PHYSICAL CHEMISTRY

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1957

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PHYSICAL CHEMISTRY

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ADSORPTION OF ALIPHATIC ALCOHOLS FROM SOLUTIONS ON SILICA GEL AND WHITE SOOT

(Presented by Academician M. M. Dubinin on 8 January 1957)

The adsorption of alcohols and acids of a homologous series from nonpolar solvents on porous hydrophilic adsorbents—silica gels and aluminosilicates—has been studied in works ([1], [2], [11]). As a result of these investigations it was established that the limiting adsorbed amount decreases with increasing hydrocarbon radical, while the limiting adsorption volume for the comparatively macroporous adsorbents studied remains constant ([3], [11]) (the rule of constancy of the limiting adsorbed volume ([4])). The observed decrease of adsorption in the homologous series was associated with volume interactions in solutions (changes in the solubility of the members of the homologous series ([1])) or was attributed to the influence of the porous structure of the adsorbent, when, instead of the formation of regularly oriented layers, dense filling of the pores by molecules of the adsorbed substance was assumed ([3], [5]).

In the case of nonporous hydrophilic adsorbents, as indicated in works ([2–4]), it may be expected that the limiting adsorbed amount of alcohols and acids of a homologous series is constant. This corresponds to the idea of such an orientation of the adsorbed molecules in which interaction with the surface occurs through the polar groups, while the chains of the hydrocarbon radicals are directed toward the solution, i.e., the molecules form a layer analogous in structure to condensed films of aliphatic compounds on the surface of water. In this case the number of molecules per unit surface will not depend on the length of the hydrocarbon radical. For nonporous hydrophobic adsorbents, measurements of the adsorption of sparingly soluble alcohols and acids from aqueous solutions ([6], [7]) showed that the adsorption limit increases with increasing number of carbon atoms in the molecule. Investigation of adsorption from solutions on porous and nonporous adsorbents of one and the same surface nature is of great interest, since it makes it possible to evaluate the influence of porous structure and to use the data obtained for judging the orientation of adsorbed molecules in the surface layer. For hydrophobic adsorbents, a comparison of adsorption isotherms of certain organic substances from aqueous solutions on carbon and on nonporous soot was made in ([8]). As far as we know, there are no corresponding data for hydrophilic adsorbents.

Fig. 1. Adsorption isotherms of n-alcohols from CCl_4 on white soot (a) and silica gel (b), calculated per 1 g (A) and per 1 m^2 (B); the numbers at the curves are the number of carbon atoms in the alcohol molecule

Figure 1: Fig. 1. Adsorption isotherms of n-alcohols from CCl_4 on white soot (a) and silica gel (b), calculated per 1 g (A) and per 1 m^2 (B); the numbers at the curves are the number of carbon atoms in the alcohol molecule

In the present work we carried out measurements of the adsorption of a series of normal aliphatic alcohols from solutions in CCl_4 on two samples of silica of different structure. The porous sample was KSK-2 silica gel (^{9}) with a predominant pore diameter of 60 Å and a specific surface area of 400 m^2/g. As the nonporous sample, so-called white soot was used, which was obtained in the form of a very loose powder (bulk density 0.025 g/cm^3) by burning vapors of ethyl orthosilicate. Its specific surface area was determined by the BET method from the adsorption isotherm of nitrogen vapor, and also from statistical treatment of electron-

microphotographs and proved to be, in the first case, 240 m^2/g, and in the second, 220 m^2/g*. The closeness of these values indicates that white soot is a practically nonporous adsorbent. The same conclusion follows from the data of work (^{10}), in which the adsorption of Freon vapor (CCl_2F_2) was studied on a similar silica preparation. The content of structural water in the prepared samples was: for soot, 4.2 μM/m^2, and for silica gel, 4.1 μM/m^2. Thus these adsorbents, while differing sharply in their structure, had practically the same hydrated surface.

Fig. 1. Adsorption isotherms of *n*-alcohols from CCl_4 on white soot (*a*) and silica gel (*b*), calculated per 1 g (*A*) and per 1 m^2 (*B*); the numbers at the curves are the number of carbon atoms in the alcohol molecule.

Owing to the large volume occupied by the soot powder, and to the considerable decrease, as a result, in the relative extraction of the adsorbed substance from solution, it was difficult to carry out adsorption measurements in the region of high concentrations. We therefore confined ourselves to measuring the portions of the isotherms corresponding to a constant adsorption, which was reached for all the alcohols studied at concentrations of about 5% of the concentration of the pure liquid (^{11}).

As follows from Fig. 1*A*, the data obtained on soot and on silica gel do not differ qualitatively from one another. In both cases, as the hydrocarbon radical increases, a decrease is observed in the limiting value of the adsorption and a shift of it into the region of lower equilibrium concentrations (^{12}). Similar results were obtained by us on this silica gel when *n*-heptane was used as the solvent (with the exception of the data for methyl alcohol, which is only sparingly soluble in heptane, whose isotherm had an S-shaped form) (^{13}).

* The first of these determinations was carried out by E. A. Sysoev, the second

by E. A. Leont’ ev, to whom the authors express their gratitude.

If one assumes that the observed decrease in the limiting adsorbed amount in the homologous series may be caused by competition from the solvent, then adsorption of the latter will obviously increase as adsorption of the alcohol decreases, i.e., on going to the higher alcohols. We attempted to estimate the adsorption of the solvent in these systems. For this purpose, the adsorption isotherm of octyl alcohol on silica gel was extended into the region of high concentrations. Extrapolation of its inclined portion to its intersection with the abscissa axis gave a value close to the concentration of the pure alcohol. Since such an extrapolation cannot give sufficiently accurate results, we additionally carried out a series of experiments to determine the adsorption of CCl_4 from its solutions in octyl alcohol in the concentration range of interest to us, but within the limits of measurement error no appreciable adsorption was found. From the isotherms obtained, the values of the total content of adsorbed substance in the surface layer, a, were calculated (Table 1).

Thus, the decrease in adsorption of alcohols as their hydrocarbon radical grows is not connected with the influence of the porous structure of the adsorbent and, apparently, cannot be attributed to competition from the solvent. This phenomenon may be explained if it is assumed that alcohol molecules in the dense adsorption layer are oriented in such a way that the chains of the hydrocarbon radicals preferentially "lie" on the surface. Similar conclusions concerning the orientation of molecules in the surface layer were drawn in work ([14]) in a study of the adsorption of benzene from solutions in heptane on silica gel, and also of the adsorption of fatty acids from aqueous solutions on charcoal ([15]). Obviously, in this case the area occupied by a molecule in the surface layer will depend on the length of the hydrocarbon radical. However, as follows from Fig. 2, where this dependence is presented, direct proportionality is not observed. The area per one CH_2 group, which for the first members of the series is about 8 Å^2,* decreases markedly with increasing length of the hydrocarbon radical. At the same time, the thickness of the layer of adsorbed molecules increases from 4.2 Å in the case of the lower alcohols to 7.1 Å on soot and 13.0 Å on silica gel for octadecyl alcohol. From this one may conclude that the orientation of adsorbed alcohol molecules on the partially dehydrated surface of silica ([16]) changes from the lower alcohols to the higher ones. The molecules of the latter are apparently arranged at some angle to the surface. It is necessary, however, to bear in mind that in the case of silica gel the possibility of a change in orientation of adsorbed molecules in fine pores may be limited by their geometrical dimensions. Therefore, the values of the landing areas and the thickness of the adsorption layer for the higher alcohols may be regarded as certain average quantities referring to the silica-gel sample studied.

Fig. 2. Values of landing areas ω, thicknesses of the adsorbed layer τ, and limiting adsorption volume av_m of n-alcohols on silica gel (1) and white soot (2)

In order to determine the influence of porous structure on the magnitude of

Fig. 2. Values of landing areas ω, thicknesses of the adsorbed layer τ, and limiting adsorption volume av_m of n-alcohols on silica gel (1) and white soot (2)

Figure 2: Fig. 2. Values of landing areas ω, thicknesses of the adsorbed layer τ, and limiting adsorption volume av_m of n-alcohols on silica gel (1) and white soot (2)

limiting adsorption, the data obtained were referred to 1 m^2 of surface. A comparison of such isotherms on soot and silica gel for each of the alcohols is given in Fig. 1B. As follows from this figure, the adsorption isotherms of methyl alcohol coincide for both adsorbents. Further, as the in— with an increase in the number of carbon atoms in the alcohol molecule, adsorption on the porous sample—silica gel—becomes relatively higher than the corresponding value on nonporous soot. An increase in the adsorption limit on going from a coarse-porous to a fine-porous silica gel was noted in (^{14}) and was explained by the authors as due to an enhancement of the adsorption potential in fine pores. A similar explanation may be given in the present case as well; however, unlike (^{14}), where this effect was found upon a decrease in the adsorbent pore size, in our experiments it appeared at an unchanged pore size and with an increase in the size of the adsorbed molecules.

Table 1

Limiting adsorbed amounts and their volumes for a series of *n*-alcohols on white soot and silica gel

Alcohols	White soot: x, mM/g	White soot: a, mM/g	White soot: av_m, cm^3/g	Silica gel: x, mM/g	Silica gel: a, mM/g	Silica gel: av_m, cm^3/g
Methyl	2.40	2.49	0.10	4.10	4.25	0.17
Ethyl	1.60	1.69	0.10	2.75	2.90	0.17
Propyl	1.18	1.26	0.10	2.10	2.23	0.17
Butyl	1.00	1.05	0.10	1.80	1.90	0.17
Hexyl	0.80	0.85	0.11	1.54	1.65	0.21
Octyl	0.67	0.73	0.12	1.45	1.58	0.25
Octadecyl	0.51	0.51	0.17	1.56	1.56	0.52

As follows from Table 1 and Fig. 2, the limiting adsorption volume of all the alcohols studied on nonporous soot changes little. Even if one restricts consideration to the first members of the series, up to and including butyl alcohol,

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* According to data (^{15}), the cross section of the hydrocarbon chain may be represented by a rectangle with sides 4.12 and 4.49 Å.

the constancy of the adsorption volume observed in this case is evidently not connected with the influence of the porous structure, but is a consequence of the indicated orientation of molecules in the surface layer. On going to the higher alcohols, the limiting adsorption volume on the silica gel studied by us increases noticeably. On the other hand, it is known that for fine-porous samples a decrease in the limiting adsorption volume may occur owing to the effect of ultraporosity ([11]). In the case where the pore sizes of the adsorbent and the character of their distribution are such that these oppositely acting effects can compensate one another, the limiting adsorption volume for members of a homologous series will remain constant.

The authors express their deep gratitude to Academician M. M. Dubinin and B. V. Il’ in for their interest in this work and for discussion of the results.

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named after M. V. Lomonosov

Received
29 XII 1956

CITED LITERATURE

1. F. E. Bartell, G. H. Scheffler, *J. Am. Chem. Soc.*, **53**, 2507 (1931).
2. A. V. Kiselev, I. A. Vorms et al., *ZhFKh*, **19**, 83 (1946).
3. A. V. Kiselev, *ZhFKh*, **23**, 452 (1949).
4. K. D. Shcherbakova, A. V. Kiselev, in: *Collected Works on Physical Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1947, p. 225.
5. R. D. Hansen, R. S. Hansen, *J. Coll. Sci.*, **9**, 1 (1954).
6. R. S. Hansen, R. P. Craig, *J. Phys. Chem.*, **58**, 211 (1954).
7. A. V. Kiselev, I. V. Shikalova, *ZhFKh*, **30**, 94 (1956).
8. A. V. Kiselev, Yu. S. Nikitin, Yu. A. Eltekov, *ZhFKh*, **30**, 334 (1956).
9. M. M. Egorov, T. S. Egorova, V. F. Kiselev, K. G. Krasil’ nikov, *DAN*, **114**, No. 3 (1957).
10. P. C. Carman, F. A. Raal, *Proc. Roy. Soc.*, **A 209**, 59 (1951).
11. A. V. Kiselev, in: *Collected Volume: Investigations in the Field of Chromatography*, Publishing House of the Academy of Sciences of the

USSR, 1952, p. 71.

12. V. K. Semenchenko, *Koll. zhurn.*, **9**, 125 (1947).
13. O. M. Dzhigit, A. V. Kiselev, K. G. Krasil' nikov, *DAN*, **58**, 413 (1947).
14. A. V. Kiselev, Yu. A. Eltekov, *DAN*, **100**, 107 (1955).
15. A. Blackburn, J. J. Kipling, *J. Chem. Soc.*, 1955, 1493.
16. G. I. Aleksandrova, V. F. Kiselev et al., *DAN*, **108**, 283 (1956.)

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