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APPLICATION OF DTA TO THE DETERMINATION OF THE PROPERTIES OF MIXED MONOLAYERS ON SOLID SURFACES

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Differential thermal analysis was used as a complementary method to "inverse" gas chromatography in the investigation of phase transition in mixed monolayers of hydrocarbon and alcohol deposited on a silica gel surface. It was found that in certain cases the DTA method provides more information about the behaviour of mixed monolayers than does gas chromatography. This is for monolayers with a low alcohol amount. Two endothermic peaks were produced as a result of disintegration of the hydrocarbon film. The presence of two mixed monolayer forms was found at alcohol concentrations greater than 65%.

It was previously shown that mixtures of long-chain aliphatic alcohols and hydrocarbons form oriented, mixed two-dimensional films on the surface of water, glycerol and silica gel [1].

The most characteristic feature of these monolayers is the surface area occupied by a single molecule. Irrespective of the nature of the molecule, this surface area is equal to 0.21 nm^2. Further, phase transitions of solid compact – liquid expanded type take place in these monolayers, as in the monolayers formed by pure alcohol on hydroxylated surfaces [2–4]. The temperature of a phase transition depends on the monolayer composition. In the case of 2% alcohol in the hydrocarbon monolayer, this temperature is a few degrees higher than the melting temperature of the pure hydrocarbon. As a result of the transition a certain proportion of the molecules (primarily the hydrocarbon ones) are ejected from the monolayer to the three-dimensional phase, and the surface occupied by a single molecule in the monolayer increases. Of course, the concentration of alcohol in the expanded monolayer increases, too. The temperature of the phase transition increases with the increase of the alcohol concentration in the mixed monolayer. It was found that the monolayer characterized by a composition of about 1:1 is particularly stable. This is especially clear in the case of the mixed monolayer deposited on water [1]. This is probably related to the high energetic homogeneity of the water surface.

If the alcohol concentration in the monolayer exceeds 50%, two types of mixed films may be found on the hydroxylated surface: a film characterized by a 1:1 composition, and a second one richer in alcohol. The two forms of film differ distinctly in the temperature of the phase transition [1].

The properties of these mixed monolayers were investigated by means of "inverse" gas chromatography. With this method information is acquired about the state of a surface film by examination of the retention volume of an arbitrarily chosen substance as a function of temperature, while the investigated surface film is used as a stationary phase in the gas chromatographic column [5]. In the case of mixed monolayers deposited on a water surface, the data obtained by means of this method were confirmed and supplemented by direct investigation of their properties by the Langmuir balance method [1]. Of course, application of the Langmuir balance is impossible when surface films are deposited on a solid surface. However, differential thermal analysis may be applied to such systems as a direct method of investigating their properties. This method was previously successfully used for surface film investigations [6–8].

Experimental

Materials

(a) Commercial medium pore silica gel for gas chromatography (Schuchardt, Munich, F.R.G.), 0.1–0.2 mm fraction, was heated with water in an autoclave during 1 h at 200° and under 18 atm pressure. The specific surface area of the obtained product was 47.4 m^2/g.

(b) *n*-Octadecanol (Fluka A.G., Switzerland) was purified by distillation in vacuum and crystallized twice from methanol solution before use.

(c) *n*-Nonadecane (Fluka A.G., Switzerland) was purified by crystallization from redistilled ethyl acetate, repeated four times.

(d) As a test substance for gas chromatographic measurements, *n*-hexane was used (Reakchim, U.S.S.R.).

Methods and apparatus

(a) "Inverse" gas chromatographic measurements were performed with a Chrom 4 gas chromatograph (Laboratorni Pristroje, Prague, Czechoslovakia). Packings were placed into glass columns 1 m long and 2 mm in i.d. Hydrogen was used as carrier gas at a flow rate of 40 cm^3/min. The volume of the *n*-hexane samples introduced into the column with a 1 μl Hamilton microsyringe was 0.02 μl.

(b) Calorimetric measurements were carried out with a DTA microcalorimeter constructed in our laboratory. The measuring and reference cylindrical cells, each with a volume of 0.3 cm^3, were drilled in a block of solid copper. The temperature difference between them was measured with a Ni–NiCr thermocouple. In order to ensure better transport of heat from the cell packing to the thermocouple, the junctions of the thermocouple wires were welded to thin copper plates placed in the centre of the cells.

The thermocouple signal was amplified with a V623 (Meratronik, Poland) microvoltmeter with measuring ranges of 10, 30 and 100 μV, changed according to the temperature difference between the cells. The output range of the amplifier was 1 V. The amplified signal was recorded with a TZ 21S (Laboratorni Pristroje, Prague, Czechoslovakia) line recorder. The temperature inside the reference cell was measured with an additional thermocouple. The heating rate of the microcalorimeter was 4 deg/min. As heater, a GChF 18.3 gas chromatograph with a good temperature programmer was used.

It was found that the sensitivity of this apparatus was about 20 μV/mcal. sec, or 1 cm^2 of a recorded endothermic peak area was equivalent to 0.0082 cal, when the sensitivity range of the microvoltmeter was 30 μV, the recorder worked in the sensitivity range 1 V/25 cm (i.e. full recorder chart width) and the chart speed was 20 mm/min (these parameters were used in all measurements reported in this paper).

The measuring cell contained 0.2 g of packing containing about 0.02 g of film-forming substance.

The reproducibility of the heat measurements was ±1.5% and the precision of the temperature measurement inside the reference cell was ±0.2°. More details concerning the apparatus and mode of operation are given in ref. [6].

Results and discussion

Plots of the logarithm of the retention volume V_S *vs.* $1/T$ are presented in Fig. 1. The relationships were obtained for *n*-hexane as a test substance and for mixed monolayers of *n*-octadecanol (ODL) and *n*-nonadecane (ND) deposited on silica gel. The composition of the monolayers varies from 100% ODL to 100% ND.

The diagrams in Fig. 1 are very similar to the previously presented curves (1). Their shape and the position of the inflection points confirm the above-described model of mixed monolayers of alcohol and hydrocarbon deposited on a hydroxylated silica gel surface.

Some additional information concerning the changes taking place in such monolayers is provided by the DTA curves in Fig. 2. Curve *A* presents a picture of the endothermic transitions occurring in the surface film of pure hydrocarbon. The first peak, with maximum at 29.5°, corresponds to a polymorphic transition in the solid hydrocarbon [9]. The melting temperature of ND is 32° [10]. Since curve *A* displays no peak with a maximum at this temperature, it may be presumed that the whole amount of the ND on the silica gel surface is arranged into an ordered surface film. The existence of well-ordered films on a silica gel surface was previously proved [11]. The structure of such films disintegrates at a temperature not much higher (~ 3°) than the melting temperature of the hydrocarbon forming the film. This phenomenon is seen in curve *A* as a double peak, with maxima at 33.6 and 36°.

The explanation for the presence of the two peaks corresponding to the change in structure of the ND film is very difficult. It is possible that ND forms a film the structure of which is different than that of ODL, i.e. the molecules of ND are not oriented perpendicularly to the silica gel surface. In such a case, two- or multilayer

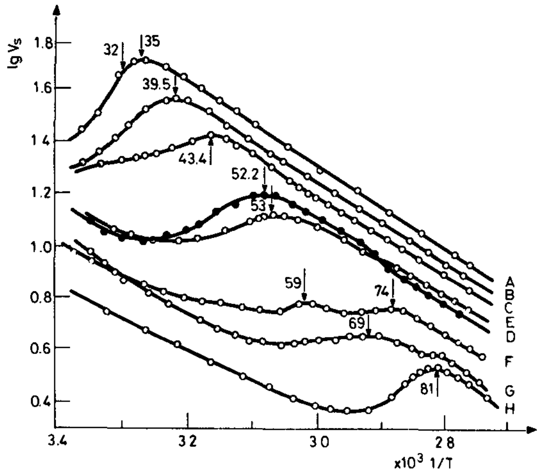

Fig. 1 Plots of log V_S *vs.* $1/T$ relationships for the chromatographic column packings containing the monolayers composed of *n*-octadecanol (ODL) and *n*-nonadecane (ND), deposited on silica gel surface. The amount of monolayer-forming substances changed from 10.14% w/w for ODL to 10.04% w/w for ND. Composition of monolayers: A – 100% ND; B – 80% ND and 20% ODL; C – 65% ND and 35% ODL; D – 50% ND and 50% ODL; E – 35% ND and 65% ODL; F – 20% ND and 80% ODL; G – 10% ND and 90% ODL; H – 100% ODL

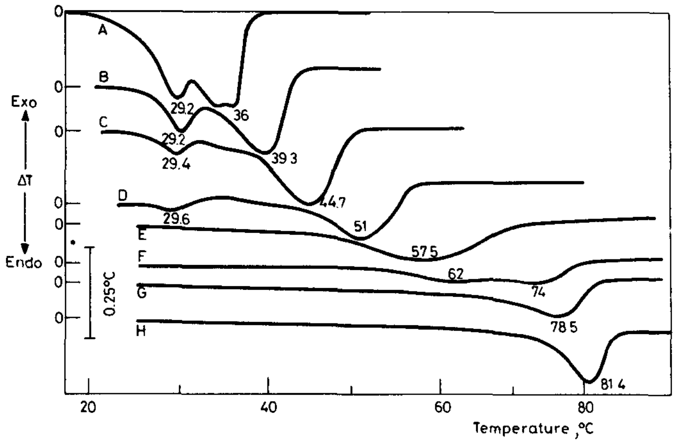

Fig. 2 The DTA curves of mixed monolayers on silica gel surface. Composition of monolayers: A – 100% ND; B – 80% ND and 20% ODL; C – 65% ND and 35% ODL; D – 50% ND and 50% ODL; E – 35% ND and 65% ODL; F – 20% ND and 80% ODL; G – 10% ND and 90% ODL; H – 100% ODL

domains of ND molecules can be formed on the solid surface. Thus, the peak with maximum at 33.6° probably represents the destruction energy of the second layer, and the peak with maximum at 36° corresponds to disintegration of the layer of ND molecules clinging directly to the silica gel surface.

A comparison of the $\log V_S = f(1/T)$ diagram and curve *A*, both obtained for the hydrocarbon film, reveals that the DTA curve provides more information about the behaviour of this film.

The addition of alcohol to the ND monolayer radically changes the picture of the phase transition (Fig. 2, curves *B–G*). The peak area representing the heat of the polymorphic transition at 29.5° diminishes, and the peak disappears if the concentration of ODL in the mixed monolayer exceeds 50%. At the same time, the temperature of the peak representing the heat of the phase transition in the mixed monolayers increases (Fig. 2, curves *B–E*). The shape of the peaks changes as well. They become more and more diffuse, just as the maxima in the $\log V_S$ *vs.* $1/T$ plots in Fig. 1.

Curves *F* and *G* in Fig. 2, for ODL concentrations greater than 65%, differ distinctly from those previously mentioned: two peaks appear at temperatures higher than 32°. Two maxima may also be found in the $\log V_S$ *vs.* $1/T$ diagrams (Fig. 1, curves *F* and *G*).

As explained in [1], the increase of the phase transition temperature in mixed monolayers is caused by the stabilizing influence of ODL, and the broadening of the temperature range of this phase transition is probably the result of a large pore size distribution of the silica gel used and of the energetic non-homogeneity of its surface. The presence of two peaks in the DTA curves, and of two maxima in the $\log V_S = f(1/T)$ diagrams, shows that two forms of mixed monolayer exist on the silica gel surface [1]. One of them is richer in ODL and the second in ND. The higher-temperature peak corresponds to the heat of the phase transition in the part of the monolayer richer in alcohol.

Curves *H* (Figs 1 and 2) present the effect of heating of the monolayer composed of ODL only. The inflection point in the $\log V_S = f(1/T)$ plot and the peak at 81–82° confirm that at this temperature the phase transition occurs in the alcohol monolayer on the silica gel surface, as described previously [3–6].

In Fig. 3 the relationship between V_S and the composition of the monolayer deposited on the silica gel surface is presented. The retention volumes of *n*-hexane were determined at 84°. It is interesting that the run of this diagram is non-linear. The elucidation of this phenomenon is as follows: At 84° the following system exists on the silica gel surface: a mixed monolayer in liquid expanded state and drops of ODL solution in ND. The compositions of the monolayers and solutions are not the same: it may be expected that the monolayer is always richer in ODL, due to the hydrogen-bonding between the hydroxyl and silanol groups. Solutions of ODL in ND are non-ideal [12]. Therefore, the relationship between the retention volume and their composition cannot be linear. Likewise, the contribution of the adsorption of hexane has a non-linear character [13]. Due to the two effects, the $\log V_S$ *vs.* monolayer composition diagram is as seen in Fig. 3.

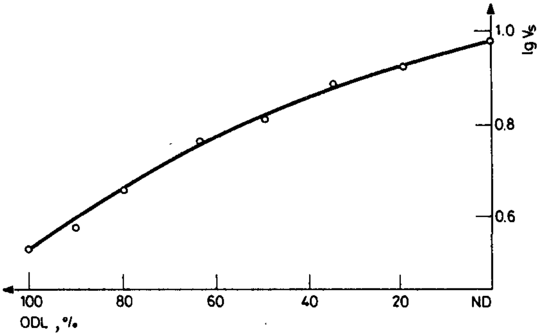

Fig. 3 Plot of log V_S of *n*-hexane at 84° *vs.* composition of monolayers on silica gel surface

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Zusammenfassung — In der Untersuchung der Phasenübergänge der auf Silikageläoberfläche angebrachten, gemischten Hydrokarbonat- und Alkohol-Monomolekularschichten wurde als Ergänzungsmethode der "inversen" Gaschromatographie die Differentialthermoanalyse verwendet. Es wurde festgestellt, dass die DTA-Methode mehr Information über das Benehmen der gemischten Monomolekularschichten als die Gaschromatographie gibt. So ist es bei den Monomolekularschichten mit niedriger Alkoholmenge. Zwei endothermische Peaks entstanden als Ergebnis der Zersetzung des Hydrokarbonat-Films. Bei Alkoholkonzentrationen über 65% wurden zwei Formen des gemischten Monomolekularschichtes gefunden.

Резюме — Дифференциальный термический анализ был использован в качестве дополняющего метода к *"обратной" газовой хроматографии для исследования фазовых переходов* в смешанных слоях углеводорода и спирта, нанесенных на поверхность силикагеля. Установлено, что в определенных случаях, метод ДТА дает больше информации о поведении смешанных монослоев, чем газовая хроматография. Это прежде всего касается монослоев с малым количеством спирта. Были найдены два эндотермические пики, обусловленные разрушением углеводородной пленки Установлено также наличие двух форм смешанного монослоя при концентрации спирта выше 65%.