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THE EFFECTIVE INFLUENCE OF ADSORBATE-ADSORBATE ASSOCIATIONS ON THE TWO-DIMENSIONAL CONDENSATION OF A MOBILE ADSORPTION MONOLAYER ON A HOMOGENEOUS SOLID ADSORBENT SURFACE

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ABSTRACT

The study employed the formalism of the canonical ensemble to analyze adsorption equilibrium, assuming that linear association of molecules is the only type of attractive interaction in the mobile monolayer on a homogeneous solid adsorbent surface. The partition function of the canonical ensemble was related to the free energy and the chemical potential of the adsorbate. The initial model did not show the possibility of two-dimensional condensation of the adsorbate, confirming the analogy to the one-dimensional Ising model.
The generalization of the model, assuming a branched form of adsorbate-adsorbate associates, leads to a new adsorption equation that takes into account the number of centers favorable for association. The introduction of the concept of multidimensional association enabled the derivation of an adsorption equation, which was analyzed with respect to the critical point of the adsorption layer condensation. This analysis showed that condensation is possible if the number of such centers is greater than two. The critical values of the association constant and the degree of surface coverage are functions of the number of association centers. These results demonstrate that the formalism of the canonical ensemble is effective for describing adsorption equilibrium with linear association of molecules, and that generalizing the model to include branched associates leads to a new adsorption equation predicting two-dimensional condensation of the adsorbate under certain conditions.
The described model introduces new solutions in the use of sorbents in diving apparatus with a closed circuit and thus increasing their efficiency in military applications.
Keywords: adsorption, monolayer, association, condensation, isotherm.

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INTRODUCTION

In our previous work [1], we discussed the problem of molecule association in a localized adsorption monolayer on a homogeneous surface of a solid adsorbent. During the discussion, we demonstrated the complete equivalence of two alternative methods for describing adsorption equilibrium: the statistical method and the phenomenological method. The first method was based on the formalism of the canonical ensemble, while the second was applied in the variant proposed by A.V. Kiselev in the mid-20th century [2]. By eliminating the obvious thermodynamic inconsistencies in Kiselev's concept, we obtained an adsorption equation identical to the special case of the relationship given by Fowler and Guggenheim [3], derived using equilibrium statistical thermodynamics. The direct result of our considerations concerned the case of linear association of adsorbate molecules and, like the equations of Kiselev [2] and Berezina-Kiselev [4], did not predict the possibility of two-dimensional condensation of the adsorption layer. The obvious reason for this deficiency in the discussed concept stemmed from the analogy between the linear association of molecules and the Ising model [5], whose one-dimensional variant excludes any phase transition. Accepting this observation as a methodological premise allowed for a generalization of the description, in which two-dimensional condensation of the adsorption layer became a natural consequence of adsorbate-adsorbate association. The issue of the association of adsorbed molecules, especially regarding the effect of this phenomenon on the possibility of two-dimensional condensation of the adsorption layer, is also the subject of this work. This time, however, the considerations pertain to a mobile monolayer, where each molecule has, in addition to vibrational (external and/or intramolecular), two degrees of freedom of translation parallel to the surface of the adsorbent. Therefore, the aim of this work is to formulate a description of adsorption equilibrium that is, on one hand, complementary to the solution concerning the localized monolayer, and on the other hand, completes, along with that solution, the theoretical framework of adsorbate-adsorbate association for both mutually alternative surface phase models.

APARAT FORMALNY

To maximize the clarity of our considerations, we will choose the statistical method using the canonical ensemble. Recall that this is an ensemble with constant temperature, constant volume, and a constant number of molecules. In our case, this means a constant temperature, a constant adsorbent surface area, and a constant total number of adsorbate molecules, regardless of the groupings in which these molecules occur (for adsorbate-adsorbate association, this last condition should be expressed as $N = \sum_i iN_i = \text{const}$, where N_i denotes the number of molecules with multiplicity i). The partition function of the canonical ensemble, in our case, is the sum of the states of the adsorption layer, Z_a, which has the following relationships with the free energy F_a and the chemical potential of the adsorbate μ_a:

$$F_a = -kT\ln Z_a \qquad (1)$$

and

$$\mu_a = -kT\left(\frac{\partial \ln Z_a}{\partial N}\right)_{T.A}. \qquad (2)$$

where k and T denote the Boltzmann constant and the absolute temperature, respectively.

In the state of internal equilibrium of the adsorption layer, the free energy, as the thermodynamic potential of the isoplanar-isothermal process, reaches a minimum. This implies, due to equation (1), a maximum of the logarithm of Z_a. Therefore, the task of determining the most probable distribution of adsorbate molecules among the various associates reduces to formulating the conditions for this maximum, taking into account the constraint N=const.

According to the Lagrange method [6], we thus construct the function:

$$\chi = \ln Z_a + \alpha \sum_i iN_i \qquad (3)$$

where α s the undetermined factor, and the coordinates of the maximum of this function (where all N_i are treated as independent variables) constitute the solution to our problem. If, therefore, $Z_a = Z_a(T,A,N_1,N_2, \dots)$, then, according to the equation: (3).

$$(d\chi)_{T.A} = \sum_i \left[\left(\frac{\partial \ln Z_a}{\partial N_i}\right)_{T.A.N_{j\neq i}} + i\alpha\right] dN_i \quad (4)$$

At the absolute maximum of the function χ each square bracket in the above equation equals zero. Therefore, for each i,

$$\mu_i = ikT\alpha. \qquad (5)$$

where $\mu_i = -kT\left(\frac{\partial \ln Z_a}{\partial N_i}\right)_{T.A.N_{j\neq i}}$ is the chemical potential of the associate with multiplicity *i*.

On the other hand, we can also treat Z_a as a function of T , A and N, and rewrite equation (4) in the form:

$$(d\alpha)_{T,A} = \left[\left(\frac{\partial \ln Z_a}{\partial N}\right)_{T,A} + \alpha\right] dN \quad (4')$$

Similarly, in this case, i.e., in equation (4'), in the state of internal equilibrium of the adsorbate, the interior of the square brackets equals zero, hence

$$\mu_a = kT\alpha, \qquad (5)$$

where the chemical potential of the entire adsorption layer, μ_a (equal to $-kT(\partial \ln Z_a / \partial N)_{T,A}$), turns out to be, according to equation (5), identical in value to the chemical potential of the individual (unassociated) adsorbate molecules, μ_1.

Ultimately, the condition for the most probable distribution of adsorbate molecules among the various associates can be written as follows:

$$\mu_i = i\mu_1 = i\mu_a \; ; \; i = 1.2.3. \dots \qquad (6)$$

Completing the current considerations requires the determination of the equilibrium condition between the adsorbate and the non-adsorbed gas (adsorptive). This aspect does not pose a particular problem, as it is well known that the equilibrium condition in a multiphase system is the equality of the chemical potential of a given component in all phases of the system. Thus, in our case, $\mu_a = \mu_g$, and by virtue of equation (6), also $\mu_1 = \mu_g$, where μ_g denotes the chemical potential of the adsorptive.

Additionally, a significant simplification of the problem is the commonly accepted assumption of the ideality of the non-adsorbed gas, for which [6]:

where p and j_g denote, respectively, the pressure of the gas and the internal partition function of a single gas molecule, while ttt is the translational factor in the form: [6]:

$$t = \frac{h}{\sqrt{2\pi mkT}} \qquad (8)$$

with Planck's constant, h and the mass of a molecule, m.

The result of our considerations can thus be presented in general form as follows:

$$p = kTt^{-3} j_g \exp\left(\frac{\mu_i}{kT}\right) \qquad (9)$$

Specifying the relationship (9) still requires adopting a specific model (physical representation) of the adsorption layer and formulating, based on it, the relationship between μ_1 and the total concentration of the adsorbate on the adsorbent surface. The implementation of this stage is the aim of the subsequent part of this study.

MODEL OF THE ASSOCIATED MOBILE ADSORPTION MONOLAYER

In this study, we assume that adsorbate-adsorbate association is the only type of lateral attractive interaction in the adsorption layer. This implies identifying the mobile phase of the adsorbate with a mixture of two-dimensional ideal gases, whose components are defined by the multiplicity of molecules – associates. Consequently, for the simplest variant of the considered layer, that is, linear association, we can postulate the following form of the canonical partition function:

$$Z_a = \prod_i \left(\frac{t_i^{-2N_i}}{N_i!} j_i^{N_i}\right) A_f^{\sum_i N_i} \exp\frac{E^0 \sum_i iN_i + E^{as} \sum_i (i-1)N_i}{kT} \qquad (10)$$

where E^0 i E^{as} are the adsorption and association potentials, respectively (conventionally marked as positive), while A_f denotes the effective surface area associated with the available surface area of the adsorbent, A^*, by the relationship;

$$\ln A_f = \int \frac{1}{A^*} dA + C \qquad (11)$$

where the integration constant, C, should be chosen in such a way that the total surface area of the adsorbent, A, represents the low-density limit of A_f.

Quation (10), transformed according to formula (4), leads to the expression for μ_i in the form:

$$\mu_i = kT \ln\left\{\frac{t_i^2}{j_i} \exp\left[-\frac{iE^0 + (i-1)E^{as}}{kT}\right] \frac{N_i}{A_f} \exp\left[-i\left(\sum_i N_i\right)\left(\frac{\partial \ln A_f}{\partial N}\right)_{T,A}\right]\right\} \qquad (12)$$

and, in particular, for i=1

$$\mu_1 = kT \ln\left\{\frac{t_1^2}{j_1} \exp\left[-\frac{E^0}{kT}\right] \frac{N_1}{A_f} \exp\left[-\left(\sum_i N_i\right)\left(\frac{\partial \ln A_f}{\partial N}\right)_{T,A}\right]\right\} \qquad (13)$$

Substituting equation (13) into formula (9) gives the general adsorption equation in the form:

$$p = kTt^{-1} \frac{j_g}{j_a} \exp\left(-\frac{E^0}{kT}\right) \frac{N_1}{A_f} \exp\left[-\left(\sum_i N_i\right)\left(\frac{\partial \ln A_f}{\partial N}\right)_{T,A}\right] \qquad (14)$$

where $j_a = j_1$.

In turn, equations (12) and (13) give, by virtue of condition (6), an important relationship:

$$N_i = \left[\frac{t_1^{2i} j_i}{t_i^2 j_1^i} \exp\left(\frac{E^{as}}{kT}\right)\right]^{i-1} N_1^i \qquad (15)$$

Let us now consider two possible solutions based on the use of equations (14) and (15).

In the first case, we assume that adsorbate-adsorbate association is at most dimerization. This means that:

$$N = N_1 + 2N_2 \qquad (16)$$

and

$$\sum_i N_i = N_1 + N_2 \qquad (17)$$

Equation (16) associated with (13) gives:

$$N_1 = \frac{2N}{\sqrt{8K_2' \frac{N}{A_f}} + 1 + 1}, \qquad (18)$$

whereas

$$\sum_i N_i = 1 - \frac{4K_2' \frac{N}{A_f}}{\left(\sqrt{8K_2' \frac{N}{A_f}} + 1 + 1\right)^2} \qquad (19)$$

where:

$$K_2' = \frac{t_1^4 j_2}{t_2^2 j_1^2} \exp\left(\frac{K^{as}}{kT}\right) \qquad (20)$$

To simplify the notation of the adsorption equation, let us define the degree of association of the adsorption layer, γ, as a dimensionless quantity satisfying the double inequality, $0 \le \gamma \le 1$. With reference to the subject of our considerations, this condition is satisfied by the expression:

$$\gamma = \frac{N - N^{as}}{N}, \qquad (21)$$

in which the sum $\sum_i N_i$ is replaced by the more convenient symbol N^{as}.

In view of the above definition of the degree of association, γ, it is easy to demonstrate that for the discussed case of adsorbate dimerization:

$$\gamma = \frac{4K_2' \frac{N}{A_f}}{\left(\sqrt{8K_2' \frac{N}{A_f}} + 1 + 1\right)^2} \qquad (22)$$

consequently, the adsorption equation (14) takes the form:

$$p = kTt^{-1} \frac{j_g}{j_a} \exp\left(-\frac{E^0}{kT}\right) \frac{N}{A_f} (1 - 2\gamma) \exp\left[-N(1 - \gamma)\left(\frac{\partial \ln A_f}{\partial N}\right)_{T,A}\right] \qquad (23)$$

Let us now proceed to the second variant of the solution, in which we allow the possibility of forming associates of unlimited multiplicity.

In this case:

$$N = N_1 + 2N_2 + 3N_3 + \ldots \qquad (24)$$

and

$$N^{as} = N_1 + N_2 + N_3 + \ldots, \qquad (25)$$

where the right-hand sides of both of the above equations are series that are, by assumption, infinite and convergent. If we further assume that the pre-exponential factor in equation (15) does not depend on the multiplicity of the associate, then the association constant K_i' can be written as $(K_2')^{i-1}$ and based on equations (24) and (25), we obtain:

$$N^{as} = N\left[1 - \frac{4K_2'\frac{N}{A_f}}{\left(\sqrt{4K_2'\frac{N}{A_f}+1}+1\right)^2}\right], (27)$$

and according to the definition (21)

$$\gamma = \frac{4K_2'\frac{N}{A_f}}{\left(\sqrt{4K_2'\frac{N}{A_f}+1}+1\right)^2}. \quad (28)$$

The adsorption equation resulting from the above determinations is thus given as follows:

$$p = kTt^{-1}\frac{j_g}{j_a}\exp\left(-\frac{E^0}{kT}\right)\frac{N}{A_f}(1-\gamma)^2\exp\left[-N(1-\gamma)\left(\frac{\partial \ln A_f}{\partial N}\right)_{T,A}\right] \quad (29)$$

By comparing the properties of equations (23) and (29), we find that in both cases, the degree of association tends to zero when K_2' and/or $N/A_f \to 0$, however, for K_2' and/or $N/A_f \to \infty$, equations (23) and (29) yield, respectively, $\gamma = 1/2$ i $\gamma = 1$. Given the assumed physical model of the adsorption layer in both cases, this result can certainly be regarded as an indication of the formal consistency of solutions (23) and (29).

TWO-DIMENSIONAL CONDENSATION OF THE ADSORPTION LAYER

The derived expressions (23) and (29) include, among other things, the effective surface area of the adsorbent, A_f, whose specific form depends on the adopted model of the adsorption layer. ach of these expressions, therefore, represents a family of adsorption equations that differ in the form of this variable. For the purposes of this work, we will use, for example, the two-dimensional analog of the van der Waals equation, where $A^* = A - Nb_0$, and the second virial coefficient of a hard disk fluid, b0b_0b0, represents the area effectively blocked by the adsorbed molecule. After integration, according to equation (11), we obtain: $A_f = A\text{-}Nb_0$, which is thus identical to A^* (it should be noted, however, that such an identity is not generally the rule, but an exception).

To eliminate the extensive quantities A and N from the discussed equations, we introduce the dimensionless surface coverage, θ, with values in the range (0.1). The simple definition of this variable: $\theta = (Nb_0/A)$, also gives us:

$$K_2'\frac{N}{A_f} = K^{as}\frac{\theta}{1-\theta} \quad (30)$$

and

$$K_H = \left(kT\frac{t^{-1}j_g}{b_0\, j_a}\right)^{-1}\exp\left(-\frac{E^0}{kT}\right) \quad (31)$$

The isothermal constants K^{as} and K_H will be referred to as the association constant and Henry's constant, respectively.

hanks to the above substitutions, we can write the adsorption equations and the corresponding formulas for the degree of association as follows:

for dimerizationsi

$$p = \frac{\theta}{K_H(1-\theta)}(1-2\gamma)\exp\left[(1-\gamma)\frac{\theta}{1-\theta}\right] (32)$$

and

$$\gamma = \frac{4K^{as}\frac{\theta}{1-\theta}}{\left(\sqrt{8K^{as}\frac{\theta}{1-\theta}}+1+1\right)^2} \quad (33)$$

for unlimited multiplicity of associates.

$$p = \frac{\theta}{K_H(1-\theta)}(1-\gamma)^2\exp\left[(1-\gamma)\frac{\theta}{1-\theta}\right] (34)$$

and

$$\gamma = \frac{4K^{as}\frac{\theta}{1-\theta}}{\left(\sqrt{4K^{as}\frac{\theta}{1-\theta}}+1+1\right)^2} \quad (35)$$

Let's now analyze the relationships (32) and (34), along with their accompanying expressions (33) and (35), for the possibility of a critical point occurring on the adsorption isotherm, where both the first and second derivatives of the adsorptive pressure with respect to the degree of surface coverage of the adsorbent equal zero. The isotherm containing such a point (the critical isotherm) divides, as is known, the equilibrium description space of adsorption into a subcritical region, allowing liquid-gas equilibrium (both phases are two-dimensional in our case), and a supercritical region, excluding two-dimensional condensation of the adsorbate. To obtain the critical values of the association constant, K_c^{as} and the degree of coverage, θ_c, the system of equations must be solved: $\left(\frac{\partial p}{\partial \theta}\right)_T = 0$ and $\left(\frac{\partial^2 p}{\partial \theta^2}\right)_T = 0$. Since $\left(\frac{\partial p}{\partial \theta}\right)_T = p\left(\frac{\partial \ln p}{\partial \theta}\right)_T$, the equivalent, and due to the form of our equations more convenient, system has the form:

$$\begin{cases}\left(\frac{\partial \ln p}{\partial \theta}\right)_T = 0\\ \left(\frac{\partial^2 \ln p}{\partial \theta^2}\right)_T = 0\end{cases} \quad (36)$$

Unfortunately, the result of the conducted analysis is negative for both equation (23) and (29). In both cases, there is no finite value of K^{as} that is a solution to the system (36). This result should not be surprising, as the proposed model so far assumes the formation of only linear adsorbate-adsorbate associates. It is, therefore, somewhat analogous to the Ising model [5], which unequivocally excludes the possibility of condensation in a one-dimensional system but allows this effect in multiple dimensions. From this perspective, the failure of our analysis concerning equations (23) and (29) can, paradoxically, be seen as a positive indication, suggesting the correct direction for generalizing our description to include the formation of branched associates. Naturally, further analysis should exclude the case of dimerization, as here the distinction between linearity and non-linearity becomes meaningless.

Let's begin the concept of "multidimensional" adsorbate-adsorbate association with the rather uncontroversial statement that an adsorbate molecule may, due to its spatial structure or the presence of specific functional groups, have centers that facilitate specific interactions with other molecules. In a single-component system, where the molecules are identical, the number of such centers, z, can therefore be considered a characteristic parameter of the given adsorbate. From this point of view, solutions (23) and (29) should be regarded as examples where z equals 1 and 2, respectively, which is exactly the same as the exponent in the pre-exponential factors $(1\text{-}2\gamma)$ oraz $(1\text{-}\gamma)^2$. It should be noted that each of these factors, varying in the range

(0,1), expresses the probability that a randomly chosen molecule is an "associate" of multiplicity i=1, i.e., simply a single adsorbate molecule. This probability is equal to 1 for γ=0, and equal to, 1/2 and 1 respectively, for a fully associated adsorption layer. It is important from our point of view that the pre-exponential factor (1-γ) appears to the first power regardless of the value of zzz. Based on these observations, we postulate that the observed regularities apply for any value of the numer z. Na podstawie powyższych konstatacji stawiamy postulat, że zaobserwowane prawidłowości obowiązują dla dowolnej wartości liczby z.

According to this postulate, the adsorption equation for unlimited multiplicity of adsorbate-adsorbate associates can be presented as follows:

$$p = \frac{\theta}{K_H(1-\theta)}(1-\gamma)^z \exp\left[(1-\gamma)\frac{\theta}{1-\theta}\right] \quad (37)$$

Let us now analyze the above formula with respect to the critical point of two-dimensional condensation of the adsorption layer. We will demonstrate that an exact solution to the problem is possible without the need for the tedious and uncertain task of solving the system of equations (36). Instead, we propose an alternative method based on a single differentiation of the logarithm of the pressure with respect to the surface area of the adsorbent. Performing the appropriate transformations leads to the solution equation in the form:

$$(z-2)^2 K^{as}\theta^2 - (z-2)[(z-2)K^{as}+1]\theta + z - 1 = 0 \quad (38)$$

This equation, like any quadratic equation, has two solutions. However, since there is only one critical point, we require its discriminant to be equal to zero, which guarantees a solution in the form of a double root.

Thus, we have:

$$(z-2)^2 K^{as2} - 2zK^{as} + 1 = 0 \quad (39)$$

which for any z gives::

$$K_c^{as} = \frac{z+2\sqrt{z-1}}{(z-2)^2} \quad (40)$$

Substituting the solution (40) into equation (38) determines the critical value of the degree of coverage, θ_c, in the form:

$$\theta_c = \frac{z-1+\sqrt{z-1}}{z+2\sqrt{z-1}} \quad (41)$$

Equations (40) and (41) provide an answer to the question of the possibility of two-dimensional condensation of the adsorption layer in the absence of interactions between adsorbate molecules other than association. This answer is conditional; adsorbate-adsorbate association alone can lead to the discussed phase transition if z>2, which implies a branched nature of the associates. For exclusively linear associates (z=2) we have, according to equation (41), θ_c =1/2, but the corresponding association constant, K_c^{as}, is, as follows from equation (40), infinite.

From both of the last equations also follows the interdependence relationship between K_c^{as} i θ_c, the form of which is:

$$K_c^{as}\theta_c = \frac{z-1+\sqrt{z-1}}{(z-2)^2} \quad (42)$$

It allows, for any z>2, the calculation of the value of one of the critical parameters provided the other is known. Table 1 summarizes the results of the calculations of K_c^{as}, θ_c and their product depending on the number z. Exact solutions (for z=2, 5 i 10) are given in fractional form, while the remaining values are accurate to five significant digits. The choice of the range of values for z>6, may correspond only marginally to the reality of the phenomenon, but it more clearly reflects the properties of the corresponding functions.

Tab. 1

Values of K_c^{as}. θ_c and their product depending on the number z.

z	K_C^{as}	Θ_C	$\Theta_C * K_C^{as}$
2	∞	1/2	∞
3	5.8284	0.58579	3.4142
4	1.8660	0.63397	1.1829
5	1	2/3	2/3
6	0.65451	0.69098	0.45225
7	0.47596	0.71010	0.33798
8	0.36921	0.72571	0.26794
9	0.29912	0.73880	0.22099
10	1/4	3/16	0.04687
11	0.21388	0.75975	0.16250
12	0.18633	0.76834	0.14316

The results presented in Table 1 are illustrated in Figures 1 and 2. These figures show the dependencies of, K_c^{as} and θ_c on z respectively. The solid lines here represent the general nature of the corresponding functions, while the points placed on them emphasize the discrete variability of the number *z*.

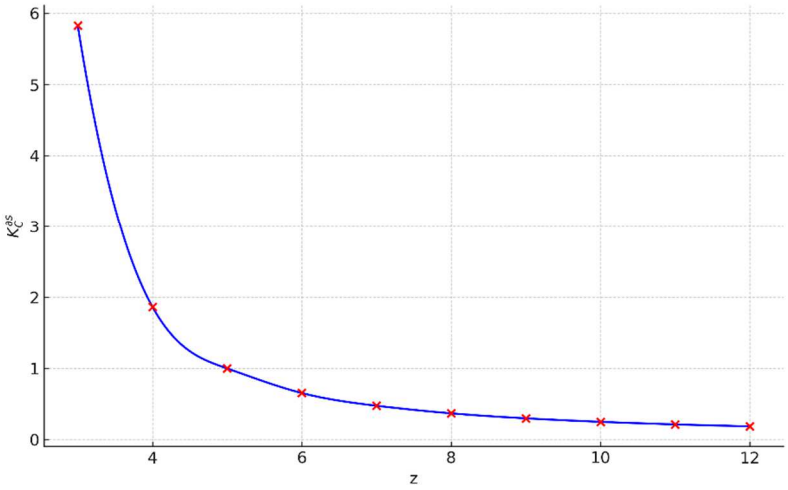

Fig. 1 Graph of the K_C^{as} as a function of the numer z.

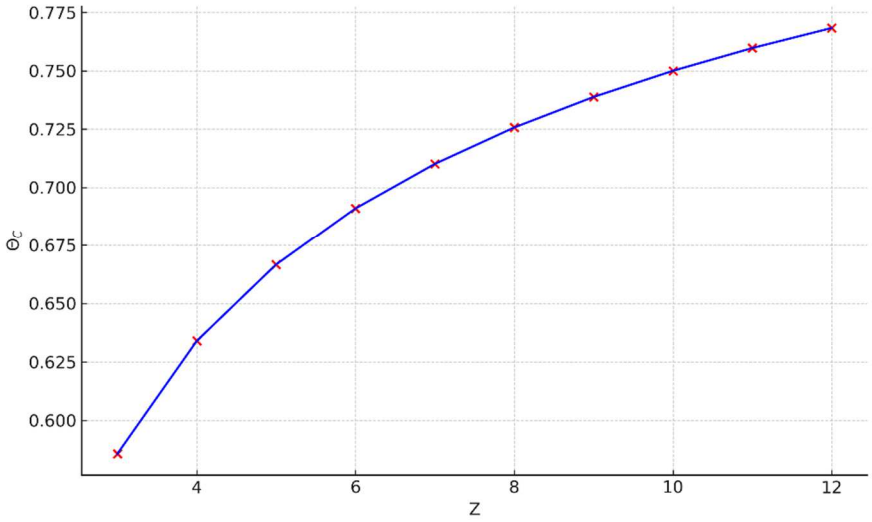

Fig. 2 Graph of the θ_c as a function of the numer z.

CONCLUSIONS

1) The formalism of the canonical ensemble used in this study proved effective in formulating the description of adsorption equilibrium under the assumption that linear association of molecules is the only type of attractive interaction in the mobile monolayer on a homogeneous surface of a solid adsorbent.
2) The analysis of the adsorption equation obtained in the first step, with respect to the possibility of two-dimensional condensation of the adsorbate, gives a negative result, confirming the analogy of linear association to the one-dimensional Ising model.
3) Generalizing the model to assume a branched form of adsorbate-adsorbate associates, along with a postulate regarding the probability of unassociated molecules, leads to a new adsorption equation that considers the number of association centers possessed by an adsorbate molecule. From this perspective, the previous adsorption equation turns out to be a special case for z=2.
4) A repeated analysis with respect to the critical point of adsorbate condensation gives a conditionally positive result, proving that such condensation is possible even in the absence of interactions other than association, provided that the number z is greater than 2. Simultaneously, the critical value of the association constant and the degree of surface coverage are unambiguous functions of z. Theoretically, in the range $2 \leq z < \infty$, the former decreases from infinity to zero, while the latter increases from 1/2 to 1.

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