

A Model of Adsorption at Liquid—Solid Interface Involving Association in the Bulk Phase

Małgorzata Borówko*, Jacek Goworek, and Mieczysław Jaroniec

Institute of Chemistry, MCS University, PL-20 031 Lublin, Poland

(Received 4 August 1981. Accepted 30 November 1981)

A model of monolayer adsorption of binary liquid mixtures on homogeneous and heterogeneous solid surfaces involving association of one component in the bulk phase is discussed. Suitable model calculations, illustrating association and heterogeneity effects, have been performed according to an equation derived for adsorption excess. This equation has been examined by using the experimental data of adsorption of alcohols from benzene and *n*-heptane on silica gel.

(*Keywords: Adsorption on heterogeneous surfaces; Association; Adsorption from solutions*)

Adsorptionsmodell für die Grenzfläche Feststoff—Flüssigkeit unter Berücksichtigung der Assoziation in der Flüssigkeitsphase

Es wird ein Adsorptionsmodell binärer, flüssiger Mischungen an homogenen und heterogenen Oberflächen von Feststoffen unter Beachtung der Assoziation eines der Bestandteile in der Flüssigkeitsphase diskutiert. Mit der aus dem Oberflächenüberschuß abgeleiteten Gleichung wurden entsprechende Modellberechnungen durchgeführt, die die mit Assoziation und Heterogenität verbundenen Effekte illustrieren. Die Gleichung wurde für die experimentellen Daten der Alkoholadsorption aus Benzol und *n*-Heptan an Kieselgel überprüft.

Introduction

The majority of papers on liquid adsorption concern binary solutions and homogeneous adsorbents (see references in reviews^{1,2}). Recently, a general formulation of adsorption from liquid mixtures on heterogeneous solid surfaces has been proposed^{3,4}. From this treatment follows that the theoretical investigations of liquid adsorption, involving heterogeneity of the adsorbent surface and nonideality of solution present great difficulties. Therefore, in many descriptions of this problem some simplifying assumptions have been used. In the majority

of papers the model of ideal adsorbed phase was considered⁵⁻⁷. The extensive theoretical investigations concerning the effects of surface heterogeneity and nonideality of bulk solution have been recently presented by *Dabrowski et al.*^{6,7}. Until now there are no theoretical studies describing a strong specific adsorbate—adsorbate interactions in liquid adsorption on solids. According to the opinion of many authors association in the solution play a considerable role in adsorption processes⁸⁻¹¹.

In this paper a simple model for adsorption of binary solution on energetically homogeneous and heterogeneous solid surfaces involving association of one component in the bulk phase is proposed. A general equation describing adsorption equilibria is presented. Model calculations illustrating the influence of association constant and type of the associates on adsorption excess were performed by using derived equations. Moreover, the mutual influence of adsorbent heterogeneity and association in the bulk solution on shape of the excess adsorption isotherms is discussed. The adsorption isotherm of *Langmuir-Freundlich* type is applied to interpret the experimental data of adsorption of alcohols from benzene and *n*-heptane on silica gel.

Theory

Let the adsorption system consist of the binary liquid mixture *A—B* (adsorbate) and an insoluble solid (adsorbent). Next, let us assume that the component *A* forms associates in the bulk phase.

The following assumptions are made for the mathematical description of the adsorption equilibrium:

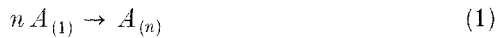
- (a) the molecular sizes of both components of the mixture are identical,
- (b) after the establishment of adsorption equilibrium the original solution may be divided into two phases: adsorbed phase (containing N^s moles) and bulk phase (containing N moles),
- (c) adsorption is supposed to be a monolayer one,
- (d) the total number of molecules in the adsorbed phase is constant,
- (e) the adsorbed phase is ideal,
- (f) the component *A* forms associates in the bulk phase.

The assumptions (a)-(d) are frequently used in the theory of adsorption from solutions on solids¹⁻³.

According to some investigations the adsorbed phase is frequently more ideal than the bulk phase¹². The assumption (e) is justified for many adsorption systems, for example: silica gel/alcohol/*n*-heptane. In the case of the component *A* which can form hydrogen bonds formation of double associates in the bulk solution is a reasonable assumption.

However, in the adsorbed phase the silanol groups of the silica surface would compete with AA associates in the surface layer. Thus, a strong interaction of A with the surface silanols would preclude AA interactions in the adsorbed phase.

First, we take into consideration the association of the component A in the bulk solution. The strong specific interactions cause the formation of the following associates:



where n denotes the number of atoms A in a given complex $A_{(n)}$ ($n = 1, 2, \dots$).

Let us assume that only one type of associates can be formed in the bulk solution. Then, the association constant L_n can be expressed as:

$$L_n = x_{A_{(n)}}^l / n (x_{A_{(1)}}^l)^n \quad (2)$$

where $x_{A_{(n)}}^l$ denotes the mole fraction of complex $A_{(n)}$ in the bulk phase. The mole fraction of any associate is defined by:

$$x_\sigma^\rho = n N_\sigma^\rho / N^\rho \quad (3)$$

where N_σ^ρ is a number of moles of the associate $\sigma = (A_{(1)}, A_{(n)}, A_{(1)}^s, B_{(1)}^s)$ in the ρ -th phase ($\rho = l, s$); the superscripts l and s refer to the bulk and adsorbed phases, respectively, and N^ρ is the total number of moles of both components in the ρ -th phase. In our case the mole fraction of components A and B in the bulk phase can be found from the following equations:

$$x_A^l = x_{A_{(1)}}^l + x_{A_{(n)}}^l \quad (4)$$

$$x_B^l = x_{B_{(1)}}^l \quad (5)$$

Combination of eqs. (2) and (4) leads to:

$$n L_n (x_{A_{(1)}}^l)^n + x_{A_{(1)}}^l - x_A^l = 0 \quad (6)$$

From this equation the mole fraction of monomer $A_{(1)}$ in the bulk phase can be calculated as a function of the mole fraction x_A^l .

It is easy to prove that only one solution of eq. (6) exists in the interval $(0, 1)$.

The analytical solution of eq. (6) for $n = 2$ have been presented by Jaroniec and Piotrowska¹⁰.

In the case of trimers formation it can be written:

$$x_{A(1)3}^l = \left[\left(\frac{x_A^l}{2} + F \right)^{1/3} - \left(F - \frac{x_A^l}{2} \right)^{1/3} \right] / (3L_3)^{1/3} \quad (7)$$

where

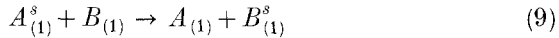
$$F = \left[\frac{(x_A^l)^2}{4} + 1/81 L_3 \right]^{1/2} \quad (8)$$

Now, let us discuss the adsorption process which is a fundamental phenomenon occurring in the system.

The mathematical form of equations describing the adsorption equilibrium depend upon the assumed surface model.

Homogeneous Surfaces

The adsorption process can be described by the following exchange reaction:



The equilibrium constant describing the reaction (9) is defined as follows:

$$K = x_{A(1)}^s x_{B(1)}^l / x_{A(1)}^l x_{B(1)}^s \quad (10)$$

If the association in the adsorbed phase is neglected we can write: $x_{v(1)}^s = x_v^s$ for $v = A, B$. Then, from eq. (10) we obtain the following form of adsorption isotherm:

$$x_A^s = x_A^s(z; K) = Kz / (Kz + 1) \quad (11)$$

where

$$z = x_{A(1)}^l / (1 - x_A^l) \quad (12)$$

Thus, the analytical form of each adsorption isotherm depends upon type of the function: $x_{A(1)}^l = x_{A(1)}^l(x_A^l; L_n)$, e.g. upon the assumed association model.

Eq. (11) is analogous to *Everett's* isotherm for ideal behaviour of both phases¹³:

$$x_A^s = x_A^s(x_{AB}^l; K) = K x_{AB}^l / (K x_{AB}^l + 1) \quad (13)$$

where $x_{AB}^l = x_A^l / x_B^l$.

The surface excess of the component A is given by:

$$n_A^e = N^s (x_A^s - x_A^l) \quad (14)$$

The influence of association on the shape of the excess adsorption isotherm has been investigated on the basis of eqs. (11), (12) and (6). All calculations have been performed for the monolayer capacity equal to unity ($N^s = 1$).

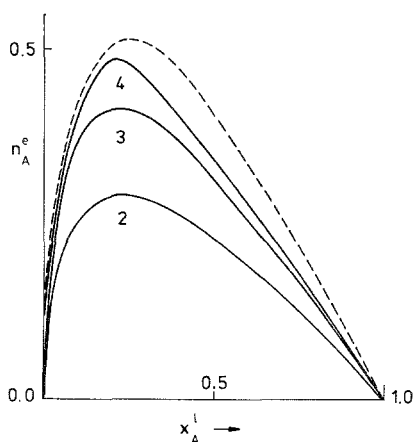


Fig. 1. Excess adsorption isotherms calculated according to eqs. (14), (11) for $N^s = 1$, $K = 10$, $L_2 = L_3 = L_4 = 10$ and various values of the parameter $n = 2, 3, 4$ (solid lines). Excess adsorption isotherm calculated from *Everett's* equation (13) (dashed line)

Fig. 1 shows the excess adsorption isotherms calculated for $K = 10$, $L_2 = L_3 = L_4 = 10$ and different values of $n = 2, 3, 4$ (solid lines). The dashed line denotes the adsorption excess calculated from eqs. (13) and (14) for ideal solution. From comparison of these curves follows that association of component A in the bulk phase always causes a considerable reduction of the adsorption. The largest deviations from *Everett's* equation occur for dimers and gradually decrease with increasing n . However, it should be noted that the assumption of constancy of the association constant for associates having different number of molecules is not very likely. In fact the influence of associate size on the shape of the adsorption isotherm may be smaller because simultaneously the respective change of L_n will occur.

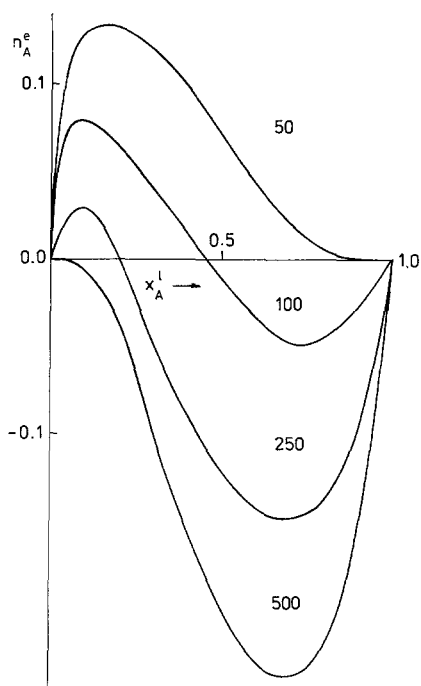


Fig. 2. Excess adsorption isotherms calculated for dimers ($n = 2$) according to eqs. (14), (11) for $N^s = 1$, $K = 10$ and various values of the association constant $L_2 = 50, 100, 250, 500$

The purpose of the next model calculations was to study the influence of the association constant on the shape of the excess adsorption isotherms. Fig. 2 shows the results obtained for the case of formation of double associates $A_{(2)}$ in bulk phase. The diagrams presented in Fig. 2 prove that a change in the association constant L_2 causes a drastic change in the type of excess adsorption isotherms. The isotherm curves change from type II ($L_2 = 10$), through type III ($L_2 = 50$) and type IV ($L_2 = 100$) to type V in Nagy and Schay classification^{14, 15} (see Fig. 1 and 2). For high values of L_2 ($L_2 = 500$) a negative adsorption of component A is observed in the whole concentration range. The curve calculated for $L_2 = 50$ is especially interesting because such adsorption isotherms are often measured for alcohol solutions¹⁶. Summing up the model investigations we can draw the conclusion that an increase in the association constant causes a reduction of adsorption excess n_A^e and range of preference adsorption of A .

Heterogeneous Surfaces

The theory of adsorption from ideal solutions on energetically heterogeneous surfaces gives the following adsorption isotherm³:

$$X_A^s = \int_{\Delta} K x_{AB}^l / (1 + K x_{AB}^l) F(\varepsilon_{AB}) d\varepsilon_{AB} \quad (15)$$

where X_A^s denotes the mole fraction of component A in the adsorbed phase for heterogeneous surfaces, $F(\varepsilon_{AB})$ is the distribution function, $\varepsilon_{AB} = \varepsilon_A - \varepsilon_B$, ε_v denotes the adsorption energy of the v -th component ($v = A, B$) and Δ is the integration region.

The integral adsorption isotherm (15) can be solved analytically for several distribution functions^{3, 5, 6}. Then X_A^s can be written as a function of x_{AB}^l and two parameters:

$$X_A^s = X_A^s(x_{AB}^l; \bar{K}, m)$$

where the constant \bar{K} characterizes mean difference of adsorption energies while heterogeneity parameter m determines the shape of the distribution function $F(\varepsilon_{AB})$.

It is easy to show that for associating substance we have:

$$X_A^s = X_A^s(z; \bar{K}, m) = \int_{\Delta} z K (Kz + 1)^{-1} F(\varepsilon_{AB}) d\varepsilon_{AB} \quad (16)$$

It follows from comparison of eqs. (15) and (16) that all adsorption isotherms known in the theory of adsorption from ideal solutions on heterogeneous solids can be generalized to the adsorption with association of one component in the bulk phase. The equations describing adsorption with association may be obtained by a simple replacement of the ratio x_{AB}^l by the variable z . In this way we can generalize *DR*⁵, *Freundlich*⁵ and *Toth*¹⁶ type equations. Detailed studies of *Dabrowski* and *Jaroniec*⁷ concerning the adsorption of binary liquid mixtures on heterogeneous surfaces show, that the isotherm of *Langmuir-Freundlich* type gives particularly good results. The generalized form of this equation is:

$$X_A^s = \bar{K} z^m / (\bar{K} z^m + 1), \quad 0 < m \leq 1 \quad (17)$$

where $\ln \bar{K} = m \ln \bar{K}_0 \approx m \varepsilon_{AB} / RT$ and ε_{AB} is the difference of adsorption energies of both components for which quasi-gaussian distribution $F(\varepsilon_{AB})$ reaches a maximum.

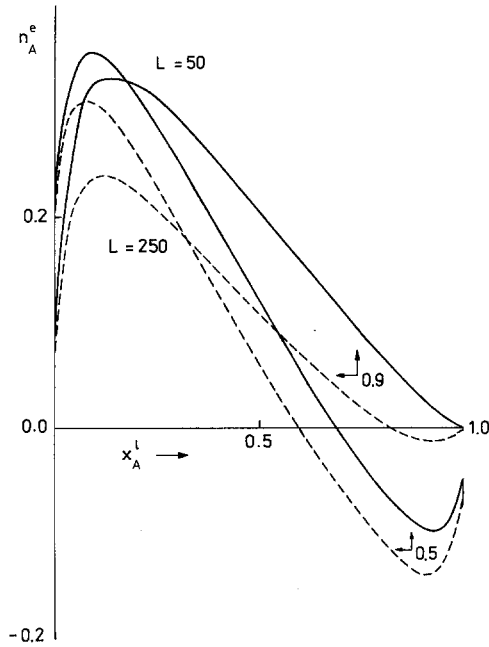


Fig. 3. Excess adsorption isotherms calculated for trimers according to eqs. (14), (17) for $N^s = 1$, $\bar{K}_0 = 10$, $L_3 = 50$ and $m = 0.5, 0.9$ (solid lines), $L_3 = 250$ and $m = 0.5, 0.9$ (dashed lines)

The mathematical analysis of eq. (17) shows that the curves n_A^e vs. x_A^l drawn for constant N^s , \bar{K}_0 , L_n and different values of heterogeneity parameter m intersect in the point \bar{x}_A^l such that:

$$x_{A(1)n}^l(\bar{x}_A^l) = \bar{x}_B^l / \bar{K}_0 \quad (18)$$

If the solution is an ideal one then $\bar{x}_A^l = (\bar{K}_0 + 1)^{-1}$. However, for the associated bulk solution $\bar{x}_A^l \in [(\bar{K}_0 + 1)^{-1}, 1]$. It is easy to check that for $x_A^l < \bar{x}_A^l$ an increase of the parameter m causes a reduction of surface excess n_A^e . The opposite relation is observed for $x_A^l > \bar{x}_A^l$. The point \bar{x}_A^l tends to unity in two cases: as the association constant L_n increases or as the parameter n decreases.

The illustrative calculations concerning the simultaneous influence of association in the bulk phase and heterogeneity of the adsorbent surface were carried out on the basis of eqs. (17) and (7)-(8). The results are presented in Fig. 3.

The isotherm (17) can be rewritten in the following linear form:

$$\ln [X_A^s / (1 - X_A^s)] = m \ln z + \ln \bar{K} \quad (19)$$

The above equation is analogous to that used by *Dabrowski* and *Jaroniec* for adsorption from nonideal solutions⁷.

When the monolayer capacity is known the real adsorption X_A^s can be obtained from experimental data. The association constant can be often determined by using ultrasonic¹⁷, NMR¹⁸, IR¹⁹ or viscosity method²⁰. Then, the variable z can be calculated from equations (12) and (6). In this case the parameters \bar{K} and m may be determined from experimental dependence $\ln (X_A^s / X_B^s)$ vs. $\ln z$ by using graphical method.

Experimental

Experiments were conducted in order to test eq. (17) for the following adsorption systems:

- (a) *sec.*-butanol (*A*)—*n*-heptane (*B*)—silica gel
- (b) *tert.*-butanol (*A*)—benzene (*B*)—silica gel
- (c) *sec.*-butanol (*A*)—benzene (*B*)—silica gel
- (d) *tert.*-butanol (*A*)—*n*-heptane (*B*)—silica gel

Chemicals: The solvents benzene (POCh Gliwice), *n*-heptane, *tert.*-butanol (Aldrich) and *sec.*-butanol (Reanal) puriss. grade were dried over silica gel and were then used without further purification. The silica gel 0.2-0.5 mm from Merck was used as the adsorbent. The specific surface area of the adsorbent determined by the B.E.T. method using nitrogen at 78 K was found to be 300 m² per gram.

Procedure: Adsorption isotherms were measured at 293 K by using a static method described earlier²¹. The silica gel before adsorption was dried at 453 K for 24 h. The equilibrium solution concentrations were analyzed by gas-liquid chromatography.

Results and Discussion

According to the opinion of many authors some alcohols, for example *tert.*-butyl alcohol, associate forming the trimers^{18, 22-24}. Therefore, in order to describe the association equilibrium in the bulk phase the eq. (7) have been used. Unfortunately, the association constants of the investigated alcohols in *n*-heptane and benzene are not available in literature. Thus, eq. (17) is virtually a four-parameter one. The parameters N^s , $\ln \bar{K}$, m and L were determined from the adsorption data in the following way:

- (1) the monolayer capacity N^s have been found by means of the well known method of *Schay* and *Nagy*²⁵,

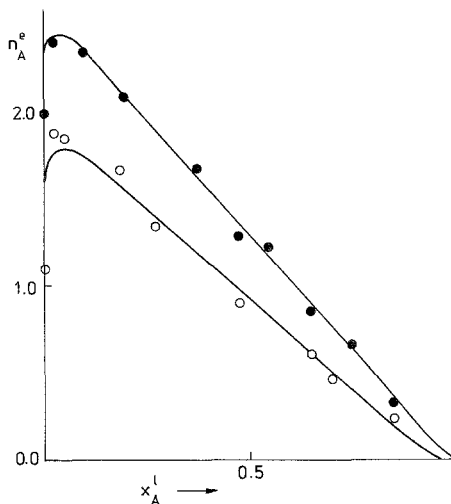


Fig. 4. Comparison of the experimental values for the excess adsorption of *sec.*-butanol from benzene (○) and *n*-heptane (●) with the theoretical excess adsorption isotherms calculated from eqs. (14), (7) and (17)

- (2) the x_A^s have been calculated from eq. (14) for a given value of N^s ,
- (3) the parameter $\ln \bar{K}$ and m were determined numerically by means of eq. (18) for different values of L_3 ,
- (4) the standard deviation SD were calculated for all L_3 and corresponding values of \bar{K} and m :

$$SD = \left[\sum_{i=1}^k (n_{\text{exp}}^e(x_{A_i}^l) - n_{\text{theor}}^e(x_{A_i}^l))^2 / (k - 1) \right]^{1/2}$$

where k denotes number of experimental points whereas $n_{\text{exp}}^e(x_{A_i}^l)$ and $n_{\text{theor}}^e(x_{A_i}^l)$ are experimental and theoretical values of the surface excess for given $x_{A_i}^l$.

- (5) the optimal values of parameters \bar{K} , m , L_3 are those for which the dependence SD vs. L_3 reaches a minimum.

The approximation coefficients $\ln \bar{K}$, m and the optimal values of constants N^s , $\ln \bar{K}_0$, L_3 are summarized in the Table 1. As follows from the analysis of the results the total number of moles in the adsorbed phase N^s is similar for all investigated systems. The monolayer capacity for *sec.*-butanol is slightly greater than for *tert.*-butanol in the both solvents. The heterogeneity parameters m are also similar for those adsorption systems. As follows from comparison of values $\ln \bar{K}_0$ the mean difference between adsorption energies of both alcohols and

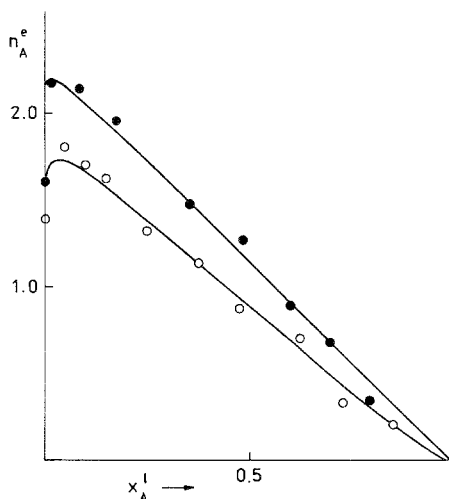


Fig. 5. Comparison of the experimental values for the excess adsorption of *tert.*-butanol from benzene (o) and *n*-heptane (●) with the theoretical excess adsorption isotherms calculated from eqs. (14), (7) and (17)

Table 1. Adsorption parameters of equation (17)

Adsorption system	N^s (mmol g ⁻¹)	$\ln \bar{K}$	m	L_3	$\ln \bar{K}_0$
(a)	2.8	3.688	0.39	10	9.457
(b)	2.4	2.704	0.39	150	6.932
(c)	2.4	4.453	0.45	25	9.895
(d)	2.1	2.886	0.30	50	9.622

solvents is greater for *n*-heptane than for benzene. A considerable influence of solvent on the values of association constant L_3 is observed. This conclusion is confirmed by the immediate measurements²⁶.

It should be noted that the method of determination of the association constant does not seem to be precise enough because the dependence SD vs. L_3 has a distinct minimum. On the other hand the values of association constant obtained for a given compound by using different methods are not identical. Thus, the determination of precise values of the association constant is a very difficult problem. In such a situation the above method may be useful for characterization the experimental adsorption systems with the associated bulk phase.

The Figs. 4 and 5 show the excess adsorption isotherms calculated

according to eqs. (19), (14) and (5) for the parameters summarized in the Table 1. The agreement of experimental points (circles) with the theoretical excess isotherms (solid lines) is satisfactory.

The presented analysis of the experimental data testifies to a practical usefulness of the proposed equations. The model calculations discussed in a previous section show that those equations may be used for approximation of different types of the adsorption isotherms. The investigations prove that the association may play a considerable role in the many adsorption systems.

References

- 1 *Everett D. H.*, in: *Colloid Science (Everett D. H., ed.)*, Specialist Periodical Reports, Vol. 1. London: Chem. Soc. 1973.
- 2 *Brown C. E., Everett D. H.*, in: *Colloid Science (Everett D. H., ed.)*, Specialist Periodical Reports, Vol. 2. London: Chem. Soc. 1975.
- 3 *Jaroniec M., Patrykiewicz A., Borówko M.*, in: *Progress in Surface and Membrane Science*, Vol. 14. New York: Academic Press. 1981.
- 4 *Borówko M., Jaroniec M.*, *Rev. Roum. Chim.* **25**, 475 (1980).
- 5 *Ościk J., Dabrowski A., Jaroniec M., Rudziński W.*, *J. Colloid Interface Sci.* **56**, 403 (1976).
- 6 *Dabrowski A., Ościk J., Rudziński W., Jaroniec M.*, *J. Colloid Interface Sci.* **69**, 287 (1979).
- 7 *Dabrowski A., Jaroniec M.*, *J. Colloid Interface Sci.* **73**, 475 (1980).
- 8 *Ościk J.*, *Przem. Chem.* **44**, 129 (1969).
- 9 *Soczewiński E.*, *Anal. Chem.* **41**, 179 (1969).
- 10 *Jaroniec M., Piotrowska J.*, *Journal of HRC & CC* **3**, 257 (1980).
- 11 *Jaroniec M., Jaroniec J. A.*, *J. Chromatogr.* **210**, 130 (1981).
- 12 *Coltharp M. T.*, *J. Colloid Interface Sci.* **54**, 311 (1976).
- 13 *Everett D. H.*, *Trans. Faraday Soc.* **60**, 1803 (1964).
- 14 *Schay G., Nagy L., Szekrenyesy T.*, *Period. Polytechnica* **4**, 95 (1960).
- 15 *Nagy L., Schay G.*, *Magyar Kem. Folyoirat* **60**, 31 (1960).
- 16 *Ościk J., Goworek J., Kusak R.*, *J. Colloid Interface Sci.* **79**, 308 (1981).
- 17 *Musa R. S., Eisner M.*, *J. Chem. Phys.* **36**, 227 (1959).
- 18 *Feeney J., Walkner S. M.*, *J. Chem. Soc. A* **1966**, 1148.
- 19 *Lidded V., Becker F. D.*, *Spectrochim. Acta* **10**, 70 (1957).
- 20 *Thomas L. H., Meatyard R.*, *J. Chem. Soc.* **1963**, 1986.
- 21 *Ościk J., Goworek J.*, *Polish J. Chem.* **52**, 775 (1978).
- 22 *Saunders M., Hyne J. B.*, *J. Chem. Phys.* **29**, 1319 (1958).
- 23 *Saunders M., Hyne J. B.*, *J. Chem. Phys.* **29**, 253 (1958).
- 24 *Fletcher A. N., Heller C. A.*, *J. Phys. Chem.* **71**, 3742 (1967).
- 25 *Schay G., Nagy L.*, *J. Chim. Phys.* **58**, 149 (1961).
- 26 *Kunst M., van Duijn D., Bordewijk P.*, *Ber. Bunsenges. Phys. Chem.* **83**, 840 (1979).