DESICCATION THERMOGRAMS FOR DISPERSE MATERIALS MOISTENED BY VARIOUS LIQUIDS

II. DESICCATION THERMOGRAMS FOR ARGILLACEOUS MINERALS

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It is shown here that the method of desiccation thermograms with various moistening liquids makes it possible to thoroughly study the sorptive properties and the fine porous structure of argillaceous minerals.

In the earlier article [1] the authors have shown that the method of desiccation thermograms with the test specimens moistened by various liquids is useful for studying rather thoroughly the sorptive properties and the microporous structure of those capillary-porous materials (macrogels) whose porous structure is permanent and independent of the moistening liquid. In this article we will describe the results of analyzing the desiccation thermograms for argillaceous minerals (capillary-porous colloidal materials), also moistened by various liquids.

TABLE 1. Comparison of Results Obtained by the Sorption Method and by the Desiccation Thermograms Method

Specimen	Moistening liquid	Mass content at the critical points on desication thermograms (·10^3 mM/g)			Quantity of liquid at φ =1 (from adsorption isotherms) ·10^3 mM/g
		W_1	W_2	W_{1a}	
Mountain leather	Water	74	7,5	21,2	23 [4]
	Methanol	13,6	5,3	11,5	15 [4]
	Butanol	7,6	4,7	6,1	—
	Benzene	9,9	1,5	5,6	5,5 [4]
	Cyclohexane	2,9	0,9	2,0	3,6 [6]
	Heptane	2,4	0,9	1,6	1,8 [5]
Montmorillonite	Water	35,0	6,0	16,9	17,0 [7]
	Methanol	11,3	4,0	6,5	7,2 [8]
	Butanol	9,5	1,5	2,3	—
	Benzene	2,4	1,3	1,6	1,6 [8]
	Cyclohexane	1,3	0,6	0,7	0,6 [6]
	Heptane	1,0	0,5	0,5	0,4 [5]
Hydromica	Water	56,0	3,1	16,0	14,0 [9]
	Methanol	13,0	9,5	10,7	—
	Butanol	9,1	3,1	3,5	—
	Benzene	3,0	1,1	2,0	—
	Cyclohexane	4,7	1,1	2,1	2,4 [6]
	Heptane	2,1	1,8	1,9	2,0 [5]
Kaolinite	Water	69,3	2,7	12,8	13,0 [10]
	Methanol	13,2	1,8	7,8	—
	Butanol	6,4	0,6	2,3	—
	Benzene	6,5	1,5	2,5	—
	Cyclohexane	9,0	0,6	1,4	1,0 [6]
	Heptane	2,8	0,5	1,3	—

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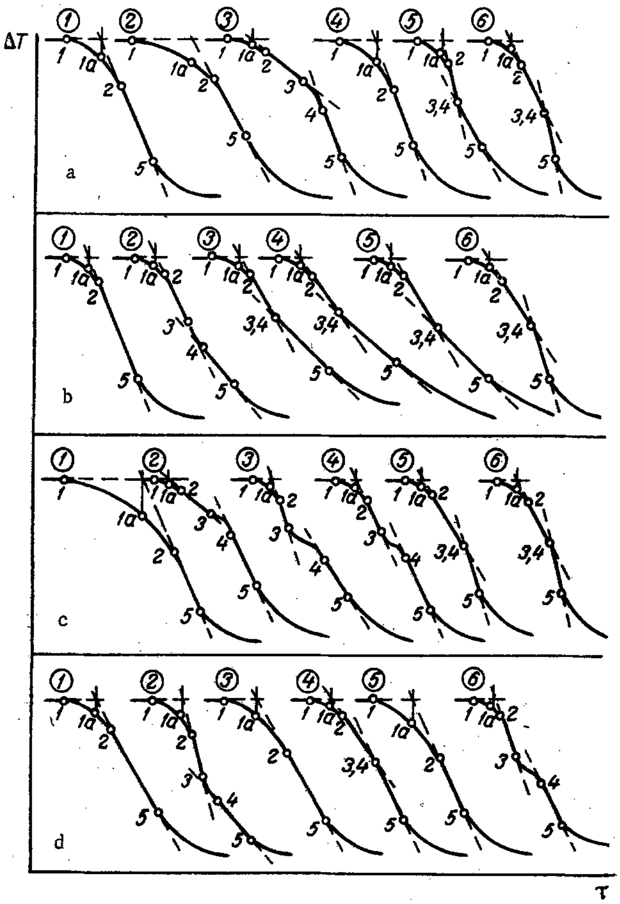

Fig. 1. Desiccation thermograms for: montmorillonite (a), hydromica (b), kaolinite (c), moistened by water (1), by methanol (2), by n-butanol (3), by benzene (4), by cyclohexane (5), by n-heptane (6). Temperature difference between specimen and air ΔT, testing time τ.

Here, as before, we considered two problems. The first one was to establish the kinetic laws governing the evaporation of liquids with various properties from various capillary-porous materials. The second one was to determine aqueous properties and the porous structure of argillaceous minerals from desiccation kinetic curves. Both aspects of the study are of interest for the analysis and the design of heat and mass transfer processes in the treatment of capillary-porous colloidal materials.

Argillaceous minerals are highly disperse systems whose porous structure is not permanent but formative during interaction with one or another liquid. The very concept of "pore dimensions" does not apply here in a unique sense, because the latter depend not only on the properties of these minerals but also on the physico-chemical properties of the liquid. Moistening an argillaceous mineral by one liquid such as water, for example, and plotting the desiccation thermogram will not, therefore, yield all the information about the porous structure. Meanwhile, plotting the desiccation thermograms for the same argillaceous mineral moistened by liquids whose physicochemical properties and molecule sizes are different, polar and apolar liquids used as "molecular probes," can yield more complete information about the porous structure of such a capillary-porous colloidal material.

For this study we had selected four typical argillaceous minerals with different structural-sorptive characteristics: mountain leather, montmorillonite, hydromica, and kaolinite. They were moistened by six liquids of different size molecules, both polar ones (water, methanol, n-butanol) and apolar ones (benzene, cyclohexane, n-pentane). The properties of these liquids were listed in [1].

The preparation of specimens and the test procedure for plotting the thermograms and the desiccation kinetics curves were as described earlier [1]. The tests were performed at various temperatures and

TABLE 2. Capacity of Adsorptive Monolayer in tne Test Specimens

Specimen	Moistening liquid	Quantity of moisture in monolayer ($\cdot 10^3$mM/g)		Specific surface (m^2/g)	
		according to desiccation thermograms	according to BET	according to point 5 on the thermograms	according to BET
Mountain leather	Water	5,2	5,9 [13]	340	380 [13]
	"		4,5 [14]		290 [14]
	Methanol	2,8	2,1 [4]	310	218 [4]
	Butanol	1,3	—	226	— [5]
	Benzene	0,8	0,5 [5]	152	120 [6]
	Cyclohexane	0,4	0,42 [6]	93	99 [5]
	Heptane	0,5	0,42 [5]	142	160
Montmorillonite	Water	4,0	4,8 [14]	250	310 [14]
	Methanol	1,8	—	194	—
	Butanol	0,8	—	145	—
	Benzene	0,6	0,25 [5]	112	60 [5]
	"		0,90 [15]		212 [15]
	Cyclohexane	0,3	0,21 [6]	52	49 [6]
	Heptane	0,2	0,18 [5]	73	71 [5]
Hydromica	Water	2,2	2,4 [14]	136	157 [14]
	Methanol	1,5	—	160	—
	Butanol	0,8	—	132	—
	Benzene	0,6	0,5 [5]	110	118 [5]
	Cyclohexane	0,5	0,42 [6]	98	99 [6]
	Heptane	0,4	—	115	—
Kaolinite from Glukhov	Water	1,4	1,4 [10]	88	94,2 [10]
	"		1,1 [15]		76,0 [15]
	Methanol	0,6	—	68	—
	Butanol	0,4	—	73	—
	Benzene	0,4	—	76	—
	Cyclohexane	0,3	0,29 [6]	70	68 [6]
	Heptane	0,2	—	67	—

pressures in a thermobarometric chamber shown in [16]. The data in Tables 1 and 2 were obtained in air at a 310°K temperature and an approximately $2.6 \cdot 10^3 N/m^2$ pressure.

Typical desiccation thermograms obtained in our tests for various argillaceous minerals are shown in Fig. 1.

All the argillaceous minerals moistened by water have S-shape desiccation thermograms with one straight-line segment between the critical points 2 and 5, unlike the thermograms for polycapillary-porous materials (macrogels) with two such sloping segments [1]. This shape of the thermograms is explained by the flexible structure of argillaceous minerals moistened by water and, consequently, the absence in it of macropores. We note that in this study macropores and micropores are, according to [2], differentiated on the thermograms on the basis of the relative equilibrium vapor pressure, which is close to unity in macropores but less than unity in micropores. On the other hand, the high plasticity and fluidity of argillaceous suspensions with a high moisture content is related to the presence of large quantities of osmotic water with a very low bond energy. The first critical point on a thermogram corresponds here to the beginning of evaporation of osmotic water, as has been confirmed in recent tests with ion-substituted clay [3] by a comparison of desiccation thermogram data with nuclear-magnetic-resonance data.

In Table 1 are given the mass contents in the argillaceous minerals which correspond to points 1, 2, and 1a on their thermograms (the critical point 1a, as can be seen, lies on the intersection of the straight-line thermogram segments). For comparison, in Table 1 are also given the maximum hygroscopic mass holding capacity of the same specimens, which has been obtained from adsorption isotherms at $\varphi = 1$. It is evident here that the maximum hygroscopic moisture holding capacity of argillaceous minerals corresponds closely to the moisture content at the critical point 1a between points 1 and 2. During the desiccation of argillaceous minerals moistened by water, therefore, osmotic water evaporates first along the segment between the critical points 1 and 1a, whereupon past the critical point 1a water evaporates from microcapillaries.

For argillaceous minerals moistened by any other liquid, the mass content at the critical point 1a on a thermogram also corresponds closely to the maximum hygroscopic mass holding capacity of specimens, as determined from isotherms and shown in Table 1. The physical significance of segment 1-1a is different here, however. Specimens dried prior to the experiment and sifted into grains 0.25-0.50 mm in size do not, after having been moistened by any liquid other than water, spontaneously disperse but, instead, remain in the granular state. In thermogram plotting tests, therefore, until the first critical point 1a there occurs evaporation not only of osmotically bonded liquid but also essentially of liquid from macropores of the intergranular space. After the critical point 1a on the thermograms for all specimens, liquid from microcapillaries begins to evaporate under an equilibrium vapor pressure (relative) less than unity.

Curves 2-6 on the diagram indicate that the shape of thermograms and the number of critical points on them differ for the same specimen moistened by different liquids. The obvious dependence of the lower thermogram range on the energy of interaction between the adsorbed liquid and the solid phase [11] leads to the hypothesis, as shown in [12], that the presence of several straight-line segments on the thermograms here is due to different energy levels of the bond between liquid molecules and solid surface.

The mass content at the critical point 5 on the thermograms for all specimens moistened by any liquid corresponds closely to the quantity of adsorbed liquid with the strongest bond, usually called the quantity of liquid in a monolayer. This has been confirmed by a comparison between the mass content at the critical point 5 on a thermogram, with the quantity of liquid in a monolayer determined from adsorption isotherms according to the BET procedure (Table 2).

From the quantity of liquid corresponding to the critical point 5 on a thermogram, we have determined the specific surfaces of the test specimens. These data are also listed in Table 2 along with analogous specific surfaces obtained by the BET procedure. According to this table, the method of desiccation thermograms yields values of specific surface which agree closely with those obtained by the BET procedure. For this reason, the method of desiccation thermograms may be considered entirely suitable for determining the specific surface of a capillary-porous colloidal material, on par with the widely used sorption methods.

A comparison between the values of specific surface obtained when the same specimen has been moistened by different liquids indicates that the sorptive properties of the tested argillaceous minerals depend not only on the molecule size of the moistening liquid but also, above all, on the peculiarities of interaction between the solid phase and one or another liquid. Thus, mountain leather crystals have a strongly developed inner surface owing to canals with very definite dimensions (6.4 × 3.7 Å) [15]. In consequence, relatively small water or methanol molecules can penetrate and be sorbed in the canals without obstacles, while large benzene, cyclohexane, or heptane molecules are sorbed essentially at the outer surface of mountain leather particles. For this reaon, probably, the specific surface of mountain leather is largest with respect to water and methanol. An essential factor here is also the shape of molecules: the specific surface with respect to cyclohexane with molecules in the shape of disks is much smaller than with respect to heptane with elongated molecules, although the molal volume of the former is smaller than that of the latter. At the same time, the adsorption level of different liquids by mountain leather depends not only on the size and the shape of molecules but also on the properties of these molecules, especially on their dipole moment.

In the case of montmorillonite, as in the case of mountain leather, adsorption occurs essentially within the interlayer space between argillaceous particles and only partly at the outer surface. Unlike in mountain leather, however, the crystal lattice in montmorillonite is mobile and, as a result, the structure of this mineral changes during adsorption. Molecules of the moistening liquid penetrate the interlayer space and widen the interplanar distance in unit cells of a crystal. At that time, the degree of "flexibility" depends strongly on the dipole moment of the sorbate molecules [8]. For this reason, the specific surface of montmorillonite is much larger with respect to water, methanol, and butanol than with respect to benzene, cyclohexane, and heptane.

A different pattern is noted in the case of hydromica and kaolinite. The structure of these minerals is determined basically by the intercrystalline pores. Hydromica crystals are of a regular round shape with a weakly developed microporous structure, while kaolinite has a rigid linkage between intracrystalline clusters [8, 15]. As a consequence, all liquids are adsorbed only behind the outer crystal surface. Accordingly, as can be seen in Table 2, the specific surface of hydromica depends very little on the dimensions and the dipole moments of the moistening liquid molecules (no dependence at all exists in the case of kaolinite).

Thus, our experiments have established that desiccation thermograms for argillaceous minerals moistened by various liquids are determined, with regard to the shape of the curves and the locations of the critical points on them, by the structural properties of these materials as well as by the interaction characteristics of the moistening liquid and the solid phase. The pattern of moisture extraction in successive stages, one form and with one kind of bond after another, prevails here not only in the case of water but also in the case of various liquids with other physicochemical properties. It has been shown, furthermore, that the method of desiccation thermograms with various liquids used as "molecular probes" is suitable for a rather complete study of the sorptive properties and the structure of argillaceous minerals.

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