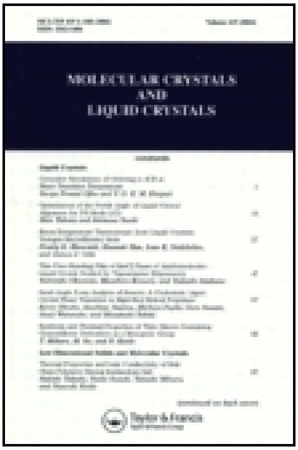

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Dorota Ziółkowska [a]

[a] Department of Technology and Engineering, University of Technology and Agriculture, Seminaryjna 3, Bydgoszcz, 85-326, Poland

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THEORETICAL DESCRIPTION OF ADSORPTION PHENOMENA IN THE SYSTEMS: BINARY NON-ELECTROLYTE SOLUTION/ACTIVE CARBON

Dorota Ziółkowska
University of Technology and Agriculture, Department of Technology and Engineering, Seminaryjna 3, 85-326 Bydgoszcz, Poland

The solution analog of the exponential equation of adsorption on to microporous solids has been formulated. The derived expression has been applied for the description of the experimental systems consisting of binary liquid non-electrolyte solution and microporous carbon.

Keywords: adsorption from solutions; microporous adsorbents; exponential adsorption equation

INTRODUCTION

Adsorption on structurally heterogeneous surfaces, particulary when they contain micropores, requires a special form of description. Considerations of this problem have led to the theory of volume filling of micropores (VFMT) [1]. It concerns adsorption from the gaseous phase but have found equally wide application for the description of this phenomenon in the case of porous solid/liquid adsorbate systems. VFMT postulates were the theoretical basis for the considerations presented in great deal of works.

The problem of theoretical description of adsorption from binary liquid non-electrolyte solutions on to microporous solids has also been the subject of studies undertaken by author and co-workers. We considered the possibility of adapting four single gas adsorption equations (LF, GL, LF-GL and T), creating a kind of "family" in both the mathematical and physical sense, for the description of two-component solution/microporous solid systems [2,3]. We accepted VFMT postulates as a basis for our derivation, too. Calculations have confirmed that for each adsorption system, as well as for each "solution" adsorption equation in which the different sizes of the components of the bulk phase were taken into account, a similar and high (in terms of the correlation coefficient, q, value) accuracy was obtained for the description of the experimental data. Moreover all equations let us to obtain satisfactory forms of distribution functions of standard chemical affinity.

THEORETICAL

The present work refers to so-called exponential adsorption isotherm [4,5] as one of the stages in the development of VFMT. Solution analog of this equation formulated by Garbacz *et al.* [6] for the case of limited miscibility of the bulk phase components has the form:

$$x_1^s = \exp\left\{-\left[\frac{RT}{E}\ln\left[\left(a_1^*(a_2^*)^{(1-x_1^*)/x_1^*}\right)\Big/\left(a_1^l(a_2^l)^{(1-x_1^l)/x_1^l}\right)\right]\right]^n\right\} \tag{1}$$

where: x_1^s denotes molar fraction of component "1" in the adsorption phase; R, T, E and n stand for gas constant, temperature, characteristic energy $[E = A(1-F(A)) = e^{-1}]$ and the Weibull function parameter, respectively; a_i^l and a_i^* $(i = 1 \text{ or } 2)$ as well as x_i^l and x_i^* denote activities (a) and the molar fractions (x) of component "i" in the equilibrium (l) and saturated (*) bulk phases.

In present work the VFMT postulates are accepted in their new forms. Lets assume now that: (i) distribution function of standard chemical affinity, F(A), is expressed with the aid of expansion of the exponent, $F(A) = 1-\exp[-\sum c_i(A/E)^i]$, where c_i are coefficients of expansion, (ii) $1-F(A)$ is equal not, like previously, x_1^s, but its function, $x_1^s(1-x_1^s)^{(1-x_1^s)/x_1^s}$, which fulfils the same edge conditions.

In this way we obtain the new solution analog of exponential adsorption equation. It can be written down as follows:

$$x_1^s(1-x_1^s)^{(1-x_1^s)/x_1^s} = \exp\left[-\sum_n c_n\left(\frac{RT}{E}\ln\frac{a_1^*(a_2^*)^{(1-x_1^*)/x_1^*}}{a_1^l(a_2^l)^{(1-x_1^l)/x_1^l}}\right)^n\right] \tag{2}$$

RESULTS AND CONCLUSIONS

New solution analog of exponential equation of adsorption has been used for the description of the experimental excess adsorption isotherms. The calculations have been carried out for the systems consisted of binary non-electrolyte solution and microporous adsorbent. In this work there are shown results obtained for the three exemplary systems: solution of iodine (io) in benzene (be)/active carbon. Adsorbents are marked as follows: 01-carbon CWZ-3 oxidized with the aid of concentrated HNO_3 at ambient temperature, 02-carbon CWZ-3 oxidized with the aid of concentrated HNO_3

at high temperature, 03-carbon M-22. All measurments were taken at 293 K [7,8].

All the solutions were assumed to be ideal. Low values of the mole fraction of iodine in the saturated state (0.0478) provide the justification for such an approximation. Under these circumstances, one can assume that $a_1^l = x_1^l$ and, according to the Gibbs-Duhem equation, that $a_2^l = 1 - x_1^l$.

Equation (2) with the four-term expansion of the exponent was used as a real adsorption isotherm in the following excess adsorption equation:

$$n_1^{\sigma(n)} = n^s(x_1^s - x_1^l) \tag{3}$$

were n^s stands for the number of moles of both solution components in the adsorption phase (per adsorbent mass unit) and is, in general, the composition function for this phase.

Calculations have been carried out in two ways:

a) under the assumption that adsorbed molecules are of the same sizes,
b) with regard to the fact, that molar volumes ratio of admolecules, $r = V_1/V_2$, differs from unity and for the system iodine + benzene is equal 0.854.

Optimized values of parameters of Eq. (2) obtained for the described adsorption systems are presented in Table 1. Accordance between the experimental data and the theoretical curves for the variant "b" of calculations is illustrated in Figure 1.

Analyses of the results of optimization lead to the following conclusions:

1. For each adsorption system and for both ways of calculations values of correlation coefficients are high. Moreover, in the majority of cases, when the different sizes of the bulk phase components were taking into consideration, more precisious description of experimental data has been obtained.
2. The values of coefficients c_n vary non-monotonically with the increase of n number but c_2, c_3 and c_4 are usually so close to 0 that they provide

TABLE 1 Results of Optimization of Eq. (2) Parameters

System	c_1	c_2	c_3	c_4	n^s	RT/E	Q
iobe01(r = 1)	1.000	$3*10^{-21}$	$9*10^{-22}$	$4*10^{-22}$	3.0846	0.7048	0.9986
iobe01(r ≠ 1)	1.000	$1*10^{-20}$	$1*10^{-21}$	$9*10^{-22}$	3.0974	0.6579	0.9993
iobe02(r = 1)	1.000	$6*10^{-21}$	$2*10^{-21}$	$7*10^{-22}$	1.6330	0.7391	0.9920
iobe02(r ≠ 1)	1.000	$7*10^{-20}$	$3*10^{-21}$	$1*10^{-22}$	1.6388	0.6890	0.9935
iobe03(r = 1)	1.000	$8*10^{-22}$	$2*10^{-21}$	$9*10^{-22}$	4.1328	0.6990	0.9959
iobe03(r ≠ 1)	1.000	$6*10^{-23}$	$6*10^{-22}$	$7*10^{-22}$	4.1468	0.6570	0.9973

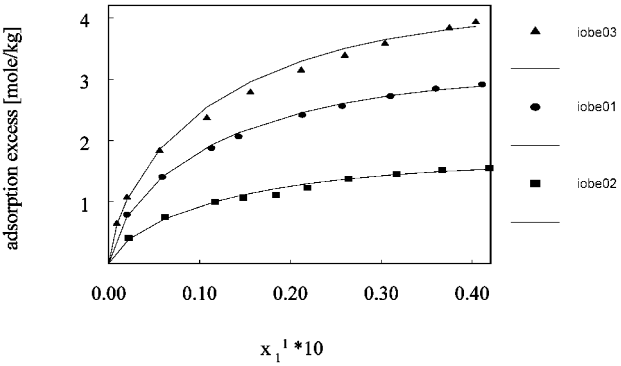

FIGURE 1 Experimental (points) and theoretical (lines) isotherms of adsorption for variant $r = 1$.

the quick convergence of the Eq. (2) exponent. That is why one can accept Eq. (2) in the shorter form:

$$x_1^s(1 - x_1^s)^{(1-x_1^s)/x_1^s} = \left(a_1^*(a_2^*)^{(1-x_1^*)/x_1^*}/a_1^l(a_2^l)^{(1-x_1^l)/x^l{}_1}\right)^{E/RT}$$

for calculations in the systems containing active carbon and binary liquid non-electrolyte solution with limited miscibility of the bulk phase components.

3. The n^s values obtained for individual active carbons vary according to the change in the micropore volumes of the adsorbents used which (in m^2/g) amount to: 01–1240, 02–1255 and 03–1225, respectively [7,8]. This confirms, at least indirectly, the adsorption mechanism according to the VFMT.

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