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Abstract

Full Text

PHYSICAL CHEMISTRY

I. V. SMIRNOVA, A. A. KUBASOV, MARTIN BÜLOW, K. V. TOPCHIEVA

HEATS OF WETTING OF ALUMINUM OXIDE
BY SOLUTIONS OF METHYLCYCLOHEXENES IN *n*-HEPTANE

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On the basis of measurements of adsorption isotherms ([1]) and isotherms of heats of wetting ([2]), it was shown that, as the concentration of cyclohexene in an *n*-heptane solution increases, the arrangement of the cyclene molecules relative to the surface of aluminum oxide changes. From orientation with the principal plane of the ring parallel to the surface of aluminum oxide ("flat" orientation), the cyclohexene molecules pass to an edgewise orientation, while remaining attached to the surface by the double bond. Similar behavior of adsorbed molecules was observed in the adsorption of 1-methylcyclohexene-1 from solutions in *n*-heptane on the same adsorbent ([3]). In the present work, the heats of wetting of aluminum oxide by solutions of 1-methylcyclohexene-1 and 1-methylcyclohexene-3 in *n*-heptane are studied over the entire concentration range at 20°.

Fig. 1. Isotherms of the heats of wetting of aluminum oxide by solutions in *n*-heptane: industrial 1-methylcyclohexene-1 (*a*) and 1-methylcyclohexene-3 (*b*), and synthetic 1-methylcyclohexene-1 (*c*) at 20°.

Measurements of the heats of wetting were carried out in a calorimeter with constant heat exchange ([2]). The treatment of the industrial aluminum oxide used and its structural characteristics are given in the same work. The synthesis and purification of 1-methylcyclohexene-1, as well as the purification of *n*-heptane, were described previously ([3]). 1-Methylcyclohexene-3 was synthesized by dehydration of para-methylcyclohexanol, obtained by hydrogenation of para-cresol in an autoclave according to known methods ([4,5]). The physicochemical constants of 1-methylcyclohexene-3 purified by distillation were: b.p. 102.3° (743); d_4^{20} 0.8000; n_D^{20} 1.4419, in agreement with literature data ([6]). The purity of all

hydrocarbons was confirmed by gas-liquid chromatographic analysis.

The isotherms of the heats of wetting of aluminum oxide by 1-methylcyclohexene-1 and 1-methylcyclohexene-3 from solutions in *n*-heptane at 20° are shown in Fig. 1. The isotherms of the heats of wetting of both methylcyclohexenes practically coincide. Consequently, adsorption from solutions under these conditions for the methylcyclohexenes studied must be identical in ···

in nature and close in magnitude. The form of both isotherms is similar to the form of the isotherm of heats of wetting of aluminum oxide by solutions of cyclohexene in *n*-heptane ([2]). An analogous dependence of the energetic interaction with the surface in the process of adsorption from solutions of cyclohexene and its methyl derivatives makes it possible to speak of an identical adsorption mechanism of these hydrocarbons on aluminum oxide. Thus, the reorientation of methylcyclohexene molecules on the surface of aluminum oxide, shown in the study of their adsorption isotherms ([3]), is confirmed by the established similarity of the isotherms of heats of wetting. The steeper step in the bend region of the isotherms of heats of wetting for methylcyclohexenes, compared with cyclohexene, is probably associated with the greater difference in the heats of wetting of this adsorbent by molecules differently oriented on the surface.

When a methyl group is attached to the cyclohexene molecule, a significant decrease was noted ([3]) in adsorption from solutions in *n*-heptane on aluminum oxide, as well as a decrease in its selectivity. Therefore, for methylcyclohexenes, calculation of the ω_m area occupied by a molecule in the dense monolayer on the adsorbent surface from the adsorption isotherm was impracticable. This value, necessary for comparing the energetic characteristics of adsorbed hydrocarbons, was calculated as follows. Using the methods of vector analysis described in ([7]), we calculated conformational structures in the form of a "half-chair" and a "half-bath" for both methylcyclohexenes. For 1-methylcyclohexene-3, both the axial and the equatorial position of the methyl group were taken into account. In calculating the structures, the following values of carbon–carbon bond lengths were used: single bond 1.55 Å, double bond 1.34 Å; bond lengths $\geqslant$ C–H 1.09 Å and $\geqslant$ C–H 1.07 Å; the values of the tetrahedral angle of carbon 109°28′ and of the hydrogen–carbon bond angle with a double bond 125°16′ ([7-9]). Then, by the method described in ([9]), the values of ω_m were calculated for all variants of the conformational structures of methylcyclohexenes at different orientations relative to the surface for dense and loose packings ([10]). In the calculation, the following van der Waals radii were adopted: C –1.8 Å; H –1.2 Å and CH_3 –2.0 Å. The calculation showed that the difference in the values of ω_m for the "half-chair" and "half-bath" conformational structures for both methylcyclohexenes, both in the "flat" and in the edge-on orientations relative to the surface, does not exceed 1 Å^2. In the case of the "flat" orientation of the 1-methylcyclohexene-3 molecule, ω_m is substantially larger with the equatorial position of the methyl group than with the axial position (by 8 Å^2). With an axial position of the methyl group, the molecule becomes almost spherical, and its different orientations relative to the surface differ only slightly (by no more than 1.5 Å^2). On the

basis of the literature concepts of the stereochemistry of six-membered cyclic hydrocarbons ([11]), it may be considered that, for methyl derivatives of cyclohexene, the principal structure should be the "half-chair" conformation, with an equatorial position of the methyl group in 1-methylcyclohexene-3. In this case, for the "flat" orientation of the molecules the calculated values of ω_m are 56.4 Å^2 for 1-methylcyclohexene-1 and 56.1 Å^2 for 1-methylcyclohexene-3. For the edge-on orientation of the molecules along the double bond, the values of ω_m are 38.0 Å^2 for 1-methylcyclohexene-1 and 38.5 Å^2 for 1-methylcyclohexene-3. These values were calculated for loose packing of the adsorbed molecules, which corresponds to the adsorption isotherm of 1-methylcyclohexene-1 from solutions in *n*-heptane ([3]). Thus, when the orientation of methylcyclohexene molecules on the surface changes, the value of ω_m can decrease by approximately a factor of 1.5, whereas when the orientation of cyclohexene molecules changes, this value, on the basis of experimental data ([1]), decreases approximately twofold. This circumstance, together with the increase in the size of the cyclene molecule due to introduction of the methyl group, may serve as the reason for a less

a sharp change in the shape of the adsorption isotherm of methylcyclohexenes from solutions, caused by reorientation of the molecules on the surface.

Proceeding from the reorientation of molecules during adsorption, it should be assumed that the heat of wetting of alumina by pure methylcyclohexenes pertains to the interaction with the surface of edgewise-oriented molecules. Using the experimental values of the heats of wetting of alumina by the individual hydrocarbons, amounting to 7.7 cal/g for 1-methylcyclohexene-1 and 7.4 cal/g for 1-methylcyclohexene-3, and the values of ω_m calculated for the edgewise orientation of these molecules, molar values of the heats of wetting were obtained. They are equal to 7.1 kcal/mole for 1-methylcyclohexene-1 and 6.9 kcal/mole for 1-methylcyclohexene-3. These values are higher than the heat of wetting of the same alumina by pure cyclohexene (4.6 kcal/mole ([2])). The same relationship was found for the heats of adsorption of cyclohexene and its methyl derivatives, measured by the gas-chromatographic method on this adsorbent ([12]).

Since temperature has practically no effect on the magnitude of the heat of wetting ([16]), let us compare the results obtained in the present work with the heats of wetting of alumina known from the literature at 0° by toluene: $2.64 \cdot 10^{-2}$ cal/m^2 ([13]) and 3.4—$3.6 \cdot 10^{-2}$ cal/m^2 ([14]), and by methylcyclohexane $3.03 \cdot 10^{-2}$ cal/m^2 ([13]). In all cases the specific surface area of alumina was measured by adsorption of nitrogen vapors. The values of the heats of wetting, calculated in the same units, for the alumina used by us (specific surface area with respect to nitrogen 290 m^2/g ([15])) are $2.65 \cdot 10^{-2}$ cal/m^2 for 1-methylcyclohexene-1 and $2.55 \cdot 10^{-2}$ cal/m^2 for 1-methylcyclohexene-3. Despite the existing difference in the surface properties of different alumina samples, it should be noted that the heat of wetting of alumina by methylcyclohexenes is lower than by methylcyclohexane and toluene. This agrees with our results on the study of the heats of wetting of alumina by benzene, cyclohexene, and cyclohexane. In this series a lower heat of wetting was also observed for cyclene ([2]). For the heats of adsorp-

tion of hydrocarbons of both these series, measured by the gas-chromatographic method on alumina ([12]), the same dependence was established as for the heats of wetting. In studying the wetting of silica gel (25°) by benzene, cyclohexene, and cyclohexane, no such dependence was observed for any orientations of the cyclene molecules ([17]). Apparently, the reason for the different behavior of this series of hydrocarbons on alumina and silica gel is the edgewise orientation of cyclene molecules on the surface of catalytically active alumina, which causes a decrease in the energy of their interaction with the surface.

Figure 1 also gives an isotherm of the heats of wetting of synthetic alumina by solutions of 1-methylcyclohexene-1 in *n*-heptane at 20° in the region of high cyclene concentrations. The specific surface area of this alumina sample,* determined by the BET method from adsorption of methyl alcohol vapors, is 290 m^2/g. The predominant pore radius is 70 Å. Preliminary treatment of the sample was carried out by the same procedure. On this isotherm of heats of wetting, a distinct bend is noticeable in the same concentration region as in wetting industrial alumina. Consequently, also on alumina prepared by another method, the form of the isotherm of heats of wetting indicates reorientation of cyclene molecules during adsorption from solutions. The heat of wetting of synthetic alumina by 1-methylcyclohexene-1 is, for edgewise orientation, 9.2 kcal/mole. The rise on the isotherm of heats of wetting in the concentration region close to pure 1-methylcyclohexene-1 is retained for synthetic alumina as well. The values

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heats of wetting, referred to unit surface area of the adsorbent, are 130 erg/cm^2 for the industrial sample and 167 erg/cm^2 for the synthetic aluminum oxide sample. The larger value for the more broadly porous synthetic sample is consistent with the study of the effect of the porosity of silica gel on the heats of wetting by paraffinic and aromatic hydrocarbons (18, 19).

Moscow State University
named after M. V. Lomonosov

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Note: Figure translations are in progress. See original paper for figures.