M. P. VOLAROVICH, I. I. LISHTVAN, and N. V. CHURAEV

1962

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

M. P. VOLAROVICH, I. I. LISHTVAN, and N. V. CHURAEV

STUDY OF THE IMMOBILIZATION OF A DISPERSION MEDIUM UNDER THE INFLUENCE OF STRUCTURE-FORMING ADDITIVES

(Presented by Academician P. A. Rehbinder on 30 XI 1961)

As is known (^{1}), hydrophilic disperse systems, in addition to bound water W_{ph}, retained by forces of a physicochemical nature, also contain immobilized water W_{i}, mechanically captured during the formation of gel-like structures. Quantitative study of the latter encounters considerable difficulties because immobilized water, in its properties, does not differ in any way from free water. To determine its content one may use the method of the nonsolvent volume (^{2}), bearing in mind that penetration of the indicator into immobilized water is hindered in comparison with free water, in which the equilibrium concentration of the indicator is rapidly established. Since the accuracy of measuring W_{i} is the greater, the lower the indicator concentration and the shorter the contact time, it is most convenient for these purposes to use solutions of a radioactive indicator (^{3}). In this case, samples of the dispersion medium are taken immediately after addition of the indicator and stirring of the suspension. During stirring, the indicator does not have time to diffuse through the fine pores of the gel structure; as a result, to the nonsolvent volume of water W_c will be attributed not only physicochemically bound water, but also immobilized water, i.e.

$$W_c = W_{\text{ph}} + W_{\text{i}}.$$

Fig. 1

The use of low indicator concentrations also makes it possible to avoid errors associated with changes in the properties of the disperse system under investigation when significant amounts of sugar or electrolytes, usually employed as indicators, are added to it. By determining W_c directly by the indicated method and knowing the value of W_{ph} (^{3}), one can determine W_{i} by difference.

Figure 1a shows the change in the content of W_c in a hydrophilic semicolloidal system (humic substances isolated from peat) when solutions of $CaCl_2$ of different concentrations are added to it. The same graph shows the corresponding values of the limiting shear stress, obtained by the method described by us earlier (4). As the radioactive indicator, the compound Na_2SO_4, labeled with radioac-

···to the active isotope S^{35}, which is not sorbed by peat (3). To study the mechanism of interaction of calcium salts with the hydrophilic colloids of peat, a radioactive label, $CaCl_2$ with Ca^{45}, was used. The amount of absorbed cations was calculated taking into account the undissolving volume, determined from $S^{35}O_4$ or Cl. In the latter case W_c was determined from the concentration of chlorine ions (by titration according to Volhard). The content of Ca^{45} and S^{35} in the analyzed samples was determined by radiometric methods using the different energies of the β-radiation of these isotopes.

The use of a double label ($S^{35}O_4$ or Cl and Ca^{45}) made it possible to establish that the interaction of calcium with humic substances proceeds by the type of ion-exchange sorption. Absorption of calcium ions leads to a shift of the dynamic equilibrium gel $\rightleftarrows$ sol $\rightleftarrows$ true solution toward the gel, as is also indicated by the decrease in dispersity observed by methods of sedimentometric analysis (4). Electron-microscopic study of the aggregates that arise showed that they are not compact formations and have considerable internal porosity (5). The yield shear stress θ increases upon absorption of Ca ions up to a certain limit, corresponding to the maximum development of gel structures immobilizing the greatest amount of the dispersion medium. It should be noted that the observed changes in W_c upon calcium additions occurred mainly through immobilization of the dispersion medium, and not through a change in the content of physicochemically bound water. As was shown earlier by A. V. Dumanskii and co-workers (6), the content W_{ph} in humic substances does not exceed 70%. Investigations carried out by N. V. Churaev led to the conclusion that the bound water of the hydrophilic colloids of peat is represented mainly by water of solvation of the active groups of high-molecular compounds (humic substances, hemicelluloses), as evidenced by the good agreement of the measured values of W_{ph} with those calculated from the number of active groups, analogous to the way this was done by I. N. Putilova for proteins (7). Confirmation of this character of the physicochemical binding of water in peat is also the insignificant change in the content of W_{ph} during its mechanical dispersion.

A decrease in the content of immobilized water upon further absorption of Ca (Fig. 1,a) indicates the beginning of compact coagulation, which also leads to a decrease in the strength of the system. The observed change in the content of W_i in accordance with the change in the structural-rheological properties of hydrophilic humic substances agrees with the data of P. A. Rebinder and N. N. Serb-Serbina (1,8). We note that interaction with sodium ions, on the contrary, led to a significant decrease in the structural-rheological properties (4) as a result of a shift of the equilibrium toward the solution during the formation of sodium

Fig. 2

Figure 2: Fig. 2

humates, and was accompanied by the release of immobilized water.

Observations of the immobilization of the dispersion medium and its reverse transition into the free state upon a shift of the gel $\rightleftarrows$ sol equilibrium were carried out in a series of special experiments. A fraction of medium peat smaller than 1 mm was placed on a funnel with filter paper, and through it a solution of a radioactive indicator (S^{35}) was filtered until all free water was completely displaced, which was noted from equality of the specific activity of the filtrate and of the filtering solution. After this, by filtration through the sample of a $CaCl_2$ solution, the dispersion equilibrium was artificially shifted toward the gel, which, in forming, immobilized part of the labeled dispersion medium. Filtration of $CaCl_2$ was likewise carried out until complete displacement from the pores of the free water containing the radioactive indicator.

Figure 1,b shows the change in concentration of the radioactive indicator (N impulses/min) in the filtrate after the start ($\tau = 0$) of filtration of calcium chloride. As is seen from the graph, after 25–30 min the displacement of labeled water was practically completed. After this, at 50 min, filtration was begun···

tion through the specimen of NaOH solution, which led to a shift of the equilibrium in the colloidal fraction of the peat toward the sol and the true solution. The graph in this case shows the appearance of activity in the filtrate, indicating the transition of the labeled immobilized water into free water. The results of the experiments show that a shift of the dispersion equilibrium in hydrophilic colloids toward the gel does indeed lead to immobilization of the dispersion medium, while destruction of the structure of associates and gels leads to its release. The content of immobilized water in the humic colloids of peat reaches 1000–2000% and depends on their structure, determined by the amount and composition of the absorbed cations, as well as by the concentration of dry matter. The high content of immobilized water, as well as of other categories of mechanically retained water—intracellular and capillary water ([3])—is a specific feature of peat as a disperse system and has a considerable influence on the kinetics of moisture transfer and on the nature of the course of various technological processes.

Fig. 2

Figure 2 shows the isotherm, obtained by applying the methods described above, of sorption of Ca^{45} from a $CaCl_2$ solution by a specimen of sedge peat, and the values of W_c measured simultaneously with the aid of the radioactive indicator S^{35}. The experiments were carried out at pH values of the medium close to natural ones. The absorption capacity for Ca of lowland peat was found to be approximately 90 mg-eq. per 100 g of dry matter, whereas for raised medium peat it amounted to only 10–15 mg-eq., which may be explained by suppression of exchange processes at low pH values (9). The considerable exchange capacity of lowland peats leads, in particular, to the fact that their physicochemical properties, unlike those of raised peats, may vary within substantially wider limits depending on the mineral composition of the groundwaters feeding the peat deposit.

The measured quantity W_c in the case of natural peats includes not only immobilized and physicochemically bound water, but also intracellular water W_{vnk}, i.e.

$$W_c = W_{\mathrm{ph}} + W_i + W_{\mathrm{vnk}}.$$

The content of the latter, however, changes little under the action of additives. On the basis of the data obtained, the content of intracellular water in sedge peat can be estimated as $W_{\mathrm{vnk}} = 160\%$ (Fig. 2, $W_c = 200\%$ at $C > 50$ mg-eq. Ca/l, when $W_i = 0$), bearing in mind that $W_{\mathrm{ph}} = 40\%$.

The content of immobilized water, equal to $W_i = W_c - 200\%$, changes upon absorption of calcium by lowland peat over rather wide limits. The maximum amount of immobilized water, $W_i = 200\%$, corresponds to its absorption of 40 mg-eq. Ca per 100 g of dry matter, which corresponds to approximately half the absorption capacity of the peat. Similar results were obtained in the study of hydrophilic humic colloids isolated from peat, where the maximum W_i corresponds to absorption of 80-90 mg-eq. Ca per 100 g of dry matter (at pH 3.7-4.0). As is known, the absorption capacity of humic substances under these conditions is about 160-170 mg-eq. per 100 g of dry matter (9). Thus, the transition to compact coagulation in the hydrophilic colloids of peat occurs upon replacement of approximately 50% of the exchange capacity, which confirms the results of studies by Chiang Lung, P. A. Rehbinder, and N. N. Serb-Serbina (10).

The observed changes in the water properties and structure of hydrophilic

peat colloids under the action of Ca and Na additives and changes in the pH of the medium can be used to control the properties of disperse systems in directions required by practice.

Kalinin Peat Institute

Received
25 XI 1961

REFERENCES

[1] P. A. Rebinder, All-Union Scientific and Technical Conference on the Intensification of Processes and Improvement of the Quality of Materials during Drying. Plenary Sessions, Moscow, 1956, 1958, p. 20; A. V. Lykov, *Phenomena of Transfer in Capillary-Porous Bodies*, Moscow, 1954.

[2] A. V. Dumanskii, *Lyophilicity of Disperse Systems*, Kiev, 1960.
[3] M. P. Volarovich, N. V. Churaev, *Investigation of the Properties of Peat and the Processes Occurring in It by Means of Radioactive Isotopes*, Publishing House of the USSR Academy of Sciences, 1960.
[4] M. P. Volarovich, I. I. Lishtvan, N. V. Churaev, *Kolloidnyi zhurnal*, **22**, No. 5, 546 (1960).
[5] M. P. Volarovich, T. S. Mukhina et al., *Kolloidnyi zhurnal*, **22**, No. 5, 553 (1960).
[6] A. V. Dumanskii, M. V. Chapek et al., *Kolloidnyi zhurnal*, **2**, No. 2 (1936); **3**, No. 2, 99 (1937).
[7] I. N. Putilova, Transactions of the All-Union Conference on Colloid Chemistry, Kiev, 1952, p. 16.
[8] P. A. Rebinder, *Kolloidnyi zhurnal*, **20**, No. 5, 527 (1958); N. N. Serb-Serbina, ibid., p. 563.
[9] M. M. Kononova, *The Problem of Soil Humus and Contemporary Tasks of Its Study*, Publishing House of the USSR Academy of Sciences, 1951.
[10] Qian Lun, N. N. Serb-Serbina et al., *Kolloidnyi zhurnal*, **23**, No. 1 (1961); Qian Lun, N. N. Serb-Serbina, P. A. Rebinder, *Kolloidnyi zhurnal*, **23**, No. 3 (1961).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.