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CALORIMETRIC INVESTIGATIONS ON MOLECULAR INTERACTIONS IN A MIXED LAYER ADSORBED ON A HOMOGENEOUS SURFACE

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The adsorption and differential heats of adsorption of mixtures of methanol and tetrahydrofuran (mole ratio 1:1), methanol and cyclopentane (1:1 and 1:4) and tetrahydrofuran and cyclopentane (1:1 and 1:4) on a graphitized carbon black (Sterling MT) surface were determined.

The dependence of the intermolecular interactions on the composition of the adsorbed layer was established. From an analysis of the experimental results, the mechanism of adsorption of the equimolar methanol-tetrahydrofuran mixture was described, in which both homomolecular and heteromolecular association were taken into consideration.

Keywords: adsorption, calorimetry, differential heats of adsorption

Introduction

In a heteromolecular liquid layer adsorbed on a homogeneous surface, intermolecular adsorbate-adsorbate interactions of different natures may exist. These depend on the structures and chemical properties of the adsorbate molecules and the mole ratio of the components in the adsorbed layer. The interactions may cause homo- or heteromolecular association and also molecular deformation (compared with the equilibrium gas-phase geometry) [1]. Among other things, measurements of the heat of adsorption of a vapour mixture on a homogeneous surface of graphitized carbon black permits the identification of surface individuals.

Investigations of the effects of modification of the concentrations of the mixture components may give additional information. The aim of the present paper was to determine the influence of modification of the concentrations of methanol and tetrahydrofuran in the gas phase on their ability to undergo homomolecular interactions in the adsorbed layer. A knowledge of this influence might allow a

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more detailed explanation of the mechanism of adsorption of a methanol – tetrahydrofuran mixture on a graphitized carbon black surface.

Experimental

The adsorption and differential heats of adsorption of the following vapour mixtures were measured:

- methanol and tetrahydrofuran (mole ratio 1:1),
- methanol and cyclopentane (mole ratio 1:1 and 1:4),
- tetrahydrofuran and cyclopentane (mole ratio 1:1 and 1:4).

The adsorption was carried out on the surface of carbon black Sterling MT, graphitized at 3273 K.

The specific surface of the carbon black was 20.2 m^2/g, based on the low-temperature sorption of argon.

Isotherms of adsorption were determined by the volumetric method at 298 K.

Differential heats of adsorption were measured with the non-isothermal non-adiabatic microcalorimeter [2] constructed in our laboratory [3].

The equilibrium composition of the gaseous phase was measured in a gas cell by using IR spectroscopy.

The results of the investigations are presented in Figs 1–6.

Results and discussion

The increase in the differential heat of adsorption in parallel with the surface coverage at $\Theta << 1$ indicates that intermolecular, interactions occur in this region

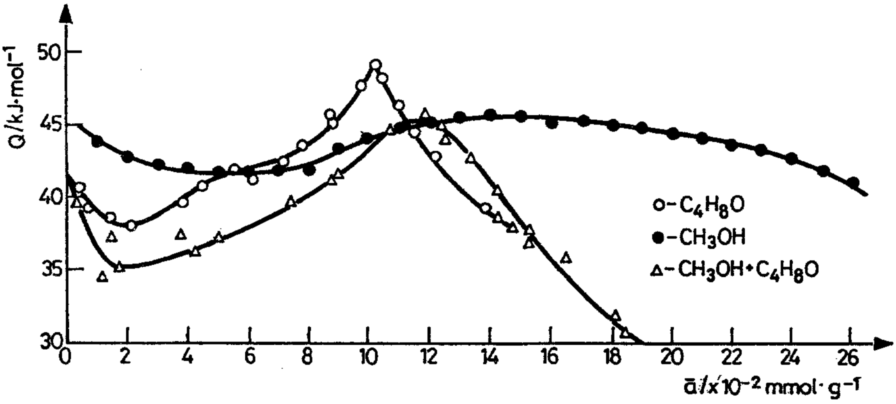

Fig. 1 Differential heats of adsorption of methanol, tetrahydrofuran and their mixture

of coverage (Fig. 1). These interactions could imply the association of methanol with tetrahydrofuran or the homomolecular association of methanol. The energy effects of the two types of association are similar, considering the approximate values of the dipole moments of the adsorbates and the fact that the association is in both cases a consequence of formation of a hydrogen-bond with the oxygen atom. It is possible that the increasing differential heat of adsorption is due only to dipole interactions between the large, polar molecules of tetrahydrofuran.

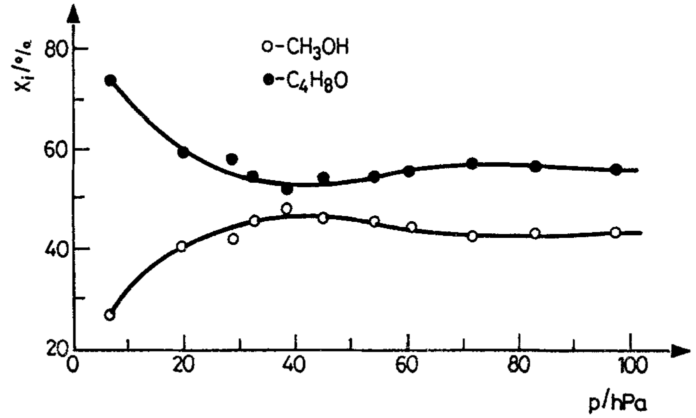

Fig. 2 Percentage mole fractions of methanol and tetrahydrofuran in the adsorbed layer

Hence, in order to differentiate the interactions in the mixed adsorbed layer, the influence of dilution of the methanol and tetrahydrofuran on their ability to undergo homomolecular association was tested. Cyclopentane, with a dipole moment equal to 0, was used as diluent, reducing the concentrations of the adsorbates in the surface layer.

Molecules of cyclopentane are selectively adsorbed initially from the equimolar mixture of methanol and cyclopentane (Fig. 3). With rise in surface coverage, the competitive influence of dispersive interactions with the adsorbent surface declines and intermolecular interactions occur. This is manifested by an increase in the mole fraction of methanol in the adsorbed layer and an increase in the differential heat of adsorption of the mixture (Fig. 4). Both effects take place at monolayer coverage. Such changes in the mole fraction of the components in the adsorbed layer and in the differential heat of adsorption of the mixture indicate that the 1:1 dilution of methanol causes the adsorption of single molecules of methanol initially and the association of alcohol molecules takes place in the monolayer coverage region.

Only the 1:4 dilution of methanol brings almost complete disappearance of the associate interactions of alcohol in the adsorbed layer. At all surface coverages studied, cyclopentane is the main component of the adsorbed layer (Fig. 3) and the differential heat of adsorption decreases (Fig. 4).

Calorimetric investigations of the adsorption of tetrahydrofuran and cyclopentane mixtures yield interesting information.

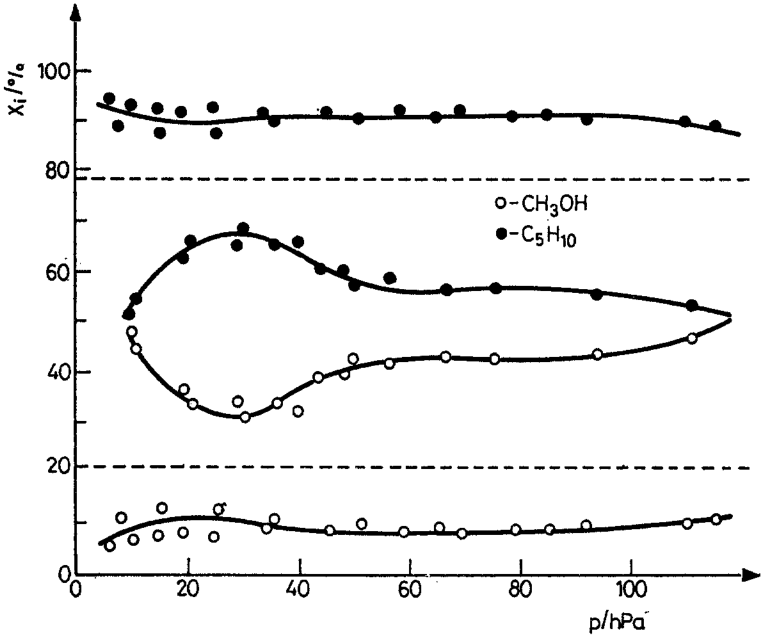

Fig. 3 Percentage mole fractions of methanol and cyclopentane in the adsorbed layers

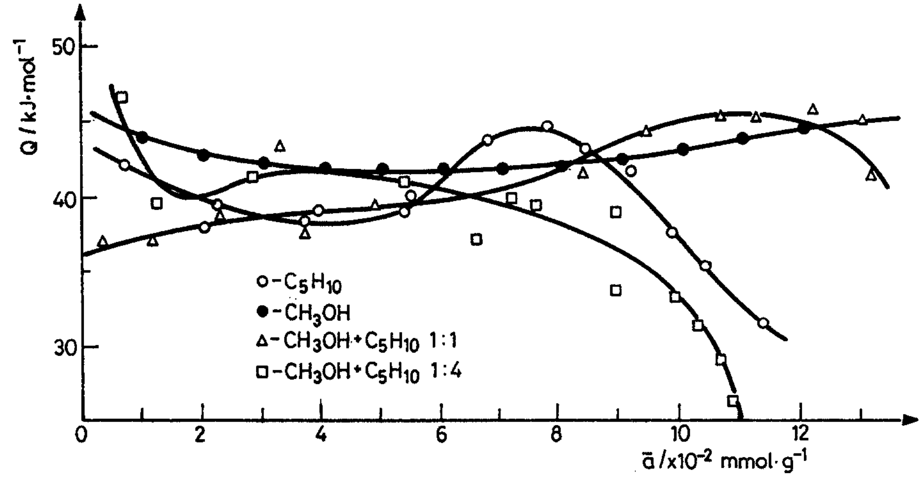

Fig. 4 Differential heats of adsorption of methanol, cyclopentane and their mixtures

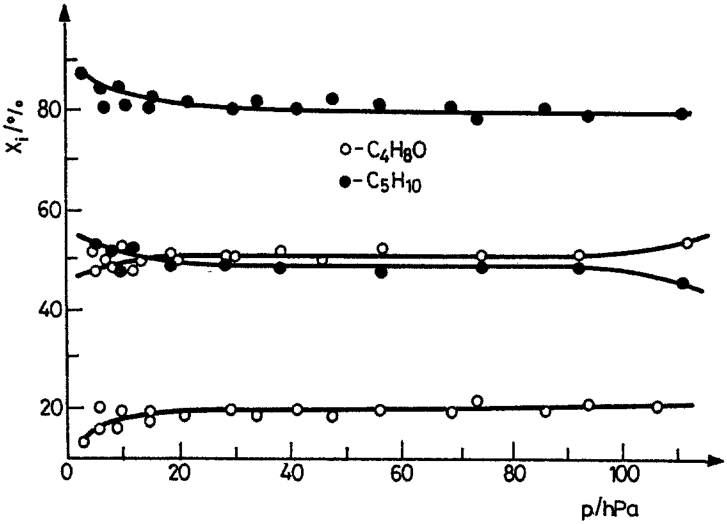

Fig. 5 Percentage mole fraction of tetrahydrofuran and cyclopentane in the adsorbed layers

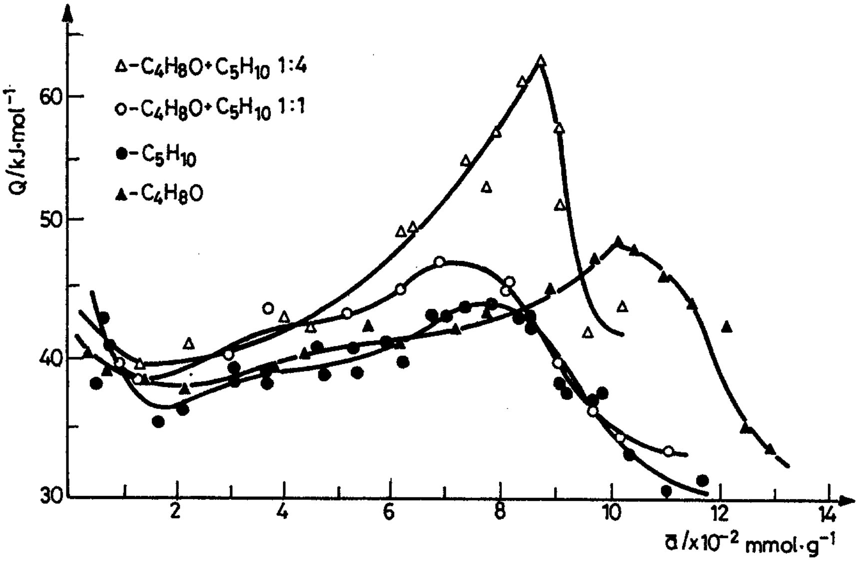

Fig. 6 Differential heats of adsorption of tetrahydrofuran, cyclopentane and their mixtures

The composition of the layer adsorbed from an equimolar mixture of C_4H_8O and C_5H_{10} is practically constant throughout the region of coverage under study, and it is equal to the mole fraction of the components in the initial mixture (Fig. 5). This fact may suggest the independent adsorption of both mixture components. However, the heat of adsorption of this mixture is higher than the sum of the heats of adsorption of its single components (Fig. 6). The curve $Q_d = f(a)$ has a similar course when a mixture of C_4H_8O and C_5H_{10} with a mole fraction of tetrahydrofuran equal to 0.2 is adsorbed (Fig. 6). Both mixtures have maximum heat of adsorption near the region of full monolayer coverage. This maximum is higher for the mixture with the greater dilution of tetrahydrofuran. Such a course of differential heat of adsorption of tetrahydrofuran-cyclopentane mixtures reflects the appearance of intermolecular interactions even at low coverage of adsorbent on the surface. The distinctly higher heat of adsorption of the 1:4 mixture of C_4H_8O and C_5H_{10} indicates that cyclopentane causes the observed exothermic effect.

The molecular structure of cyclopentane may be responsible for this phenomenon. In the five-membered ring of cyclopentane, the hydrogen atoms interact slightly, introducing a small amount of strain. Cyclopentane therefore has a nonplanar arrangement of its carbon atoms, this decreasing the ring strain [4].

The dispersive interactions of cyclopentane with the adsorbent surface limit the mobility of its molecules, causing a certain torsional strain. Coadsorption of strong dipole molecules of tetrahydrofuran may decrease this strain. This may cause stronger dispersive interactions of cyclopentane with the surface because of the planar arrangement of its carbon atoms. The fact that the observed differential heat of mixture adsorption is higher than the differential heat of adsorption of its single components may be a consequence of these exothermic effects.

On the basis of the above analysis of the results of calorimetric investigations of mixture adsorption, it is evident that a 1:1 dilution of methanol and tetrahydrofuran does not prevent homomolecular association.

Homomolecular associates are definitely formed in the monolayer coverage region. The mechanism of adsorption of a methanol and tetrahydrofuran vapour mixture onto a graphitized carbon black surface may be presented by the following scheme:

I – $\Theta << 1$: adsorption of single molecules of methanol and tetrahydrofuran:

$$n\ CH_3OH_{(g)} + m\ C_4H_8O_{(g)} \rightarrow n\ CH_3OH_{(ad)} + m\ C_4H_8O_{(ad)} + Q$$

where the indices *g* and *ad* indicate gaseous and adsorbed phases, respectively.

II – $\Theta \leq 1$: appearance of methanol-tetrahydrofuran interactions:

$$CH_3OH_{(g)} + C_4H_8O_{(g)} \rightarrow (CH_3OH\text{–}OH_8C_4)_{(ad)} + Q_{as}$$

III – $\Theta \geq 1$:additionally, homomoleculars interactions:

$$CH_3OH_{(g)} + C_4H_8O_{(g)} + CH_3OH_{(ad)} \rightarrow$$

$$\rightarrow (CH_3OH)_2(ad) + C_4H_8O(ad) + (C_4H_8O)_2(ad) + Q_1 + Q_2$$

References

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Zusammenfassung — Es wurde die Adsorption und die differentiellen Adsorptionswärmen äquimolarer Gemische aus Methanol mit Tetrahydrofuran bzw. aus Methanol und Tetra-hydrofuran mit Cyclopentan (Molverhältnis 1:1 bzw. 1:4) an mit Graphit überzogenen Ruß Sterling MT Oberflächen bestimmt.

Dabei wurde die Abhängigkeit der intermolekularen Wechselwirkungen von der Zusammensetzung der adsorbierten Schicht aufgedeckt. Ausgehend von der Analyse der experimentellen Ergebnisse wurde der Mechanismus der Adsorption eines Methanol-Tetrahydrofurangemisches beschrieben, wobei sowohl homo- als auch heteromolekulare Assoziation berücksichtigt wurde.