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Abstract

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ADSORPTION OF METHYLCYCLOHEXENE FROM SOLUTIONS AT ELEVATED TEMPERATURE

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Adsorption studies carried out at elevated temperatures are of theoretical interest for the chromatographic separation of hydrocarbons. In addition, determination of the adsorption characteristics of reacting molecules at temperatures close to those of catalytic conversion is important for establishing the mechanism of any heterogeneous catalytic process occurring both in the gas and in the liquid phases. The study of adsorption of liquid hydrocarbon mixtures is usually carried out by the interferometric method ([1],[2]), which makes it possible to analyze binary mixtures independently of the chemical properties of the components. In this method, speed and simplicity of measurement are combined with high accuracy. However, because of the design of the interferometer, calibration of the instrument and determination of the equilibrium concentrations of the solutions under investigation from calibration curves are limited to temperatures close to room temperature. In earlier measurements of the adsorption of liquid hydrocarbon mixtures up to 40° ([3]), we used ultrathermostating of the interferometer cuvette at the temperature of the adsorption experiment. This approach was unsuitable for accurate concentration measurements over a broader temperature range because of the volatility of the components.

To carry out such experiments, we developed a method for reliably separating the equilibrium solution from the adsorbent at a high experimental temperature. The interferometric measurements were then made under ordinary conditions. The adsorption ampoule was a U-shaped glass tube with a narrow constriction at the junction of the arms. Weighing of the adsorbent and filling of the ampoules with the solutions under study were carried out at 20°. The sealed ampoules were placed in a thermostated shaker in such a way that the liquid and the adsorbent were in one arm of the ampoule. After adsorption equilibrium had been established at the experimental temperature, the solution was separated from the adsorbent by pouring it into the other arm of the ampoule without removing it from the thermostat. The ampoule was then turned with the constriction upward, and both its arms were lowered into a vessel with liquid nitrogen. The vacuum produced in the ampoule made it possible to seal it off at the constriction. The entire operation of separating the solution took less than one minute.

By this method, an adsorption isotherm was obtained at 80° for solutions of 1-methylcyclohexene-1 in *n*-heptane on alumina. It was compared with the isotherm of the same binary system measured at 20°.

1-Methylcyclohexene-1 was synthesized by the method of (^{4}). The physicochemical constants of the purified hydrocarbons were as follows: 1-methylcyclohexene-1—b.p. 110° (758 mm); d_4^{20} 0.8088; n_D^{20} 1.4500; *n*-heptane—b.p. 98.4° (756 mm); d_4^{20} 0.6832; n_D^{20} 1.3872. The purity of 1-methylcyclohexene-1 was confirmed by the Raman spectrum recorded by E. G. Treshchova. The characteristics and preliminary treatment of the adsorbent are given in work (^{5}).

For the system 1-methylcyclohexene-1—*n*-heptane at 20°, in the investigated concentration range from 0 to 6 mol/l, six calibration straight lines were constructed (Fig. 1). The standard solutions were selected in such a way as to avoid fringe displacements. Adsorption equilibrium in the system under study

was established in 12-13 h at 80° and in 18-21 h at 20°. The equilibrium concentrations of the solution separated from the adsorbent were measured on an ITR-1 interferometer at 20° using known calibration lines. The amount of adsorption was determined from the difference in the concentrations of the second component in the initial solution C_2^0 and in the solution in equilibrium with the adsorbent $C_2^{(6)}$.

The concentrations determined at 20° were recalculated to the temperature of the adsorption experiment, taking into account the change in the volume of the solution and the vapor pressure of the components. The calculation of the molar-volume concentration at 80° was based on the assumption that solutions of 1-methylcyclohexene-1 in *n*-heptane obey Raoult' s law.

For checking the closeness of the solutions under study to ideal solutions, the specific gravities of the pure components (g/cm^3) were determined experimentally in the temperature range 20-80°; the data are given in Table 1.

Fig. 1. Calibration lines for the system 1-methylcyclohexene-1—*n*-heptane at 20°.

The values of the specific gravities decreased linearly with increasing temperature. The values of *k*—the coefficient of expansion of the liquid—determined from the dependence of specific gravity on temperature were used in the additive calculation of the increase in the volume of the solutions with increasing temperature from 20 to 80° according to Mendeleev' s equation

Table 1

Hydrocarbon	20	40	60	80
1-Methylcyclohexene-1	0.8088	0.7912	0.7735	0.7566
n-Heptane	0.6831	0.6656	0.6479	0.6304

$$v = \frac{v_0}{1 - kt}.$$

The volumes of solutions of different concentrations calculated in this way were compared with these same volumes measured in specially designed experiments at 80° (Table 2).

Table 2

Concentration of 1-methylcyclohexene-1, mol/l	Solution volume, cm^3, found	Solution volume, cm^3, calculated
0	6.048	6.042
0.1452	6.032	6.040
0.9886	6.042	6.034
1.9380	6.032	6.026

The difference between the experimental and calculated values of the volumes was no more than 0.2%; i.e., the additive calculation scheme adopted by us was practically suitable in the concentration range studied. Calculation of the change in solution concentrations, taking into account the increase in evaporation of the solution components with increasing temperature, likewise gave a rectilinear dependence of C_2^0 at 20° on C_2^0 at 80°. For the system studied, the changes in solution concentration due to evaporation under the experimental conditions were small.

The experimental adsorption isotherms of 1-methylcyclohexene-1, measured at 20 and 80°, are shown in Fig. 2, where the symbatic nature of the curves is visible. The adsorption isotherm obtained at 80° has a step in the concentration region approximately from 0.5 to 1 mol/l. A step is also indicated in the same concentration region at 20°. Thereafter the adsorption values on both curves increase and pass through a maximum. In the region of high concentrations, a linear decrease in adsorption is observed.

The form of the adsorption curves of 1-methylcyclohexene-1 resembles the adsorption isotherms of cyclohexene, measured from solutions in *n*-heptane on the same alumina at 20 and 30° (^{7}).

Fig. 2. Adsorption isotherms of 1-methylcyclohexene-1 from solutions in *n*-heptane on alumina at 20° *(1)* and 80° *(2)*

Fig. 2

Figure 1: Fig. 2

Comparison of the adsorption isotherms of 1-methylcyclohexene-1 and cyclohexene at 20° shows that the maximum adsorption value of 1-methylcyclohexene-1 is approximately four times smaller than that of cyclohexene. Consequently, introduction of a methyl radical into the cycloolefin molecule leads to a considerable decrease in the magnitude of adsorption. A decrease in adsorption had previously been noted upon introduction of a methyl group into the aromatic ring in the adsorption from *n*-heptane of benzene and toluene on silica gel (^{2}). Probably, in the case of cyclohexenes, whose molecules do not possess a planar structure, the attachment of substituents has a stronger influence on adsorption of the ring itself on alumina.

The close structure of the molecules of cyclohexene and of its derivative—1-methylcyclohexene-1—and the analogous form of their adsorption isotherms, obtained under the same conditions, make it possible to suppose that the adsorption of these hydrocarbons on alumina is of the same character. In studying the adsorption of cyclohexene from vapors and solutions ($^{7-9}$), it was established that its molecules change their orientation on the surface during the adsorption process. Apparently, the bend in the adsorption isotherm of 1-methylcyclohexene-1 in the concentration region of about 1.2–1.3 mol/l also corresponds to a closer packing of its molecules in the adsorption layer, probably leading to a more inclined arrangement of the molecules of 1-methylcyclohexene-1 on the alumina surface. The presence of a methyl radical at the unsaturated bond in 1-methylcyclohexene-1 may impede the transition of the molecules of the hydrocarbon under investigation to an edgewise orientation.

With the comparatively small magnitude of adsorption of 1-methylcyclohexene-1 and the rather diffuse maximum of the adsorption isotherm at 20°, it is hardly possible to speak of complete displacement of the solvent and formation on the alumina surface of a dense monolayer of adsorbed 1-methylcyclohexene-1 molecules. Its existence at 80° is still less probable, since with increasing temperature the adsorbed molecules acquire greater mobility (^{5}). Indeed, calculation of the experimental isotherms, carried out by the usual accepted methods (^{6,10}), showed that the layer corresponding to the maximum adsorption of 1-methylcyclohexene-1 has a thickness of about 2.3 Å, i.e., it is not dense. Calculation of molecular characteristics under this condition is therefore inappropriate.

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