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TEMPERATURE DEPENDENCE OF HETP FOR COLUMNS WITH SMALL AMOUNTS OF LIQUID STATIONARY PHASE

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SUMMARY

It was found that the plate number of a column depends strongly on the physical state of the monomolecular layer formed by the liquid stationary phase on the support surface. Phase transitions in the monolayer modify the distribution of liquid in the column packing and, as a result, change the height equivalent to a theoretical plate for a given column.

INTRODUCTION

The basic equation describing the dependence of the height equivalent to a theoretical plate (HETP) on the linear velocity of the carrier gas in gas chromatography may also be the basis for the determination of temperature dependence of HETP. The succesful trial of such calculations was performed by Kambara and Kodama[1]. Taking the Van Deemter[2] equation as the basis of their considerations, Kambara and Kodama[1] predicted that the logarithm of HETP plotted against the reciprocal of the absolute temperature gives two straight lines, and the maximal plate number for a column is at a temperature close to the boiling point of the solute. This is true for the columns that contain a considerable amount of liquid stationary phase. One may assume that this is the result of the difference in the values of the partition coefficient below and above the boiling point of the solute.

For columns with low loadings the chromatographic process is more complicated, and one cannot speak about the solubility phenomenon or partition coefficient in their commonly used senses, especially when the amount of liquid stationary phase is sufficient only to form one or a few layers on the support surface. The properties of a stationary phase in a such thin film are considerably different than those in its bulk phase[3] and the partition of the solute molecules between the gas and liquid phases in a column becomes intermediate between the solubility and adsorption processes.

Hence the temperature dependence of HETP for the columns with low loadings should be different to that described by Kambara and Kodama. It may be predicted that this dependence will depend strongly on the physical state of the stationary phase film and on the manner of solute sorption in this film. Thus, every change in film structure due to a temperature increase should involve an appropriate change in the plate number of a column.

EXPERIMENTAL

Materials

n-Octadecanol (purum grade; Fluka, Buchs, Switzerland) was purified before use as described in a previous paper[4].

Silica gel MIK, characterized with a specific surface area of 37 m^2/g and a mean pore diameter of 530 Å was obtained from wide-pore silica gel (P.O.Ch., Gliwice, Poland) as described previously[4].

n-Hexane (Fluka) was used as the test substance in gas chromatographic measurements.

Methods

The adsorbent was coated with n-octadecanol by the slurry method, as described by Littlewood[5]. Dichloromethane (P.O.Ch.) was used as a volatile solvent.

Differential thermal analysis (DTA) measurements were performed with a differential microcalorimeter constructed in our laboratory[4].

Measurements by the "inverse" gas chromatographic method were carried out with a G.Ch.F. 18.3 gas chromatograph (Chromatron, Berlin, G.D.R.). Hydrogen was used as the carrier gas. Silica gel MIK with n-octadecanol deposited on its surface was packed into a glass column (1.5 m × 4 mm I.D.) and 0.04 μl of the test substance was introduced into the chromatograph with a 1-μl Hamilton microsyringe.

The number of the theoretical plates was obtained by means of the equation

$$n = 5.55 \frac{t_R}{w_h}$$

where w_h is the peak width at half-height and t_R is the distance from the starting point to the maximum of the peak on the chromatogram.

RESULTS AND DISCUSSION

An excellent example of low-loaded columns packings is the systems investigated by Serpinet[6,7], who used a wide-pore silica gel as the support and n-octadecanol as the stationary phase. It was found that n-octadecanol first creates an oriented monomolecular film on the adsorbent surface and then an amount of alcohol exceeding that necessary to form the monolayer accumulates in the form of small droplets in the adsorbent pores when the temperature of the column is higher than the melting point of the alcohol.

A graph of the logarithm of the retention volume (V_S) against the reciprocal of the absolute temperature is shown in Fig. 1, which illustrates the changes in the column properties generated by a temperature increase. The increase in V_S at about 58°C is due to the melting of n-octadecanol present in the support pores, *i.e.*, to a change in the retention mechanism: below 58°C the adsorption of the solute molecules on the surface of the n-octadecanol monolayer and its crystals decides the value of the retention volume, and above this temperature, after melting of the n-octadecanol crystals, the dominant process becomes the dissolution of solute in the liquid n-octadecanol.
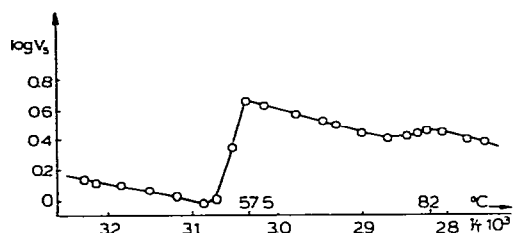
Fig. 1. Variation of log V_S with $1/T$ for n-hexane as solute on silica gel MIK covered with 17.4 % of n-octadecanol.

The second increase in V_S, at about 82°C, is the result of the phase transition which takes place in the oriented monolayer of n-octadecanol. During this transition the surface area occupied by a single molecule in the monolayer changes from 21 to about 27 Å^2 (refs. 6 and 7) and some of the molecules are ejected from the two-dimensional monolayer to the three-dimensional drops. This increase in the amount of liquid n-octadecanol leads to an increase in V_S.

The above changes in the retention mechanism influences the plate number of the column, as shown in Fig. 2. There is a clear maximum at about 86°C on all three curves corresponding to different amounts of n-octadecanol deposited on silica gel. These maxima occur at a temperature about 4°C higher than the temperature of the phase transition in the monomolecular film, determined by "inverse" gas chromato-graphy.
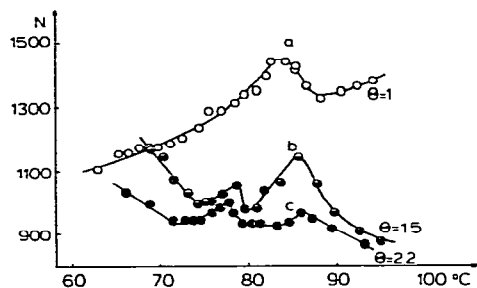

Fig. 2. Variation of plate number with temperature: (a) silica gel MIK covered with 7.9 % of n-octadecanol; (b) silica gel MIK covered with 11.8 % of n-octadecanol; (c) silica gel MIK covered with 17.4 % of n-octadecanol. n-Hexane was used as the solute.

The second, weaker, maximum occurs at about 78°C and has no corresponding feature in Fig. 1. It seems, however, that this maximum corresponds to peak III on the thermogram obtained during the heating of silica gel covered with n-octadecanol (Fig. 3). This peak represents the heat effect that arises as a result of the change in the interaction between the three-dimensional excess and monomolecular film of n-octadecanol[8]. The change, which is also manifested by a decrease in the contact angle between the drop and monolayer of n-octadecanol, takes place at about 74°C, i.e., at a temperature 4°C below the maximum of the plate number (Fig. 2b and c).

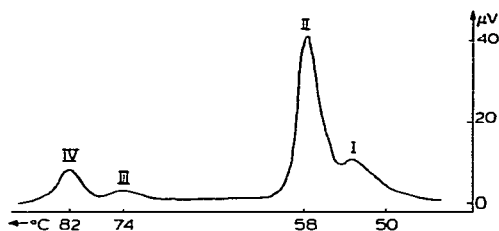It is not completely clear what the mechanism of the change in the interaction

Fig. 3. Thermogram of *n*-octadecanol obtained during the heating of silica gel MIK covered with *n*-octadecanol.

between the *n*-octadecanol drop and its monolayer is: it may be the effect of the polymorphic transition in the monomolecular film, as it is in the case of crystals of long-chain aliphatic compounds[9]; it may also be, as was pointed out by Serpinet[6,7], that the part of a monolayer covered by the drops of liquid *n*-octadecanol "melts" at a temperature lower than this part which is not in contact with the alcohol drops.

Nevertheless, the result of both possible changes in the monolayer structure is, as predicted by Fowkes[10], an increase in the surface energy of the monolayer. This fact. which has been confirmed experimentally[8], leads to a decrease in the contact angle between the drop and the monolayer of *n*-octadecanol, so the layer of liquid *n*-octadecanol on the adsorbent surface becomes thinner. Thus the influence of diffusion in the liquid phase on the shape of the solute peak diminishes and one observes an increase in the plate number of a column. This effect cannot occur if the amount of *n*-octadecanol on the support surface is sufficient to form only a monolayer. This is confirmed by the lack of a maximum in Fig. 2a at 78°C.

It is much more difficult to elucidate the reason for the increase in plate number at 86°C. Probably two processes cause this phenomenon: the change in the monolayer structure on the support surface and the increase in the amount of liquid *n*-octadecanol in the column packing. Both processes lead to modification of the distribution of liquid *n*-octadecanol in the column packing and consequently to a change in the plate number of the column.

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