitude of the temperature signal on n_c lies in the region of positive temperatures; on water vapour it passes into the negative region.

It is also of interest to examine the shape of the temperature curves. In the nitrogen flow (Fig. 3) the temperature curve usually coincides in shape with that of the concentration curve in elution chromatography. This is explained by the low magnitude of the temperature signal, which determines the size of the second term on the right-hand side of eqn. 1. At sufficiently high values of θ the adiabatic conditions

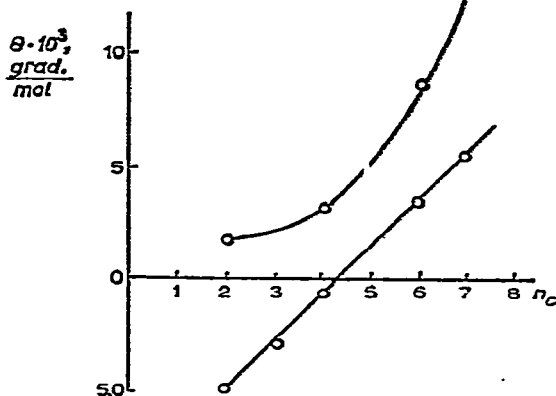
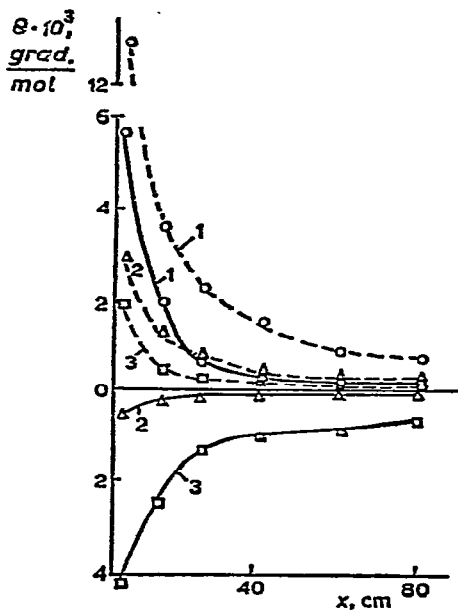


Fig. 1. Magnitude of the temperature signal at different sections of the sorbent layer in a flow of nitrogen (---) or water vapour (—) for hexanol (1), butanol (2) and ethanol (3).

Fig. 2. Dependence of the magnitude of the temperature signal on the number of carbon atoms in *n*-alcohols in a flow of nitrogen (upper curve) or water vapour (lower curve).

of the process are not met. In these cases, at the rear edge of the temperature curve, we see a negative "tumble", associated with the partial removal of the heat evolved during the passage of the band.

When an unsorbed (or weakly sorbed) substance was introduced into the flow of water vapour the temperature response was negative, and on its sorption branch (*i.e.*, the water vapour sorption) a positive "tumble" is observed. In this case it would be natural to associate the "tumble", as above, with a non-adiabatic process, but here resulting from the heat absorbed on displacement of the band of the substance. When a strongly sorbed component, *e.g.*, hexanol, is introduced into the water vapour flow, a positive temperature response is obtained. Its shape may be exactly the same as that observed in nitrogen, but can also be different. At temperatures below 125°C a negative "tumble" is seen at the leading edge. This is probably associated with the fact that at the moment of entry of the band into the sorbent section saturated with water the extent of water desorption is greater than the sorption of the substance.

From these experiments it can be concluded that the temperature effect in chromatography with a vapour mobile phase is quite different from the temperature effect in conventional elution chromatography. Scott¹ showed that in elution chromatography this effect produces an additional tailing of the peak. In chromatography with a vapour mobile phase the temperature effect result in more pronounced leading edges for unsorbed and weakly sorbed substances, and in a decrease in peak

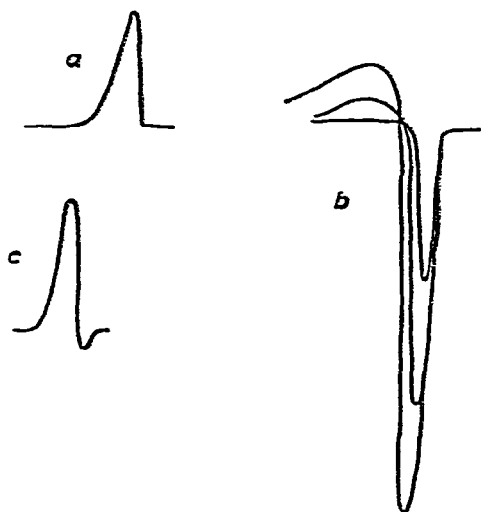


Fig. 3. Shape of the temperature signal for the elution of butanol by nitrogen (a) and water vapour (b), and of hexanol by water vapour (c).

tailing for strongly sorbed substances. It is thus seen that on the whole the temperature effect increases the influence of the sorption effect³ on the shape of the peak.

Let us now examine the effect of replacement of nitrogen by water vapour on the main separation parameters in preparative chromatography, using benzene-toluene, ethanol-propanol and octane-decane as sorbates. The stationary phases, 20% PEGA and Apiezon N, were applied on refractory brick (grain size 0.4–0.6 mm) and on Chromosorb W. When calculating the resolution, R , only the two adjacent half-widths of the peaks (Fig. 4) were taken into account:

$$R = \Delta l / (\Delta S_1 + \Delta S_2)$$

In this way the resolution for asymmetric peaks correctly reflects their separation and is directly correlated with the purity of fractions.

From Fig. 5 it is seen that when PEGA, which is a good sorbent for water, is used as the stationary phase, R increases for ethanol-propanol on changing from nitrogen to water vapour, and decreases for the other pairs of substances. When Apiezon N is used the resolution does not depend significantly on the type of mobile phase.

We showed previously⁴ that, for members of an homologous series, the replacement of nitrogen by water vapour has little effect on the separation coefficient, α . The present variation of R can therefore be explained mostly by the variation of the distribution coefficient. It is known⁵ that, with an increase in the latter, R usually increases under conditions of overloading. We have also shown⁴ that, on changing from nitrogen to water vapour, the distribution coefficient increases for ethanol and propanol and decreases for benzene, toluene and paraffins, in accordance with the present results.

A most important characteristic of separation in industrial preparative chromatography is the throughput, $P = q/\tau$, where q is the dose introduced. There are

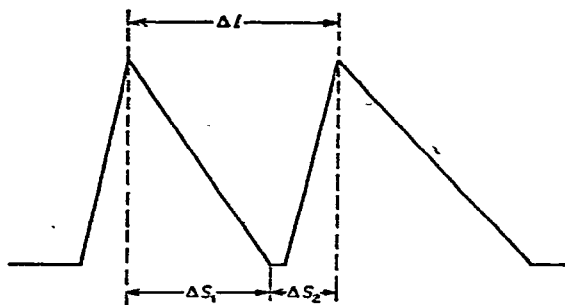


Fig. 4. Calculation of R for asymmetric peaks.

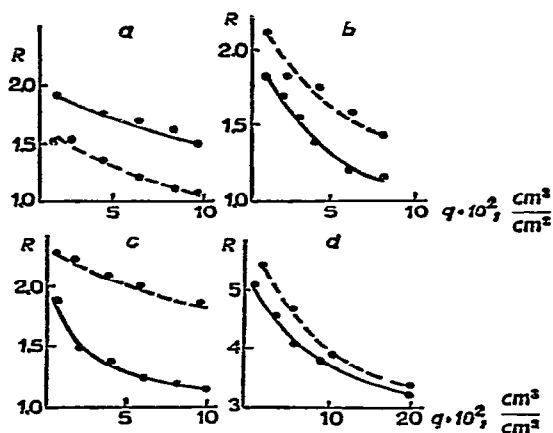


Fig. 5. Dependence of R on specific loading in a flow of nitrogen (---) or water vapour (—) at 120°C : a, ethanol-propanol on PEGA; b, benzene-toluene on PEGA; c, octane-decane on PEGA; d, octane-decane on Apiezon L.

two possible modes of operation of a preparative installation. In the first mode the next dose is introduced after the complete elution of all the components of the previous batch, then $\tau = \tau_p$ is the time between the input and the output of all the components of the batch. In the second mode the next dose is introduced before all the components of the previous mixture have been completely eluted, in this case $\tau = \tau_s$ is the time from the start of the elution of the first component of the mixture to the end of the elution of its last component. The method of calculation of P is described in ref. 6.

Table I shows the experimental values of P determined for both modes of operation (P_p and P_s). The throughput in preparative chromatography for all the studied mixtures is higher in water vapour than in nitrogen, despite the fact that the size of the dose at which $R = 1$ is lower for the benzene-toluene and octane-decane mixtures in water vapour. The throughput is increased by shortening the separation time, τ_p and τ_s .

It should be noted that the formation in the water vapour flow of peaks with a steep rear edge produces a favourable effect when the main component is free from heavy impurities. In a number of cases, the use of water vapour can thus improve the characteristics of preparative separation.

TABLE I
THROUGHPUT IN NITROGEN AND WATER VAPOUR FLOWS AT 120°C

| Mixture | Eluent | τ_p (sec) | τ_a (sec) | $P_p \cdot 10^3$ ($\text{cm}^3/\text{cm}^2 \cdot \text{sec}$) | $P_a \cdot 10^3$ ($\text{cm}^3/\text{cm}^2 \cdot \text{sec}$) |
|------------------|----------|-------------------|-------------------|--|--|
| Ethanol-propanol | Nitrogen | 115 | 81 | 0.87 | 1.66 |
| | Steam | 90 | 49 | 1.45 | 2.63 |
| Benzene-toluene | Nitrogen | 150 | 70 | 0.80 | 1.72 |
| | Steam | 82.5 | 57 | 1.21 | 1.75 |
| Octane-decane | Nitrogen | 135 | 105 | 1.41 | 1.81 |
| | Steam | 60.5 | 45.5 | 1.65 | 2.20 |

CONCLUSIONS

This study has shown that in chromatography with vapour eluents the shape of the peak at high sorbate concentrations is strongly affected by the sorption and temperature effects which facilitate the formation of peaks with predominant leading edges. In a number of cases, the characteristics of preparative separation in a flow of water vapour are better than in flows of the conventional carrier gases.

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