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Abstract

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THE INFLUENCE OF DISSOLVED TEMPLATES ON THE FORMATION OF SPECIFIC ADSORPTION PROPERTIES OF THE SURFACE OF SILICA GELS

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An analysis of works on the preparation of specific adsorbents (3–10) makes it possible to suppose that, for obtaining silica gels with high selectivity of adsorption with respect to a previously specified substance, a very promising method is their preparation (3) with the aid of dissolved templates. In work (1) it was indicated that the hypothesis (2,3) concerning the formation of "imprints" of template molecules on the surface of silica gel, responsible for adsorption specificity, is of great importance for the theory of adsorption; however, the question of the presence or absence of such "imprints" has still not been resolved.

The present work is devoted to an investigation of the mechanism of formation of adsorption specificity with the aid of dissolved templates—azo dyes, in particular to the role of the so-called nonextractable dye—template—in creating the specificity of silica gels.

We prepared 3 series of specific silica gels: in series I,* a sodium silicate solution was added to a sulfuric acid solution to which the dye-template had previously been added—methyl orange (MO), ethyl orange (EO), propyl orange (PO), or methyl red (MR); otherwise the procedure did not differ from that described in (3). In series II the template was only MO; in one sample MO was introduced into the initial acid solution, in the second—into the sol 4 hours after its preparation, in the third—into the hydrogel after syneresis (by immersing the hydrogel in an acidified saturated aqueous solution of MO), and in the fourth—into the hydrogel washed free of salts and dried in air; the dye was extracted in all cases from the dry silica gel with methanol in a Soxhlet apparatus. In series III, in contrast to the preceding series, the dye (MO) for all samples was introduced into the initial acid solution, and the samples differed from one another in that in the first of them extraction of MO with methanol (by decantation) was carried out immediately after syneresis of the hydrogel, while in the others—at different stages (from 10 to 90%) of drying of the samples; the salt residue was washed out with distilled water, after which the gels were dried, ground in a mortar, and fractions of 0.25-0.5 and 0.5-1.0 mm were screened off and used in adsorption experiments.

In all cases, in parallel with the preparation of the specific gels, under the same conditions and with analogous subsequent treatment, control samples of silica gels were prepared—without dyes.

On gels of series I (Fig. 1), under conditions analogous to those described in (3,6,9), adsorption isotherms of all four dyes were recorded on an SF-5 spectrophotometer and, in accordance with the data of works (3–9), it was found that adsorption of dyes on the control gels is 2–4 times less than on the corresponding specific samples. It is seen from Fig. 1 that the gel obtained in the presence of MO (a, curve 1) selectively absorbs MO; the sample prepared in the presence of EO (b, curve 1) selectively adsorbs EO, etc.—in all cases without exception there is observed specific—

* V. F. Gamaleya took part in the experiments on the preparation and investigation of the properties of silica gels of series I.

···specific adsorption of the former. It is interesting to note that on the MR gel (g, curve 1) MO is, in general, adsorbed better than EO and PO; this fact is apparently explained by the fact that substantial fragments of the MO and MR molecules coincide and, during formation, can give similar "imprints" in structure on the surface of the silica gel, whereas in EO (PO) and MR the molecular structures differ to a greater extent.

For silica gels of series II and III, adsorption isotherms of MO and sorption isotherms of methanol vapor were recorded in a vacuum apparatus with McBain balances at 20°, and the amounts of dye not extractable by methanol were determined under conditions analogous to those described in (6).

Figure 2a presents typical adsorption isotherms of MO on a control and a specific gel, indicating the selectivity of MO uptake by the specific samples. Figure 2b gives isotherms of specific adsorption (curves of the excess adsorption of MO on the specific gels in comparison with the corresponding controls) for gels of series II; it is seen here that the content of nonextractable dye in these samples (Fig. 2b) changes in parallel with the magnitude of the selective uptake of MO, which agrees with the results of (9). However, the conclusion of these authors that this fact serves as decisive proof of an associative mechanism of the specific adsorption of MO molecules on identical nonextractable MO molecules in the silica-gel skeleton is evidently incorrect, as is seen from the following.

In series II, as in (9), we extracted MO from completely dried gels; as a result, both we and the authors cited should have expected a correspondence between the concentration of nonextractable MO molecules inside the particles of the gel skeleton and the concentration of MO molecules on their surface, extractable by methanol and leaving the corresponding "imprints," which determine the magnitude of the specific adsorption. In series III, extracting MO at different stages of gel formation, we obtained specific sam—

Fig. 1. Adsorption isotherms of dyes on specific silica gels.
a —on MO gel: 1 —MO, 2 —EO, 3 —PO; *b* —on EO gel: 1 —MO, 2 —EO; *v* —on

Fig. 3. Absorption spectra of MO in solution (1), adsorbed on silica gel (2), and captured by the silica-gel framework (3). The absorption intensities are given, for convenience, on different scales.

Figure 1: Fig. 3. Absorption spectra of MO in solution (1), adsorbed on silica gel (2), and captured by the silica-gel framework (3). The absorption intensities are given, for convenience, on different scales.

PO gel: 1 –MO, 2 –EO, 3 –PO; *g* –on MR gel: 1 –MO, 2 –EO, 3 –PO, 4 –MR.

Fig. 2. Adsorption isotherms of MO on silica gels: *a* –on the specific (1) and control (2) gel of series II; *b* –specific adsorption on gels of series II. Amount of nonextractable dye (M/kg $\cdot 10^5$): 1 –13.5; 2 –37.5; 3 –10.8; 4 –1.5; *v* –on the specific (1) and control (2) gel of series III; *g* –specific adsorption on gels of series III. Amount of nonextractable dye (M/kg $\cdot 10^5$): 1 –0; 2 –3.5; 3 –0.3; 4 –0; 5 –0.9.

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samples (an example is given in Fig. 2b), in which there is no correspondence between the amount of non-extractable and specifically adsorbed MO (Fig. 2a). The specific surface areas of the silica gels, calculated from methanol-vapor sorption isotherms, proved to be practically identical (790-810 m^2/g), i.e., when recalculated per unit surface area, the relative position of the specific-adsorption isotherms does not change. It is interesting to note that the authors of work (5), who began extraction of the dye with methanol at 50% humidity of the hydrogel, obtained colorless gels in the case of MO and EO, whereas in the case of PO and butyl orange the gels were slightly pinkish.

Fig. 3. Absorption spectra of MO in solution (1), adsorbed on silica gel (2), and in the state captured by the silica-gel framework (3). The absorption intensities are given, for convenience, on different scales.

Thus, the conclusion of the authors of (9) concerning an associative mechanism of specific adsorption is premature. Our results and the data of work (5) indicate that the hypothesis advanced by one of us (2), concerning "imprints" of the template molecules on silica gel that are responsible for specific adsorption, is at present better substantiated.

In this connection, the question of the state of the molecules of the non-extracted dye in the gel becomes of special interest. In work (3) it was found that non-extracted MO, in comparison with MO dissolved or ordinarily adsorbed on silica gel, possesses increased resistance to the action of powerful ultraviolet irradiation and strong oxidizing agents. A direct spectral study of the state of the dye in silica gel has hitherto been complicated by the fact that silica gels are usually obtained in the form of grains or spherical granules. By a special method we obtained control silica gels and silica gels specific to MO in the form of transparent disks up to 5 mm thick, and recorded the absorption spectra of MO in three states: in an aqueous phosphate buffer solution (pH 4.64); in the adsorbed state on a control silica-gel plate immersed in the same solution; and in the form of non-extracted MO in a plate of specific gel, likewise soaked in the same buffer solution for a week (Fig. 3).

It is seen from Fig. 3 that in all three cases the state of the MO molecules is different; if, in addition, one takes into account the experimental facts cited above from (3), it may be assumed that the molecules of non-extracted MO are probably located inside the elementary particles constituting the silica-gel framework and, consequently, cannot be the cause of the adsorption specificity of the silica gels.

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REFERENCES CITED

1. M. V. Polyakov, Z. Z. Vysotskii, Proceedings of the Scientific-Technical Conference on Adsorption, L., 1959.
2. M. V. Polyakov, *ZhFKh*, **2**, 799 (1931); *ZhFKh*, **10**, 100 (1937).
3. F. H. Dickey, *Proc. Natl. Acad. Sci.*, **35**, 227 (1949); F. H. Dickey, *J. Phys. Chem.*, **59**, 695 (1955).
4. R. Curti, U. Colombo, *Chimia e industria*, **33**, 103 (1951).
5. R. Curti, U. Colombo, F. Glerici, *Gazz. chim. Ital.*, **82**, 491 (1952).
6. R. G. Haldeman, P. H. Emmett, *J. Phys. Chem.*, **59**, 1039 (1955).
7. A. H. Beckett, P. Anderson, *Nature*, **179**, No. 4569, 1075 (1957).
8. A. Waksmundsky, *Roczniki Chemii*, **32**, 323 (1958).
9. J. L. Morrison, M. Worsley, D. R. Shaw, G. W. Hodgson, *Canad. J. Chem.*, **37**, 1986 (1959).
10. V. V. Patrikeev, A. A. Balandin, E. I. Klabunovskii, Yu. S. Mardashev, G. I. Maksimova, *DAN*, **132**, 850 (1960).