Physical Chemistry

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1961

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Abstract

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HEATS OF WETTING OF ALUMINUM OXIDE BY SOLUTIONS OF BENZENE, CYCLOHEXANE, AND CYCLOHEXENE IN *n*-HEPTANE

(Presented by Academician P. A. Rebinder on 22 II 1961)

The study of the adsorption of various hydrocarbons on oxide contacts is of great interest both for understanding heterogeneous catalytic processes and for the chromatographic separation of hydrocarbon mixtures. Measurements of adsorption isotherms of vapors and solutions of benzene, cyclohexane, and cyclohexene on aluminum oxide, published in ([1–3]) and in the present work, made it possible to determine the arrangement of the molecules of these hydrocarbons on the surface of the adsorbent and to calculate their molecular characteristics.

It was established that, during adsorption on aluminum oxide, as the concentration of cyclohexene increases, its molecules change their orientation on the catalyst surface. From a flat position relative to the aluminum oxide surface they turn onto an edge, with the double bond toward the surface; moreover, with increasing adsorption temperature and its approach to the temperature of the catalytic isomerization of cyclohexene, an ever lower concentration of cyclohexene molecules on the surface is required for such reorientation. In all probability, the edgewise orientation of cyclohexene molecules precedes its catalytic transformation. Adsorption isotherms of benzene and cyclohexane, measured under the same conditions, showed that the molecules of these hydrocarbons are arranged with the principal plane of the ring parallel to the catalyst surface.

Further development of adsorption studies is aided by the investigation of the energetic properties of adsorbed molecules of the same hydrocarbons. To this end we measured the heats of wetting of the aluminum oxide surface by pure liquids—benzene, cyclohexane, and cyclohexene—and by their solutions in *n*-heptane. The isotherms of the heats of wetting were compared with the adsorption isotherms.

The adsorbent used was an industrial catalyst—bead aluminum oxide with a specific surface area of 250 m^2/g and a predominant pore radius of 40 Å ([4]). For the calorimetric experiments the adsorbent was crushed and the 0.1-0.25 mm fraction was selected. The powder was washed with bidistillate to remove dust, dried, and calcined at 500° for 5 hours. It was then weighed into calorimetric

ampoules and evacuated under vacuum with gradual heating to 200° and at a pressure of about $5 \cdot 10^{-5}$ mm Hg.

Chemically pure *n*-heptane and cyclohexane, and previously freeze-out cryoscopically pure benzene, were repeatedly distilled over metallic sodium in a rectification column with an efficiency of 70 theoretical plates. Cyclohexene, obtained by catalytic dehydration of cyclohexanol over magnesium sulfate ([5]), was purified in a similar manner. The constants of the hydrocarbons used coincided with literature data ([6,7]). All purified hydrocarbons were stored over bead aluminum oxide calcined at 500° ···

activated alumina and, before the experiment, were additionally dried with a freshly calcined portion of alumina.

Measurements of the heats of wetting were carried out in a calorimeter with constant heat exchange, analogous to that described under No. 2 in ([8])*. The calorimeter had a temperature sensitivity of $1—5 \cdot 10^{-5}$° and a calorimetric sensitivity of $2—4 \cdot 10^{-3}$ cal. The procedure was similar to that described in ([9]).

To avoid traces of moisture, in addition to thorough preliminary dehydration of the hydrocarbons studied, before the experiment the calorimeter was blown through with air dried over concentrated sulfuric acid and calcined calcium chloride and silica gel.

In the calorimetric experiment, three ampoules with alumina were broken successively, the first of which, especially when working with benzene, gave an overestimated result because of traces of water; the other two ampoules, as a rule, gave coinciding values. The heats of wetting were calculated from the data of the last two ampoules. After the experiment, three calibrations of the heat capacity of the calorimeter were carried out and the equilibrium concentration of the solution was determined. It was measured interferometrically from calibration curves previously constructed for each of the systems studied. The accuracy of measurement of the heat of wetting was ±5%.

Table 1

Hydrocarbon	Heat of wetting, cal/g	Heat of wetting, kcal/mole
Benzene	7.2	7.6
Cyclohexane	5.8	8.4
Cyclohexene	7.0	4.6
n-Heptane	4.5	–

Fig. 1. Isotherms of heats of wetting (1) and adsorption (2) of benzene from solutions in *n*-heptane on activated alumina at 20°

The results of calorimetric measurements of the heats of wetting of activated alumina at 20° by pure hydrocarbons—benzene, cyclohexane, cyclohexene, and

Fig. 1. Isotherms of heats of wetting (1) and adsorption (2) of benzene from solutions in n-heptane on activated alumina at 20°

Figure 1: Fig. 1. Isotherms of heats of wetting (1) and adsorption (2) of benzene from solutions in n-heptane on activated alumina at 20°

Fig. 2

Figure 2: Fig. 2

n-heptane—are given in Table 1.

The measured heats of wetting of activated alumina by solutions of benzene, cyclohexane, and cyclohexene in *n*-heptane at 20° over the entire concentration range from pure *n*-heptane to the pure isocyclic hydrocarbon are shown in Figs. 1, 2, and 3.

From the data of Table 1 it is seen that the heats of wetting of the alumina surface by pure hydrocarbons, expressed in calories per 1 g of adsorbent—the aromatic hydrocarbon benzene and the cyclene cyclohexene—are close to one another. On going to the cyclane cyclohexane, the magnitude of the heat of wetting decreases, and for the alkane *n*-heptane it has the smallest value. The higher interaction energy of molecules of benzene, cyclohexene, and cyclohexane with the alumina surface, compared with that of *n*-heptane, explains the displacement by them of *n*-heptane molecules from the surface of this adsorbent during adsorption of liquid binary mixtures of these hydrocarbons with *n*-heptane.

* The authors express their deep gratitude to V. F. Kiselev and K. G. Krasil' nikov, who made it possible to use the calorimetric apparatus.

However, in order to judge the energetic properties of the surface of bead alumina, it is necessary to take into account the different adsorbability of the hydrocarbons studied on the catalyst.*

Figures 1, 2, and 3 show the adsorption isotherms of benzene ([2]), cyclohexane, and cyclohexene ([3]) from solutions in *n*-heptane, obtained at the same temperature as the heats of wetting. The numbers of hydrocarbon molecules adsorbed in a dense monolayer, found from the isotherms, make it possible

Fig. 2. Isotherms of the heats of wetting (1) and adsorption (2) of cyclohexane from solutions in *n*-heptane on bead alumina at 20°.

to calculate the values of the heats of wetting referred to 1 mole of adsorbed hydrocarbon (Table 1). It is found that, of the three hydrocarbons studied, apart from *n*-heptane, the smallest amount of heat is released when the surface of alumina is wetted by an adsorbed mole of cyclohexene. The values of the heats of wetting calculated per 1 mole of adsorbed benzene and cyclohexane differ little from one another. The reason for this phenomenon will be discussed

Fig. 3

Figure 3: Fig. 3

later.

Fig. 3. Isotherms of the heats of wetting (1) and adsorption (2) of cyclohexene from solutions in *n*-heptane on bead alumina at 20°. The black circles denote experiments carried out on a new calorimetric setup assembled by us according to the model of the calorimeter ([8]).

Let us consider the isotherms of the heats of wetting of bead alumina by solutions of benzene and cyclohexane in *n*-heptane, shown in Figs. 1 and 2. The course of these curves is similar to that described in the literature ([10]) and coincides with the experimental adsorption isotherms. From Figs. 1 and 2 it is seen that the isotherms of the heats of wetting rise in the region of low concentrations, more steeply for benzene than for cyclohexane. Then, over a wide concentration range, an almost constant amount of heat is evolved. At the end of the isotherm, when the concentration of the solution becomes close to that of pure benzene or cyclohexane, the heat increases to a value equal to the heat of wetting by the pure hydrocarbon. In the case of benzene and cyclohexane, the rise on the iso-

* The small difference in the values of the heats of wetting of the solution components does not make it possible to calculate, with sufficient accuracy ([9]), the differential values of the heats of adsorption from the solutions studied.

on the heat-of-wetting isotherms in the region of low concentrations coincides with the rise on the adsorption isotherms shown in the same figures. This rise corresponds to the process of formation of a monolayer by the more strongly adsorbed component as its concentration in the solution increases. After the monolayer is filled, the increase in the heat of wetting ceases. This once again confirms the monomolecular character of the adsorption of these hydrocarbons from solutions. An increase in the heat in the region of concentrations close to the pure liquids was observed earlier for some systems (⁀10); however, it is still difficult to explain it.

The isotherm of the heats of wetting of bayonet alumina by cyclohexene from solutions in *n*-heptane (Fig. 3), at low concentrations and at concentrations close to the limiting concentration, has a form similar to the isotherms discussed above. But, in contrast to the heat-of-wetting isotherms for benzene and cyclohexane, it has a step in the concentration region around 2.6 mole/l. On the adsorption isotherm of cyclohexene in the same concentration region, an inflection is observed, explained by reorientation of cyclohexene molecules on the alumina surface from a flat position to an edgewise one (⁀2). Comparison of these two isotherms shows that the calorimetrically measured heats of wetting agree with the idea of reorientation of cyclohexene molecules. The heat released in the concentration region up to 2.6 mole/l apparently corresponds to wetting of the alumina surface by flat-oriented cyclohexene molecules. At

higher concentration it is determined by the energy of interaction with the surface of edgewise-oriented cyclohexene molecules. The magnitude of the heat of wetting of cyclohexene, equal to 4.6 kcal/mole for the edgewise orientation of its molecules, is approximately twice as large when they are arranged flat.

It is known from the literature that, among the hydrocarbons considered, cyclohexene has the greatest catalytic activity on alumina; its catalytic isomerization occurs already at 40° (⁓3), and at the precatalytic temperature (30°), as adsorption studies have shown, the main part of the cyclohexene molecules is oriented edgewise to the surface. We believe that this is connected with the decrease in the heat of wetting of the alumina surface by cyclohexene upon transition from the flat position to the edgewise one, which is apparently precatalytic.

Benzene and cyclohexane are less active on alumina and undergo catalytic transformations only at high temperatures (11-13). These hydrocarbons, as the results of our calorimetric measurements show, have higher values of the heats of wetting on alumina.

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Received
21 II 1961

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