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THEORETICAL ISOTHERMS FOR MONOLAYER ADSORPTION ON HETEROGENEOUS SURFACES

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Theoretical isotherms for monolayer adsorption on heterogeneous surfaces have been obtained on the basis of the Langmuirian local isotherm and three different distribution functions of adsorption energies (Boltzmann, quasi-Gaussian and shifted quasi-Gaussian distribution functions). The isotherm obtained with the Boltzmann distribution function proposed 40 years ago by Glueckauf predicts well the maximum surface coverage, Freundlich region, as well as Henry behaviour at extremely low surface coverages. It has been demonstrated that the so–called Dubinin - Radushkevich isotherm appears in the transition between the Freundlich and Henry regions if the upper limit to the energy of adsorption is high enough. The isotherm obtained with the quasi-Gaussian distribution function also predicts well the maximum surface coverage and reduces to the Henry region at low surface coverages. Shifted quasi-Gaussian adsorption energy distribution function suggested by Cerofolini et al. results in mixed isotherms between these two extreme cases. Transition between these two types of adsorption energy distributions can also result in the appearance of the so–called Dubinin - Radushkevich behaviour in a certain range of adsorbate concentrations . The characteristics of the correspond-

[1]A part of this work was made during a visit to the Department of Chemistry at the University of Aarhus, Denmark.

ing isotherms are discussed in detail and advantages of Glueckauf's suggestions are demonstrated.

1. Introduction

The reasons why the theory of homogeneous submonolayer adsorption cannot always explain the experimental results are very often the effects of surface irregularities. Surface imperfections of molecular dimensions have as a result the energetic inhomogeneity of the surface, and this has a profound effect on the adsorption isotherms determined experimentally. The theory of submonolayer adsorption on heterogeneous surfaces has been the subject of many scientific papers [1-8]. It was developed for adsorption of gases at heterogeneous surfaces and later for adsorption of solutes at different solid-liquid interfaces. Recently, these theoretical results were applied to interaction of solutes with biological and geological interfaces. The basic concepts of this theory can be summarised in the following way. If $\mathrm{d}F = f(Q)\mathrm{d}Q$ is the distribution function of sites available for adsorption of adsorption energy between Q and $\mathrm{d}Q$, and if the local adsorption isotherm is defined by function $\Theta(Q, KC)$, K being the strength of adsorption (i.e. adsorption equilibrium constant) corresponding to a ground state of energy and C the concentration (assuming that the activity coefficient is close to unity) of adsorbate to be adsorbed at the interface from a homogeneous phase, then the net surface coverage should be [9]:

$$\Theta_T = \int\limits_{-\infty}^{\infty} \Theta(Q, KC) f(Q)\mathrm{d}Q = \int\limits_{0}^{\infty} \Theta(Q, KC)\mathrm{d}F. \tag{1}$$

For example, as shown by several authors, if the local adsorption is described by the Langmuir isotherm:

$$\Theta(Q, KC) = \frac{1}{1 + e^{-Q/RT}/KC} \tag{2}$$

and if a Boltzmann distribution function is selected as a model of site heterogeneities:

$$F = e^{-Q/nRT} \tag{3}$$

where n is the parameter of the heterogeneity, the resulting net surface coverage will follow the known Freundlich adsorption isotherm:

$$\Theta_T = A(KC)^{1/n} \tag{4}$$

where A is a constant. This result has been obtained both by a semi-empirical approach [10-12] and by a rigorous treatment [9]. The reverse problem, i.e., determination of the distribution function, was first discussed by Roginskii [12] and analyzed in a rigorous way by Sips [13]. He derived the Boltzmann distribution for the Freundlich isotherm using this procedure. Later, House and Jaycock [14] developed a computer program for numerical evaluation of the distribution function for a given local adsorption isotherm on the basis of such methodology. Cerofolini and coworkers [15,16] state that the analytical solution can also be obtained on the basis of the Langmuir type of local isotherm and the quasi-Gaussian type of adsorption energy distribution :

$$F = e^{-QQ/bRT} \tag{5}$$

assuming that only positive values of Q are possible (i.e. $Q > 0$), where b is the parameter of the distribution function. They stated that, using the so–called condensation approximation [17], known Freundlich (Eq. (4)) and Dubinin-Radushkevich [18]:

$$\log \Theta = A + B(\log(KC)^2) \tag{6}$$

isotherms can be derived from the distribution functions (3) and (5), respectively. This statement disagrees with the existing rigorous solutions reported in literature [10,13]. We discovered the same interpretation of the results of Sips in the book written by Adamson [6], where $Q > 0$ limit is mentioned for the classical Freundlich isotherm (instead of the infinite limit which is valid for this case). For the combination of the Langmuir and Freundlich isotherms:

$$\Theta_T(KC) = \frac{1}{1 + 1/A(KC)^{1/n}} \tag{7}$$

Sips [13] reported using his reverse method, a complex distribution function which is very similar to the Gaussian one only for $n = 2$. In his paper Sips mentions the difficulties in calculating the adsorption isotherm for a Gaussian adsorption energy distribution (due to the "intractable definite integrals"). Cerofolini and coworkers [15,16] proposed a shifted quasi-Gaussian distribution:

$$F = e^{-Q(1 + Q/b)/nRT} \tag{8}$$

and solved it numerically for the Langmuirian type of local adsorption isotherm. They concluded that this isotherm produces, within a sufficiently large scale of surface coverages, a transition between the Henry ($\Theta = KC$), Dubinin–Radushkevich and Freundlich isotherms, while individual distributions, as they claim, produce Freundlich (see Eq. (4)) or Dubinin–Radushkevich isotherms (see Eq. (6)). Both of these isotherms fail to produce the Henry region at very low surface coverages and at the same time they don't predict the formation of the complete monolayer.

2. *Why Henry behaviour does not appear at low coverages*

If we study the shape of the overall adsorption isotherm for the Langmuirian type of local adsorption isotherm with different adsorption energies (see Eq. (2)), we can conclude that it is impossible to obtain pure Henry conditions at very low coverages, assuming validity of Eq. (2) and that $-\infty < Q < \infty$, or $0 < \exp(-Q/RT) < 1$. The reason is, however small adsorbant concentration is present in the homogeneous phase from which the adsorption takes place, high adsorption energies will always be available that will make the term $\exp(-Q/RT)/KC$ small enough in comparison with unity. This will make the change of total coverage due to high energy sites comparable to the change of the distribution function:

$$\mathrm{d}\Theta_T = f(Q)\mathrm{d}Q = dF \quad \text{for} \quad Q >> RT\ln(1/KC). \tag{9}$$

Taking into account the fact that all other changes of total coverage could be only smaller than the change in the distribution function, the Henry conditions could never be reached, a fact well known for the classical Freundlich isotherm (see Eq. (4)). The question arises whether both the Boltzmann and quasi-Gaussian distributions lead to adsorption isotherms which do not reach the Henry conditions at very low surface coverages (as stated by Cerofolini et al. [15,16]) and how their combination could produce the Henry condition for the same limiting conditions. At the first moment our impression was that numerical errors may cause an appearance of the Henry isotherm at very low coverages. If d, a certain increment of distribution function F is used, then there is a limit of Q values (let us call it q) which would limit the integration procedure. In fact, this could allow the adsorbate concentration to become so small that $\exp(-q/RT) \gg KC$ and, consequently, the local adsorption isotherm described by Eq. (2) would yield:

$$\Theta(Q, KC) = KCe^{Q/RT}. \tag{10}$$

This is the Henry (the so–called linear or ideal) adsorption isotherm. This numerical error is equivalent to the solution of the integral :

$$\Theta_T = \int_{-\infty}^{q} \Theta(Q, KC)f(Q)\mathrm{d}Q = \int_{d}^{\infty} \Theta(Q, KC)\mathrm{d}F \tag{11}$$

which should produce a linear domain of the adsorption isotherm for sufficiently low surface coverages. We have, therefore, decided to use a numerical method to reexamine the findings of Cerofolini and coworkers [15,16].

3. Development of the simple numerical method

We developed a simple numerical method for integration of Eq. (1) and tested it for the well–known analytical solution, for the Boltzmann distribution and the Langmuir type of local adsorption isotherm. The simplest possible method was used to avoid any error and to have the results of integration under full control. Introducing $F = \exp(-Q/nRT)$, i.e., $\exp(-Q/RT) = F^n$, the change of total coverage is:

$$DT = \frac{DF}{1 + F^n/KC} \tag{12}$$

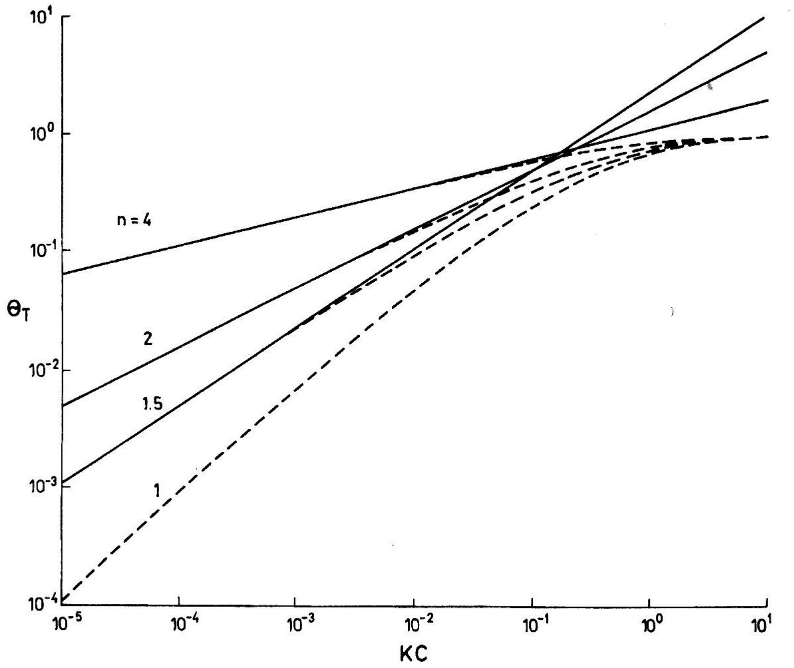

Fig. 1. Results of the numerical integration of Eq. (12) within the limits $0 < F < \infty$ *(solid lines are equivalent to the classical Freundlich isotherm) and* $0 < F < 1$ *(dashed lines, producing new adsorption isotherms) for different values of the* n *parameter.*

where DT is the change of the total surface coverage and $DF = 1/N$, N being the number of iterations during the integration. The limits for F were from 0 to ∞. The results are shown in Fig. 1. Obviously, this simple procedure produces very good results. The perfect classical Freundlich isotherm was obtained as expected. Then, we repeated the calculations in order to evaluate the integral described by Eq. (11) in the following way:

$$\int_{d}^{\infty} \Theta(Q, KC)\mathrm{d}F = \int_{0}^{\infty} \Theta(Q, KC)\mathrm{d}F - \int_{0}^{d} \Theta(Q, KC)\mathrm{d}F. \tag{13}$$

This can be easily achieved by storing the value of TH for a given F value (which corresponds to the energy q) and later subtracting it from the total integral. The results are presented in Fig. 2. One can see that an increase of the value d (i.e., the upper limit of adsorption energy $q = RT\ln(1/d)$) causes appearance of the Henry behaviour at lower values of surface coverages. From this we can conclude that an improper use of the numerical method could produce the effect of the apearance of Henry behaviour at energies of adsorption higher than the one corresponding to the increment of the distribution function. However, we can draw an even more important conclusion. Because the energy of adsorption is limited and therefore has a maximum value, then at low surface coverages the Henry behaviour should arise, decreasing the range of concentrations of adsorbate in the homogeneous phase for which a Freundlich isotherm can be observed. The intersection of the Freundlich and Henry slopes in the corresponding log-log plot of surface coverage vs. concentration of adsorbate in homogeneous phase can, then, serve for determination of such a limit of adsorption energies. This has been found out first by Glueckauf [19] about 40 years ago, and rediscovered later by several authors [8,20,21], without any reference to the old Glueckauf's work.

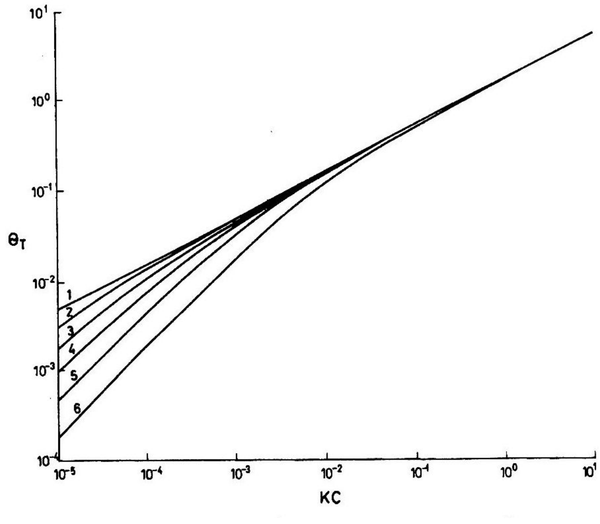

Fig. 2. Results of the numerical integration of Eq. (11) within the limits $d < F < \infty$ (corresponding to the limits of adsorption energy $0 < Q < q$, where $q = nRT\ln(1/d)$). (1) $d = 0$; (2) $d = 0.002$; (3) $d = 0.005$; (4) $d = 0.01$; (5) d=0.02; (6) $d = 0.05$.

4. Prediction of the complete monolayer

The Freundlich isotherm has also been criticized for the fact that it does not predict well the maximum surface coverage corresponding to the complete monolayer. It seems that invention of special isotherms, such as those proposed by Sips [13], is actually unnecessary for this purpose. Here, we refer to Eq. (6) and the following equation:

$$\Theta_T(KC) = 1/(1 + 1/KC)^{1/n} \tag{14}$$

or, for example, even the more unusual one:

$$\Theta_T(KC) \log k = \log \frac{kKC + 1}{KC + 1} \tag{15}$$

reported later in Refs. 22-24. We will show that this can be achieved simply by accepting the comments of Hill [25] and Tompkins [26], who complained about the other limit to the negative energies necessary to perform an analytical derivation of the classical Feundlich isotherm. We performed additional numerical calculations for the Freundlich isotherm only up to the limit $F = 1$ (which corresponds to the energy of the ground state and to the strength of adsorption K). The results are presented in Fig. 1 (dashed lines). They show that when the negative energies are not taken into account, the prediction of maximum coverage is obtained and Eq. (4) is valid only in the range of low adsorbant concentrations. In this way, we could come to the conclusion that the statement of Hepler [27], who claimed that the integral between the limits $1 < F < \infty$ is very small compared to that between $0 < F < 1$, is not generally true. It is true only at very low surface coverages. However, how can we explain the fact that the numerical solution for $F \leq 1$ produces a logical limit $\Theta \leq 1$, while the analytical solution and numerical solution for $F \gg 1$ does not? If we turn our attention back to Eq. (2), then, for extremely negative energies, $\exp(-Q/RT)$ will become so large that, however large is the adsorbant concentration in the homogeneous phase, $\exp(-Q/RT) \gg KC$ will eventually become true. Then the Freundlich isotherm (see Eq. (4)) will appear as a result of the integration. We expect this to happen for energies lower than about $Q = -5nRT$ (at least for adsorbant concentrations $KC < 10$) which would correspond to $F = 148$. Of course, the consequence of the adsorption energy limit with $F \leq 1$ is the prediction of correct maximum coverages $\Theta_T \leq 1$. In the case of formation of multiple layers, negative adsorption energies could also have a physical meaning. It would be interesting to study the shape of the part of the isotherm obtained for the limit $F \leq 1$ and compare it with some other isotherms of a similar type (see, for example, Eqs. (7), (14) and (15)). We compared the shapes of some of these isotherms in Fig. 3. The conclusion is that each of these special isotherms does not coincide with the shape of the isotherm obtained rigorously by numerical integration of the Langmuirian local isotherm with the Boltzmann distribution of adsorption energies. Therefore, these special isotherms should not be named "generalized Freundlich isotherms" because they do not possess the common origin from the point of view of the nonhomogeneity of the adsorption sites on the interface. In conclusion, we could say that the combination of the Langmuirian local isotherm and the Boltzmann adsorption energy distribution, if integrated within the energy limits $0 < Q < q$ where q is a certain maximum adsorption energy (the limits which correspond to $d < F < 1$, which have been mentioned fourty years ago by Glueckauf [19]), produces a new theoretical isotherm which, at extremely low surface coverages, reduces to the Henry isotherm. At very high adsorbate concentrations, it predicts well the maximum monolayer surface coverage and, in the intermediate range of surface covarages, corresponds to the known Freundlich isotherm. We will show that under certain conditions the so–called Dubinin–Radushkevich isotherm appears as the transition between the Freundlich and Henry behaviour.

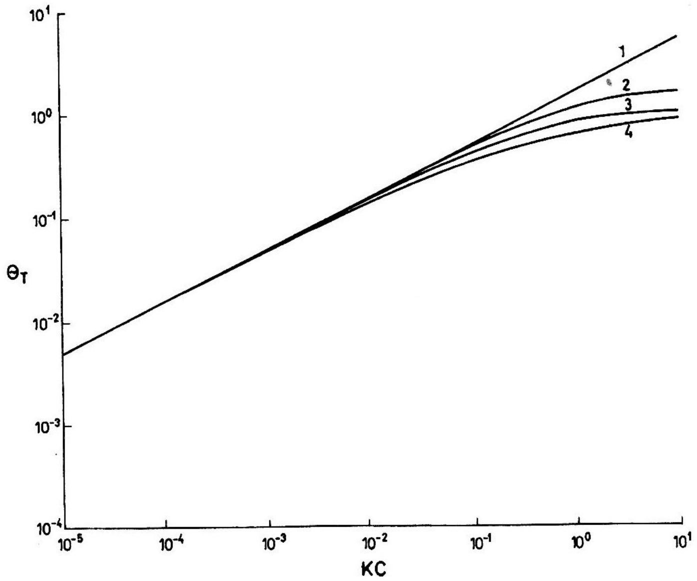

Fig. 3. Comparison of different types of theoretical adsorption isotherms. (1) Classical Freundlich isotherm for $n = 2$ (see Eq.(4)); (2) Sips isotherm defined by Eq. (6); (3) new isotherm proposed here for the limits of integration $0 < Q < \infty$ (i.e., $0 < F < 1$); (4) Sips isotherm defined by Eq. (17).

5. *Adsorption isotherm for a quasi-Gaussian distribution function*

Now we use the same numerical approach to solve the adsorption isotherm for the case when the local adsorption isotherm is still of the Langmuirian type, but assuming the quasi-Gaussian distribution of adsorption energies (see Eq. (5)).

In this case $F = \exp(-QQ/bRT)$ and, consequently, $\exp(-Q/RT) = F^x$, where $x = (b/RT \ln(1/F))^{1/2}$. Therefore, the numerical integration should be performed using the following difference equation:

$$DT = \frac{DF}{1 + F^x/KC} \tag{16}$$

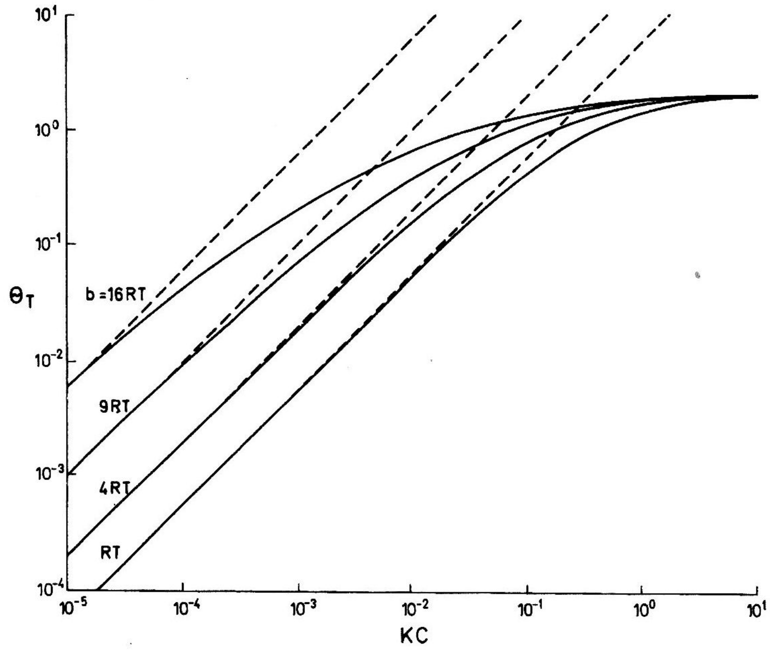

Fig. 4. Results of the numerical integration of Eq. (16), using $x = (b/RT \ln(1/F))^{1/2}$ and the integration limits $0 < F < \infty$ (solid lines) and the corresponding Henry isotherms (dashed lines) for different b values.

instead of Eq. (12). The results of the calculations are shown in Fig. 4. We were surprised to see that isotherms similar to Henry behaviour were obtained instead of the Dubinin–Radushkevich ones at lower adsorbate concentrations. In addition, this isotherm predicts well the maximum coverage if the constant factor $A = 1/2$ is added to obtain $\Theta_T = 1$ for high adsorbate concentrations in the homogeneous phase. Therefore, it is probable that the numerical method of Cerofolini and coworkers [16] is correct, but they used it only for the shifted and not for pure quasi-Gaussian distribution function, for which they assumed the Dubinin–Radushkevich isotherm should be valid. Of course, if Henry behaviour can be obtained with a quasi-Gaussian distribution function alone, then the shifted quasi-Gaussian distribution function should produce the same result. Let us see if we could obtain the quasi-Gaussian distribution from the Dubinin - Radushkevich isotherm. For this purpose, we could used the method of Sips [13] and the result is the following:

$$f = A\sin(Q/aRT)e^{-QQ/bRT} \tag{17}$$

and this is certainly not the quasi-Gaussian distribution (mentioned above, see Eq. (5)). For small adsorption energies, this distribution function reduces to the simpler form:

$$f = A\frac{Q}{aRT}e^{-QQ/bRT} \tag{18}$$

which is equivalent to the first derivative of Eq. (5). Only for adsorption energies $Q = aRT(n + 1/2)\pi$, the distribution function (17) reduces to the quasi-Gaussian values. Due to the fact that Eq. (17) generates also negative distribution function values makes the Dubinin–Radushkevich isotherm rather unnatural. It could well be that this type of adsorption isotherm appears in the transition range between the Boltzmann and quasi-Gaussian distributions, as suggested by Cerofolini and coworkers [16]. Therefore, we tried to recalculate their results to check this possibility. For this purpose, we used the shifted quasi-Gaussian distribution function $F = \exp(-Q(1 + Q/b)/nRT)$ and, consequently, $\exp(-Q/RT) = F^x$ where:

$$x = 2n/(1 + \sqrt{1 + (4nRT/b)\ln(1/F)}). \tag{19}$$

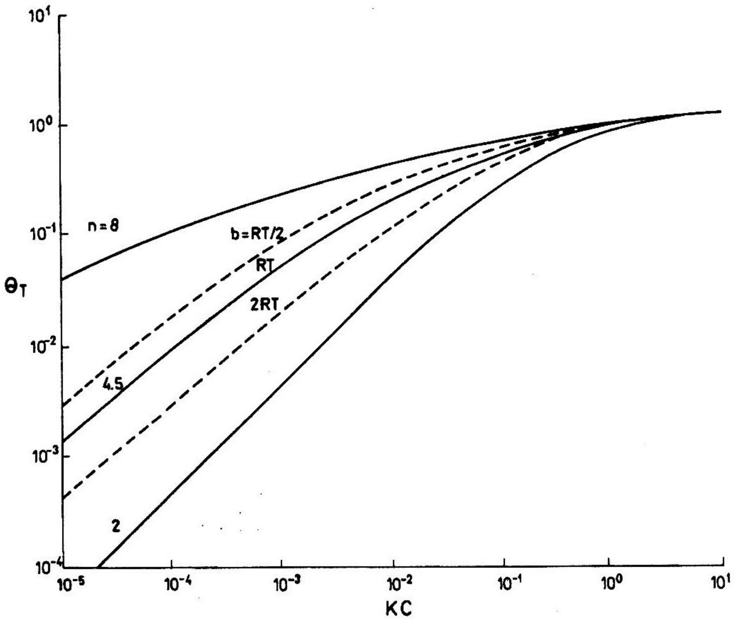

Fig. 5. Results of the numerical integration of Eq. (16), using x from Eq. (19), and the integration limits $0 < F < \infty$, for $b = RT$ and different n values (solid lines), as well as for $n = 4.5$ and different b values (dashed lines).

Numerical calculation were performed using the same difference equation (16) with the new meaning of x according to Eq. (19). The results are presented in Fig. 5. If these results are plotted vs. $(\ln KC)^2$, one can see that the values in a transition between the Boltzmann and quasi-Gaussian distributions sometimes show, in a certain range of adsorbate concentrations, a straight line corresponding to what is known as the Dubinin - Radushkevich isotherm. In fact, any transition between Freundlich and Henry behaviour will also produce the same result. This is true of some of the plots from Fig. 2 that have not been obtained using the quasi-Gaussian distribution (see Fig. 6.).

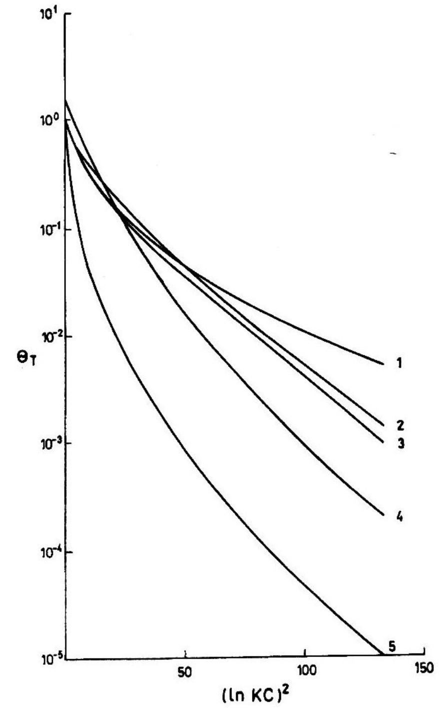

Fig. 6. Plots of Θ_T vs. $(\ln KC)^2$ for different models of adsorption at heterogeneous surfaces. (1) Boltzmann distribution function with $n = 2$; (2) Shifted quasi-Gaussian distribution function with $n = 4.5$ and $b = RT$; (3) Boltzmann distribution function with $n = 2$ and $q = 4.6nRT$; (4) Quasi-Gaussian distribution function with $b = 4RT$; (5) Henry isotherm.

6. The meaning of Dubinin-Radushkevich isotherm

While Freundlich and Henry isotherms have a definite physical meaning (the first is a result of nonhomogeneities of active binding sites, and the second is a consequence of the equation of state for the ideal two–dimensional gas model), it seems that the so–called Dubinin–Radushkevich isotherm represents only a transitional region between the first two isotherms. From the results obtained here it is not surprising that the Dubinin–Radushkevich isotherm has been discovered empirically. Cerofolini et al. [15,16] have assumed the relation between the pure quasi-Guassian adsorption energy distribution and the Dubinin–Radushkevich isotherm. One cannot find any evidence for such conclusions in the literature. Dubinin himself illustrated the form of such an isotherm with experimental data only within the range of at the most one and a half order of magnitude in the volume of adsorption space for gases on different surfaces [29]. One should mention, however, the experimental results have been reported by some other authors who obtained the shape of the Dubinin–Radushkevich [18] type of isotherm for a range of several orders of magnitude in KC values [30-32]. In addition, Dubinin [29] described also some data with clear deviations from his isotherm (the same is true for some other experimental data [31]) and proposed the use of several different isotherms of the same kind to fit the experimental data. As one can see from Fig. 6, rigorous solutions can explain this fact without any additional formal interventions in the equation of the overall isotherm. Dubinin–Radushkevich isotherm has been correlated [33,34] with Brunauer–Emmett–Teller (BET) and Sips isotherms. However, if it is true what we are suggesting in this paper, the connection between them is unreasonable. BET, Sips and Dubinin–Radushkevich isotherms appear in completely different regions of surface coverages. Some authors [35,36] suggested the use of Dubinin–Radushkevich isotherm (fitting only a part of the total isotherm at heterogeneous surfaces) for the choice of the local isotherm. This suggestion appears to have no physical meaning. Cerofolini and coworkers [16] assumed that a combination of Boltzmann and quasi-Gaussian distributions are necessary to "explain the Freundlich and the Dubinin–Radushkevich behaviours". We demonstrated in this work that this is not the necessary condition.

7. *Discussion*

In this paper we proved that several authors [6,16] did not correctly interpret the conditions for the appearance of classical Freundlich isotherm. For this purpose, rigorous solutions of Eq. (1) should be used as shown by many authors [9-11,13] and in this paper. The similar rigorous solution for the quasi-Gaussian distribution function of adsorption energies is derived in this paper. We demonstrated that it does not produce the Dubinin–Radushkevich isotherm as suggested by Cerofolini et al. [16]. It is interesting to learn that a pure quasi-Gaussian distribution of adsorption energies with the Langmuirian type of local adsorption isotherm reduces to an isotherm with a total surface coverage of the Henry type, in the range of very low adsorbant concentrations in the homogeneous phase from which the adsorption takes place. This is true for both cases, when negative values for Q are, or are not permitted. This can be explained by the fact that the high energy side of the quasi-Gaussian distribution function is a gradual equivalent to the sharp cut-off for the high energy limit in the case of the Boltzmann distribution function which generates the Henry behaviour at small surface coverages. However, the reverse procedure developed by Sips [13] generates only the simple Boltzmann adsorption energy distribution function from the adsorption isotherm of the Henry type. In addition, the adsorption isotherm obtained using the quasi-Gaussian distribution of adsorption energies predicts well the maximum coverage, which is not the case of the Freundlich isotherm (see Eq. (4)) obtained with the Boltzmann distribution of adsorption energies without the cut-off in the region $Q < 0$. This is again not surprising because the low energy side of the quasi-Gaussian distribution function is a gradual equivalent to the sharp cut-off for negative adsorption energies in the case of the Boltzmann distribution function when the complete monolayer is formed. Boltzmann distribution function of adsorption energies has been verified experimentally with data on surface complexation processes in the region of moderate and high surface coverages. In the same region of adsorbate concentrations, gas/solid interaction usually undergoes multilayer adsorption, and submonolayer adsorption isotherms cannot be applied in studies of such systems. Using sequential analysis of the experimental results for surface complexation processes, it has been shown [38,39] that weak binding sites are more abundant than the stronger binding sites. Such behaviour can be explained only with the Boltzmann type of distribution function. At low surface coverages only the high energy binding sites are active, and in a certain narrow region of adsorbant concentrations different distribution functions could fit well the same experimental data. Therefore, different distribution functions cannot be always distinguished well under such conditions. Energy distributions very often include $\exp(-E/k_BT)$ term, where k_B is the Boltzmann constant, (this is the case for example in the Boltzmann, Fermi and Bose distribution functions). Unfortunately, the possibilities of using the Boltzmann distribution function with appropriate limits to the energy of adsorption was almost neglected during last 40 years. On the contrary, different types of quasi-Gaussian, symmetric and nonsymmetric, distribution functions have been widely used for derivation of a number of semi-empirical isotherms, but all of them applicable only in a certain narrow region of surface coverages. Some authors tried to resolve this problem using more sophisticated distribution functions [15,16,28,40] or complex isotherms [13,22,28,41]. As we illustrated in the present paper, based of the suggestion made by Glueckauf [19], a straightforward solution of this problem is relatively simple by using Boltzmann distribution function with proper limits to the energy of adsorption. From the results obtained in this work we can conclude that the shape of the so-called Dubinin–Radushkevich isotherm can be obtained from the Langmuirian type of local isotherm and Boltzmann distribution of adsorption energies if a sufficiently high maximum energy of adsorption is assumed. It does not appear without the upper limit of adsorption energies. It also does not appear if this limit is not high enough. Therefore, the transition between the Henry, Dubinin–Radushkevich, Freundlich and Langmuir isotherms can be obtained using the Langmuirian local isotherm and only the Boltzmann distribution of adsorption energies. These theoretical arguments can be verified by reinterpretation of very fine experimental results available in the literature. Preliminary results in fitting the data for adsorption of noble gases on Pyrex glass [30,31] with rigorous solution for pure Boltzmann distribution function are very encouraging. In addition, the comparison of complexation data for Cu(II) in lake waters rich in organic matter with this rigorous solution clearly illustrates its advantages over the semi- empirical isotherms mentioned above [38].

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TEORIJSKE IZOTERME ZA JEDNOSLOJNU ADSORPCIJU NA HETEROGENIM POVRŠINAMA

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Dobivene su teorijske izoterme za jednoslojnu adsorpciju na heterogenim površinama koje se zasnivaju na Langmuirovskoj lokalnoj izotermi i tri različite funkcije raspodjele energije adsorpcije (Boltzmannova, kvazi-Gaussova i pomaknuta kvazi-Gaussova funkcija raspodjele). Izoterma dobivena za Boltzmannovu funkciju raspodjele predložena od strane Glueckaufa pred 40 godina predviđa dobro maksimalnu pokrivenost površine, Freundlichovo područje, kao i Henryevo ponašanje na vrlo niskim pokrivenostima površine. Pokazano je da se tzv. Dubinin–Raduškevičeva izoterma javlja na prijelazu između Freundlichovog područja i Henryevog područja. Izoterma koja je dobivena za kvazi-Gaussovu funkciju raspodjele također predviđa dobro maksimalnu pokrivenost površine i prelazi u Henryevo područje na niskim pokrivenostima površine. Pomaknuta kvazi-Gaussova funkcija raspodjele energije adsorpcije predložena od strane Cerofolinija i suradnika ima za rezultat miješanu izotermu. Na prijelazu između ta dva različita tipa raspodjele energije adsorpcije, unutar određenog područja koncentracija adsorbata, također se javlja Dubinin–Raduškevičeva izoterma. Raspravljene su karakteristike spomenutih izotermi i prikazane su prednosti Glueckaufovih prijedloga.