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Abstract

Full Text

Physical Chemistry

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HEAT CAPACITY OF A LIQUID IN DISPERSE SYSTEMS

In previous works by one of the authors ([1,2]) it was shown that the mean heat capacity of nitrobenzene in the disperse system nitrobenzene–glass powder is significantly smaller than that of the bulk liquid. In disperse systems of this type, the properties of the solid phase change little upon formation of the disperse system, and the properties of the latter are determined mainly by the liquid interlayers between the individual particles of the solid phase. Such disperse systems are convenient and comparatively simple models; their study makes it possible to find regularities determining the properties of practically more important systems.

In the present work the heat capacity of the systems nitrobenzene–glass powder, nitrobenzene–silica gel, benzene–glass powder, and benzene–potassium iodide powder was measured. The temperature interval of the heat-capacity measurements was 10—80°. For the measurements an adiabatic calorimeter with continuous heat input was used. The inner shell, made of thin (0.08 mm) brass, was heated by a current whose strength was regulated by means of a thermocouple. The small thermal inertia of such a shell and the possibility of easily controlling its heating made it possible to work with a temperature difference between the calorimetric vessel and the shell of 0.005—0.01°. During heat-capacity measurements the operating regime (heating rate, amount of substance in the vessel) was maintained the same as during calibration of the instrument, which made it possible to introduce a correction caused by the thermal nonuniformity of the calorimetric vessel. The error of heat-capacity measurement did not exceed 0.2—0.3%.

The glass powder (specific surface 0.73 m^2/g) was prepared in the same way as in work ([2]). To activate the surface, the glass powder was kept for 30 min in a glow discharge with continuous shaking. The discharge parameters (I, U, gas pressure) were basically the same as in work ([3]), where purification of surfaces by a glow discharge was studied.

The silica gel used in the work (U-333), with a total specific surface of 280 m^2/g, contains many dead-end pores into which the liquid did not penetrate.* When the silica gel was wetted with nitrobenzene, only through pores were filled; their specific surface, determined by the method of filtration of a rarefied gas ([4]), was

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

87 m^2/g.

The liquids (nitrobenzene, benzene) used in the work were purified by distillation. In the reference literature ([5–7]) the heat capacity of nitrobenzene is given at one temperature only; only in ([8]) are there values of the heat capacity of nitrobenzene at various temperatures, but these data (1912) are incorrect. We measured the true heat capacity of free nitrobenzene in two calorimeters with periodic and continuous heat input (Fig. 1, curve 1). The heat capacity of benzene measured by us agrees with the literature data ([9]).

The mean thickness of the liquid interlayers in the disperse system nitrobenzene –glass powder was 200—300 $\mu\mu$. The mean thickness of the liquid interlayers in the disperse system nitrobenzene–silica gel was 17 $\mu\mu$, which corresponds to approximately 35 layers of nitrobenzene molecules.

* The calorimetric vessel with the disperse system nitrobenzene-silica gel was evacuated for 1 hour to a pressure of 0.1 mm Hg for partial removal of air.

The heat capacity of the liquid was calculated as the difference between the heat capacities of the disperse system and the solid phase. The results of measurements of the heat capacity of nitrobenzene in the disperse system nitrobenzene –glass powder are given in Fig. 1.

Fig. 1. Heat capacity of nitrobenzene in the disperse system nitrobenzene–glass powder.
1 –heat capacity of free nitrobenzene (a), heat capacity of nitrobenzene in the system with a nonactivated surface (b). **2** –heat capacity of nitrobenzene in the system with an activated surface (c).

Fig. 2. Heat capacity of nitrobenzene in the system nitrobenzene–silica gel.
1 –heat capacity of free nitrobenzene, **2** –heat capacity of nitrobenzene in the system nitrobenzene–silica gel.

On the nonactivated glass surface the heat capacity of nitrobenzene is the same as in the bulk liquid, while in the disperse system with an activated glass surface the heat capacity of nitrobenzene is considerably lower than in the free liquid and, up to 50°, almost does not depend on temperature; thereafter it increases rapidly, approaching the corresponding value for the bulk liquid. Repeated heating to 70-80° does not change the heat capacity of the disperse system; however, after heating to 110-120° the activity of the glass surface disappears and the heat capacity of nitrobenzene in the disperse system becomes the same

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Fig. 3

Figure 3: Fig. 3

Fig. 4. Scheme of adsorption of nitrobenzene on surface hydroxyl groups

Figure 4: Fig. 4. Scheme of adsorption of nitrobenzene on surface hydroxyl groups

as in the bulk liquid.

Fig. 3. Heat capacity of benzene in disperse systems.
1 –heat capacity of free benzene (*a*), heat capacity of benzene in the system benzene–glass powder (*b*), heat capacity of benzene in the system benzene–KJ (*c*). **2** –heat capacity of benzene (+0.024% nitrobenzene) in the system benzene –glass powder (*d*).

Figure 2 shows the heat capacity of nitrobenzene in the disperse system nitrobenzene–silica gel. In this disperse system the heat capacity of nitrobenzene is somewhat increased in comparison with the bulk liquid, which is opposite to the effect observed in the system nitrobenzene–activated glass powder. It may be assumed that the increase in the heat capacity of nitrobenzene in the system nitrobenzene–silica gel is connected primarily with the very small thickness of the liquid layers in it, so that in this case, in the observed effect, the contribution of the heat capacity of the adsorbed···

ionosol. As shown in a number of works ([9], [10]), the heat capacity of adsorbed monolayers is considerably greater than the heat capacity of the liquid in bulk, and, apparently, it was this effect of increased heat capacity that we observed in the nitrobenzene–silica-gel system.

In the nitrobenzene–glass-powder system, where the average thickness of the liquid interlayers was considerably greater, the influence of the heat capacity of the monolayer on the total heat capacity was masked by a considerable decrease in the heat capacity of the liquid as a result of "ordering" of its boundary layer.

Figure 3 shows the heat capacity of benzene in various disperse systems. The heat capacity of benzene in disperse systems–benzene–glass powder with an activated surface, benzene–potassium iodide–is the same as that of the free liquid. However, the addition to benzene of 0.024% nitrobenzene in the system glass powder with an activated surface–benzene leads to a considerable decrease in the heat capacity of the latter (Fig. 3, curve 2). An analogous effect of induction of boundary anomalies in benzene was observed by us earlier in measuring the disjoining pressure of thin films of nitrobenzene and benzene ([11]). Heating to 40–50° destroys the anomalous properties of the benzene layer, but on cooling they are restored again. It should also be noted that the maximum of the heat capacity at 20° in the disperse system benzene–glass powder apparently indicates a phase transition in the boundary layer of benzene.

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Fig. 4. Scheme of adsorption of nitrobenzene on surface hydroxyl groups

All this can be explained by assuming that nitrobenzene is adsorbed on the surface of glass, forming hydrogen bonds with surface hydroxyl groups (Fig. 4), and that an oriented monolayer of nitrobenzene molecules is formed on the surface, with their benzene rings directed outward. Then a polymolecular layer of the boundary phase of benzene is formed on it, repeating the structure of its substrate and possessing a lower heat capacity.

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