ISSN 1061-933X, Colloid Journal, 2016, Vol. 78, No. 3, pp. 391–396. © Pleiades Publishing, Ltd., 2016.
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Thermogravimetric Determination of Specific Surface Area for Soil Colloids

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Recieved May 30, 2015

Abstract—A simple and easy method based on differential drying of samples at different temperatures has been proposed for quantitative determination of the specific surface areas of colloidal disperse systems. The following fundamental dependence of moisture thermodynamic potential [Ψ] on absolute drying temperature T is used in the method: $\Psi = Q - aT$, where Q is the specific heat of evaporation and a is a parameter related to the initial temperature and relative air humidity in an external thermodynamic reservoir (laboratory apartment). Gravimetric data on moisture mass fraction W and the value of Ψ have been used to plot Polanyi potential curves $W(\Psi)$ for the studied samples. The curves have been employed to calculate the isotherms of moisture sorption. The capacity of a monolayer and the effective specific surface area have been determined from these isotherms in terms of the BET theory. The surface area estimated from the published results of classical experiments is about 1000 m^2/g. The problem of the "absolute zero of humidity," which is of great importance for determining the properties of colloidal disperse bodies normalized with respect to the solid phase mass, has been discussed.

DOI: 10.1134/S1061933X16030170

INTRODUCTION

Effective specific surface area S is one of the most frequently used quantitative parameters of dispersity. Several methods and instruments have been proposed for its determination by measuring the adsorption of different substances on the surface of examined disperse bodies [1–4]. In some cases, the S values of samples are found by comparing the amount of an adsorbed (desorbed) substance with that obtained for a reference adsorbent with a known specific surface area; however, S is, more frequently, calculated from the experimentally measured sorption isotherms (SIs) using the BET model for their approximation [1, 3, 4]. This model is believed to enable one to calculate more precisely, as compared with its prototype, the Langmuir equation, monolayer capacity W_m, i.e., the amount of a vaporous adsorbate that covers the particles of a disperse body with a monomolecular layer, for three-phase disperse systems. If parameter W_m and area s_0 per adsorbate molecule are known, it is easy to estimate required parameter S by the following formula [3, 4]:

$$S = \frac{W_m s_0 N_A}{M}, \qquad (1)$$

where N_A is Avogadro's number and M is adsorbate molecular mass.

Thus, in order to estimate S it is, in most cases, necessary and sufficient to obtain the isotherm of adsorbate sorption on a studied disperse body. Excluding the expensive special equipment used for determining SIs by thermal desorption or gas chromatography [2, 4], the classical method for their measurement that involves the exposure of samples in an adsorbate atmosphere with a preset pressure (concentration) of its vapor and implies the establishment of absorption equilibrium in the adsorbent–adsorbate system appears to be most available.

In soil science and pedology, this method is referred to as "saturation over salts," because, according to this method, relative pressure P/P_0 of water vapor, which is used as an adsorbate, is preset in a closed volume of a dessicator containing a sample using saturated solutions of different salts [5]. An essential drawback of this method is its duration (1 month and more for 5- to 10-g samples) governed by the characteristic time of the establishment of sorption equilibrium. A second problem is the small number of experimental points (seldom more than two) lying in an SI range of $0 < P/P_0 < 0.3$ (0.4) that is suitable for calculating W_m by the BET method. This number is limited by the standard set of salts used in this method (lithium and zinc chlorides, $P/P_0 = 0.10$–0.15, and calcium chloride, $P/P_0 = 0.32$) [5].

At the same time, there is a theoretical possibility of an essentially different method for determining SIs and, consequently, specific surface areas. This method is based on successive drying of samples at different temperatures, weighing them at each stage, and calcu-

Table 1. Experimental data on humidity and calculated values of moisture potential and specific surface area for the examined samples of soil colloids

Sample no.	1	2	3	4	$\lvert\Psi\rvert$, kJ/kg
T, °C	W, %				
27	39.8	33.3	39.9	45.8	145
47	23.0	18.8	24.3	24.8	305
70	11.6	9.0	13.4	16.4	489
110	8.7	7.3	11.4	15.6	809
200	7.4	6.1	9.3	14.0	1529
340	3.9	3.6	6.7	4.0	2649
400	2.0	0.8	3.4	1.6	3129
500	0.0	0.0	0.0	0.0	3929
S, m^2/g	1022.3	864.6	1005.8	1157.1	

lation of the thermodynamic potential (specific Gibbs free energy) of the moisture in the atmosphere of a drying oven connected with the laboratory apartment, which maintains a constant content of water vapor in air, from the drying temperature [6]. The goal of this work is to substantiate the use of the thermogravimetric method for determining S and to show that this method can be applied for the investigation of soil colloids.

EXPERIMENTAL

The results of the classical experiments [7] on dehydration of colloids isolated from the following four Californian soils were used as the experimental data: (1) Altamont, (2) Yolo, (3) Vina, and (4) Aiken, which are attributed to Aridic Haploxerets and Mollic xerofluvents families (Table 1). Before the isolation of the colloidal fraction, soil samples were, according to [7], purified from an organic moiety, and their absorbing complex was saturated with hydrogen. Drying was carried out at temperatures T ranging from 27 to 500°C. In the calculations of humidity, the "absolutely dry" (anhydrous) state of soil colloids corresponded to sample mass after drying at the final stage at 500°C.

Numerical values of physically substantiated parameters that enter into the model used for estimating the moisture thermodynamic potential as a function of drying temperature were evaluated from the reference data on the temperature dependence of saturation vapor pressure of water in a range of $0 \leq T \leq 374$°C, i.e., from the state of freezing to the critical point of water.

For the same purpose, an alternative estimation was carried out from the data of a laboratory experiment implying air heating in a KD 200 drying oven (NUVE OVEN, China) with forced circulation and ventilation of air and simultaneous control over relative air humidity and temperature using DS 1923 "gigrochrone" programmed electronic sensors [8]. The statistical processing of the results was performed using the MS EXCEL 3 software.

The proposed method is theoretically substantiated as follows. Required parameter S is estimated by the common method using the approximation of the isotherms of water vapor sorption on studied samples by the BET model [3]:

$$\frac{P/P_0}{W(1-P/P_0)} = \frac{1}{W_m K} + \frac{(K-1)}{W_m K}\left(\frac{P}{P_0}\right), \tag{2}$$

where W is the mass fraction of water (humidity, kg/kg) and K and W_m are model parameters. In the $x = P/P_0$, $y = (P/P_0)/W(1 - P/P_0)$ coordinates, the model SI has the form of $y = ax + b$ linear dependence. Approximating experimental SIs by this dependence and determining approximation parameters a and b, the required S value is easily calculated as follows [3]:

$$S = \frac{36.14}{a+b}, \tag{3}$$

where 36.16 is the numerical expression of the combination of all constants in equation (1) for water molecules and $(a + b) = 1/W_m$.

Let us derive SIs from the thermogravimetric data using the Polanyi potential theory [1, 9]. As applied to water vapor as an adsorbate, this theory implies that the dependence between moisture thermodynamic potential Ψ and humidity $W(\Psi)$ must be invariant with respect to temperature. The thermodynamic potential is related to relative water vapor pressure P/P_0 or the value of relative air humidity, which is numerically equal to it under the ideal gas approximation, by the known fundamental equation [10]:

$$\Psi = \frac{RT}{M}\ln\left(\frac{P}{P_0}\right). \tag{4}$$

Here, Ψ is the specific thermodynamic potential (J/kg), T is the absolute temperature (K), M is the molar mass (kg/mol), and R is the gas constant (J/(mol K)).

The function inverse to relation (4) has the following form:

$$\frac{P}{P_0} = \exp\left(-\frac{|\Psi| M}{RT}\right), \quad (5)$$

Having known the $W(\Psi)$ dependence, function (5) can be used to easily calculate the isotherms for specified temperature T in the form of the $W(P/P_0)$ functions.

In turn, the $W(\Psi)$ dependence may be found from the data on the drying of samples at different temperatures using the approach described in [6]. In the volume of the laboratory apartment, which is infinite, as compared with the volume of the drying oven, a constant relative pressure of water vapor or relative air humidity f is maintained at room temperature T_r. Under these conditions, air heating in the drying oven must reduce the P/P_0 value relative to the initial value of f via an increase in the denominator, i.e., saturation vapor pressure P_0. Relation $P_0(T)$ is, as a first approximation, determined by Kirchhoff–Rankin model (6), which is obtained by integrating the Clausius–Clapeyron equation under the assumption of the constancy (independence from temperature) of specific heat Q of evaporation [11]

$$\ln(P_0) = -\frac{QM}{RT} + B, \quad (6)$$

where B is the integration constant.

Having written relation (6) for two temperatures, i.e., the constant one (T_r) and an arbitrary (T), and subtracted one equation from the other, it is easy to obtain the following dependence, taking into account that, at $T = T_r$, $P_0 = P/f$ [6]:

$$\ln\left(\frac{P}{P_0}\right) = \frac{QM}{RT} - \left(\frac{QM}{RT_r} - \ln f\right). \quad (7)$$

Substituting it into Eq. (4), we derive the following basic theoretical formula used in the method for calculating the thermodynamic potential as a function of the temperature upon drying the samples:

$$\Psi = Q - aT, \quad (8)$$

where $a = \{Q/T_r - (R/M)\ln f\}$ is the parameter that is governed by the conditions in the laboratory apartment.

RESULTS AND DISCUSSION

To carry out the calculations by the above-proposed scheme, let us determine the value of parameter Q in Eq. (8). Figure 1a shows the result of such direct determination performed via the approximation of the reference data [12] by Kirchhoff–Rankin equation (6). In the $y = \ln P_0$, $x = 1/T$ coordinates, the experimental data are approximated by linear regression function $-mx + n$, where m and n are regression parameters. Values of $m = 4882.2 \pm 6.3$ and $n = 24.5 \pm 0.02$ obtained at significance level $p < 0.0001$, standard error of approximation $s = 0.07$, and correlation coefficient $R^2 = 0.999$ indicate the high accuracy of functional dependence (6). Since $Q = mR/M$, we obtain parameter value $Q = 2255 \pm 3$ kJ/kg.

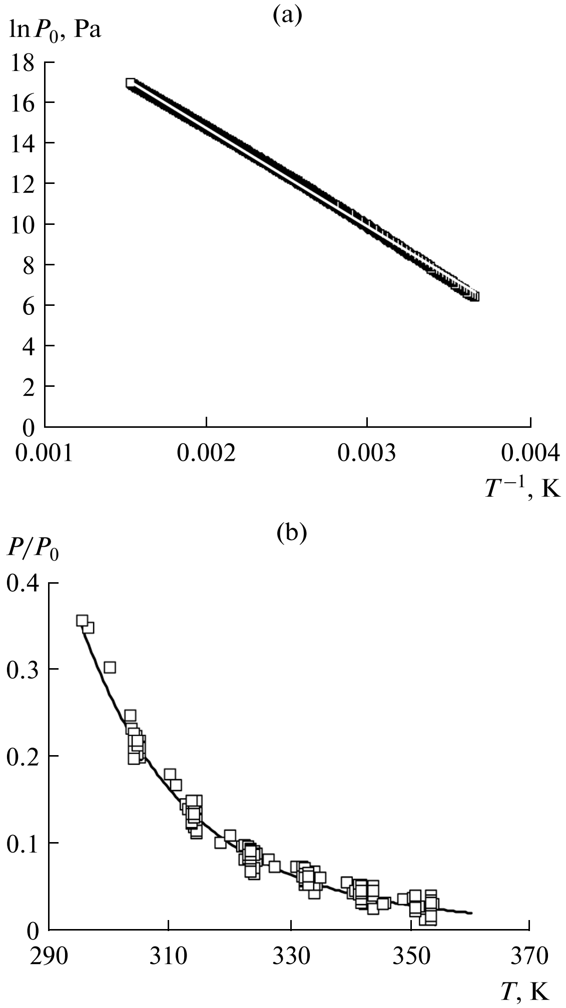

Fig. 1. Temperature dependences of saturation vapor pressure P_0 and relative air humidity P/P_0 plotted based on the data of (a) [12] and (b) laboratory experiment with air heating in the drying oven and Eqs. (6) and (7), respectively.

The results of alternative experimental estimation from the data on the dependence of relative air humidity on the temperature (Fig. 1b) in the drying oven and their approximation by dependence (7) (equation of linear regression in the $y = \ln(P/P_0)$, $x = 1/T$ coordinates has the form of $y = 4853.8x - 17.49$, $R^2 = 0.952$) gave $Q = 2241 \pm 33$ kJ/kg. Taking into account the broader confidence interval (33 kJ/kg), this estimate may be considered to be identical to the previous one. The experiment, which was performed using DS 1923 off-line programmed sensors for automated

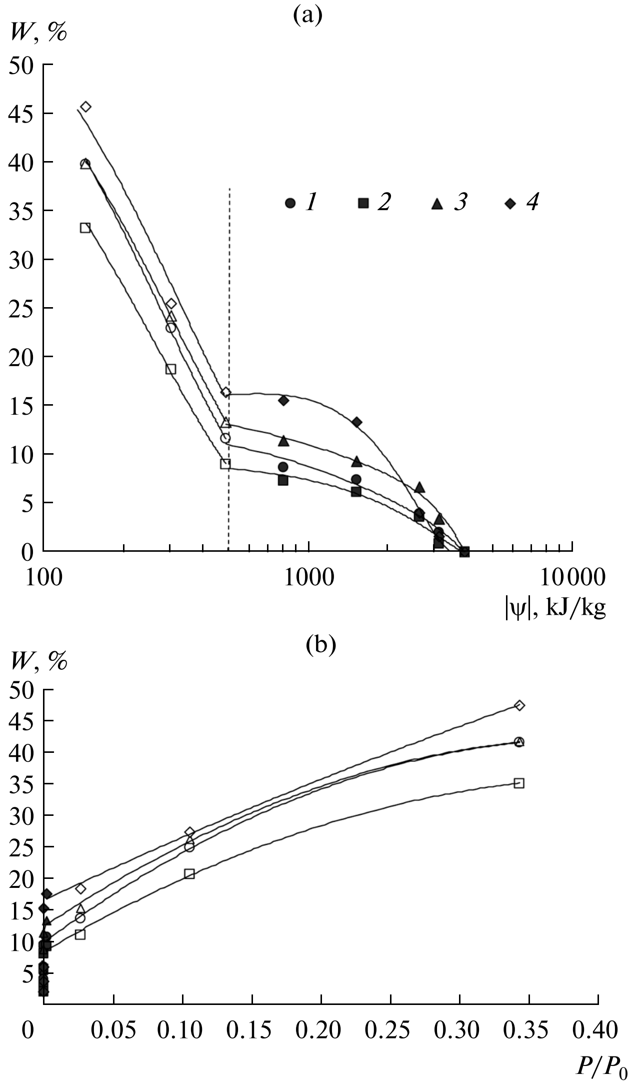

Fig. 2. (a) Polanyi potential curves and (b) SIs calculated from them for soil colloids. The numbers of curves *1–4* correspond to the numbers of soil colloid samples; filled symbols refer to the conditionally isolated layer of strongly bound moisture, which cannot be removed at temperatures of nearly 100°C and above.

simultaneous control over P/P_0 and T, also enabled us to determine (seemingly, for the first time) the functional relation between these values obtained in the standard mode of drying the samples of disperse materials and to show the complete coincidence of this relation with theoretical formula (7).

Using above-determined parameter Q = 2255 kJ/kg and conventionally chosen (for the regime of the experiment [7]) parameters of the external laboratory apartment $T_r = 20$°C (293 K) and $f = 0.5$ (50% relative air humidity), we may estimate the values of moisture thermodynamic potential for different stages of drying soil colloids by basic formula (8). The resulting absolute values of Ψ are listed in Table 1. As can be seen from the presented data, the values of Ψ varied from 145 to 3929 kJ/kg within the temperature range of the experiments on colloid dehydration of 27–500°C. Since, at the last step of the experiment, the drying temperature was higher than the critical point of water, adsorbed moisture was seemingly unable to form a continuous phase (solvation layer). This is indirectly evident from the values of the pressure equivalent to the thermodynamic potential (26000–40000 atm), which exceed all estimates known for molecular pressure of liquid water (10000–24000 atm [13, 14]).

The sorption isotherms calculated from the data of Table 1 by formula (5) according to the Polanyi potential theory are presented in Fig. 2. To make the analysis more convenient, Fig. 2a shows the initial Polanyi curves (the $W(\Psi)$ dependences), while Fig. 2b depicts the sorption isotherms. Both dependences clearly show the region, in which the absolute values of the potential are higher than 500 kJ/kg and the values of P/P_0 are lower than 0.03 units, with this region corresponding to drying temperatures higher than 70°C (dotted line in Fig. 2a), at which the physical mechanism of water retention is obviously changed. In this region, the values of humidity for the examined colloids varied from 9 to 16.4% and amounted to at least a third of the initial amount of water at room temperature, i.e., a rather large fraction of it.

The aforementioned results indicate that, when determining the effective specific surface area by the BET method, the pressure range should be confined to $0.03 \le P/P_0 \le 0.34$, i.e., to the data on drying the colloids in a range from room temperature to 70°C. This temperature range ensures the presence of solvation layers, including monolayer W_m, which is required for estimating S by the BET method. This is of importance from the methodological point of view, because, when determining specific surface area by the proposed method, the differential drying of samples should obviously be carried out in the mentioned temperature range (below 70°C). Indeed, within this range, the SIs represented in the BET coordinates are almost ideal straight lines with correlation coefficients R^2 = 0.99–1, as they must be in accordance with the BET theory (Fig. 3). The corresponding equations of linear regression in the $x = P/P_0$, $y = F_{\text{BET}} = (P/P_0)/W(1 - P/P_0)$ coordinates have the following forms: sample 1, $y = 3.38x + 0.15$, $R^2 = 1$; sample 2, $y = 3.98x + 0.20$, $R^2 = 1$; sample 3, $y = 3.18x + 0.12$, $R^2 = 1$; and sample 4, $y = 3.01x + 0.12$, $R^2 = 0.995$. The desired S values were calculated from the regression parameters of the equations by formula (3) (Table 1, the bottom line). As can be seen from the aforementioned data, the estimates obtained for different colloids had close values of about 1000 m^2/g (865–1160 m^2/g).

The following result is also of interest. Drying at 105°C does not completely remove moisture from soil colloids and finely disperse powders; i.e., it does not

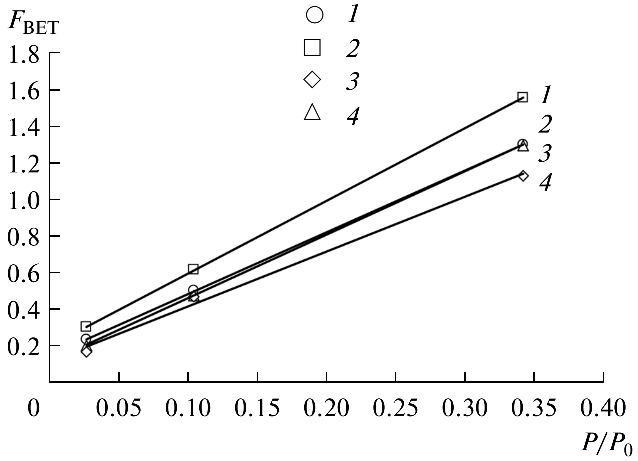

Fig. 3. Fragments of SIs plotted for soil colloids in the BET coordinates. The denotations are the same as in Fig. 2.

result in an "absolutely dry" state. Therefore, the standard drying of colloidal materials with a surface area of about 1000 m^2/g at water boiling temperature (commonly accepted in soil science, pedology, and materials science) with the aim to achieve the "absolutely dry" state may lead to large errors. Let us recalculate the data on the "absolute zero" of humidity obtained at 500°C (Table 1) for the standard "zero" approved in soil science (pedology) and obtained at 100°C. For this purpose, we use the following simple algebraic formula, which follows from the determination of the humidity as the ratio of the difference between the masses of a humid and an "absolutely dry" material to the latter mass:

$$W(T) = 100 \times \frac{W_0(T) + 100}{W_{100} + 100} - 100, \qquad (9)$$

where $W(T)$ is the desired new "absolute zero" humidity reached at 100°C and $W_0(T)$ is the corresponding initial "absolute zero" humidity attained at 500°C. At $W_0(T) = W_{100}$, the formula will obviously yield a zero value of $W(T)$.

The new values of humidity obtained for samples 1–4 by formula (9) are listed in Table 2. They were used to estimate once again the corresponding values of effective specific surface area using equation (2) and the BET model. The comparison of these values with the initial estimate (Table 1) revealed differences that were rather large even for colloids and equal to 100–260 m^2/g or 10–25% of the initial value, which we assume to be the true one. That is, the drying of colloids, in which the layer of strongly bound moisture reaches humidity values W_0 of 10–15%, at the standard temperature of about 100°C, which is too low for removal of such humidity, leads to an essentially overestimated mass of an absolutely dry soil. As a consequence, the humidity, effective specific surface area, and all calculated characteristics relevant to the normalization with respect to the mass of the solid phase appear to be artificially understated. Among real natural objects, such a situation is likely to arise in active slits, whose specific surface area is about 1000 m^2/g. This also concerns numerous modern synthetic nanomaterials, of which the quantitative characteristics relevant to the retention of moisture and other chemical compounds, exchange properties, etc., may be severely inaccurate, when the mass of the solid phase is determined by the "standard" dehydration at water boiling temperature.

Table 2. Recalculation of the data on humidity and specific surface area for the examined samples of colloids for the "standard" zero humidity reached at 100°C

T, °C	W, %				$\lvert\Psi\rvert$, kJ/kg
	1	2	3	4	
27	28.6	24.2	25.6	26.1	145
47	13.2	10.7	11.6	8.0	305
70	2.7	1.6	1.8	0.7	489
110	0.0	0.0	0.0	0.0	809
S, m^2/g	822.8	712.7	742.3	1052.7	

This work was supported by the Russian Foundation for Basic Research (project no. 16-04-00284).

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Translated by K. Aleksanyan