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Physical Chemistry

D. N. Nekrasov and M. M. Kusakov

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Abstract

Full Text

Physical Chemistry

D. N. Nekrasov and M. M. Kusakov

CAPILLARY RISE OF A LIQUID IN POROUS MEDIA AND CAPILLARY HYSTERESIS

(Presented by Academician A. V. Topchiev, 11 IV 1960)

As shown in ([1]), during the rise of a nonviscous liquid in capillary tubes of circular variable cross section there may exist several equilibrium heights of rise (capillary hysteresis), depending on the shape of the capillary. In the case of a porous medium consisting of an infinitely large number of capillaries of different cross section, of complex shape, and communicating with one another, the problem of capillary rise cannot be solved analytically. However, if one proceeds from the notion of a vertically arranged equivalent capillary with circular variable cross section*, then, using the method set forth in ([1]) and experimental data on the capillary rise and lowering of a liquid in real porous media, it can be shown that in this case capillary hysteresis is expressed in the existence of an infinite number of heights of rise lying between two limiting (minimum and maximum) values.

For such an equivalent capillary the system of equations

$$h\rho g = \frac{2\sigma}{r};$$

$$r = f(h), \tag{1}$$

where h is the height of capillary rise, ρ is the density of the liquid, g is the acceleration due to gravity, σ is the surface tension of the liquid at the boundary with its saturated vapor, and r is the radius of the capillary, will have an infinite number of roots $(h_1)_{\min} < h_2 < \cdots < (h_n)_{\max}$. The potential energy U of the wetting liquid for this case will have the form

$$U = -\rho g \int_0^V (p_k - h)\, dV, \tag{2}$$

where p_k is the capillary pressure, expressed in the same units as the height h of the liquid column, and V is the volume of liquid in the capillary. For a real porous medium the potential energy U will have a form analogous to (2), but the quantities $p_k - h$ and V can be measured experimentally. Having obtained

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Fig. 1. Dependence of the potential energy of the forces of gravity and capillary forces acting on a liquid in a porous medium on the mean height of capillary rise of the liquid

Figure 1: Fig. 1. Dependence of the potential energy of the forces of gravity and capillary forces acting on a liquid in a porous medium on the mean height of capillary rise of the liquid

from experiment the graph of the dependence $V = f(p_k - h)$, one can graphically calculate the value of U for each value of the mean height $\bar{h} = \frac{V}{S}$, where S is the porosity of the porous medium (which may be regarded as constant), and thus obtain the graph of the dependence $U = f(\bar{h})$. From the condition $\frac{\partial U}{\partial h} = 0$, the equilibrium heights of capillary rise of the liquid can be found.

* In this case the shape of the capillary, determined by the equation $r = f(h)$, may be arbitrarily complex.

Experimental verification of this method was carried out on the capillary rise of water in porous media consisting of hydrophilic quartz sand with grain sizes from 0.075 to 0.45 mm. The apparatus made it possible to observe the capillary rise and lowering of the liquid in the porous medium and to measure quite accurately the change in the volume of water in the porous medium at different values of $\rho_k - h$.

Fig. 1. Dependence of the potential energy of the forces of gravity and capillary forces acting on a liquid in a porous medium on the mean height of capillary rise of the liquid

Figure 1 shows the graph of the function $U = f(\bar{h})$ for one of such porous media (grain size from 0.35 to 0.42 mm). Curve 1 corresponds to capillary rise. The minimum value $U = 0$* corresponds to the minimum mean height $(\bar{h}_1)_{\text{min}} = 15.42$ cm of the equilibrium capillary rise of water in the porous medium. The curves 2–6, calculated as examples (the number of such curves may be arbitrarily large), correspond to the lowering of water from heights $h > (\bar{h}_1)_{\text{min}}$. Raising the liquid to a height greater than $(\bar{h}_1)_{\text{min}}$ was achieved by a corresponding change in the magnitude and sign of $\rho_k - h$.

As can be seen from Fig. 1, each of the curves 2–6 has a minimum corresponding to the equilibrium height of capillary retention of the liquid as it is lowered in the porous medium. The locus of points corresponding to the minima of the potential energy forms curve 7, which passes into the straight line $h = (\bar{h}_n)_{\text{max}}$, where $(\bar{h}_n)_{\text{max}}$ is the maximum value of the mean height of capillary rise of water in the porous medium. When the liquid is raised to a height $h > (\bar{h}_n)_{\text{max}}$ and then subsequently lowered, the liquid is retained in the position corresponding to the height $h = (\bar{h}_n)_{\text{max}}$. For the case shown in Fig. 1, $(\bar{h}_n)_{\text{max}} = 24.28$ cm. All the other experimentally observed heights of capillary rise of water in the porous medium satisfy the condition 15.42 cm $< \bar{h} <$ 24.28 cm. The most stable is the minimum height $(\bar{h}_1)_{\text{min}}$, corresponding to the smallest value of

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the potential energy U.

Thus, from consideration of the general conditions of equilibrium of a liquid and experimental verification of these conditions, it follows that in the case of porous media capillary hysteresis is expressed in the existence of an infinitely large number of equilibrium heights of capillary rise, lying between the minimum and maximum values.

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* As in (1), on the graph $U = f(\bar{h})$ the value $U = 0$ is conventionally combined with the minimum value of the energy.

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

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