

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON COLLOID AND SURFACE CHEMISTRY
INCLUDING CATALYSIS*

REPORTING DATA ON ADSORPTION
FROM SOLUTION AT THE
SOLID/SOLUTION INTERFACE

(Recommendations 1986)

Prepared for publication by

D. H. EVERETT

School of Chemistry, University of Bristol, UK

*Membership of the Commission during the period (1979–85) in which the report was prepared was as follows:

Chairman: 1979–83 J. Lyklema (Netherlands); 1983–85 K. S. W. Sing (UK); *Vice-Chairman:* 1979–85 J. Haber (Poland); *Secretary:* 1979–83 M. Kerker (USA); 1983–85 E. Wolfram (Hungary); *Members:* J. H. Block (FRG; Titular 1983–85, Associate 1979–83); N. V. Churaev (USSR; Associate 1979–85); D. H. Everett (UK; National Representative 1979–85); G. F. Froment (Belgium; National Representative 1981–85); P. C. Gravelle (France; Associate 1979–85); G. L. Haller (USA; Associate 1979–81); R. S. Hansen (USA; Titular 1979–83); R. A. W. Haul (FRG; National Representative 1979–83); J. W. Hightower (USA; Associate 1983–85); R. J. Hunter (Australia; Associate 1979–85); L. G. Ionescu (Brazil; National Representative 1983–85); A. S. Kertes (Israel; National Representative 1979–85); A. Kitahara (Japan; National Representative 1979–85); J. C. Kuriacose (India; National Representative 1983–85); J. Lyklema (Netherlands; National Representative 1983–85); A. Maroto (Argentina; Associate 1983–85, National Representative 1981–83); S. G. Mason (Canada; National Representative 1979–85); K. Meyer (GDR; National Representative 1981–85); P. Mukerjee (USA; Associate 1979–83); L. G. Nagy (Hungary; National Representative 1979–85); H. van Olphen (Netherlands; Associate 1979–83); J. A. Pajares (Spain; National Representative 1981–83); M. W. Roberts (UK; Titular 1979–83); J. Rouquérol (France; Associate 1983–85); K. S. W. Sing (UK; Associate 1979–83); P. J. Stenius (Sweden; Titular 1983–85, Associate 1981–83); M. S. Suwandi (Malaysia; National Representative 1983–85); K. Tamaru (Japan; Titular 1979–83); L. Terminassian-Saraga (France; Titular 1983–85, Associate 1979–83); A. Weiss (FRG; National Representative 1983–85); P. B. Wells (UK; Associate 1983–85); E. Wolfram (Hungary; Titular 1979–83).

Considerable assistance in the preparation of this report was given by G. Schay (Hungary), who produced the first draft.

Republication of this report is permitted without the need for formal IUPAC permission on condition that an acknowledgement, with full reference together with IUPAC copyright symbol (© 1986 IUPAC), is printed. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.

Reporting data on adsorption from solution at the solid/solution interface (Recommendations 1986)

ABSTRACT This document is a companion to that on Reporting Physisorption Data for Gas/Solid Systems, and is designed to supplement the discussion of adsorption at the solid/solution interface given in the Manual of Symbols and Terminology for Physico-chemical Quantities and Units, Appendix II, part 1: Definitions, Terminology and Symbols in Colloid and Surface Chemistry, Pure Appl. Chem. 31, 579-638 (1972), section 1.1.10.

The definitions of adsorption from solution used here are essentially those adopted in the Manual. A discussion is then given of the operational determination of adsorption from solution, and includes an outline of various available experimental techniques, and recommendations concerning the precautions which need to be taken to ensure reliable results. Recommendations are made regarding the form in which results should be published.

The interpretation of adsorption data in thermodynamic terms is discussed as is the role of adsorption models in elucidating the molecular processes involved in adsorption. Attention is also drawn to the problems associated with the effects of surface heterogeneity on adsorption from solution.

CONTENTS

SECTION 1.	INTRODUCTION
SECTION 2.	DEFINITIONS OF ADSORPTION FROM SOLUTION
	2.1 Introduction
	2.2 Use of a Gibbs dividing surface
	2.3 Special case of pure liquids
SECTION 3.	OPERATIONAL DETERMINATION OF ADSORPTION FROM SOLUTION
	3.1 Methodology
	3.2 Practical considerations and precautions
	3.3 Immersion method
	3.4 Circulation method
	3.5 Chromatographic method
	3.6 Slurry method
	3.7 Null method
	3.8 Radioactive method for low surface areas
	3.9 Other methods
	3.10 Guidance on choice of methods
SECTION 4.	EVALUATION OF ADSORPTION DATA
	4.1 Presentation of primary data
	4.2 Classification of adsorption isotherms
SECTION 5.	INTERPRETATION OF ADSORPTION DATA: THERMODYNAMIC METHODS
	5.1 Interfacial tension of the fluid/solid interface
	5.2 Enthalpy and entropy of immersion (or wetting)
	5.3 Interpretation
SECTION 6.	INTERPRETATION OF ADSORPTION DATA: USE OF ADSORPTION MODELS
	6.1 General
	6.2 Surface phase model
	6.3 The layer model
	6.4 Pore filling model
	6.5 Other models
SECTION 7.	SURFACE HETEROGENEITY
SECTION 8.	GENERAL CONCLUSIONS AND RECOMMENDATIONS
	NOTES AND REFERENCES
	LIST OF SYMBOLS

1 INTRODUCTION

The study of adsorption from liquid solutions by solids has expanded rapidly in recent years, and various procedures have been adopted by different workers in presenting and interpreting their work. To ensure that experimental studies contribute most effectively to the understanding of the basic phenomena it is desirable that work from different laboratories be presented in a way which encourages the intercomparison of results and their assimilation into a reliable body of scientific information.

This manual is intended to present a definitive summary of the basis upon which an understanding of the phenomenon of adsorption is founded, to outline various possible experimental techniques for obtaining adsorption isotherms and to consider the ways in which such data can be interpreted. A major objective is to ensure that the data are obtained by reliable techniques and are presented in the literature in a manner that enables them to be interpreted by other workers.

The scope of this report is limited to the reversible adsorption of small non-ionic species by inert solids. It thus excludes adsorption from solutions of strong electrolytes, ion-exchange processes and polymer adsorption. On the other hand, weak electrolytes are not excluded when it can safely be assumed that adsorption of the molecular (uncharged) form predominates. Also excluded are phenomena involving the penetration of the adsorbate into the structure of the adsorbent (e.g. swelling of clay minerals) and adsorption into swollen gels. Note (a)*.

Consideration is in the main restricted to binary solutions or liquid mixtures. Although adsorption from multicomponent systems is of growing importance, e.g. in liquid chromatography and in many practical purification processes, the presentation of a completely general treatment would lead to complications that would obscure some of the underlying features. In very dilute solutions certain approximations to the equations are often justified.

The symbols and terminology used are generally in accordance with the IUPAC Manual of Symbols and Terminology for Physicochemical Quantities and Units, Appendix II, part 1, which deals with Colloid and Surface Chemistry (Note b). The notations for surface excesses in this Manual, although strictly logical tend to be somewhat clumsy and it would seem desirable to adopt simpler abbreviations for the specific excess quantities $n_1^{\sigma(n)}/m$, $n_1^{\sigma(v)}/m$ etc. Alternative symbols that have been used are χ, Ω and n_1^e (the latter particularly by chemical engineers). If authors employ one of these alternatives they should take care to define clearly its relationship to the more explicit quantities $n_1^{\sigma(n)}/m$ etc. The use of Γ for areal excess quantities (e.g. $n_1^{\sigma(n)}/A_s$) is well established. However, since the specific surface areas of particulate solids and porous adsorbents are not always known reliably it is not always possible, nor even desirable, to report experimental data in terms of Γ .

2 DEFINITIONS OF ADSORPTION FROM SOLUTION

2.1 Introduction

The primary experimental observation leading to the concept of adsorption from solution by a solid is that there is a discrepancy between the overall stoichiometric composition and that calculated from the known concentration in the bulk liquid phase and its volume (or mass), assuming that this concentration is uniform throughout the liquid phase. These discrepancies, which for a given component may be positive or negative, are then attributed to non-uniform composition of the liquid phase in the immediate neighbourhood of the phase boundary.

A quantitative mathematical description of the phenomenon of adsorption may be developed either in terms of the concept of a Gibbs dividing surface, or in purely algebraic terms (Note c).

2.2 Use of a Gibbs dividing surface

The concept of a Gibbs dividing surface in its general form is outlined in the Manual, Appendix II. For each interface the adsorption or surface excess of a given component is defined as the difference between the amount of component actually present in the system, and that which would be present (in a reference system) if the bulk concentrations in the adjoining phases were maintained up to a chosen geometrical dividing surface (Gibbs dividing surface, or GDS). In the particular case of a solid/liquid interface in which no component of the liquid phase penetrates into the solid, the situation may be depicted schematically as in figure 1, where the local concentration of a specified component i is plotted as a function of the distance z from a plane solid surface.

* Explanations of all Notes are provided in the Section NOTES AND REFERENCES on page 982.

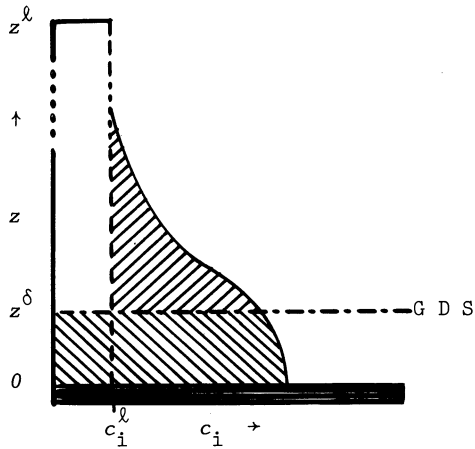


Figure 1: Concentration profile of component i as function of distance z from a plane solid surface (schematic).

If the volume of the liquid phase up to an arbitrarily chosen GDS at z^δ is V^ℓ , then the surface excess, or adsorption, of component i is defined as

$$n_i^\sigma = n_i - V^\ell c_i^\ell, \tag{1}$$

where n_i is the total amount of i in the system and c_i^ℓ is its bulk concentration in the liquid. (Note d)

The total amount of i is given in terms of the local concentrations by

$$n_i = A_s \int_0^{z^\ell} c_i dz,$$

where A_s is the area of the dividing surface, so that since

$$V^\ell = A_s \int_0^{z^\ell} dz,$$

$$n_i^\sigma = A_s \left[\int_{z^\delta}^{z^\ell} (c_i - c_i^\ell) dz + \int_0^{z^\delta} c_i dz \right]; \tag{2}$$

i.e. n_i^σ per unit area is given by the sum of the areas of the two shaded portions of the diagram. The surface excess concentration (or areal surface excess) is denoted by $\Gamma_i = n_i^\sigma / A_s$.

The value to be ascribed to Γ_i clearly depends on the choice of the location of the GDS:

$$(d\Gamma_i / dz^\delta) = c_i^\ell. \tag{3}$$

For a binary solution the variation of Γ_1, Γ_2 with z^δ can be represented as in figure 2.

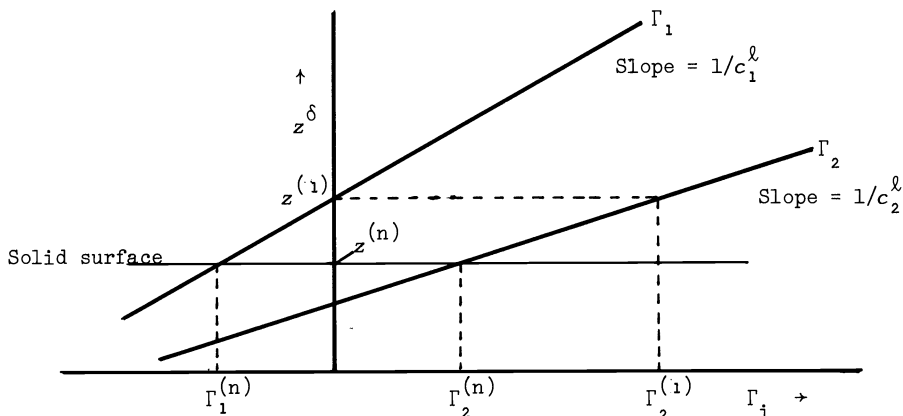


Figure 2: Variation of Γ_1 and Γ_2 as functions of choice of position z^δ of the G.D.S.

To obtain a well-defined measure of adsorption it is necessary to formulate a definition that is independent of the choice of the GDS. Two convenient alternative definitions may be derived as follows.

The surface excesses of 1 and 2 may be written

$$n_1^\sigma = n_1 - V^l c_1^l, \quad (4a)$$

$$n_2^\sigma = n_2 - V^l c_2^l, \quad (4b)$$

where V^l is the volume of the liquid phase up to the arbitrarily chosen GDS. Elimination of V^l from these equations leads to the *relative surface excess of 2 with respect to 1*:

$$n_2^{\sigma(1)} = n_2^\sigma - n_1^\sigma (c_2^l/c_1^l) = n_2 - n_1 (c_2^l/c_1^l). \quad (5)$$

Since the right-hand side of this equation contains only experimental quantities, the left-hand side must be independent of the position of the GDS. On division by A_s ,

one defines $\Gamma_2^{(1)}$, the *areal relative surface excess of 2 with respect to 1*, by

$$\Gamma_2^{(1)} = n_2^{\sigma(1)}/A_s = \frac{1}{A_s} \left[n_2 - n_1 \left(\frac{c_2^l}{c_1^l} \right) \right] = \Gamma_2 - \Gamma_1 \left(\frac{c_2^l}{c_1^l} \right) = \Gamma_2 - \Gamma_1 \left(\frac{x_2^l}{x_1^l} \right), \quad (6)$$

where x_2^l is the mole fraction of 2 in the bulk liquid.

$\Gamma_2^{(1)}$ as defined by (6) is independent of the choice of GDS. However, if the GDS is chosen such that $\Gamma_1 = 0$, then $\Gamma_2^{(1)}$ is the value of Γ_2 for this particular choice. This is illustrated in figure 2, where $\Gamma_2^{(1)}$ is the value of Γ_2 when z^δ is chosen at $z^{(1)}$. The relation (6) follows immediately from the geometry of this figure.

Alternatively, the surface excess of 2 and the total surface excess may be written

$$n_2^\sigma = n_2 - V^l c_2^l, \quad (7a)$$

$$n^\sigma = n^0 - V^l c^l, \quad (7b)$$

where n^0 is the total amount of substance present and c^l the total concentration.

Eliminating V^l leads to the *reduced surface excess*:

$$n_2^{\sigma(n)} = n_2^\sigma - n^\sigma (c_2^l/c^l) = n_2^\sigma - n^\sigma x_2^l = n_2 - n^0 x_2^l. \quad (8)$$

Again the right-hand side is an experimental quantity so that the left-hand side is independent of the GDS. On division by A_s , the *areal reduced surface excess*, denoted by $\Gamma_2^{(n)}$, is defined as

$$\Gamma_2^{(n)} = n_2^{\sigma(n)}/A_s = \Gamma_2 - \Gamma x_2^l = \frac{1}{A_s} (n_2 - n^0 x_2^l). \quad (9)$$

$\Gamma_2^{(n)}$ as defined in equation (9) is independent of the GDS. However, if the GDS is defined such that $\Gamma = \Gamma_1 + \Gamma_2 = 0$, then $\Gamma_2^{(n)}$ is the value of Γ_2 for this particular choice. It follows therefore that

$$\Gamma_1^{(n)} = -\Gamma_2^{(n)}. \quad (10)$$

This is also illustrated in figure 2 where $\Gamma_2^{(n)}$ is the value of Γ_2 when z^δ is chosen at $z^{(n)}$, which also co-incides with the surface of the solid.

The relationship between $\Gamma_2^{(1)}$ and $\Gamma_2^{(n)}$ follows if in equation (6) we insert $\Gamma_1^{(n)} = -\Gamma_2^{(n)}$, in place of Γ_1 and Γ_2 respectively, whence

$$\Gamma_2^{(1)} = \Gamma_2^{(n)}/x_1^l. \quad (11)$$

The importance of this equation arises because in many experimental methods it is $\Gamma_2^{(n)}$ that is measured, while $\Gamma_2^{(1)}$ is the quantity which occurs in the fundamental thermodynamic equations.

For dilute solutions $x_1^l \rightarrow 1$ and $\Gamma_2^{(1)} \rightarrow \Gamma_2^{(n)}$.

If the composition of the bulk solution is expressed in mass fractions w_1^l, w_2^l then the surface excess masses of the components are given by

$$m_2^{\sigma(1)} = m_2^{\sigma} - m_1^{\sigma} \left(\frac{w_2^{\ell}}{w_1^{\ell}} \right) = m_2 - m_1 \left(\frac{w_2^{\ell}}{w_1^{\ell}} \right), \quad (12a)$$

$$m_2^{\sigma(m)} = m_2^{\sigma} - m^{\sigma} w_2^{\ell} = m_2 - m^{\sigma} w_2^{\ell}, \quad (12b)$$

with

$$m_2^{\sigma(1)} = m_2^{\sigma(m)} / w_1^{\ell}. \quad (12c)$$

Equations (9) and (12b) lead immediately to a prescription for measuring the reduced surface excess amount or reduced surface excess mass. In each case the first term on the right of the last equality sign is the total amount, or total mass, of component 2. This is known from the composition (x_2° or w_2°) of the solution before equilibration with the solid sample:

$$n_2 = n^{\circ} x_2^{\circ}; \quad m_2 = m^{\circ} w_2^{\circ}.$$

Hence

$$n_2^{\sigma(n)} = n^{\circ} (x_2^{\circ} - x_2^{\ell}) = n^{\circ} \Delta x_2^{\ell}, \quad (13a)$$

$$m_2^{\sigma(m)} = m^{\circ} (w_2^{\circ} - w_2^{\ell}) = m^{\circ} \Delta w_2^{\ell}. \quad (13b)$$

Alternatively, since $n^{\circ} = n_1 + n_2$, and $m^{\circ} = m_1 + m_2$,

$$n_2^{\sigma(n)} = n_2 x_1^{\ell} - n_1 x_2^{\ell}, \quad (14a)$$

$$m_2^{\sigma(m)} = m_2 w_1^{\ell} - m_1 w_2^{\ell}. \quad (14b)$$

These two quantities are related by

$$m_2^{\sigma(m)} = n_2^{\sigma(n)} (w_1^{\ell} M_2 + w_2^{\ell} M_1) = n_2^{\sigma(n)} \frac{M_1 M_2}{x_1^{\ell} M_1 + x_2^{\ell} M_2}, \quad (14c)$$

where M_1 and M_2 are the molar masses of the two components.

In most earlier work and in much recent work, adsorption from solution is reported in terms of liquid volumes and volume concentrations. If V° is the initial volume of liquid (Note e)

$$n_2^{\sigma(v)} = V^{\circ} \Delta c_2^{\ell}. \quad (15)$$

Provided that the partial molar volumes, v_1 and v_2 of the components are constant in the concentration interval considered, then the following relation holds:

$$n_2^{\sigma(v)} = \left[1 + (v_1 - v_2) c_2^{\ell} \right] n_2^{\sigma(n)}. \quad (16)$$

v_1 and v_2 are in general concentration dependent (except for perfect or ideal dilute solutions). However, if $(v_1 - v_2)$ is small enough (say less than $10^{-1} \text{ dm}^3 \text{ mol}^{-1}$) and the equilibrium solution sufficiently dilute (say $c_2^{\ell} < 10^{-1} \text{ mol dm}^{-3}$) the second term in the brackets on the right-hand side of (16) will be practically negligible and the two measures of the surface excess will be approximately equal. Since, however, we are often interested in the course of the adsorption isotherm at higher concentrations, or in the case of completely miscible systems over the whole concentration range, the use of $n_2^{\sigma(v)}$ is to be discouraged especially since the collection of data necessary for the representation of the data according to equations (13a or b) is hardly more cumbersome from the experimental point of view.

2.3 Special case of pure liquids (Note f)

In the case of a pure liquid, despite its low compressibility, the variation of density near a solid surface can be detected and measured. The total volume V of a system consisting of solid and pure liquid is different from (usually less than) that calculated assuming a constant liquid density. If the densities of bulk solid (ρ^{sol}) and liquid (ρ^{ℓ}) are known then an excess volume (usually negative) can be defined as:

$$V^{\sigma} = V - V^{\text{sol}} - V^{\circ} = V - m^{\text{sol}} / \rho^{\text{sol}} - m^{\ell} / \rho^{\ell}; \quad (17)$$

here m^{sol} is the mass of solid and V^{sol} its volume calculated from the bulk density, and m^{ℓ} is the mass of liquid. Alternatively the excess mass is

$$m^{\sigma} = m^{\ell} - (V - V^{\text{sol}}) \rho^{\ell}, \quad (18)$$

and the areal excess mass

$$\Gamma = \{m^{\ell} - (V - V^{\text{sol}}) \rho^{\ell}\} / A_S. \quad (19)$$

If the compressibility of the solid is much less than that of the liquid, these excesses can be attributed to changes in the density of the liquid in close proximity to the solid surface. Such changes must also occur in the case of mixtures, but they do not affect the definitions in equations (13).

3 OPERATIONAL DETERMINATION OF ADSORPTION FROM SOLUTION

3.1 Methodology

The basic experimental method of determining adsorption from solution takes, in effect, the solid surface as the GDS, and measures $\Gamma_2^{(n)}$.

The simplest method follows from equation (13a). A sample of liquid containing an amount n_2^0 at a mole fraction x_2^0 is equilibrated with a mass m of solid and the final mole fraction x_2^l is measured. The reduced surface excess of component 2 is then given by equation (13a):

$$n_2^{\sigma(n)} = n_2^0 \Delta x_2^l \quad (13a)$$

The specific reduced surface excess and the areal reduced surface excess are then

$$n_2^{\sigma(n)}/m = n_2^0 \Delta x_2^l / m \quad (20)$$

and

$$\Gamma_2^{(n)} = n_2^0 \Delta x_2^l / (m a_s) \quad (21)$$

where a_s is the specific surface area of the solid. Similar equations, following from equation (13b) apply if mass and mass fractions are measured. The alternative method using equation (15) may be used if the solutions are sufficiently dilute so that $\Gamma_2^{(v)} \approx \Gamma_2^{(n)}$. It is not recommended for use at higher concentrations.

Experiments are repeated with different concentrations of liquid to build up an adsorption isotherm (specific reduced surface excess isotherm, sometimes called the 'composite isotherm') in which $n_2^{\sigma(n)}/m$ or $\Gamma_2^{(n)}$ is given as a function of x_2^l .

3.2 Practical considerations and precautions

- (i) In selecting systems for the study of adsorption from solution it is important to check that the adsorbent does not swell, dissolve or otherwise deteriorate in contact with the solution, and that the adsorption is reversible with respect to changes of temperature and/or composition of the liquid phase. If these criteria are not met, then caution is required in the interpretation of the results.
- (ii) In certain circumstances it may be necessary to eliminate or allow for adsorption on, or reaction of the components of the liquid with, the walls of the experimental apparatus. Particular care is needed if a filter is used to separate the solid from the liquid.
- (iii) If the surface of the solid is contaminated with a soluble constituent, then previous rinsing or leaching of the adsorbent with a suitable solvent may remove the contamination, but in unfavourable cases this may alter the structure of the surface and/or its specific surface area.
- (iv) It is preferable that the adsorbent should be outgassed before use, bearing in mind the precautions outlined in 'Reporting Physisorption Data for Gas/Solid Systems' (Note g).
- (v) In some techniques each measurement is made with a fresh sample of adsorbent. Consequently the homogeneity of the adsorbent must be checked carefully. The homogeneity of commercial adsorbents may sometimes be poor, and a comparatively large number of replicate measurements on randomised samples may be needed to obtain sufficiently reliable results. Such replications should all be carried out at the same liquid/solid ratio. In many cases proper attention must be paid to the method of sampling the adsorbent to obtain a representative sample.
- (vi) The purity of the components of the solution and the avoidance of contamination during preparation and handling are essential. When working with organic media, contamination with water can have a drastic effect on the measurements.
- (vii) After equilibration, the adsorbent together with the adsorbate bound to it must be separated from the bulk equilibrium liquid by sedimentation, centrifugation or filtration. The separation must be carried out at the same temperature as that at which equilibrium was established, and for experiments far from ambient temperatures special techniques (e.g. a thermostatted centrifuge) are needed.
- (viii) The supernatant liquid has to be subjected to chemical analysis to obtain Δx_2^l . Any analytical method which is sensitive and accurate enough can be used, but in practice optical methods are most frequently employed e.g. refractometry, colorimetry or spectrophotometry. The latter can also be used for uncoloured substances that can be transformed into coloured ones by the addition of suitable reagents. By using radio-labelled adsorptives, measurement of changes of radioactivity can also be employed.

In the case of volatile liquids, appropriate measures have to be taken at all stages in the experiment to minimise losses by evaporation which may change the concentration of the liquid. This is a particular problem if the concentration of the equilibrium liquid is determined using a conventional refractometer (i.e. Abbé or Pulfrich). It should also be noted, in work aiming at high precision, that the refractive index of liquid mixtures can be affected significantly by dissolved air. To avoid the necessity of the conversion of volume fractions to mole fractions, it is advisable to determine the calibration curve for any analytical method with solutions prepared on a weight/weight basis.

- (ix) The liquid/solid ratio has to be chosen appropriately. The smaller the ratio the greater will be the resulting change Δx_2^l and thus the accuracy.

(x) It is important to check that equilibrium has been achieved: this may take as little as 1-2h. with non-porous adsorbents, but may extend to 1-2 days with porous adsorbents since diffusion within pores cannot be influenced by agitation. A reduction in grain size of the adsorbent may increase the speed of equilibration, but may also alter the adsorption capacity either by increasing the accessibility of the pores, or increasing the external surface area.

(xi) If the excess isotherm is determined with the objective of finding the best conditions for the practical use of the adsorbent, exhaustive treatment with the solvent to be used subsequently is recommended. Great care and circumspection is needed if the aim of the investigation is the intercomparison of the adsorption behaviour of an adsorbent with different solutions in various solvents.

3.3 Immersion method (Note h)

The traditional method of determining adsorption from solution is to add a known mass of solid to a measured amount of solution of known composition in a convenient container which is then sealed and equilibrated, usually with agitation, in a thermostat. Violent agitation which may lead to abrasion of the solid particles is to be avoided. A sample of supernatant liquid is withdrawn and analysed to obtain the change in mole fraction or of concentration.

This method, although widely used in the past, and still popular for less precise work, is tedious and suffers from a number of important disadvantages for accurate work.

Among the factors that have to be borne in mind when using this method are the following.

- (i) Preliminary work is needed to establish the time needed to establish equilibrium.
- (ii) Outgassing of the components of the solution and of the solid, and their mixing out of contact with the atmosphere requires an elaborate technique.
- (iii) Problems also arise in the separation of adsorbent and supernatant liquid if experiments are carried out at temperatures other than ambient, or if the system is sensitive to atmospheric contamination.
- (iv) Since each experiment is usually made with a fresh sample of adsorbent, random sampling errors may become important.
- (v) In choosing an appropriate liquid/solid ratio, this must be large enough to ensure the retrieval of a sample of bulk liquid sufficient for analysis - preferably for duplicate or replicate determinations.

3.4 Circulation method (Note i)

Many of the problems associated with the classical immersion method may be eliminated if the procedure is carried out in the absence of air and equilibrium is achieved by circulating the liquid over a sample of solid, the concentration of the liquid being monitored continuously by passage through a flow refractometer or other convenient concentration measuring device. A differential method in which solution of the initial concentration is circulated through the reference cell of the refractometer is particularly convenient.

Among the advantages of such a technique are the following.

- (i) The adsorption cell may be accurately thermostatted and the temperature dependence of the adsorption determined by varying the cell temperature without the need to refill the apparatus.
- (ii) The same sample of adsorbent can be used throughout, and the constancy of its properties checked from time to time. If the components of the liquid are volatile the adsorbent can be outgassed under controlled conditions before and between measurements, while if one or both of the components is of low volatility the adsorbent can be contained in a demountable (e.g. stainless steel) cell and can be washed with a suitable solvent, replaced and outgassed.
- (iii) The solutions can be made up from thoroughly purified and outgassed components on a vacuum line and transferred in vacuo to the outgassed measuring line.
- (iv) The approach to equilibrium can be monitored continuously.
- (v) Calibrations can be associated with each experiment by injecting samples of the non-preferentially adsorbed component into the reference circuit.

A number of relatively minor limitations of this method remain. Thus an accurate value of n^0 is needed, so that the quantitative accuracy of the transfer of solution from the preparation cell into the apparatus must be checked. Care has to be taken to ensure that there are no stagnant regions in the circulation system where the solution concentration may not be at the equilibrium value. Consideration also has to be given to the design of suitable pumps that will neither adsorb the solution components, contaminate the system, nor be corroded when used with aggressive solutions. Difficulties may also arise if the solid pack is not readily permeable to the circulating liquid. Some materials may tend to gel in contact with the solution and in such cases the method may not be practicable. The method also becomes less accurate in very dilute solution.

3.5 Chromatographic method (Note j)

In this technique the solid adsorbent is used as the column packing and measurements are made of the concentrations of ingoing and outgoing solution. The difference between them Δc_2 , may again be monitored conveniently using a differential refractometer. The volume of liquid V , passing through the column must also be measured, and the experiment continued until the inlet and outlet concentrations are equal. The reduced surface excess at this concentration is given by

$$n^{\sigma(n)} = \int_0^{V_f} \Delta c_2 dV, \quad (22)$$

where V_f is a value greater than that needed to bring Δc_2 back to zero. This technique is particularly useful when working with very dilute solutions, although it may have the disadvantage that large volumes of solution are used up in each run.

3.6 Slurry method (Note k)

This variant on the immersion method overcomes the difficulty of rigorous separation of the supernatant. The sample after equilibration is centrifuged and a weighed sample of the slurry is taken and analysed. In effect, use is made of equation (6):

$$n_2^{\sigma(1)}/m = \frac{1}{m} \left[n_2 - n_1 \left(\frac{c_2}{c_1} \right) \right] = \frac{n_1}{m} \left[\frac{n_2}{n_1} - \frac{c_2}{c_1} \right], \quad (23)$$

where m is the mass of solid in the slurry sample, n_1 and n_2 the amounts of components 1 and 2 in the slurry and c_1 and c_2 the concentrations in the bulk solution. If the liquid/solid ratio in the equilibration step is large, then c_1 and c_2 will be the same as those in the original solution. By having a small liquid/solid ratio in the slurry n_1/m is small and consequently the term in brackets is correspondingly large and can be determined accurately.

3.7 Null method (Note l)

An alternative procedure is to equilibrate an amount n^0 of initial solution of mole fraction x_2^0 with a mass m of solid, and then add to the system an amount Δn^a of a solution of mole fraction x_2^a such that the final concentration of solution returns to x_2^0 . The total amount of component 2 in the system is $(n^0 x_2^0 + \Delta n^a x_2^a)$. If the mole fraction in the liquid phase were constant up to the solid surface the amount of 2 present would be $(n^0 + \Delta n^a) x_2^0$. The reduced surface excess amount of 2 is therefore

$$\begin{aligned} n_2^{\sigma(n)} &= (n^0 x_2^0 + \Delta n^a x_2^a) - (n^0 + \Delta n^a) x_2^0 \\ &= \Delta n^a (x_2^a - x_2^0), \end{aligned} \quad (24)$$

or

$$\Gamma_2(n) = \frac{\Delta n^a}{m a_s} (x_2^a - x_2^0). \quad (25)$$

In the particular case in which pure component 2 is added

$$\Gamma_2(n) = \frac{\Delta n_2^a}{m a_s} (1 - x_2^0). \quad (26)$$

It follows, from (11), that for a binary system the relative adsorption of component 2 is given by

$$\Gamma_2(1) = \frac{\Delta n_2^a}{m a_s} \quad (27)$$

i.e. Δn_2^a is a direct measure of the relative adsorption. (Note m)

Experimentally this procedure is easily realised using a circulation technique. It is in fact not necessary to inject exactly the correct amount of pure component 2 to bring the solution concentration back to x_2^0 , since the injection of several aliquots enables the required quantity to be obtained either by interpolation or extrapolation.

The important feature of this method is that it does not require a knowledge of n^0 , nor is it necessary to calibrate the detection system. It retains all the advantages of the circulation method, but in addition it has the major advantage that it is unnecessary to know the amount of solution with which the solid is equilibrated.

3.8 Radioactive method for low surface areas

Certain specialised techniques have been developed to meet specific problems. For example, the radioactive method may be used for the adsorption, or co-adsorption, of radio-chemically labelled substances from dilute solution at the surface of a thin extended solid sample transparent to the radiation emitted by the labelling nuclides. One side of the solid is equilibrated with the solution, and the other side faces an appropriate detector. If co-adsorption is to be studied then it is necessary to use specifically labelled co-adsorptives.

3.9 Other methods

Adsorption from solution may also be studied by a variety of other techniques such as various forms of spectroscopy (i.r., u.v., n.m.r., e.s.r.), neutron scattering, and ellipsometry. These

provide important information on the molecular state of the interfacial region, but do not usually lead to a strictly defined measure of the amount adsorbed.

3.10 Guidance on choice of methods

The choice of method of measuring adsorption from solution by solids with high specific surface areas depends on the type of system being studied and the objectives of the work. The immersion method is often chosen because of the simplicity of the apparatus needed and the use of standard laboratory techniques. It may be the preferred method for a preliminary study in which relatively few experimental points are needed to establish the general pattern of behaviour. However, even in such cases care must be taken when using volatile liquids and especially when the preferential adsorption is small: it appears that some early work is in serious error because of failure to take adequate precautions.

The slurry method has a number of advantages in that the total amount of the components in the slurry, and not their concentrations, are measured. The chromatographic method is particularly useful when working with dilute solutions, where the circulation method becomes less accurate. For work of highest accuracy, especially if temperature coefficients are to be measured, one or other form of circulation apparatus is recommended. This method, however, involves the use of more sophisticated equipment including vacuum pumps, suitable liquid-circulating pumps, and some form of flow-through detector. However, equipment of this kind is readily constructed from the standard components which are now available for high performance liquid chromatography. The null method is a development of the circulation method and is to be particularly recommended for future work. The main types of system to which circulation methods are inapplicable are those in which the solid tends to form a gel in contact with the solution.

4 EVALUATION OF ADSORPTION DATA

4.1 Presentation of primary data

Adsorption data are most commonly presented in the form of *specific reduced surface excess isotherms* in which $n_2^{\sigma(n)}/m$, conveniently expressed in mmol g^{-1} (i.e. mol kg^{-1}), or $n_2^{\sigma(m)}/m$ in mg g^{-1} , is plotted against the mole fraction or mass fraction of the equilibrium bulk solution. Whenever possible, tabulated data should also be provided, or deposited in a readily accessible library or data store. It is particularly important that the preferentially adsorbed component should be clearly indicated. The tabulated data should be those derived directly from experiment and not those interpolated from a smoothed graph. Information should also be provided on the relevant details of the particular technique employed.

In all cases the following should be reported:

- (i) Characterisation of the adsorbent: chemical identity or commercial name and provenance, grain size, specific surface area (if necessary before and after pretreatment) and method of determination (Note g), mode of pretreatment, and, in the case of porous adsorbents the pore volume and pore size distribution.
- (ii) Characterisation of the solution components: chemical identity, provenance, degree of purity as supplied (e.g. analytical reagent, etc.), further purification steps, characteristic physical properties (e.g. refractive index, boiling and/or melting point, n.m.r. spectrum) chromatographic test of purity, check on absence of traces of water when this is relevant.
- (iii) Description of the experimental method: details of precautions to eliminate sources of error indicated in Section 3.2 above.
- (iv) details of the method of sampling, temperature control, analytical method, number of replicate runs and their reproducibility.

4.2 Classification of adsorption isotherms

(i) completely miscible systems

Most specific reduced surface excess isotherms measured over the whole concentration range for completely miscible liquids fall broadly into one of two classes, the so-called inverted U-shape and the S-shape isotherms (figure 3a and 3b).

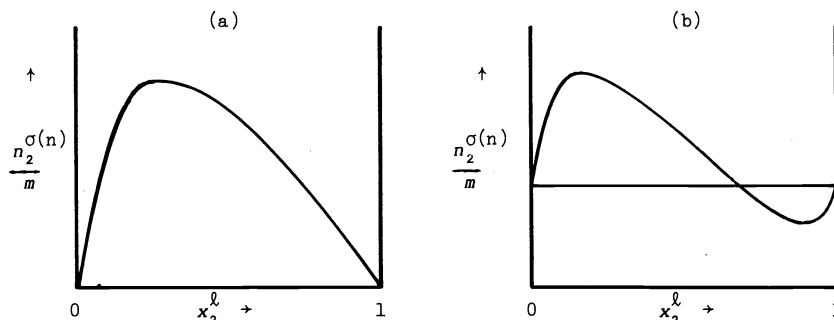


Figure 3: The two main classes of specific reduced surface excess isotherms

Variations occur in the detailed features (e.g. the length of the linear segment around the inflexion point in 3b, or the sharpness of the maximum in 3a.) A more detailed classification is possible (Note n), but the various sub-groups merge into one another, leaving as the main distinction whether or not the preferentially adsorbed component is the same over the whole concentration range, or whether there is a reversal of sign of the adsorption. In the latter case the point of intersection of the isotherm with the abscissa is called an *azeotropic point*, at which the relative composition of the surface layer is identical with that of the bulk liquid.

(ii) dilute solutions

In dilute solutions, especially when the preferentially adsorbed component is of limited solubility, the surface excess isotherms may exhibit the extreme forms shown in figures 4a and 4b.

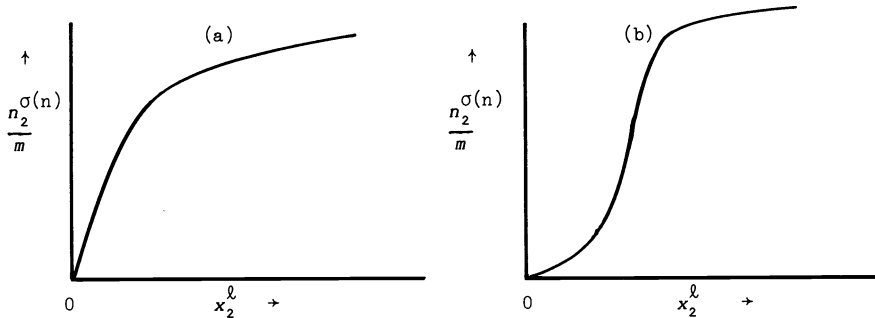


Figure 4: The two extreme types of adsorption isotherm from dilute solution

Transition from the type shown in figure 4b to that in figure 4a is often observed as the temperature is raised. Once again more detailed classifications have been proposed (Note o). At higher concentrations, if the solubility is high enough, these isotherms tend towards the shape shown in figure 3a.

(iii) special cases

In a number of special cases more complex behaviour may be observed, e.g. a point of inflexion may appear on the higher concentration limb of figure 3a, or the curve may show two maxima.

(iv) composite and individual isotherms

Specific reduced surface excess isotherms are often referred to as composite isotherms to distinguish them from so-called 'individual isotherms' which purport to give the adsorption of each component separately. As pointed out below (Section 6) the latter class of isotherms can only be calculated on the basis of some model of the interfacial region, and have no place in the primary presentation of experimental data.

5 INTERPRETATION OF ADSORPTION DATA: THERMODYNAMIC METHODS

5.1 Interfacial tension of the fluid/solid interface (Note p)

A thermodynamic analysis of adsorption from solution leads to the following equation (Gibbs equation) relating the so-called interfacial tension, σ , of the fluid/solid interface, defined by $(\partial G/\partial A_s)_{T,p,n_1,n_2}$ (where G is the Gibbs energy of the whole system), to the adsorption:

$$(\partial\sigma/\partial\mu_2)_{T,p} = -\Gamma_2^{(1)} = -\Gamma_2^{(n)}/x_1^l, \quad (28)$$

where μ_2 is the equilibrium chemical potential of component 2, which is the same in both liquid and interfacial regions.

Since

$$\mu_2 = \mu_2^* + RT \ln x_2^l \gamma_2^l, \quad (29)$$

where the asterisk refers to pure component 2, and γ_2^l is its activity coefficient at the mole fraction x_2^l ,

$$d\mu_2 = RT d \ln x_2^l \gamma_2^l,$$

and

$$d\sigma = -\frac{RT\Gamma_2^{(n)}}{x_1^l} d \ln x_2^l \gamma_2^l.$$

On integration

$$\sigma - \sigma_2^* = -\frac{RT}{a_s} \int_{x_2^l=1}^{x_2^l} \left\{ \frac{n_2^{\sigma(n)}/m}{x_1^l x_2^l \gamma_2^l} \right\} d(x_2^l \gamma_2^l). \quad (30)$$

Integration across the whole mole fraction range gives $\sigma_1^* - \sigma_2^*$. If a_s is not known, then the only quantity that can be calculated in this way is $(\sigma - \sigma_2^*)a_s$. The integration is most conveniently carried out graphically from smoothed curves of $(n_2^{\sigma(n)}/m)/(x_1^l x_2^l \gamma_2^l)$ against $x_2^l \gamma_2^l$.

The following important considerations must be borne in mind:

- (i) Adsorption measurements must be made accurately over the whole concentration range since it is necessary to extrapolate the curves both to pure component 2 and to infinite dilution of that component. This is particularly important at low concentrations when the bulk solution shows substantial deviations from ideal behaviour since the abscissa of the graph is $x_2^l \gamma_2^l$. For example, in the case of ethanol(1) + heptane(2) $\gamma_2^l=12$ at a mole fraction of 0.02, so that an adsorption measurement at this concentration will appear on the graph at $x_2^l \gamma_2^l = 0.24$.
- (ii) The calculation is critically dependent on accurate knowledge of the activity coefficients of the bulk solution, and it is the frequent absence of such information that makes a reliable thermodynamic analysis difficult or impossible. Constancy of the a_1^l 's is also implied.

5.2 Enthalpy and entropy of immersion (or wetting) (Note q)

The following equations enable the enthalpies and entropies of immersion to be calculated from the interfacial tensions derived according to the methods outlined in Section 5.1 as a function of temperature:

$$\Delta_w \hat{h} - \Delta_w \hat{h}_2^* = \frac{\partial}{\partial(1/T)} \left[\frac{\sigma - \sigma_2^*}{T} \right], \quad (31)$$

$$\Delta_w \hat{s} - \Delta_w \hat{s}_2^* = \frac{\partial}{\partial T} (\sigma - \sigma_2^*), \quad (32)$$

or

$$\Delta_w \hat{s} - \Delta_w \hat{s}_2^* = \frac{1}{T} \{ (\sigma - \sigma_2^*) - (\Delta_w \hat{h} - \Delta_w \hat{h}_2^*) \}. \quad (33)$$

The notations $\Delta_w \hat{h}$ and $\Delta_w \hat{s}$ refer to the enthalpy and entropy changes associated with the immersion of unit area of solid in the liquid.

Enthalpies of immersion may be determined independently by calorimetry and comparison of the values of the above differences obtained by the two methods provides a check on the reliability of the experimental methods and the methods of analysis of the adsorption data.

5.3 Interpretation

The thermodynamic quantities obtained by the above methods are independent of any physical model of the nature of the adsorption process. They can thus form the basis upon which the predictions of various theories can be compared with experiment.

It is important to observe that the thermodynamic quantities obtained are all relative to those of the reference liquid, in this case component 2. It is, in principle, possible to relate them to the properties of the clean solid surface if information on the vapour adsorption of component 2 is known accurately, but this is unfortunately not generally available.

If component 2 is only partially soluble in component 1, then the latter is conveniently taken as the reference component. By interchanging the suffixes in equation (30), and remembering that $n_1^{\sigma(n)} = -n_2^{\sigma(n)}$, values of $\sigma - \sigma_1^*$ can be calculated.

6 INTERPRETATION OF ADSORPTION DATA: USE OF ADSORPTION MODELS

6.1 General

A complete theory of adsorption at the solid/liquid interface will involve a detailed discussion of the shape of the concentration profile and of the orientations of molecules in the vicinity of the surface. Although progress is being made, none of the theories so far developed is expressed in a form that can be compared directly with experimental measurements.

At the present time, therefore, it is necessary to employ greatly simplified models which although not always physically realistic, nevertheless are useful in the correlation of experimental data.

In using such theories, it is important to bear their limitations in mind. In special cases they may give useful information about the molecular state of the interface, but they must not be used uncritically.

6.2 Surface phase model

The most commonly employed model of adsorption from solution (figure 5) approximates the concentration profile (the dashed curve) by a step function. In effect the liquid volume, containing a total amount of substance, n , is split into two parts within each of which the composition is constant: V^s in which the mole fraction is x_2^s defines the so-called 'surface phase' (Note r) and contains an amount of substance n^s , while V^l is the bulk homogeneous liquid of mole fraction x_2^l containing $n^l = n - n^s$.

The reduced surface excess in this model may be expressed in any of the following ways:

$$n_2^{\sigma(n)} = (x_2^s - x_2^l)n^s = n_2^s - n^s x_2^l = n_2^s x_1^l - n_1^s x_2^l. \quad (34)$$

If the adsorption of 2 is large enough, then at sufficiently low equilibrium concentrations $n^s x_2^l$ may become negligibly small so that $n_2^{\sigma(n)}$ can be equated to n_2^s , the amount of 2 bound by adsorption to the interface. Nothing can be said, however, concerning n_1^s , the amount of solvent present in the interfacial layer without making assumptions about the structure of the latter.

Two main models of the adsorbed phase may be considered, namely the layer model when the concept of surface area can be given a clear meaning, and the pore filling model appropriately applied to porous, especially microporous, materials where the notion of surface area becomes blurred. (Note g).

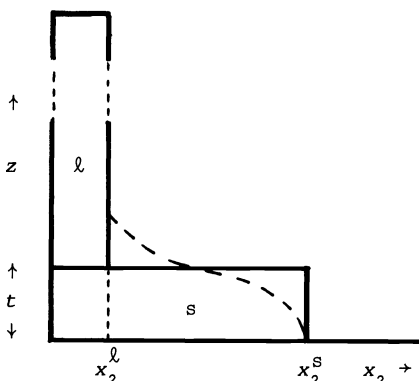


Figure 5: 'Surface phase' model in which the continuous concentration profile (dashed curve) is approximated by a step function separating the liquid phase (l) from the surface phase (s) consisting of t molecular layers

6.3 The layer model

It is assumed that the adsorbed phase consists of t layers of molecules on a plane smooth homogeneous surface. The condition that the surface is always completely covered is that

$$n_1^s a_1 + n_2^s a_2 = A_s, \quad (35a)$$

or that

$$x_1^s a_1 + x_2^s a_2 = A_s/n^s, \quad (35b)$$

where a_1 and a_2 are respectively the partial molar areas of components 1 and 2; they are approximately equal to a_1^0/t and a_2^0/t where a_1^0 and a_2^0 are the molar cross-sectional areas of the molecules. It has to be emphasised that in the case of molecules of markedly asymmetrical shape these effective cross sectional areas will depend of the orientation of the molecules with respect to the surface. As this orientation may vary along the isotherm, the values of a^0 do not necessarily remain constant, nor can it always be assumed that t is constant.

Subject to these restrictions, the mole fraction of (2) in the surface phase is given by

$$x_2^s = \frac{t x_2^l + a_1^0 \Gamma_2^{(n)}}{t - (a_2^0 - a_1^0) \Gamma_2^{(n)}}. \quad (36)$$

A widely used assumption is that $t = 1$, i.e. that the surface phase consists of a monolayer. There are strong arguments, however, partly intuitive but more precisely based on thermodynamic arguments, supporting the view that in general there must be a gradual transition in composition from that of the first layer adjoining the solid surface to that of the bulk liquid. Consequently the values attributed to x_1^s and x_2^s should more generally be regarded as mean values in the thickness t .

In many cases, however, mainly of marked preferential adsorption of one component, the monolayer model seems to be a satisfactory approximation. In these circumstances, and if the molecules are of about the same size, equation (36) reduces to

$$x_2^s = x_2^l + a \Gamma_2^{(n)}, \quad (37)$$

where a is the common value of a_1^0 and a_2^0 .

The functions $x_1^s(x_2^l)$ and $x_2^s(x_2^l)$ are often called the 'individual isotherms' for components 1 and 2 respectively, referred to in Section 4.2(iv). Before accepting a monolayer model it is essential to check its consistency by confirming that (a) values of x_1^s calculated assuming a monolayer do not exceed unity, and (b) x_1^s always increases with x_2^l i.e. $(\partial x_1^s / \partial x_2^l) > 0$. If the data fail to satisfy either of these criteria, then a minimum thickness of the surface layer may be estimated by repeating the calculation of x_1^s with increasing values of t until both criteria are satisfied.

The separation of the components brought about by adsorption can be characterised by the separation factor, S , defined as

$$S = \frac{x_2^s x_1^l}{x_2^l x_1^s} \quad (38)$$

$S > 1$ indicates preferential adsorption of component 2.

Rearrangement leads to

$$x_2^s = \frac{x_2^l/x_1^l}{1/S + x_2^l/x_1^l} \quad (39)$$

which is formally an expression of the Langmuir type with the variable x_2^l/x_1^l going from $0 \rightarrow \infty$ over the whole concentration range. This represents a true Langmuir isotherm only if S is constant.

If it is assumed that the molecules are of the same size and that both the bulk and surface phases behave ideally, then S is equal to the adsorption equilibrium constant K_a and equations (37) and (38) with (35b) and $a_1 = a_2 = a$, lead to

$$\frac{x_1^l x_2^l}{\frac{\sigma(n)}{n_2}/m} = \frac{m}{n^s} \left(x_2^l + \frac{1}{(K_a - 1)} \right) \quad (40)$$

This equation provides, in principle, a means of finding K_a and n^s/m from a graph of the left hand side against x_2^l . When n^s/m is known, the specific surface area of the solid may be calculated:

$$a_s = (n_s/m) a \quad (41)$$

In many cases, when the graphical representation of (40) is satisfactorily linear, the values of a_s derived in this way are in good agreement with those obtained by the BET method from nitrogen gas adsorption. In these instances adsorption from solution provides an alternative method of measuring specific surface areas. Even when equation (40) is not followed, other methods of using the data to estimate surface areas may often be applied (Note t).

Deviations of K from constancy may be formally associated with non-ideality of one or both of the two phases:

$$K_a = \frac{x_2^s \gamma_2^s x_1^l \gamma_1^l}{x_1^s \gamma_1^s x_2^l \gamma_2^l} = S \frac{\gamma_2^s \gamma_1^l}{\gamma_1^s \gamma_2^l} \quad (42)$$

where γ_i^s is the activity coefficient of i in the surface phase.

It is often useful to calculate the surface activity coefficients from the thermodynamically derived equation, applicable to the surface phase model (Note u):

$$\ln \gamma_i = \ln \frac{x_i^l \gamma_i^l}{x_i^s} - (\sigma - \sigma_i^*) a_i / (RT) \quad , i = 1, 2, \quad (43)$$

where $(\sigma - \sigma_i^*)$ is obtained using equation (30) and x_i^s from equation (36) or (37). The activity coefficients so derived may be compared with those for the bulk liquid. It must be stressed, however, that the concept of surface activity coefficients only has any meaning in terms of the surface phase model, and that the values calculated for these coefficients depend on what assumptions are made concerning t and a_i . These assumptions must always be stated explicitly.

6.4 Pore filling model

In the case of adsorbents with narrow pores, especially micropores, where the clear meaning of the concept of surface area, and the picture of mono- or multilayer coverage becomes blurred or even meaningless (Note g), it is more appropriate to consider the material in the pore volume V_p as the adsorbed phase. In this case one must analyse the data in terms of specific rather than areal quantities. However, in interpreting adsorption data for such systems one must bear in mind that molecular sieving effects may complicate the phenomenon.

In the absence of such complicating factors the condition for complete filling of the pores (which replaces the condition (35) for complete filling of the surface) is

$$n_1^s v_1^s + n_2^s v_2^s = V_p \quad (44)$$

where v_1^s and v_2^s are the partial molar volumes of the components in the pore space. In this picture, equilibrium bulk liquid is not supposed to be present within the pores. The phenomenological definition of the reduced surface excess is still given by equation (8). Again since the composition of the liquid contained in the pores may not be uniform throughout the whole volume of the pore, the mole fractions characterising the composition of the adsorbed phase are to be understood as mean values, in much the same way as explained in connection with the multilayer model.

For molecules of the same size, the amount of material which can be accommodated in the pore space is

$$n^s = V_p/v \quad (45)$$

where v is the common molar volume. Equation (40) still applies and it should therefore be possible to derive values of n^s and hence of V_p from adsorption isotherms in the same way as surface areas can be obtained for non-porous materials.

6.5 Other models

The simple surface phase model presented here for mixtures of molecules of the same size, may be developed in various ways. These include:

(i) extension to the case in which the ratio of the areas occupied by molecules of types 2 and 1 is r , when to maintain complete filling of the surface, equation (42) takes the form

$$K_a = \left(\frac{x_2^s \gamma_2^s}{x_2^\ell \gamma_2^\ell} \right) \left(\frac{x_1^\ell \gamma_1^\ell}{x_1^s \gamma_1^s} \right) r \quad (46)$$

no simple linearisation of the form (46) is possible, even when all the activity coefficients are unity;

(ii) theories of the behaviour of surface activity coefficients;

(iii) multilayer theories in which the single step function discussed above (figure 5) is replaced by a series of steps;

(iv) statistical mechanical theories and computer calculations of the concentration profiles;

(v) theories incorporating the effects of surface heterogeneity (see Section 7);

(vi) theories of adsorption from solution by zeolites, where molecular sieving may play an important role.

7 SURFACE HETEROGENEITY

As outlined in Section 6, adsorption from solution is often interpreted in terms of a layer model, assuming the surface to be an ideally smooth homogeneous plane, characterised by constant values of the energies of adsorption of the two components at all points on the surface. This implies that K_a is constant over the surface. However, few solid surfaces are perfectly uniform and planar, and it is important to understand how surface heterogeneity and roughness affects adsorption behaviour. A major problem is that of distinguishing between deviations from ideal behaviour arising from these factors, and those associated with non-ideality of the surface phase caused by interactions between adsorbed molecules, by molecular size differences and by orientation effects. It may not, even in principle, be possible to make such a separation since the influence of intermolecular interactions depends on whether the heterogeneity is randomly distributed or associated with different patches of the surface. Attempts to derive information on surface heterogeneity from measurements of adsorption from solution require the introduction of assumptions concerning both the nature of the adsorbed phase and the spatial distribution of the heterogeneity, e.g. it may be assumed either that the adsorbed phase is ideal, or that it deviates from ideality in the same way as the bulk solution, while the heterogeneity may be described in terms of various distribution functions. If the bulk phase is ideal it may be justified to assume that the adsorbed phase is also, so that heterogeneity effects dominate the behaviour. At the moment there is no independent check on the validity of such assumptions, and it is necessary to resort to fitting of experimental data to test alternative theoretical models. However, only rarely are such data of high enough precision to lead to a unique solution. It has been suggested that studies of the temperature dependence of adsorption, or calorimetric measurements of enthalpies of adsorption may help to resolve this problem, but this possibility has yet to be tested.

It is therefore essential, in presenting an analysis of data in terms of a model of a heterogeneous surface, to specify clearly what assumptions are involved. The resulting conclusions should also be examined critically to check that they do not conflict with other evidence. For example, one should be suspicious if strong heterogeneity is indicated for a surface that on the basis of other evidence (e.g. vapour adsorption or electron microscopy) is thought to be essentially homogeneous (e.g. graphitised carbon black). Similarly the validity of the analysis may be in doubt if the same surface appears to exhibit widely different degrees of heterogeneity based on adsorption measurements using different liquid mixtures. This will be particularly so if in the bulk these mixtures deviate from ideality to different extents, and if there is no expectation on chemical grounds for specific differences in the interactions of the molecules involved with the surface. On the other hand, if surfaces have been made deliberately heterogeneous (e.g. clays which have been ion exchanged to different extents with cationic surfactants) then clearly this fact must be reflected in the interpretation of the results.

In general, the situation with respect to the influence of surface imperfections on adsorption from solution has yet to be resolved by further work, both theoretical and experimental. Future experiments should include both adsorption and calorimetric studies, and must seek the highest attainable precision, since, as with the problem of vapour adsorption on heterogeneous surfaces, the calculated energy distribution functions are very sensitive to experimental errors in the measured isotherm.

8 GENERAL CONCLUSIONS AND RECOMMENDATIONS

- 8.1 In presenting the results of measurements on adsorption from solution, the raw data should be given in terms of the specific reduced surface excess $n_1^{\sigma(n)}/m$ or $m_1^{\sigma(m)}/m$ as a function of the equilibrium liquid mole fraction (x_1^l). The data may be presented graphically or in tabular form, but if published only as graphs, the numerical data should be available either from the authors or from a readily accessible source.
- 8.2 If the surface area of the solid is known (and stated in the paper) then the data may be expressed as areal reduced surface excesses, $\Gamma_1^{(n)}$.
- 8.3 The experimental method employed should be adequately described: a list of details which should be included is given in Section 4.1.
- 8.4 In presenting an analysis of the results the methods used and the assumptions involved should be stated explicitly.
- 8.5 If a thermodynamic analysis is presented, full details of the sources of information on the activity coefficients of the bulk solution should be given, and if the values adopted are different from those already published, they should be given either in a table or by an interpolation formula.
- 8.6 If the analysis is made in terms of the layer model the interpretation of large deviations from simple behaviour should be made with caution in view of the generally unrealistic physical assumptions involved.

NOTES AND REFERENCES

- (a) Adsorption at the *surface* of a solid may also lead to changes in volume but these are usually small and are not discussed here.
- (b) Manual of Symbols and Terminology for Physicochemical Quantities and Units, Appendix II, part 1, Definitions, Terminology and Symbols in Colloid and Surface Chemistry, prepared for publication by D.H.Everett. Pure Appl. Chem., **31**, 579-638 (1972).
- (c) The algebraic method makes no specific reference to a dividing surface, but involves a general thermodynamic discussion of the degrees of freedom of the whole system. However, it leads to the same operational equations for the adsorption (equations 6 and 9) as those based on the use of a dividing surface. See, for example, R.S.Hansen, J. Phys. Chem. **66**, 410 (1962); F.C.Goodrich, Trans. Faraday Soc. **64**, 3403 (1968); F.C.Goodrich in Surface and Colloid Science (E.Matijevic and F.Eirich, Eds.) Wiley-Interscience, New York (1969), vol.1, p.1; G.Schay, ibid, vol.2, p.155.
- (d) In the framework of the so-called algebraic method V^0 is thought of as the volume of an arbitrarily chosen amount of bulk liquid.
- (e) This definition is ambiguous in practice. V^0 is usually the volume of solution measured before immersion: it should, strictly, be the volume of the equilibrium solution. The definition in terms of initial volume is exact only when the volume is unchanged on adsorption. See A.V.Vernov and A.A.Lopatkin, Zhur. Fiz. Khim. **55**, 428 (1981) (Russ. J. Phys. Chem. **55**, 240 (1981)).
- (f) S.G.Ash and G.H.Findenegg, Spec. Disc. Faraday Soc. **1**, 105 (1970).
- (g) Reporting Physisorption Data for Gas/Solid Systems, prepared for publication by K.S.W. Sing, Pure Appl. Chem., **57**, 603 (1985).
- (h) J.J.Kipling, Adsorption from Solutions of Nonelectrolytes, Academic Press, London and New York, 1965, chap. 2; G.D.Parfitt and P.C.Thompson, Trans. Faraday Soc., **67**, 3372 (1971).
- (i) E.Kurbanbekov, O.G.Larionov, K.V.Chmutov and M.D.Yudelevich, Zhur. Fiz. Khim. **43**, 1630 (1969) (Russ. J. Phys. Chem. **43**, 916 (1969)); S.G.Ash, R.Bowen and D.H.Everett, J. Chem. Thermodynamics **5**, 239 (1973).
- (j) G.Schay, L.G.Nagy and G.Racz, Acta Chimica Acad. Sci. Hung. **71**, 23 (1972); S.C.Sharma and T.Fort, J. Coll. Interface Sci. **43**, 36 (1973); H.L.Wang, J.L.Duda and C.J.Radke, J. Coll. Interface Sci. **66**, 153 (1978).
- (k) C.Nunn, R.S.Schechter and W.H.Wade, J. Coll. Interface Sci. **80**, 598 (1981).
- (l) C.Nunn and D.H.Everett, J. Chem. Soc. Faraday Trans. I, **79**, 2953 (1983).
- (m) This equation is essentially equivalent to that discussed by C.Wagner (Nach. Akad. Wiss. Göttingen II, Math. Phys. Kl. **1973**, 37; cf. G.N.Lewis and M.Randall, Thermodynamics, 2nd. edition, revised by K.S.Pitzer and L.Brewer, McGraw-Hill, New York (1961), p.479):
- $$\Gamma_2^{(1)} = (\partial n_2 / \partial A_s)_{\text{int}, V, n_1}$$
- where int means that the intensive variables are kept constant.
- (n) e.g. G.Schay and L.G.Nagy, J. Chim. Phys. **1961**, 140.
- (o) e.g. C.H.Giles, T.H.MacEwan, S.N.Nakhwa and D.Smith, J. Chem. Soc. **1960**, 3973.

(p) The use of the term *surface tension* when applied to interfaces involving a solid phase has been the subject of much discussion since only in very special cases is it possible to devise a means of measuring the surface tension of a solid by mechanical means. Gibbs avoided this problem in the case of a fluid/solid interface by calling σ "the superficial tension of the fluid in contact with the solid" thus implying that the solid is inert and unaffected by the presence of the liquid. By adopting the term "interfacial tension of the fluid/solid interface" for the quantity defined by $(\partial G/\partial A_S)_{T,p,n_1,n_2}$ the role of interactions between the solid and fluid is acknowledged. σ as defined here plays the same part as the surface tension of a liquid in determining thermodynamic equilibrium.

As noted in Section 1, it is often not possible to assign a reliable value to A_S . In such cases it is recommended that equ.(30) be used to calculate $(\sigma - \sigma_2^*)_{a_S}$. Then σa_S may be called the *specific free energy of immersion*.

(q) If A_S is not known then eqs.(31-33) should be used to calculate $(\Delta_w \hat{h} - \Delta_w \hat{h}_2^*)_{a_S}$ and $(\Delta_w \hat{s} - \Delta_w \hat{s}_2^*)_{a_S}$. $\Delta_w \hat{h}_{a_S}$ and $\Delta_w \hat{s}_{a_S}$ are then, respectively, the *specific enthalpy of immersion* and *specific entropy of immersion*. The direct calorimetric technique of measuring enthalpies of immersion requires careful analysis to ensure that appropriate correction terms are allowed for (e.g. for stirring and bulb-breaking) (see e.g. D.H.Everett, A.G.Langdon and P.Maher, *J.Chem.Thermodynamics*, **16**, 981, (1984).

(r) See e.g. J.Davis and D.H.Everett in Specialist Periodical Reports, *Colloid Science*, Royal Society of Chemistry, London, vol.4,1983,p.85.

(s) The term "surface phase" is not strictly justified since unlike bulk phases (which are autonomous) the properties of surface phases depend on the interactions with adjacent phases (i.e. they are not autonomous). Consequently they are not phases in the sense of the phase rule.

(t) See e.g. G.Schay in *Proc.Int.Symp.on Surface Area Determination,1969* (D.H.Everett and R.H.Ottewill,Eds.)Butterworth, London,1970,p.272.

(u) See ref.(r) p.86.

LIST OF SYMBOLS

A_S	area of surface or interface
a_S	specific surface area = A_S/m
a_i	partial molar area of component i
a_i^0	molar cross sectional area of component i
c_i^l	concentration of component i in bulk liquid
c_i	local concentration of component i
$\Delta_w H$	enthalpy of immersion of solid in a given solution
$\Delta_w \hat{h}$	areal enthalpy of immersion of solid in a given solution = $\Delta_w H/A_S$
$\Delta_w \hat{h}_i^*$	areal enthalpy of immersion of solid in pure component i = $\Delta_w H_i^*/A_S$
K_a	adsorption equilibrium constant
m	mass
m_i	mass of component i
m^{sol}	mass of solid
m^0	total mass of liquid
m^σ	excess mass
$m_i^{\sigma(1)}$	relative mass adsorption of component i with respect to component 1
$m_i^{\sigma(m)}$	reduced mass adsorption of component i
M	molar mass of component i
n	amount of substance
n_i	amount of component i
n^0	total amount of liquid
n_i^σ	surface excess amount of component i
$n_i^{\sigma(1)}$	relative adsorption of component i with respect to component 1 = relative surface excess of component i with respect to component 1
$n_i^{\sigma(n)}$	reduced adsorption of component i = reduced surface excess of component i

$n_i^{\sigma(n)}/m$	specific reduced adsorption of component i
$n_i^{\sigma(n)}/A_s$	areal reduced adsorption of component i = $\Gamma_i^{(n)}$
n^s	total amount of substance in 'surface phase'
n_i^s	amount of component i in 'surface phase'
S	separation factor
$\Delta_w S$	entropy of immersion of solid in a given solution
$\Delta_w \hat{S}$	areal entropy of immersion of solid in a given solution = $\Delta_w S/A_s$
$\Delta_w S_i^*$	areal entropy of immersion of solid in pure component i
t	thickness of adsorbed layer (in molecular layers)
V	volume
V^l	total volume of liquid up to the Gibbs Dividing Surface (Section 2.2); volume ascribed to the bulk liquid in the surface phase model (Section 6.2)
V^0	initial volume of liquid
V^σ	excess surface volume
V^f	volume of solution passed in chromatographic process
V_p	pore volume
V^{sol}	volume of solid
v	molar volume
v_i^s	partial molar volume of component i in adsorption space
w	mass fraction
w_i^l	mass fraction of component i in bulk liquid
w_i^0	initial mass fraction of component i in liquid
x	mole fraction
x_i^l	mole fraction of component i in bulk liquid
x_i^0	initial mole fraction of component i in liquid
x_i^s	mole fraction of component i in 'surface phase'
z	distance normal to a surface
z^δ	z co-ordinate of Gibbs dividing surface
z^l	z co-ordinate of boundary of liquid phase
γ_i^l	activity coefficient of component i in bulk liquid
γ_i^s	activity coefficient of component i in 'surface phase'
Γ	areal adsorption (areal surface excess) = n^σ/A_s
$\Gamma_i^{(1)}$	areal relative adsorption of component i with respect to component 1 = areal relative surface excess of component i with respect to component 1 = $n_i^{\sigma(1)}/A_s$
$\Gamma_i^{(n)}$	areal reduced adsorption of component i = areal reduced surface excess of component i = $n_i^{\sigma(n)}/A_s$
$\Gamma_i^{(v)}$	areal surface excess of component i on volume basis = $n_i^{\sigma(v)}/A_s$
μ_i	chemical potential of component i
μ_i^*	chemical potential of pure component i
ρ^l	density of liquid
ρ^{sol}	density of solid
σ	surface or interfacial tension of the fluid/solid interface
σ_i^*	surface or interfacial tension of the pure component i/solid interface.