DRYING-PROCESS THERMOGRAMS OF COLLOIDAL DISPERSIONS CONTAINING VARIOUS MOISTURES

I. DRYING THERMOGRAMS OF BRITTLE GELS

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The mode of successive evaporation, which had been applied to water variously bonded to a colloidal dispersion during the drying process, is extended to other liquids and is used in an analysis of the drying thermogram. It is shown that the drying thermogram method of analysis applied to brittle gels containing various liquids makes it possible to thoroughly study their adsorption characteristics and microporous structure, with the aid of the molecular-sieving effect.

The pore structure of colloidal dispersions is now widely studied by the drying thermogram method [1], which in turn is based on the laws of evaporation kinetics for variously bonded liquids. In all such studies so far, except in [2], only water was used as the evaporating liquid. With liquids having other properties, on the other hand, new ways may become feasible in which the drying thermogram method could be used for studying the pore structure of colloidal dispersions.

In this article we will analyze the drying thermogram for typical dispersions with a rigid structure (brittle gels) containing various moistures. We set out here with two objectives: first of all, to explain the physical significance of the critical points on the drying thermograms for various liquids and, secondly, to explain the possibilities of using the drying thermogram method with various liquids for a study of the microporous structure of colloidal dispersions.

A study was made on adsorbents including seven silica gels of different porosities with the effective pore radius ranging from 10^{-9} to 10^{-8} m and also microporous activated carbon. As characteristics of their pore structure we determined the isotherms of vapor adsorption for all specimens. The effective pore radii in these specimens (without correction for the thickness of the adsorption film), calculated from the isotherms of water adsorption and also often taken from published sources [3-5], are given in Table 4. It can be seen in Table 4 that the silica gels chosen for this study adequately represent all types of structure with various porosity levels [4].

As the adsorbates we selected liquids with various sizes of molecules and various dipole moments. We used here liquids with boiling points not below 40-60°C and yet sufficiently volatile. Altogether three polar liquids (water, methanol, n-butanol) and three nonpolar liquids (benzene, cyclohexane, n-heptane) were selected. The effective diameters and areas of their molecules, calculated by conventional formulas [6] and also taken from published sources, are given in Table 1. All unreferenced data in these tables have been obtained by the authors.

Prior to the experiment, each adsorbent was dried at 105°C so as to free it of any moisture sorbed from the air, then cooled in a desiccator over phosphor anhydride, and filled directly in the desiccator with a given test liquid. In this way, each drying thermogram corresponded to the evaporation of one specific liquid without interference from the evaporation of water.

Thermograms and drying curves in these tests were recorded with laboratory instrumentation which had been described in [5]. All tests were performed under identical conditions: air temperature 50°C, air

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TABLE 1. Effective Dimensions of Molecules in the Test Liquids

Adsorbate	Molecule diameter $\cdot 10^{-10}$ m, according to the formula in [6]	Molecule area according to the formula in [6]	10^{-20} m^2 according to data in published sources
Water	3.44	10.6	11.5 [7] 14.8 [8.9] 20-25 [10]
Methanol	4.37	18.2	17.6 [11]
n-butanol	5.60	29.2	—
Benzene	5.72	30.8	30.3 [11] 40 [12.13] 49 [14]
Cyclohexane	6.06	36.1	—
n-heptane	6.74	55.1	80 [14] 57 [13]

pressure $3 \cdot 10^3$ N/m^2, and pumping rate of air constant. Such a mode of operation corresponds to approximately 0.8 kJ/g of free energy of water vapor in the drying air [16], which is equivalent to drying under atmospheric pressure at 105°C. This eliminated any possibility that a specimen would adsorb water vapor from the air while one of the other liquids was evaporating from it. At the same time, this mode of drying ensured a sufficiently high evaporation rate of any of the test liquids and, accordingly, a clear definition and a good reproducibility of their thermograms. Two of the given silica gels were, furthermore, moistened with each of the given liquids and tested in different modes corresponding to different drying rates. It has become apparent here that the mass contents which correspond to the critical points on the drying thermogram remain the same, within test accuracy, at different drying modes. The earlier conclusion [15] that the mass content at the critical points on the thermogram is independent of the drying rate in the case of water appears thus to be valid for all the liquids used in this experiment.

Typical drying thermograms obtained here are shown in Fig. 1.

As is well known [1], the initial range of a drying thermogram up to the critical point 3 corresponds to the evaporation of almost unbonded liquid from the intergranular space and from macropores larger than 10^{-7} m in radius in a colloidal dispersion. The differences between the physicochemical properties of the various evaporating liquids do not come much into evidence within this range of thermogram. The range beyond the critical point 3 corresponds to the evaporation of both a liquid from the micropores and of adsorbed liquid in a specimen. Within this range of the thermogram the physicochemical properties and the size of the liquid molecules are necessarily reflected most strongly. For that reason, we are concerned here with this range of the thermogram.

The mass content in specimens at the critical point 3 on the drying thermogram (W_3) is shown in Table 2. It is evident here that, when all specimens are moistened with water, their W_3 values approach closely their hygroscopic moisture capacity determined from the adsorption isotherms. Such a coincidence is observed also in the case of other liquids, wherever reliable sorption data are available. For all specimens, furthermore, the values of W_3 expressed in units of volume per 1 kg of adsorbent are close, which agrees with the Gurvich law [19]. Some difference in the W_3 values for the various liquids has, probably, to do with the fact that the Gurvich rule is not obeyed exactly by microporous adsorbents. The reasons for this have been discussed thoroughly in [6]. Thus, the data in Table 2 lead us to the conclusion that the critical point 3 on the drying thermogram for colloidal dispersions corresponds to the maximum hygroscopic mass capacity of specimens with respect to each of the test liquids. Unlike in sorption measurements, moreover, where determining the maximum hygroscopic mass capacity ($\varphi \to 1$) is connected with serious difficulties, point 3 on the drying thermogram is found rather easily.

The critical points 4 and 5 on the drying thermogram for brittle gels containing water corresponds to the quantity of poly- and monomolecular water adsorption [1, 15]. When specimens contain other liquids the physical significance of the critical points 4 and 5 on a drying thermogram can be explained by comparing the mass contents of specimens at these points with the quantities of adsorbed substance in a monolayer and in polylayers which have been determined from the isotherms. Such a comparison is made in Table 3.

A comparison of the data in Table 3 shows that the mass content in each specimen at the fifth critical point on the thermogram is close to the quantity of the same liquid adsorbed under a 10% relative vapor

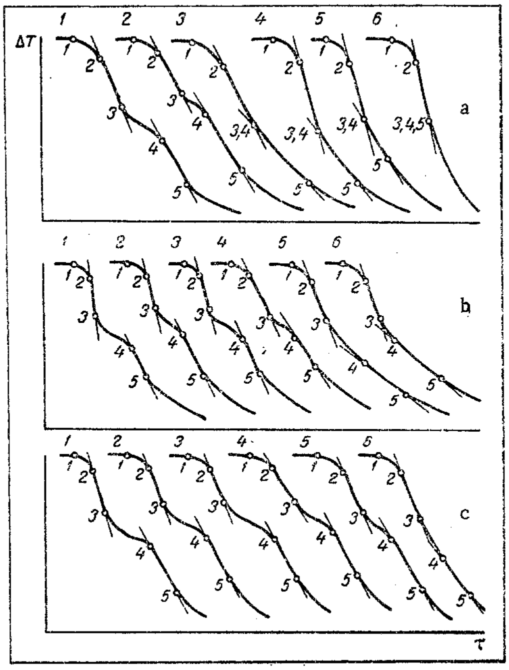

Fig. 1

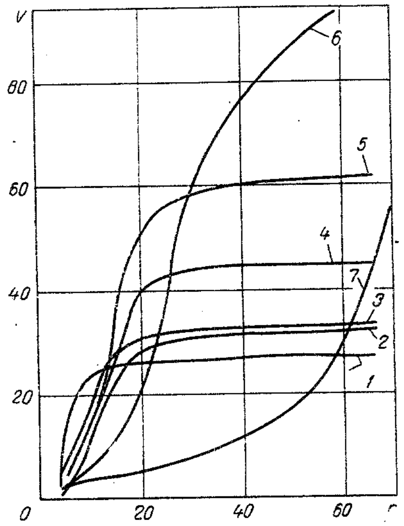

Fig. 2

Fig. 1. Drying thermograms of grade MSM silica gel and activated carbon (a), grade KSM-1 and KSM-5 silica gels (b), grade KSS-4, KSK-2, E, V silica gels (c); 1) moistened with water; 2) methanol; 3) butanol; 4) benzene; 5) cyclohexane; and 6) heptane. ΔT) Temperature difference between specimen and air; τ) test time.

Fig. 2. Integral curves of pore distributions in: 1) MSM silica gel; 2) activated carbon; 3) KSM-1 silica gel; 4) KSM-5 silica gel; 5) KSS-4 silica gel; 6) KSK-2 silica gel; 7) grade E silica gel. V) Volume of pores ($\cdot 10^{-5}$ m^3/kg); r) radius of pores ($\cdot 10^{10}$ m).

TABLE 2. Comparison of the Maximum Hygroscopic Mass Capacity of Specimens Determined from Drying Thermograms and from Adsorption Isotherms

Specimen	Mass content at the 3rd critical point on the thermogram $W_3 \cdot 10^4 m^3/kg$ when moistened						Maximum hygroscopic mass capacity of specimens $W_3 \cdot 10^4 m^3/kg$ according to the adsorption isotherms			
	with water	methanol	butanol	benzene	cyclohexane	heptane	of water	methanol	benzene	heptane
MSM	2,4	2,7	1,4	2,5	2,2	2,3	2,7 2,7 [4] 2,4 [18]	2,5 [17]	2,1 [17]	2,1 [17]
KSM-5	4,5	4,8	3,5	4,2	4,2	4,4	4,5 4,7 [10] 4,8 [4]	—	4,4 [10]	—
KSM-1	2,9	3,0	2,2	3,2	3,0	2,7	2,5 [17]	2,5 [3]	2,1 [17]	2,1 [17]
KSS-4	5,9	6,9	4,8	5,7	5,8	5,9	6,2 6,3 [10]	—	6,3 [10]	—
KSK-2	9,6	10,1	8,4	9,6	10,0	9,4	10,0 10,4 [10] 9,0 [4]	—	9,9 [10]	—
E	14,9	14,8	12,5	14,6	16,4	15,3	16,0 [4]	17,2 [3]	17,2 [3]	17,2 [3]
V	4,3	4,6	3,7	4,7	4,2	4,3	—	—	—	—
Carbon	3,0	3,3	2,5	2,8	2,9	2,4	3,2	3,1	—	—

TABLE 3. Comparing the Quantities of Adsorbed Liquid on the Basis of Drying Thermograms and on the Basis of Adsorption Isotherms

Specimen	Quantity of adsorbed liquid $W_3 \cdot 10^3$ kmole/kg at the 4th and 5th critical point on the thermogram (W_4 and W_5), determined from the adsorption isotherm at $\varphi = 0.1$ (a_1) and at the beginning of hysteresis (a_2):																				
	water				methanol			butanol			benzene				cyclohexane		heptane		
	W_5	a_1	W_4	a_2	W_5	a_1	W_4	W_5	a_1	W_4	W_5	a_1	W_4	a_2	W_5	W_4	W_5	a_1	W_4
MSM	3,9	4,0 3,8 [17] [18]	5,9	6,1 [17]	3,4	3,0 [17]	6,7	1,5	1,8 [17]	1,6	1,9		2,8		1,5	1,9	1,6		1,6
KSM-5	1,1	1,4	2,3		1,9	–	3,0	1,5		1,8	1,1	1,1 [20] 1,8 [12]	2,0	2,5 [10]	0,3	0,6	0,6		1,3
KSM-1	2,3	2,7 1,6 [17]	3,9		2,2	2,7 [17]	3,8	1,1		1,3	0,8		1,4		0,7	1,2	0,7		1,3
KSS-4	1,6	1,4 1,9 [10]	3,1		1,4		2,4	1,6		2,0	1,0		2,1		0,4	0,8	0,5		1,1
KSK-2	1,1	1,0 1,3 [10]	2,6		1,1		2,3	2,1		3,5	0,7	0,6 [20] 0,7 [12]	2,3	2,7 [12]	0,5	0,9	0,3		0,7
E	1,4	1,4 1,1 [12] 1,7 [4]	2,9	4,0 [4]	0,9	1,0 [5]	1,5	1,4		1,8	0,4	0,5 [17]	1,1		0,2	0,4	0,2	0,2 [3,17]	0,4
V	1,5	2,0	2,8		2,2		3,4	1,5		1,8	0,8		1,7		0,2	0,4	0,3		0,6
Carbon	0,7	0,8	1,2		0,6		1,2	2,5		2,8	2,4		2,9		2,4	2,8	1,6		1,6

TABLE 4. Filling the Micropores with Liquids of Various-Size Molecules

Specimen	Effective radius of pores $\cdot 10^{-10}$ m	Quantity of liquid in the micropores of specimens ($W_{3-4} \cdot 10^4$ m^3/kg) moistened with					
		water	methanol	butanol	benzene	cyclohexane	heptane
MSM	10	1,2	0,2	0	0	0	0
KSM-5	13	4,1	3,6	2,2	2,4	3,2	2,4
KSM-1	14	2,2	1,8	1,2	2,0	1,7	0,8
KSS-4	20	5,5	5,9	3,2	3,9	4,5	4,0
KSM-2	41	9,1	9,1	5,6	7,6	9,1	8,4
E	100	14,4	14,2	11,0	13,6	15,9	14,7
V	Heteroporous	3,8	3,2	2,2	3,2	3,6	3,2
Carbon	13	2,8	2,7	0	0	0	0

pressure, under which an adsorbing monolayer is filled completely [21]. The mass content in each specimen at the fourth critical point on the thermogram is approximately twice as high as at the fifth critical point (for the same liquid). If we assume that the heat of adsorption is completely released from a brittle gel by the time the second monolayer is filled up, according to [22, 23], then we may consider the fourth critical point of a thermogram to correspond to the full-capacity adsorption of liquids by the specimens. This conclusion is also supported by the fact that the mass content at the fourth critical point on a thermogram is close to the mass content which corresponds to the beginning of the hysteresis range of an adsorption isotherm (see Table 3). An exception to this rule are microporous silica gels when moistened with macromolecular liquids. In this case the micropores are filled up with a single adsorption layer and, therefore, $W_4 < 2W_5$.

The data in the table show also that, as the size of molecules increases, the quantity of adsorbed liquid in each specimen decreases regularly.

Thus, the results of our study indicate that the critical points 3, 4, and 5 on the drying thermograms of various liquids as well as of water correspond to the respective evaporation limits of variously bonded liquids from colloidal dispersion. One may, then, consider the mode of successive evaporation, which had been developed by Kazanskii [1], is also valid not only for water but also for various other liquids and it may be used for the analysis of drying thermograms where other liquids are evaporating.

The feasibility of determining the quantities of adsorbed liquid and of liquids contained in micropores on the basis of drying thermograms implies that this method can perhaps also be used for studying the microporous structure of adsorbents, with the aid of the molecular-sieving effect ("molecular feeler-gage effect") [24]. This can be seen from Fig. 1 and the data in Table 4, where pore volumes fillable with some liquid during capillary condensation (from the difference in moisture contents at the third and at the fourth critical point on a drying thermogram). Thus, in the ultramicroporous silica gels (MSM) and in activated carbon only water and methyl alcohol fill part of the pores by the mechanism of capillary condensation, while liquids with larger molecules fill up all pores of this silica gel in the primary adsorption process. For this reason, the critical points 3 and 4 separate on the drying thermograms for these specimens containing water and methyl alcohol, while they merge when these specimens contain other liquids. It is characteristic that on the adsorption isotherms for the same specimens containing liquids whose molecules are large there is no hysteresis loop (see Table 3), which indicates that no capillary condensation occurs here. Capillary condensation in the micropores of KSM-5 and KSM-1 occurs with each liquid, but the quantity of capillary condensate decreases as the molecule size increases. This is most pronounced with aliphatic molecules of butanol and heptane, less with aromatic molecules of benzene and cyclohexane. Finally, the volume of capillary condensate in macroporous silica gels is almost independent of the molecule size. This is also confirmed by the data in Fig. 2, where the integral curves of pore distributions have been calculated by the Kelvin equation on the basis of the adsorption isotherms for water vapor, without correction for the thickness of the adsorption layer. It can be seen in Fig. 2 that in the ultramicroporous silica gels (MSM) and in activated carbon more than 90% of the micropores have a radius up to $15 \cdot 10^{-10}$ m large. In the medium-porous specimens of KSM-5 and KSM-1 pores having a radius smaller than $15 \cdot 10^{-10}$ m constitute only 60-70% of the total volume of micropores. In the macroporous specimens most of the volume is taken up by pores having a radius larger than $20 \cdot 10^{-10}$ m.

Thus, the method of the drying thermogram applied to various liquids, with the aid of the molecular-sieving effect, makes it possible not only to determine the volumes of macro- and micropores but also to rather thoroughly study the adsorption characteristics and the microporous structure in colloidal dispersions. The method of the drying thermogram is also distinct from other methods, particularly the sorption method, by its comprehensiveness and speediness.

LITERATURE CITED

1. M. F. Kazanskii, Dokl. Akad. Nauk SSSR, 130, No. 5, 1059 (1960).
2. M. F. Kazanskii, Naukovi Zapiski KDPI Fizika, 25 (1957).
3. N. N. Avgul', O. M. Dzhigit, N. M. Kamakin, A. V. Kiselev, V. Luk'yanovich, I. E. Neimark, and R. Yu. Sheinfain, Dokl. Akad. Nauk SSSR, 76, No. 6, 855 (1951).
4. O. M. Dzhigit, A. V. Kiselev, and I. E. Neimark, Zh. Fiz. Khim., 28, No. 10, 1804 (1954).
5. I. E. Neimark, Ukr. Khim. Zh., 21, 4, 460 (1955).
6. S. Gregg and K. Sing, Adsorption, Specific Surface, Porosity [Russian translation], Mir (1970).
7. S. Brunauer, Adsorption of Gases and Vapors [Russian translation], IL, Moscow (1948).
8. W. D. Harkins, The Physical Chemistry of Surface Films, Reinhold Publ. Co. (1952), p. 235.
9. A. V. Kiselev, Usp. Khim., 14, No. 5 (1945).
10. V. P. Dushchenko, M. S. Panchenko, I. A. Romanovskii, and I. B. Slinyakova, Inzh.-Fiz. Zh., 15, No. 4, 633 (1968).
11. M. M. Dubinin, E. D. Zaverina, and L. V. Radushkevich, Zh. Fiz. Khim., 21, No. 11 (1947).
12. A. V. Kiselev and Yu. A. El'tekov, Dokl. Akad. Nauk SSSR, 100, No. 1 (1955).
13. A. V. Kiselev, Proceeding of the Second International Congress of Surface Activity, Butterworth Ltd., London (1957), p. 169.
14. A. V. Kiselev, Usp. Khim., 25, No. 6 (1956).
15. M. F. Kazanskii, R. V. Lutsyk, and V. M. Kazanskii, in: Heat and Mass Transfer in Dispersion Systems [in Russian], Izd. AN BSSR, Nauka i Tekhnika, Minsk (1965), p. 136.
16. V. M. Kazanskii, Inzh.-Fiz. Zh., 20, No. 5, 787 (1971).
17. A. V. Kiselev, in: Methods of Studying the Structure of Highly Dispersed and Porous Materials [in Russian], Izd. AN SSSR (1953).
18. A. V. Kiselev, in: Methods of Studying the Structure of Highly Dispersed and Porous Materials [in Russian], Izd. AN SSSR (1958).
19. L. Gurvich, Zh. Fiz. Khim., 47, 805 (1915).
20. M. M. Dubinin, in: Methods of Studying the Structure of Highly Dispersed and Porous Materials [in Russian], Izd. AN SSSR (1953).
21. A. V. Lykov, Theory of Drying [in Russian], Énergiya, Moscow (1968), p. 46.
22. A. V. Kiselev, K. G. Krasil'nikov, N. L. Pokrovskii, N. N. Avgul', O. M. Dzhigit, and K. D. Shcherbakova, Zh. Fiz. Khim., 26, No. 7, 986 (1952).
23. N. N. Avgul', O. M. Dzhigit, A. V. Kiselev, A. A. Isirikyan, and K. D. Shcherbakova, Dokl. Akad. Nauk SSSR, 77, No. 4, 625 (1951).
24. M. M. Dubinin, Vestnik Akad. Nauk SSSR, No. 3, 19 (1949).