

ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN—POLONIA

VOL. XIX, 3

SECTIO AA

1964

Z Zakładu Adsorpcji przy Katedrze Chemii Fizycznej Wydziału Mat. Fiz. Chem. UMCS
Kierownik: doc. dr Jarosław Ościk

Jarosław OŚCIK

Adsorption Affinity in Processes of Adsorption from Conformal Solutions

Powinowactwo adsorpcyjne w procesach adsorpcji z roztworów konformalnych

Адсорбционное сродство в процессах адсорбции из конформальных растворов

The idea of adsorption affinity in processes of adsorption was considered in a number of works [1—4]. These works did not, however, go beyond attempts to give a definition of adsorption affinity and no detailed analysis of the term was made.

In investigations of certain adsorption phenomena the concept of adsorption affinity is very important. That is the case in the problem of the effect of nature of the adsorption system (adsorbent — solvent) and of the molecular structure upon their adsorption ability and selectivity. The concept of adsorption affinity may be very helpful in investigations of complex adsorption phenomena in multicomponent solutions.

Therefore, it seemed purposeful to define the term „adsorption affinity” more exactly and to analyse it more closely in the process of adsorption from the broad class of conformal solutions [5].

INTRODUCTION

Each solution may be described in two ways, assuming a symmetrical or an asymmetrical reference system [6]. The chemical potential of a given substance will, of course, be identical, irrespective of the method of its description, or

$$\mu_i = \mu_i^\circ + RT \ln x_i f_i = \mu_i^\ominus + RT \ln x_i f_i^* \quad (1)$$

where x_i is the molar fraction of component i in the solution, f_i , f_i^* are activity coefficients, defined as follows:

$$\begin{aligned} f_i &\rightarrow 1 \text{ for } x_i \rightarrow 1 \\ f_i^* &\rightarrow 1 \text{ for } x_i \rightarrow 0 \end{aligned}$$

μ_i° is the chemical potential of pure component i whereas $\mu_i^\ominus$ is the standard chemical potential of component i or its chemical potential in a hypothetical ideal diluted solution at $x_i = 1$ (pure component i in the state of ideal diluted solution).

Introducing the excess function of the chemical potential, defined as

$$\mu_i^E \equiv RT \ln f_i \quad \text{and} \quad \mu_i^{E*} \equiv RT \ln f_i^* \quad (1a)$$

we can write eq. (1) in the form

$$\mu_i = \mu_i^\circ + RT \ln x_i + \mu_i^E = \mu_i^\ominus + RT \ln x_i + \mu_i^{E*} \quad (2)$$

Definition of the term „adsorption affinity”

The process of adsorption from solution may be considered as a partition of substance between two liquid phases [7]: the bulk phase and the surface phase (surface solution). In adsorption equilibrium the chemical potential of the adsorbed substance z is the same in both phases

$$(\mu_s)_z = \mu_z$$

(the index s denotes the surface phase). Assuming the asymmetrical reference system in the description of the two liquid phases, we can thus write

$$(\mu_s^\ominus)_z + RT \ln x_z^s + (\mu_s^{E*})_z = \mu_z^\ominus + RT \ln x_z + \mu_z^{E*} \quad (3)$$

or

$$(\mu_s^\ominus)_z - \mu_z^\ominus = -RT \ln \frac{x_z^s}{x_z} - [(\mu_s^{E*})_z - \mu_z^{E*}] \quad (4)$$

The difference $\Delta\mu_z^\ominus \equiv (\mu_s^\ominus)_z - \mu_z^\ominus$ is for a given substance z a function of temperature, pressure and the kind of adsorption system. It expresses the adsorption ability of the substance under given conditions. The difference $\Delta\mu_z^\ominus$ may be assumed as a measure of the adsorption affinity of substance z . We may also write

$$\Delta\mu_z^\ominus \equiv (\mu_s^\ominus)_z - \mu_z^\ominus = -RT \lim_{x_z \rightarrow 0} \ln \frac{x_z^s}{x_z} \quad (5)$$

The equation (5) permits to determine the value of adsorption affinity of substance z from its adsorption isotherm.

The adsorption affinity of substance z is also related to its excess chemical potentials in the surface and bulk phases $\left[\left(\mu_s^E \right)_z, \left(\mu_s^{E*} \right)_z \right.$ and $\left. \mu_z^E, \mu_z^{E*} \right]$. From equation (2) we can write for the bulk phase

$$\mu_z^\Theta = \mu_z^0 + \mu_z^E - \mu_z^{E*} \quad (6)$$

And, similarly, for the surface phase

$$\left(\mu_s^\Theta \right)_z = \left(\mu_s^0 \right)_z + \left(\mu_s^E \right)_z - \left(\mu_s^{E*} \right)_z \quad (7)$$

Subtraction of (6) from (7) gives

$$\Delta \mu_z^\Theta = \Delta \mu_z^E - \Delta \mu_z^{E*} \quad (8)$$

where $\Delta \mu_z^E \equiv \left(\mu_s^E \right)_z - \mu_z^E$ and $\Delta \mu_z^{E*} \equiv \left(\mu_s^{E*} \right)_z - \mu_z^{E*}$. Taking into account (2), equation (8) may also be written in the form

$$\Delta \mu_z^\Theta = \lim_{x_z \rightarrow 0} \left(\mu_s^E \right)_z - \lim_{x_z \rightarrow 0} \mu_z^E \quad (9)$$

ADSORPTION AFFINITY IN PROCESSES OF ADSORPTION FROM CONFORMAL SOLUTIONS

For conformal solutions, their molar excess free enthalpy may be expressed by [6, 7, 8]

$$G^E = \sum_{i < j} x_i x_j A_{ij} \quad (10)$$

where A_{ij} are temperature dependent constants related to conformal parameters, which are, in turn, determined by bi-molecular interactions of components i and j ; it is assumed that $A_{ii} = 0$ and $A_{ij} = A_{ji}$. Thus it can be assumed that values of these constants characterize these interactions.

The excess chemical potential of substance z in a conformal solution is given by the equation

$$\mu_z^E = \sum_i x_i A_{zi} - G^E \quad (11)$$

Thermodynamic analysis of a solution takes into account the interactions of all kinds of molecules present. Considering the surface phase as a surface solution, its thermodynamic description should take into account the interaction between the adsorbent surface (surface molecules, atoms or ions) and all molecules present in the solution. Considering a process of adsorption from a conformal solution, it may

be assumed that the surface solution is also conformal, unless mechanisms other than physical adsorption are brought into play.

The action of the adsorbent surface in such a solution may be accounted for by a change of the constants in eq. (10). Thus let us write

$$G_s^E = \sum_{i < j} x_i x_j C_{ij} \quad (12)$$

The action of the adsorbent surface on the surface solution may be also represented as the presence in the solution of an additional component in a constant amount (in a constant concentration if the volume of the surface phase is invariable). In such a case we may write

$$G_s^E = \sum_{i < j} y_i^s y_j^s \cdot A_{ij} + \sum_i y_j^s y_a A_{ai} \quad (13)$$

In equation (13) $y_a = \text{const.}$ denotes the molar fraction of molecules (atoms, ions) of the adsorbent surface in the surface solution and is related to its active area; $y_i^s (y_j^s)$ denote the molar fractions of the remaining components of the solution. In such a description of the surface solution we have, of course, $y_a + \sum y_i^s = 1$. The constants A_{ai} are related to the interactions between the adsorbent and the components of the solution.

The excess chemical potential of substance z in surface solution will be given by

$$(\mu_s^E)_z = \sum_i y_i^s A_{zi} + y_a A_{az} - G_s^E \quad (14)$$

Taking into account eq. (9), (11) and (14) we can write

$$\Delta \mu_z^{\ominus} = \sum_{i \neq z} (y_i^s - x_i) A_{zi} + y_a A_{az} - [G_{s(r)}^E - G_{(r)}^E] \quad (15)$$

where $G_{s(r)}^E$ and $G_{(r)}^E$ are excess free enthalpies of surface phase and bulk phase which do not contain the substance z . We can also write that

$$\Delta \mu_z^{\ominus} = -RT \lim_{x_z \rightarrow 0} \ln \frac{y_z^s}{x_z} \quad (16)$$

The value $\Delta \mu_z^{\ominus}$ differs from the above defined adsorption affinity $\Delta \mu_z^{\ominus}$ in view of the introduction of an additional component (atoms, ions or molecules of the adsorbent surface) into the description of the surface solution. It can be demonstrated that y_i^s and x_i^s are related by the following equation

$$y_i^s = x_i^s (1 - y_a) \quad (17)$$

thus, according to definition (5) we have

$$\Delta\mu_z^\ominus = \Delta\mu_z^{\ominus'} + RT \ln(1 - y_a) \quad (18)$$

Equation (15) is very simple in the case of adsorption from a conformational binary solution 1 + 2. For the bulk phase we have then $x_1 + x_2 = 1$, and for the surface phase $y^s + y^s + y_a = 1$. For such a case, taking into account (15) and (18), we have

$$\Delta\mu_2^\ominus = y_a [(y_a - 1) A_{a1} + A_{a2} - A_{12}] + RT \ln(1 - y_a) \quad (19)$$

Thus we have obtained a simple relationship between adsorption, affinity and constants characterizing:

- a) active surface area of adsorbent (y_a),
- b) interactions between components of solution and adsorbent surface (A_{a1} and A_{a2}),
- c) interactions between components of binary solution (A_{12}).

Assuming a symmetrical reference system, we can also write for a binary solution

$$\left(\mu_s^\ominus\right)_2 + RT \ln y_2^s + \left(\mu_s^E\right)_2' = \mu_2^\ominus + RT \ln x_2 + \mu_2^E \quad (20)$$

If the substance "2" is in the same molecular state in both phases, then $\mu_2^\ominus = \left(\mu_s^\ominus\right)_2$ and

$$RT \ln \frac{y_2^s}{x_2} = \mu_2^E - \left(\mu_s^E\right)_2' \quad (21)$$

according to (11), (13) and (14)

$$\mu_2^E = x_1^2 A_{12} \quad (21a)$$

$$\left(\mu_s^E\right)_2' = y_1^s (1 - y_2^s) A_{12} - y_1^s y_a A_{a1} - y_a (1 - y_2^s) A_{a2} \quad (21b)$$

so that we can write eq. (21) in the form

$$RT \ln \frac{y_2^s}{x_2} = [y_1^s (y_2^s - 1) + x_1^2] A_{12} + y_a [y_1^s A_{a1} - (y_1^s - 1) A_{a2}] \quad (22)$$

Taking into account eq. (17) and denoting $\varphi = 1 - y_a$ we have

$$RT \ln \frac{x_2^s}{x_2} = [x_1^s \varphi (x_2^s \varphi - 1) + x_1^2] A_{12} + y_a [x_1^s \varphi A_{a1} + (x_2^s \varphi - 1) A_{a2}] + \\ - RT \ln \varphi \quad (23)$$

CONCLUSIONS

The assumption that in processes of adsorption from solutions the surface phase also behaves as a conformational solution, permitted a detailed analysis of adsorption affinity in such systems. It also allowed to

draw a number of conclusions from experimental data on adsorption from conformational solutions, concerning the mechanism of the phenomenon.

Particularly simple relationships are obtained in the case of adsorption from binary solutions. From the experimentally determined adsorption isotherm of substance 2 from the solution 1 + 2 the function

$$RT \ln \frac{x_2^s}{x_2} = f(x_2) \quad (23a)$$

can be plotted and the constants A_{12} , A_{a1} , A_{a2} , y_a can be calculated. Thus it is possible to estimate the four essential parameters, the sum of which gives, according to eq. (19), the value of adsorption affinity. This dissection of adsorption affinity permits to estimate not only the total effect of adsorption processes but also the contributions of each of these parameters. It also permits the observation of changes of these parameters when changing the adsorption system and conditions of the process.

REFERENCES

1. Heyne W., Polanyi M.: *Z. phys. Chem.*, **132**, 384 (1928).
2. Fu Y., Hansen R. S., Bartell F. E.: *J. Phys. Colloid. Chem.*, **52**, 374 (1948).
3. Elton G. A. H.: *J. Chem. Soc.*, 1955 (1952).
4. Ościk J., Waksmundzki A.: *Ann. Univ. Mariae Curie-Skłodowska, Lublin, sectio AA*, **IX**, 9 (1954).
5. Longuet-Higgins H. C.: *Proc. Roy. Soc.*, **A. 205**, 247 (1951).
6. Prigogine J., Defay R.: *Chemical Thermodynamics*. Longmans (1954).
Prigogine J.: *Molecular Structure of Solutions*. North Holland, Amsterdam (1957).
7. Guggenheim E. A.: *Trans. Faraday Soc.*, **36**, 397 (1940).
8. Brown W. B.: *Proc. Roy. Soc.*, **A. 240**, 561 (1957).

STRESZCZENIE

W badaniach niektórych zjawisk adsorpcyjnych pojęcie powinowactwa adsorpcyjnego nabiera dużego znaczenia. Dotyczy to między innymi zagadnienia wpływu rodzaju układu adsorpcyjnego (adsorbent — rozpuszczalnik) oraz struktur cząsteczek na ich zdolność adsorbowania się i selektywność adsorpcji. Pojęcie powinowactwa adsorpcyjnego

może być także bardzo pomocne w badaniach skomplikowanych zjawisk adsorpcyjnych w układach wieloskładnikowych.

Różnica standartowych potencjałów chemicznych substancji z w fazie powierzchniowej i objętościowej

$$\Delta\mu_z^\ominus \equiv (\mu_s^\ominus)_z - \mu_z^\ominus = -RT \lim_{x_z \rightarrow 0} \ln \frac{x_z^s}{x_z} \quad (5)$$

(x_z^s i x_z — ułamki molowe substancji z w fazie powierzchniowej i objętościowej) jest funkcją temperatury, ciśnienia i rodzaju układu adsorpcyjnego. Wyraża ona zdolność adsorbowania się tej substancji w danych warunkach i można ją przyjąć jako miarę powinowactwa adsorpcyjnego.

Zakładając, że w procesach adsorpcji z roztworów konformalnych faza powierzchniowa posiada także własności roztworu konformalnego (adsorpcja fizyczna), można wyciągnąć szereg wniosków co do mechanizmu zjawiska adsorpcji.

W przypadku adsorpcji z konformalnych roztworów binarnych 1 + 2 otrzymuje się następujące zależności:

$$\Delta\mu_2^\ominus = y_a (A_{a2} - \varphi A_{a1} - A_{12}) + RT \ln \varphi \quad (19)$$

oraz

$$RT \ln \frac{x_2^s}{x_2} = [x_1^s \varphi (x_2^s \varphi - 1) + x_1^2] A_{12} + y_a [x_1^s \varphi A_{a1} + (x_2^s \varphi - 1) A_{a2}] - RT \ln \varphi \quad (23)$$

w których A_{a1} , A_{a2} , A_{12} , są stałymi będącymi funkcjami temperatury i parametrów konformalnych. Charakteryzują one:

a) oddziaływanie między składnikami roztworu a adsorbentem (A_{a1} i A_{a2});

b) wzajemne oddziaływanie między składnikami roztworu binarnego (A_{12});

y_a — charakteryzuje wielkość powierzchni czynnej adsorbentu;

$\varphi = 1 - y_a$.

W oparciu o zmierzoną izotermę adsorpcji substancji 2 można wykreślić funkcję

$$RT \ln \frac{x_2^s}{x_2} = f(x_2)$$

i przy pomocy podanej zależności (23) obliczyć stałe. W ten sposób istnieje możliwość ilościowej oceny czterech zasadniczych czynników wpływających na proces adsorpcji z roztworu. Umożliwia to także ilościową ocenę nie tylko efektu sumarycznego procesu adsorpcji, lecz także wpływu każdego z tych czynników na ten proces.

РЕЗЮМЕ

В исследованиях некоторых адсорбционных явлений, большое значение приобретает понятие адсорбционного сродства. Это касается, между прочим, проблемы влияния типа адсорбционной системы (адсорбент — растворитель) и структуры молекул на их адсорбционную способность и селективность адсорбции. Концепция адсорбционного сродства может также быть очень полезной при исследованиях сложных адсорбционных явлений в многокомпонентных системах.

Разность стандартных химических потенциалов вещества z в поверхностной и объемной фазах:

$$\Delta \mu_z^\ominus \equiv (\mu_z^\ominus)_s - \mu_z^\ominus = -RT \lim_{x_z \rightarrow 0} \ln \frac{x_z^s}{x_z} \quad (5)$$

(x_z^s и x_z — мольные доли вещества z в поверхностной и объемной фазах) является функцией температуры, давления и типа адсорбционной системы. Она выражает способность этого вещества адсорбироваться в данных условиях и может быть принята как мера адсорбционного сродства.

Предполагая, что в процессах адсорбции из конформальных растворов поверхностная фаза также обладает свойствами конформального раствора (физическая адсорбция), мы можем сделать несколько выводов относительно механизма явления адсорбции.

В случаях адсорбции из конформальных бинарных растворов 1+2 получаются следующие зависимости:

$$\Delta \mu_2^\ominus = y_a (A_{a2} - \varphi A_{a1} - A_{12}) + RT \ln \varphi \quad (19)$$

и

$$RT \ln \frac{x_2^s}{x_2} = [x_1^s \varphi (x_2^s \varphi - 1) + x_1^2] A_{12} + y_a [x_1^s \varphi A_{a1} + (x_2^s \varphi - 1) A_{a2}] - RT \ln \varphi \quad (23)$$

где A_{a1} , A_{a2} , A_{12} являются константами зависящими от температуры и связанными с конформальными параметрами. Эти константы характеризуют:

а) взаимодействия между компонентами раствора и адсорбентом (A_{a1} , A_{a2}),

б) взаимодействие между компонентами бинарного раствора (A_{12}),

y_a — характеризует величину активной поверхности адсорбента;
 $\varphi = 1 - y_a$

Из измеренной изотермы адсорбции вещества z можно построить график функции

$$RT \ln \frac{x_2^s}{x_2} = f(x_2)$$

и вычислить константы, применяя уравнение (23). Итак, существует возможность количественной оценки четырех основных параметров, определяющих процесс адсорбции из раствора. Это делает также возможным количественно оценить не только суммарный эффект процесса адсорбции, но и отдельное влияние любого из этих параметров.

Edward SOCZEWINSKI, Tadeusz WOLSKI,
Kazimierz JURKIEWICZ

On the Parallelism of Solubility and Chromatographic Behaviour
in Partition Chromatography. I. Chromatography of Some Heterocycles
in the System: Ethyl Ether/Dimethyl Sulphoxide + Water

O analogii rozpuszczalności i parametrów chromatograficznych
w chromatografii podziałowej. I. Chromatografia heterocyklicznych
w układzie: eter etylowy/dwumetylosulfotlenek + woda

O параллелизме растворимости и хроматографических параметров
в распределительной хроматографии. I. Хроматография гетероциклических
в системе: этиловый эфир/диметилсульфоксид + вода

The choice of optimal chromatographic systems aims at an appropriate distribution of the spots along the chromatogram. In partition chromatography this is effected by the control of the partition coefficients of the solutes between the two liquid phases. The methods most frequently employed for the regulation of partition coefficients involve variation of the composition of the mixed phase, or in the case of lipophilic organic electrolytes, variation of the pH of the aqueous phase. Assuming certain simplifications and a constant composition of one of the phases, it may be expected that a variation of the composition of the other phase (or its pH), changing the partition coefficient of the solute, entails also a parallel change of its solubility in the second phase (cf. [1]). This rule can only be considered as an approximation for the same

