COMPARATIVE STUDIES ON THE DETERMINATION OF SPECIFIC SURFACE AREAS BY LIQUID ADSORPTION

By

G. SCHAY, L. GY. NAGY and T. SZEKRÉNYESY

Department for Physical Chemistry, Polytechnical University, Budapest

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I. Determination of the specific surface area by a graphical method

The adsorption isotherm in the whole composition range of a completely miscible liquid pair is described in the case of a physical adsorption and of an unimolecular surface layer, by the following two relations [1—4]:

$$\chi_x = H^\circ(x^\circ - x) = n_1'(1 - x) - n_2' x \tag{1}$$

$$n_1' F_1 + n_2' F_2 = F \tag{2}$$

where H° is the amount of the original mixture (mmole/g ads.);

x° and x are the initial and equilibrium mole fractions of the first component, respectively;

n_1' and n_2' are the amounts of the two components contained in the surface layer (mmole/g ads.);

F_1 resp. F_2 are the molar areas of the components (m^2/mmole).

F is the specific surface area of the adsorbent (m^2/g ads.).

As is well-known the determination of the specific adsorption is carried out as follows:

A certain amount (H°) of a mixture of strictly two components and of a known composition (x°) is brought together with the pure and dry adsorbent. After final equilibration (6—8 hours, even in case of strong stirring), the equilibrium composition of the liquid phase is measured (x).

From equations (1) and (2) follows [5]:

$$n_1' = \frac{Fx + F_2 H^\circ (x^\circ - x)}{F_2 (1 - x) + F_1 x} \tag{3}$$

$$n_2' = \frac{F(1 - x) - F_1 H^\circ (x^\circ - x)}{F_2 (1 - x) + F_1 x} \tag{4}$$

For the systems specified in Table I, on the basis of total mixture isotherms ($\chi - x$) and of the so-called individual isotherms ($n' - x$) as computed by (3) and (4), the isotherms can be classified into five basic types *(Fig. 1)*.

Table I

Mixture	Adsorbent	Type of isotherm
acetic acid-benzene	charcoal	4
acetic acid-water	charcoal	3
acetic acid-water	silica gel	4
propionic acid-water	charcoal	3
pyridine-water	charcoal	3
pyridine-ethyl alcohol	charcoal	1
methyl alcohol-benzene	alumina	2
methyl alcohol-benzene	silica gel	2
methyl alcohol-benzene	charcoal	4
ethyl alcohol-benzene	alumina	4
ethyl alcohol-benzene	silica gel	4
ethyl alcohol-benzene	charcoal	4
ethyl alcohol-benzene	graphit	4
propyl alcohol-benzene	alumina	4
propyl alcohol-benzene	silica gel	4
propyl alcohol-benzene	charcoal	4
buthyl alcohol-benzene	alumina	4
buthyl alcohol-benzene	silica gel	3, 4
buthyl alcohol-benzene	charcoal	3, 4
diethylcarbonate-benzene	charcoal	1
dichlorethylene-benzene	silica gel	1
dichlorethylene-benzene	alumina	1
dichlorethylene-benzene	charcoal	5
carbontetrachloride methanol	charcoal	4
acetone-benzene	charcoal	4
chloroform-acetone	charcoal	5
benzene-cyclohexane	alumina	4
chloroform-benzene	alumina	1
carbontetrachloride-nitromethane	silica gel	3
nitromethane-nitrobenzene	silica gel	1
nitromethane-benzene	silica gel	1
carbontetrachloride-chloroform	charcoal	2
n-buthyl amine-benzene	silica gel	4
pyperidine-cyclohexane	silica gel	2
acetone-water	silica gel	4
ethyl alcohol-water	silica gel	4
n-propyl alcohol-water	charcoal	4

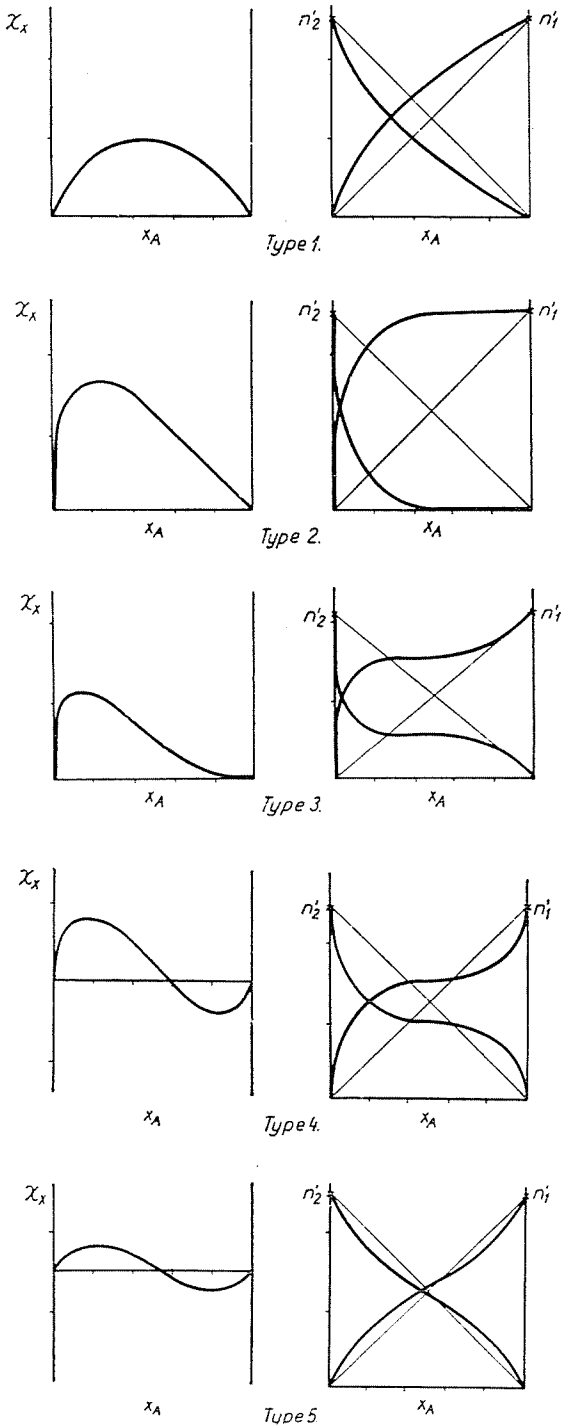

Fig. 1. Basic types of the adsorption isotherms of liquid mixtures

The types differ from each other by changing of (χ_x) sign which does not change for (1, 2 and 3) and in whether the mixture isotherm has a linear, whereas the individual isotherms a horizontal section (types 2, 3 and 4).

For simplicity's sake, the isotherm models illustrated in *Fig. 1* were calculated with identical molar areas ($F_1 = F_2$).

The comparison of the total and the individual isotherms shows that a horizontal section on the individual isotherm corresponds to any intermediate linear section on the mixture isotherm.

It can be written for the linear section of the adsorption isotherm of the mixture that:

$$n_1'(1 - x) - n_2' x = n_1' - (n_1' + n_2') x = a - bx \tag{5}$$

By comparing the coefficients it becomes evident that the mixture adsorption isotherm can have a linear section only if the composition of the surface phase remains constant in the respective region of x. From (5):

$$n_1' = a \tag{6}$$

$$n_2' = b - a \tag{7}$$

hence the absolute amount of the first component contained in the surface phase can be determined by extrapolation of the straight portion up to its intersection with axis $x = 0$, whereas its slope gives the total amount $(n_1' + n_2')$ as well as hereby also the composition of the surface layer $x' = \frac{n_1'}{n_1' + n_2'} = \frac{a}{b}$ within the linear section (graphical method). Since the relation (1) (OSTWALD'—DE IZAGUIRRE's isotherm equation) is obtained from a material balance [4] free of any neglect and of a quite general validity — hence it follows that the above graphical method is also of general validity, provided that the mixture isotherm has a linear section. Accordingly it can be applied not only in the case of physical adsorption but also in that of chemi-sorption and for unimolecular surface layers as well as for polymolecular ones.

With the amounts n_1' and n_2' determined from the mixture isotherms belonging to types 2, 3 and 4 and on the assumption of a unimolecular surface layer in case of physical adsorption, a specific surface area value can be computed by equation (2) if the molar areas of the components are known. We accepted the molar area values derived from vapour adsorption measurements. In Tables II and III, results obtained by the graphical method are compared with those obtained by the BET method. In Table II results of calculations are illustrated which were carried out from data to be found in literature, in Table III those from our own measurements.

Table II

Adsorbent	Mixture	Type of iso-therm	F_i	n_i'	F_g	n_∞^*	F	Ref.	Note
Charcoal	Ethyl alcohol / Benzene	4	120 / 180	0.76 / 2.75	587	5.1 / 3.4	612	6	
Charcoal	Benzene / Cyclohexane	3	180 / 215	2.6 / 0.4	556	BET	540	7	
Alumina gel	Methyl alcohol / Benzene	2	83;94 / 180	2.2	202 / 185	2.27 / 1.17	210 / 190	8	*
Alumina gel	Ethyl alcohol / Benzene	4	120 / 180	1.5 / 0.15	207	1.77 / 1.174	212	8	
Silica gel	Methyl acetate / Benzene	2	180 / 180	3.1 / —	560	3.21 / 3.22	580	9	
Silica gel	n-butylalcohol / Benzene	3	172 / 180	2.9 / 0.2	535	2.73 / 2.87	518 / 470	9	*
Silica gel	Ethyl alcohol / Benzene	4	120 / 180	4.6 / 0.2	586	4.5 / 3.1	550	9	
Carbon black	n-propyl alcohol / Water	2	180 / 215	0.4 / —	72	0.45 / 0.40	81 / 86	10	*
Carbon black	Benzene / Cyclohexane	4	180 / 215	0.6 / 0.1	129	BET	114	11	
Alumina gel	Pyridine / Cyclohexane	3	135 / 215	1.20 / 0,06	174	1.36 / 0.85	184	12	
Alumina gel	Piperidine / Cyclohexane	3	163 / 215	0.81 / 0.20	172	1.07 / 0.86	175 / 185	12	*
Silica gel	n-butyl-amine / Benzene	3	160 / 180	0.5 / 2.9	555	3.6 / 3.1	575 / 560	12	*

* Different specific surface area values are to be derived from the respective n_∞^* values given for two components.

So far our method of computation of specific surface areas has never failed in any case when the following three conditions were satisfied:

1. Pure physical adsorption free of chemi-sorption;
2. a reasonably long linear section on the isotherm;
3. observed concentration change due strictly to adsorption only (effectively dry adsorbent and containing no soluble materials).

Table III

Adsorbent	Mixture	Type of isotherm	F_i	n_i'	F_{BET}	F_g	Fig. Nr.
Charcoal (Nuxit AI)	Ethyl alcohol / Benzene	4	120 / 180	0.75 / 2.75	620	590	
Charcoal (Nuxit AII)	Ethyl alcohol / Benzene	4	120 / 180	1.85 / 3.25	770	807	
Charcoal (Nuxit AIII)	Ethyl alcohol / Benzene	4	120 / 180	0.85 / 4.40	840	895	(2)
Silica gel (pretreated by alcohol)	Ethyl alcohol / Benzene	4	120 / 180	3.75 / 0.4	540	522	(3)
Silica gel (pretreated by alcohol)	n-butyl alcohol / Benzene	3	172 / 180	2.2 / 0.7	540	506	
Charcoal (Nuxit AI)	Acetic acid / Benzene	4	120 / 180	1.9 / 2.2	620	624	(4)
Charcoal (Nuxit AIII)	Acetic acid / Benzene	4	120 / 180	2.2 / 3.2	840	840	

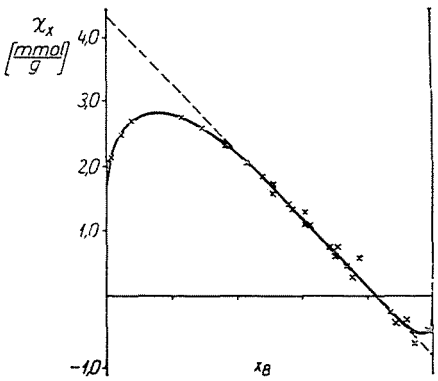

Fig. 2. The adsorption isotherm of the mixture benzene (x_B)-ethylalcohol on charcoal (Nuxit III) at 25 °C

Illustrative from the point of view of the first condition is the adsorption isotherm of the mixture ethyl alcohol-benzene on silica gel *(Fig. 3)*. Due to the chemi-sorption of alcohol on the not pretreated silica gel, the amount of the surface phase is about twice that of the surface layer built up on the adsorbent pretreated with alcohol.

The symbols used in the tables are:

F_i = molar area (m^2/mmole) of component i,
n'_i = surface mole numbers obtained by graphical method,
F_g = specific surface area of the adsorbent as computed by graphical method (m^2/g),
F_{BET} = specific surface area as computed from nitrogen adsorption by the BET method (m^2/g),
F = specific surface area as computed from the vapour adsorption of the given component (m^2/g),

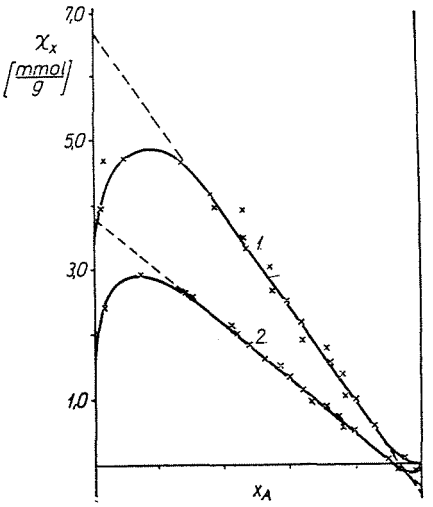

Fig. 3. The adsorption isotherm of the mixture ethylalcohol-benzene on silica gel at 25 °C. 1. Unpretreated silica gel. 2. Silica gel pretreated with alcohol

n^*_∞ = the amount (mmole/g) of the adsorbate corresponding to the complete monolayer determined from its vapour adsorption isotherm, this being mostly the quantity quoted in order to characterize the magnitude of the specific surface area.

Condition of the applicability of the graphical method is that the concentration x' in the surface layer ought to be constant over a given equilibrium concentration range. The question is how far this is realized in practice, *i. e.* whether the establishing of the types of isotherms on this basis were justified.

According to the results of surface area determinations by our computation method, the above assumption is justified for a considerable number of systems, the surface layer composition can be considered as being constant within $\pm 5\%$ over the respective range of equilibrium concentrations. (The scattering of the experimental points usually lies between ± 5 to $\pm 10\%$.)

At the same time it might happen that some experimentally found adsorption isotherm of a mixture represents a transition between two of the

above types. For systems belonging to types 4 and 5 this is a problem which rarely arises, whereas the transition between isotherms of type 1 and 2 more frequently met with. Truly only such systems can be classified as belonging to type 2 in which the adsorption potential of one of the components is high enough with respect to the other, that from an equilibrium concentration of about 0.5—0.6 on, already the surface is covered by only this sole component. This condition is rarely satisfied in practice. It very often occurs, however, that one of the components attains an interfacial concentration of 0.8—0.85 in the range of equilibrium concentrations of 0.3—0.5 already, and from this onward the interfacial concentration increases almost uniformly until $x = 1$ (for instance the pair benzene—cyclohexane on carbon black $x = 0.5$, $x' = 0.87$; $x = 0.9$, $x' = 0.98$).

For such systems a value smaller by 10—15 % is obtained for the amount of the surface phase by the graphical method (Table II), because the declining branch of the isotherm is not truly linear, having in reality a very small, scarcely observable curvature.

II. Discussion of the evaluation based on isotherms of partially miscible liquid pairs

The following isotherm equations were suggested to describe these isotherms: KISELEV, SHCHERBAKOVA [13]:

$$X_c = V^\circ \ (C^\circ - C) = n_1' - V_a C \tag{8}$$

HANSEN, YING-FU, BARTELL [14]:

$$X_c = V^\circ \ (C^\circ - C) = n_1' \ (1 - V_1 \ c) - n_2' V_2 C \tag{9}$$

WILLIAMS [3]:

$$n_1' V_1 + n_2' V_2 = V_a = \text{constant} \tag{10}$$

where V° is the volume of the starting mixture (ml/g ads.)

C° and C are the starting and equilibrium molarities of the first component (mmole/ml), resp.

V_a is the volume of the interfacial layer (ml/g ads.).

V_1 resp. V_2 are the molar volumes of the components (ml/mole).

The question arises how exact these relations are and how far their application is permissible for the description of isotherms of partially miscible systems.

With volumes and volume concentrations, the following balance equations can be written

$$V^\circ = V + V_a \tag{11}$$

for the total liquid volume and

$$V^\circ C^\circ = VC + V_a C' \tag{12}$$

for component *1*.
(V is the equilibrium volume of the bulk phase per gram adsorbent and C' the molarity of the first component in the interfacial layer).
From (11) and (12) follows

$$V^\circ \ (C^\circ - C) = V_a \ (C' - C) \tag{13}$$

It is a generally accepted convention, suggested by Gibbs, that specific adsorption or interfacial concentration should mean the excess amount of any component relating to unity of mass or unity of surface area of the adsorbent. According to Gibbs, one should place an imaginary dividing surface into the homogeneous bulk phase and consider the excess in the volume extending from there to the interface. In the case of a constant V_a, the excess amount of material defined on the basis of the Gibbs convention is given by χ_c.

From (13), we arrive to the relation (8) by substituting $V_a C' = n'_1$ and a further substitution by (10) gives the relation (9).

The relation (13) cannot be considered as one of general validity, because the balance (11) only holds if the adsorption is not accompanied by a change of volume. In the majority of cases, however, this condition is not satisfied, hence neither equation (11) nor (13) are of general validity.

In the case of physical adsorption of a unimolecular interfacial layer and in the absence of particular solvatational interactions, no considerable error is committed by using relations (11—13), the specific adsorption value belonging to a given equilibrium concentration being given within an optimal limit of error of $\pm$ 5% by an isotherm constructed from the measured data.

It is another problem as to how the value of the adsorption volume (V_a), of n'_∞ resp. of the specific surface area should be determined. The two most important methods known from literature are:

1. The isotherms, as regards their form, are similar to type I of BRUNAUER, DEMING and TELLER [25]. A substitutional analogy is inferred from the formal similarity, the isotherm is extrapolated up to the relative concentration $C/C_t = 1$ (C_t is the saturation concentration) and the value thus obtained is

considered as the amount (n'_∞) of the adsorbate corresponding to the complete unimolecular coverage. From the amount of adsorbate so determined, the surface area is computed with a given molar area. This method is used for absolute determinations of surface area by liquid adsorption, (16, 17).

2. The volume of the unimolecular interfacial layer is determined by vapour adsorption and the individual isotherm ($n'-c/c_t$) of the more strongly adsorbed component is calculated by the value V_a thus obtained, with the relation (8). The value derived by extrapolation of the individual isotherm is considered as n'_∞ [13].

The fundamental problem in connection with the first method is whether the determination of n'_∞ by extrapolation of the adsorption isotherm is permissible. The applicability of the method has three conditions:

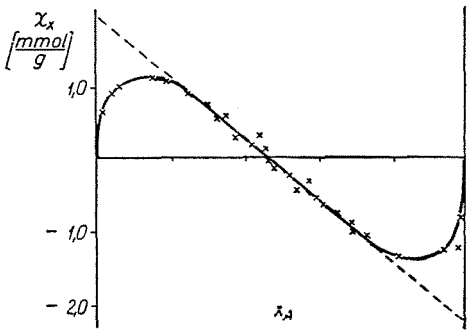

Fig. 4. The adsorption isotherm of the mixture acetic acid (x_A)-benzene on charcoal at 25 °C

1. In the neighbourhood of the saturation concentration only the more strongly adsorbable component should be present in the interfacial layer.

2. The saturation concentration should be low enough:

$$C_t \ll \frac{n'_\infty}{V_a} \quad i.e. \quad \chi_c \gg V_a C_t$$

3. The geometry of the adsorbent surface should be no hindrance to the accessibility of the surface as regards the more strongly adsorbable component.

The satisfaction of the second condition is unambigously fixed by the solubility. It cannot be decided whether the first and third conditions are fulfilled when nothing but a solution-adsorping isotherm is at our disposal. The knowledge of the pore distribution and of the specific surface area determined by vapour adsorption or by that of a completely miscible liquid pair is at least required in order to decide — assuming the simplest case (unimolecular adsorption layer) — what percentage of the surface is covered by the more strongly adsorbed component.

In Table IV, results are shown of computations carried out from isotherms of n-butyl alcohol and n-amyl alcohol *(Fig. 5)* in water on a charcoal of 840 m^2/g, and another of 620 m^2/g obtained by partially burning out the former. n'_∞ (C) is the amount needed for unimolecular coverage as calculated from the molar area (F_i) based on the assumption of flatly lying carbon chains and from the known specific surface area. n'_∞ (M) is the amount obtained by

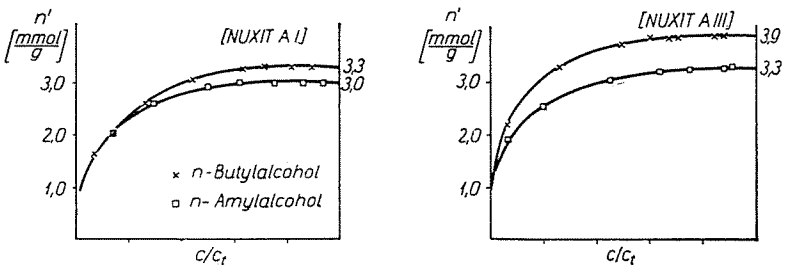

Fig. 5. The adsorption isotherm of the mixture n-butyl alcohol-water and n-amyl alcohol water on charcoal
Nuxit A I: 620 m^2/g : Nuxit A III: 840 m^2/g

the extrapolation of the individual isotherm; F is the surface calculated from n'_∞ (M); F % is the calculated surface F in percentage of the actual surface of the adsorbent.

Table IV

Adsorptivum	Fi	Nuxit AI "620 m^2/g"				Nuxit AIII "840 m^2/g"			
		$n'_\infty(C)$	$n'_\infty(M)$	F	F %	$n'_\infty(C)$	$n'_\infty(M)$	F	F %
n-butyl-alcohol	172	3.6	3.3	567	91	4.88	3.9	670	80
n-amyl alcohol	204	3.04	3.0	612	99	4.12	3.3	675	80

On the whole, it can be stated in connection with the first method that it cannot be generally applied for the absolute determination of surface area.

The second method from the very first abandons the claim to evaluate the isotherm on the basis of liquid adsorption data only, as the volume of the surface phase is calculated from vapour adsorption.

The use of an adsorption volume V_a, determined from vapour adsorption and considered as being a constant, hence independent of the adsorbate, cannot be expedient, for instance, in the case of fatty acids and aliphatic alcohols, or for the adsorption of dyestuffs. The possibility of application depends on the answer to the question, whether the error commited is greater if we disregard the fact that the specific adsorption determined from the con-

centrated solutions is not identical with the effective amount of the interfacia layer, or if we use the volume derived from it instead of the effective adsorption volume which cannot be determined by direct measurements.

Two factors should be considered to estimate the magnitude of the effects of both approximations:

1. the magnitude of solubility,
2. the accessibility of surface.

Table V

Adsorbate	F%
Cyclohexanol	14
Phenol	4
Benzoic acid	21
Salicylic acid	32
Methylenic blue	28

For poorly soluble materials (for instance fatty acids or alcohols with six or more carbon atoms in their chains, or poorly soluble large dyestuff molecules, such as methylenic blue) and with adsorbents of large specific surface areas, the use of the volume determined by vapour adsorption is not justified. It can be seen from relation (8) that, due to poor solubility, the evaluation of the isotherm is not decisively influenced by taking the adsorption volume into account. KISELEV and SHCHERBAKOVA [13] carried out surface area determinations from isotherms obtained from aqueous solutions, on a charcoal of $F_{BET} = 580$ m²/g specific surface area. Some of their results are quoted in Table V, where $\Delta F\%$ is the percentage deviation between the surface area values calculated by both methods $\Delta F\% = \frac{F_{BET} - F}{F_{BET}} \cdot 100$, F being the surface area computed from the solution isotherm. Our conclusions may be summed up in the following statements.

1. Computations from isotherms of solutions *i. e.* of but partially miscible systems are quite uncertain without the knowledge of vapour adsorption data or those of completely miscible liquid pairs. The uncertainty is mainly due to the fact that from the adsorption isotherms of partially miscible systems no information can be obtained of the amount of the second component, the solvent contained in the surface layer.

2. The knowledge of the adsorption volume (V_a), as calculated from vapour or liquid adsorption, is required for the individual isotherm to be computed on the basis of relation (8), if in the neighbourhood of the saturation concentration the concentration in the bulk phase cannot be neglected with

respect to the concentration in the interfacial layer *i. e.* if the bulk phase cannot be considered as a diluted solution in the saturation region.

3. Absolute specific surface areas can be determined but exceptionally from isotherms of solutions resp. from those of partially miscible liquids. At the same time relative surface area determinations are also problematical because an altered specific surface area also means different pore distribution and surface quality as well. There are still no suitable methods available for an unambiguous evaluation of adsorption data obtained, which are the resultants of these three different effects.

III. Surface determination by heat of immersion

1. *Definition and interpretation of the heat of immersion*

The heat of immersion is the heat effect observed when a dry solid material is plunged into a liquid. In the process, liquid molecules come into contact with the particles constituting the solid surface and interact with them. The interactions — provided there is no chemical reaction taking place — are of the van der Waals type, which can be classified into the following three categories:

a) orientation effect (interaction of permanent dipoles),

b) induction effect (the interaction of induced dipoles),

c) dispersion effect (the interaction of dipoles temporary created by deformations caused by the vibrations of the electron shells).

The heat effect is due to the fact that in the process of immersion, solid-gas and liquid-liquid interaction is substituted by some combination of the above-mentioned solid-liquid interactions and this change is always accompanied by an energy decrease in the case of a wetting liquid.

The heat of immersion is thermodynamically the total enthalpy change in the process. For simplicity's sake, we do not relate it to the two free phases but to the surface layer. If h_s is the specific enthalpy of the dry solid surface (cal/m^2), h_{sl} that of the solid-liquid interface and F the specific surface area of the solid material (m^2/g) than the heat of immersion is given by

$$Q = F(h_{sl} - h_s) \text{ cal/g} \tag{14}$$

It should be noted that the factor F with which both values have to be multiplied, is identical (as is assumed in relation 14) only if the external and internal surface area of the adsorption layer can be considered to be equal, an assumption which is certainly permissible in the case of unimolecular surface layer.

As enthalpy depends on temperature and on the quality of material, thus the magnitude of the heat of immersion is also a function of these parameters.

The heat of immersion referring to unit mass of the adsorbent also depends on the specific surface area of the adsorbent, being directly proportional to it.

2. *The theoretical possibilities of absolute or relative surface area determinations*

An apparently simple and unambiguous method of determination seems to be given by the relation (14). Provided the specific value of the heat of immersion $(h_{sl}-h_s)$ was known, by measuring the heat of immersion of an adsorbent of a given quantity, an absolute surface area determination could be carried out. Not having the knowledge of the value of $(h_{sl}-h_s)$, but performing the measurement with the same liquid on adsorbent specimens of identical quality but different specific surface areas, relative surface area determinations can be carried out.*

The enthalpy values h_{sl} and h_s are influenced, however, also by circumstances hitherto not dealt with. It should first of all be stated that these enthalpy values are not characteristic of the substances themselves, present in the two bulk phases but of the nature of the interfacial layer only, more exactly: they represent the excess enthalpy of the interfacial layer with respect to the bulk of the solid phase. (According to this point of view the effect is as a whole related to the solid, thus there is no change concerning the liquid, its free surface remains unaltered — at least during course of the immersion process here treated.)

The excess enthalpy of the surface does not depend only on the kind of its constituting atoms and molecules but also on their mutual distances and on the pattern of their arrangement. It is well known that adsorbents are frequently treated at elevated temperatures, such treatment usually being an essential part in the process of their production. It is to be expected that in such cases, as a matter of course, not only the structure of the surface but also its excess enthalpy as well as the heat of immersion vary too.

Also the pore structure might be affected by different kinds of pretreatment. The size and number of recesses and channels in the interior of the adsorbent can be very different. Larger size molecules cannot get into the narrowest pores, thus in the case of strongly microporous adsorbents it may happen that a part of the surface does not contribute to the process of wetting

* The determination of absolute surface enthalpies hence the determination of the value of h_s resp. h_{sl} for solids is — at least for the moment — an unsolved problem, only the heat effect arising from the difference of these can be experimentally observed.

and the extent of the solid-liquid interface layer is smaller than the free surface area of the solid.

So far there was no question of chemical differences. The surface of adsorbents of apparently identical composition can in reality be chemically very different, owing to various circumstances. It may happen that during production, impurities occur on the surface (even the bulk composition of different samples may not be identical, only no notice is taken of it). Ingredients used for the activation of the adsorbent (copper and zinc salts on charcoal for instance) often accumulate on the surface (such substances can be removed by a suitable solvent). Changes in the surface quality can be also brought about by effective chemical reactions. Thus, for instance, on the surface of carbon adsorbents, depending on temperature, an oxide layer may form which cannot be removed or only partly.

These statements are broadly confirmed by experience beyond the few above given examples. Hence the quality of the surface of adsorbents is in most cases very badly defined. This means that the measurement of the heat of immersion cannot be of general use for surface area determinations. Two remarks, however, should be added to this general statement:

On the one hand some time ago a method was worked out by HARKINS and JURA which fits this purpose, at least in the case of nonporous adsorbents resp. those having but wide pores [18]. The principle of their method consists in that the adsorbent is first placed into an atmosphere of the saturated vapour of the wetting liquid until equilibrium is reached. Then the surface is covered by a liquid film which is thin, but of a several molecule layers thickness. Hereby the surface area determination is made independent from the quality of the adsorbent surface. As the outer surface of the film is far enough from the surface of the solid phase, the energy conditions there are not any longer considerably affected by the latter, thus the external surface can be considered as a free liquid surface. By an immersion of the adsorbent — coated by the film — into the same liquid, thus a pure liquid surface corresponding to the area of the film ceases to exist and the enthalpy excess of this surface is observed as the measured heat effect. In this case the heat of immersion is

$$Q = F \cdot h_{lg} \tag{15}$$

where h_{lg} is the excess surface enthalpy of the wetting liquid.*

On the other hand, the fact that the magnitude of the heat of immersion is influenced by the surface quality of the adsorbent might also be of advan-

* Evidently for the reliability of the Harkins and Jura method it is a necessary condition that the adsorbed vapour film should be thick enough (polymolecular). In view of this, it may be problematic whether — even in a case of adsorbents with wide pores — such a thickness would not result in a material decrease of the external surface area of the film with respect to the uncovered adsorbent surface.

tage, namely, if just the quality of the surface should be investigated. In this case the specific surface area has to be determined by some other method and from the measurements of the heat of immersion conclusions may be drawn, for instance, as to the surface activity or the pore distribution, by applying adsorbate molecules of different sizes.

3. *Measuring technic possibilities*

Let us now examine what sensibility resp. accuracy is to be expected from the measuring methods available.

Adiabatic as well as isothermal calorimetry can be used for the measurement of heats of immersion. Our own measurements were carried out with the adiabatic method, the following estimations this method is being referred to. Object of the observation is the temperature rise caused by the heat generated and inversely proportional to the heat capacity of the calorimeter:

$$Q = \Sigma(m \cdot c) \cdot \Delta t \tag{16}$$

By far the major part of the heat capacity is supplied by the wetting liquid. As the volume of the calorimeter can hardly be reduced below of about 100 ml, let us take this value. In order to get a higher temperature rise it would be advisable to choose a wetting liquid of small specific heat (an organic one). Owing to other considerations (the ease of purification or the higher heat of immersion in some instances) the determination is often made with water. In this case the heat capacity of the calorimeter is about 100 cal/degree.

The specific value of the heat of immersion in general lies between $2 \cdot 10^{-6}$ and $12 \cdot 10^{-6}$ cal/cm^2 [19—23], whereas specific surface areas of adsorbents range, in the order of magnitude, between 10 and 10^3 m^2/g. With the mean values $7 \cdot 10^{-6}$ cal/cm^2, respectively, 100 m^2/g, and taking about 3 g of adsorbent to be wetted, the heat effect amounts to

$$Q = 7 \cdot 10^{-6} \cdot 100 \cdot 10^4 \cdot 3 \approx 20 \text{ cal}$$

effecting a temperature increase according to (16) of

$$t = \frac{20}{100} = 0.2^\circ \text{ C}$$

Let us state a required accuracy of 1% for the determination of the heat effect. In order to satisfy this requirement, at first sight it seems necessary at least to observe a temperature change of $2 \cdot 10^{-3}$ degrees. As, however, in order to increase the precision, the heat of immersion is measured as compared to a known heat effect (arising from electrical work), two temperature changes,

hence four temperature values as a final result should be determined. Inaccuracy is also increased by the fact that the calorimeter is not quite adiabatic. Therefore each of the temperature values is obtained by a suitable correction (for instance a graphical one). Considering all these items the sensibility of the thermometer should be better than 10^{-3}, say $5 \cdot 10^{-4}$ degrees.

Let us examine how this requirement can be satisfied by a commonly available temperature measuring method.

a) The limit of sensibility of the mercury thermometers is about 10^{-3} degrees. These can only be used in connection with the wetting of adsorbents with a high specific surface area $> 5 \cdot 10^2$ m²/g).

b) When using a thermopile, the sensibility of the measurement is determined by the following factors: the quality of the two metals, the number of couples constituting the pile and the sensibility of the galvanometer recording the potential difference.

The relatively high electromotive force of the copper constantan thermocouple yields a voltage of about 40 μV per degree and per pair.

Raising the number of pairs, the electromotive force (E) of the pile increases, but the gain in output voltage (E_{ff}) is less than linear, owing to the inevitable increase of the inner resistance (R_i):

$$E_{\text{eff}} = E \frac{R_e}{R_e + R_i} \tag{17}$$

where R_e is the resistance of the external part of the circuit. The multiplication of the number of pairs has to be limited owing to the increased place requirement as well.

The sensitivity of the galvanometer is a decisive factor about which the following may be mentioned: two data are characteristic of the galvanometer, its internal resistance (R_g) and its current sensibility (I_s). The sensitiveness of measurement is determined by the voltage sensibility of the galvanometer (V_s). According to Ohm's law this is the better (its value the smaller), the smaller is the value of R_g respectively I_s

$$V_s = R \cdot I_s \tag{18}$$

(R is the resistance of the total circuit comprising beyond the resistance of the thermopile and of the galvanometer also those of the leads and of the eventual potentiometer.

The voltage sensibility of available galvanometers, not having too long swinging periods, is about 0.1—0.2 μV.

If for instance a copper-constantan thermopile of 12 pairs were used and a galvanometer of a voltage sensibility of 0.2 μV, than the sensitiveness of

temperature measurement will be

$$\frac{0{,}2\ \mu V}{12 \cdot 40\ \mu V/\,^{\circ}C} = 4 \cdot 10^{-4}\ ^{\circ}C$$

by which our stipulated requirement is satisfied. Hence the heat of immersion of adsorbents having intermediate specific surface areas (100 m^2/g), they can be conveniently measured by thermopiles and by increasing the number of couples and possibly the sensibility of the galvanometer, also that of small specific surface areas (10 m^2/g) are measurable.

c) The temperature can also be measured by resistance thermometers, made of a suitable metal or of a semiconductor (thermistor).

From among the metals the temperature coefficient of the resistance of the most frequently used platinum is about 0.4%/°C and the resistance of a standard platinum thermometer is 100 Ω (at 0°C).

With a change in resistance of $10^{-3}\ \Omega$ being detectable by a Wheatstone bridge combined with a galvanometer as considered under *b)*, the sensibility of temperature measurement is, in this case

$$\frac{10^{-3}\ \Omega}{0{,}4\ \Omega/C^{\circ}} = 2.5 \cdot 10^{-3}\ ^{\circ}C$$

The temperature coefficient of thermistors is about ten times that of platinum, hence about a ten times better sensibility can be attained.

It thus follows that the platinum resistance thermometer does not serve the purpose, it does not surpass the sensibility of the much simpler mercury thermometer. The use of a thermistor proves to be the most sensitive among the discussed methods, its application requires, however, a rigorous stability, not easy to realize.

4. *Apparatus, results*

For our own measurements, adiabatic calorimetry and sensing of temperature by a thermopile was chosen. The calorimeter vessel was an especially designed Dewar flask [24] *(see Fig. 6)*.

The heat capacity of the system was determined by electrical heating. The variations of the electromotive force of the thermopile were measured with a mirror galvanometer, with a usable sensibility of $5 \cdot 10^{-7}\ \mu V$.

The results of our surface area determinations carried out at 25.0 °C on samples of charcoal and alumina gel, are shown in Table VII. The wetting liquid was water in all six cases.

Fig. 7 is to illustrate how far the experimental calorimetric plots are usable for computations. The reproducibility of the measurements depended on the magnitude of the heat effect. The values of the heats of immersion measured on a silica gel displayed, for instance the following scattering:

Water: 23.0; 22.6; 22.9 cal/g. Scattering: $\pm$ 0.2 cal/g, i. e. $\pm$ 0.9%.

n-Heptane: 9.1; 9.5; 9.9 cal/g. Scattering: $\pm$ 0.4 cal/g, i. e. $\pm$ 4.2%.

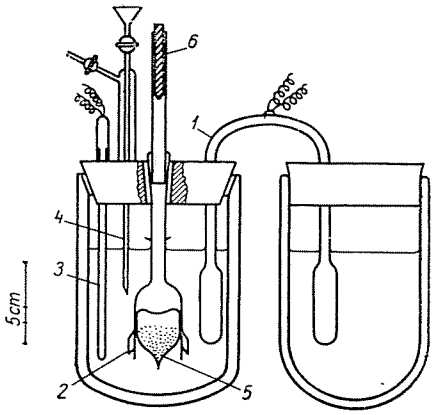

Fig. 6. Calorimeter for the measurement of the heat of immersion. 1: Thermopile (copper-constantan, 12 pairs), 2: adsorbent holder and stirrer (100 r. p. m.), 3: calorifer (2 W), 4: liquid entrance pipe piece, 5: vessel containing the adsorbent, 6: breaking rod

Table VII

Adsorbent	Heat of immersion			N_2 adsorption (BET)	
	cal/g	ratio	surface area m^2/g	surface area m^2/g	ratio
Charcoals:					
Nuxit A I	16.1	(1)	(620)	620	1
Nuxit A II	18.6	1.15	713	770	1.24
Nuxit A III	20.6	1.28	793	840	1.35
Alumina gels:					
Al-226	18.4	(1)	(274)	274	1
Contact	16.2	0.88	241	196	0.72
Rb-50	11.0	0.60	164	149	0.54

The scattering of parallel measurements is illustrated in Table VIII on a series where deviations showed medium values as compared with other series.

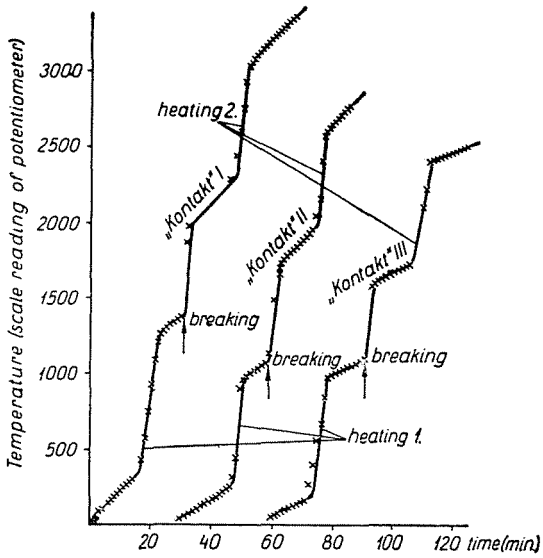

Fig. 7. Calorimetric curves (adsorbent Al_2O_3 "Contact" in water at 25 °C)
Amount of adsorbent is 2—3 g, water 150 g. It is visible that due to effective stirring, the heat effect started immediately after the vessel containing the adsorbent was broken and within about 2 minutes was already finished

Table VIII

Found values of the heats of immersion of samples of Al_2O_3, brand "Rb-50" in water at 25° C

Number	Heat of immersion cal/g	Deviation from the mean value (11.03)	
		cal/g	%
1	11.65	+ 0.62	+ 5.6
2	11.25	+ 0.22	+ 2.0
3	10.55	− 0.48	− 4.3
4	10.85	− 0.18	− 1.6
5	11.30	+ 0.27	+ 2.4
6	10.60	− 0.43	− 3.9

Mean value: 11.0 cal/g.
Standard deviation: ± 0.16 cal/g resp. ± 1.5%.

IV. Comparison of the different methods of surface area determination

In Table IX, results of surface area determinations are compiled, which were obtained by the different methods discussed in this paper.

Table IX

Adsorbent	BET		Graphical		Restrictedly miscible systems, ratio with			Heat of immersion, ratio
	F m^2/g	ratio of surface areas	F m^2/g	ratio of surface areas	n-butyl alcohol	n-amyl alcohol	methylenic blue	
Al_2O_3 (Al-226)	274 ± 5%	1	259 ± 5%	1	—	—	1	1
Al_2O_3 (Contact)	196 ± 5%	0.72	186 ± 5%	0.72	—	—	0.68	0.88
Al_2O_3 (Rb-50)	149 ± 5%	0.54	142 ± 8%	0.55	—	—	0.34	0.60
Charcoal (Nuxit AI)	620 ± 5%	1	590 ± 5%	1	1	1	1	1
Charcoal (Nuxit AII)	770 ± 5%	1.24	804 ± 5%	1.36	—	—	1.04	1.15
Charcoal (Nuxit AIII)	840 ± 5%	1.35	895 ± 5%	1.52	1.18	1.10	1.09	1.28
1	2		3		4			5

Remarks: 1. The alumina adsorbents were activated at 500 °C and dried at 120 °C, before carrying out the measurement. The samples of charcoal labelled Nuxit AI and AII were obtained from Nuxit AIII partially burning out. The charcoal samples were dried at 120 °C before measurement.

2. Specific surface area values computed with the BET method from nitrogen adsorption isotherms determined at the temperature of liquid air.

3. Specific surface areas calculated with the graphical method from the adsorption isotherms of ethyl alcohol-benzene mixtures.

4. Data obtained from the adsorption isotherms of solutes partially miscible with water.

5. Results of measurements carried out with water as a wetting liquid.

The comparison of these results and the foregoing discussion of the several methods justifies the statement that from among the methods based upon liquid adsorption only the graphical one can be considered as self-consistent *i. e.* not requiring vapour adsorption measurements. From between the two methods suitable but for relative surface area determinations, the measurement of the heat of immersion seems to be more reliable. With this method two uncertainty factors are eliminated, namely which have to be

reckoned with in the case of the adsorption of partially miscible systems. One of these is the question of accessibility of the surface. Liquids with small molecules can be used for the determination of the heat of immersion (water, methyl and ethyl alcohol) for which, even in the case of micropores, there is not the slightest danger that a considerable part of the surface could not be reached by the molecules. The other uncertainty arises from the feature of the adsorption isotherms of partially miscible systems, that no information on the extent of the adsorption of the solvent can be acquired.

Summary

The potentialities of specific surface area determination carried out by computations from isotherms of completely and of partially miscible liquid pairs and further on the basis of the measurement of heats of immersion, have been examined.

1. The isotherms of the majority of completely miscible liquid pairs have a linear section. In this case the absolute amounts of the two components constituting the interfacial layer are given by the intercepts of the extrapolated linear section with the two axes corresponding to the pure components. (Graphical method.) In case of physical adsorption, the values of specific surface areas as determined by the BET method from nitrogen adsorption and those obtained by the graphical one, assuming a unimolecular layer, are in good agreement. The graphical method is thus suitable for the absolute determination of specific surface areas.

2. In the majority of cases, no absolute surface area can be determined from the isotherms of partially miscible liquid pairs, also relative surface area determinations are uncertain as in general not only the magnitude of the surface, but also its quality as well as its structure (size of the pores) may vary from adsorbent to adsorbent, even in case of an identical chemical composition. A quantitative distinction between the three effects seems scarcely possible.

3. On adsorbents of identical type, relative surface area determinations can be carried out by the measurement of the heat of immersion. This technique is more advantageous than the surface area determination from adsorption isotherms of partially miscible liquid pairs, because here the problem of surface accessibility and the effect of the solvent are ruled out, whereas on the other hand the results may be distorted by a possible qualitative difference between the surfaces to be compared.

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PROF. G. SCHAY
L. G. NAGY
T. SZEKRÉNYESY
Budapest XI. Sztoczek u. 2. Hungary