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Abstract

Full Text

PHYSICAL CHEMISTRY

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FILM AND CAPILLARY-RETAINED WATER IN A POROUS MEDIUM

(Presented by Academician A. V. Topchiev, 13 XI 1957)

In works (^{1}-^{4}) the thickness of polymolecular layers of aqueous electrolyte solutions on the inner surface of a single capillary at various interfaces was studied. In order to determine how far the conclusions about the properties of thin layers, obtained for single capillaries, may be considered valid when applied to a porous medium and, consequently, may serve to characterize the state of bound water in the gas-bearing and oil-bearing zones of an oil reservoir, these properties were studied on samples of quartz sandstone from the Tuymazy field.

The bound water in the sandstone samples (cores) was modeled by water remaining in the porous medium after displacement of the aqueous phase by nitrogen through a low-permeability diaphragm (^{5}). The displacement of the aqueous phase took place at a pressure $p = 700$ mm Hg, which exceeded the capillary pressure in the smallest pores of the core and corresponded to the region in which the residual water saturation of the core practically no longer depended on the displacement pressure.

It was shown that the method of displacing water from cores through a low-permeability diaphragm can also be used to characterize the properties of thin layers of aqueous solutions in a porous medium.

If distilled water is used as the residual water, then after its displacement by nitrogen it is present in the cores not only in the capillary-retained state but also in the film state, since distilled water on glass and on quartz at the boundary with a gas can exist in the form of equilibrium wetting thin layers (^{6}, ^{7}).

It should be expected that if the influence of electrolyte concentration on the thickness of thin layers of aqueous solutions in a porous medium has the same character as in single capillaries (i.e., with increasing electrolyte concentration the thickness of the thin layers decreases, and at very high mineralization of the water may even become zero), then with increasing electrolyte concentration the amount of liquid displaced from the core through the low-permeability diaphragm should increase.

Figure 1 gives the results of studying the effect of NaCl concentration on the residual water saturation (expressed as a percentage of pore volume) for three cores of different permeability. From the graph (Fig. 1) it is seen that with

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

increasing NaCl concentration the amount of liquid remaining in the core decreases.

Moreover, beginning with a certain concentration C' (different for cores with different permeability), the amount of liquid remaining in the core, with further increase in electrolyte content, practically does not change (a $5N$ NaCl solution is already almost the limiting salt concentration corresponding to the formation of a saturated solution at room temperature). A similar picture was also observed when displacing $AlCl_3$ solutions of various concentrations.

The decrease in the residual water saturation of the cores, caused by the addition of an electrolyte and by an increase in its concentration, is evidently connected with the fact that, for that part of the residual water which is in the film state, the thickness of the thin layers decreases as the electrolyte concentration increases. At the same time, the quantity of liquid displaced from the cores increases. At high electrolyte concentrations, owing to the desalting action of the ions (6,7), the thin layers rupture (1,2). This circumstance makes it possible to understand why, beginning with a certain electrolyte concentration, no further change in the residual water saturation of the cores practically occurs. Apparently, in this case almost all the liquid remaining in the core is in a capillary-held state (in very narrow, subcapillary pores wholly filled with water, in annular menisci formed at narrow points of contact between grains, in blind pores), and also in the form of separate droplets remaining after rupture of the film.

Fig. 1. Dependence of residual water saturation of cores on electrolyte concentration (NaCl): a—$K = 860$ md, b—$K = 430$ md, v—$K = 39$ md

Consequently, it may be assumed that if the electrolyte concentration is less than C', the liquid is present both in capillary-held and partly in film states.

Fig. 2. Dependence of residual water saturation and the mean film thickness on core permeability: a—$5N$ NaCl solution, b—distilled water, v—thickness of the thin layer of distilled water

The decrease in the residual water saturation of the cores with increasing electrolyte concentration cannot be associated with the presence of clay particles in the cores or with a change in the contact angle of wetting.

The presence of clay particles in the cores could not have caused these changes, since their content is small (the sandstone contains 97% quartz and 3% clay

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Fig. 3

Figure 3: Fig. 3

minerals), and, moreover, this is indicated by experiments carried out on cores practically containing no clay particles. The decrease in the residual water saturation of the cores could not have been caused by a change in the contact angle of wetting of electrolyte solutions, since, on the basis of experiments on the impregnation of cores in the apparatus of Z. V. Volkova ([8,9]) with distilled water and a $5N$ NaCl solution, it was established that the values of the kinetic contact angles in both cases practically coincide, reaching 89°. The values of the contact angles measured for both liquids under static conditions (on paraffin) also proved practically identical, being 108–110°.

Thus, on the basis of the data obtained in studying the effect of electrolyte concentration on the residual water saturation of cores (as a result of which the character of the influence of the electrolyte content in the solution on the thickness of thin layers, established earlier ([1,2]) for individual capillaries, was confirmed), the quantity was determined

liquid remaining in the porous medium in a capillary-retained state.

Figure 2 shows curves expressing the dependence of the residual water saturation for distilled water and for a $5N$ NaCl solution on the permeability of the cores. It is evident from Fig. 2 that, at a permeability of the porous medium of 800–1000 md and higher, the amount of remaining liquid does not depend on permeability*. Curve 2 in Fig. 2 shows the dependence of the amount of capillary-retained liquid in the porous medium on its permeability. It follows from Table 1 that the amount of capillary-retained liquid in the porous medium is practically independent of the nature of the electrolyte.

Fig. 3. Dependence of the average thickness of a film of distilled water in a porous medium on the value σ/r

Distilled water, as residual liquid in a porous medium, consists of both film water and capillary-retained water. From the difference between the total amount of residual liquid in the cores and the amount of capillary-retained liquid, and from the value of the specific surface area of the cores, one can estimate the average thickness h of films of distilled water in cores of different permeability.

The values of the specific surface area were calculated from the permeability and porosity of the cores according to P. Carman (11). From the literature it is known that the values of specific surface area calculated by this method are lower than the actual values (12–14). On the basis of these considerations it should be assumed that the results of calculating the thickness of films in a porous medium must be somewhat smaller, and then they will agree with the results obtained earlier for equilibrium layers on simple geometric systems (6, 7). The graph of the dependence $h = f(k)$ is also shown in Fig. 2.

From Fig. 3, which gives the dependence of the average thickness of a water film (distilled) in a porous medium on the value σ/r**, proportional to the disjoining pressure of a cylindrical thin layer, it is seen that in a porous medium, just as was shown on a flat solid surface (6, 7) and in capillary systems (1–4), the average layer thickness, other conditions being equal, is determined by its disjoining pressure.

Table 1

Dependence of the amount of capillary-retained liquid in a porous medium on the nature of the electrolyte

Core No.	Permeability K, md	Residual water saturation S, %	Residual water saturation S, %	Residual water saturation S, %	Residual water saturation S, %
Core No.	Permeability K, md	$5N$ NaCl solution	$4N$ KCl solution*	$5N$ $CaCl_2$ solution	$5N$ $AlCl_3$ solution
13	39	15.7	15.0	15.0	13.3
27	430	4.0	3.8	4.0	3.9
29	850	3.2	3.3	3.0	4.0

* A $4N$ solution is the limiting concentration of KCl, above which a saturated solution forms.

The influence of the valence of the electrolyte cations on the thickness of thin layers of aqueous solutions in a porous medium was also checked by the value of the residual water saturation of the cores.

When comparing the residual saturation of the same cores with aqueous solutions of salts with monovalent and trivalent cations (NaCl and $AlCl_3$) of equal concentrations, it was established that at relatively low concentrations of the solution, for equal values of these concentrations, the residual saturation of the cores with $AlCl_3$ solutions is lower than with NaCl solutions. This result is evidently connected with the fact that, for that part of the residual liquid which at relatively low electrolyte concentrations is in the film state, the thickness of thin layers of $AlCl_3$ solutions is less than that of NaCl solutions. At high concentrations of these salts, differences in residual saturation with $AlCl_3$ and NaCl solutions were practically not observed, which may be explained by the complete destruction of the thin wetting layers at high electrolyte concentrations, noted above.

* As established in work (10), the dependence of residual water saturation on core permeability is different for different deposits.

** The radius r of the pores was taken to be the mean radius calculated from the relation $r = \sqrt{8K/m}$, where m is the porosity of the cores.

The experimental results set forth above show that the properties of thin layers, studied in single capillaries at the interface: air | aqueous electrolyte solution | glass or quartz, are fully preserved in porous media as well. Consequently, the conclusion drawn earlier (1, 4) remains valid: that the state of bound water, in particular in gas-bearing reservoirs, when it consists of electrolyte solutions, is determined by the physicochemical properties of the liquid.

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CITED LITERATURE

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