Thermodynamic parameters of adsorption described by the logarithmic Temkin isotherm

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Thermodynamic analysis of the adsorption Temkin isotherm was performed. The equations that describe the dependence of the thermodynamic functions on the amount adsorbed were obtained. A relationship between the excess differential and mean molar thermodynamic functions was found. The thermodynamic approach does not contradict the molecular statistical theory and appears to be more general.

Key words: adsorption, adsorption Temkin isotherm, thermodynamic parameters of adsorption.

The logarithmic Temkin isotherm (TI) is often used for description of adsorption on the solid surface.[1] Temkin derived this isotherm using the molecular statistical theory.[2] It has previously been shown for the Freundlich isotherm (FI)[3] that analysis of adsorption isotherms by the methods of thermodynamics supplements the data obtained using the molecular statistical approach. Therefore, it is of interest to perform a similar study for TI.

The original TI equation was written in the form $\theta = f^{-1}\ln(a_0p)$, where θ is the surface coverage, p is the partial pressure of the adsorbate, and a_0 and f are constants.[2] To analyze TI in terms of the mathematical treatment used in thermodynamics of excess quantities, this equation can conveniently be presented in the form $\Gamma/\Gamma_m = f^{-1}\ln(a_0p)$, *i.e.*, it should be assumed that $\theta = \Gamma/\Gamma_m$. Here Γ is the excessive adsorption, and Γ_m is the adsorption corresponding to the monolayer coverage.

This form is based on the fact that adsorption quantities found from experiment are excessive adsorption values.[4]

The coefficients of the TI equation are calculated as

$$f = \Delta/(RT),\ a_0 = A_0 \cdot \exp[q_0/(RT)],$$

where $\Delta = (q_0 - q_1)$, q_0 and q_1 are the highest and lowest characteristic heats of adsorption, respectively, and A_0 is a constant. In his works, Temkin postulated that Δ is independent of temperature (T).

The equation of state for the adsorption phase is related to the adsorption isotherm as follows[4]:

$$\varphi = RT\int_0^p \Gamma p^{-1}\mathrm{d}p, \tag{1}$$

where φ is the surface pressure. The direct insertion of the TI formula into Eq. (1) does not lead to the equation of state because the integral $\int_0^p p^{-1}\ln(a_0p)\mathrm{d}p$ does not converge at the lower limit (at $p \to 0$ $\lim[p^{-1}\ln(a_0p)] = \infty$). The TI equation cannot be used in the region of zero coverages because at $p \to 0$

$$\Gamma = \Gamma_m f^{-1}\ln(a_0p) \to -\infty,$$

which has no physical sense.

At the same time, at low coverages of the surface, *i.e.*, in the Henry region, adsorption is described by the linear Henry isotherm (HI)

$$\Gamma = \Gamma_m Kp,$$

where K is the coefficient of adsorption equilibrium. Taking into account this fact, the adsorption isotherm, which is also valid for the region of low coverages, can be presented in the following combined form:

$$\begin{cases} p \le p_t;\ \Gamma = \Gamma_m Kp \\ p > p_t;\ \Gamma = \Gamma_m f^{-1}\ln(a_0p), \end{cases} \tag{2}$$

where p_t is the threshold pressure of the adsorbate. Adsorption is described by the HI or TI equation below and above this value, respectively.

Transition from the HI to TI equation occurs not at a single p_t value, but in some pressure interval. Since any point inside this interval can be accepted as p_t, the uncertainty in the choice of p_t arises.

Using the boundary equation

$$\Gamma_m Kp_t = \Gamma_m f^{-1}\ln(a_0p_t), \tag{3}$$

the p_t value cannot be calculated because this equation, in which physically substantiated values of adsorption constants are included, has no solution. It can be demonstrated that HI and TI inscribed into a monotonic,

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convex towards the Γ axis adsorption isotherm do not intersect. In fact, the Henry isotherm is a tangent to the curve that describes the "real" adsorption isotherm at the point $p = 0$. By definition, the tangent to the curve that describes a convex function lies above this curve and contacts the curve only in one point. A certain portion of a "real" isotherm can be described by the TI, but at lower pressures the TI would cross the pressure axis at $p > 0$. Thus, HI and TI cannot intersect.

Using the system of equations (2), the integral in Eq. (1) can be divided into two integrals

$$\int_0^p \Gamma p^{-1}\mathrm{d}p = \int_0^{p_\mathrm{t}} \Gamma_\mathrm{m} K\mathrm{d}p + \int_{p_\mathrm{t}}^p \Gamma_\mathrm{m}(fp)^{-1}\ln(a_0 p)\mathrm{d}p.$$

Since $\Gamma_\mathrm{m}Kp_\mathrm{t} = \Gamma_\mathrm{m}f^{-1}\ln(a_0p_\mathrm{t}) = \Gamma_\mathrm{t}$, the solution of Eq. (1) gives

$$\varphi = RT\cdot[\Gamma_\mathrm{t} + f(\Gamma^2 - \Gamma_\mathrm{t}^2)/(2\Gamma_\mathrm{m})]. \quad (4)$$

Equation (4) is valid only in the region of applicability of TI, *i.e.*, for $\Gamma > \Gamma_\mathrm{t}$. At the point $\Gamma = \Gamma_\mathrm{t}$ the φ value becomes equal to the surface pressure, which is considered in the model of the ideal two-dimensional gas

$$\varphi(\Gamma = \Gamma_\mathrm{t}) = \varphi_\mathrm{id}(\Gamma = \Gamma_\mathrm{t}) = RT\Gamma_\mathrm{t}.$$

At $\Gamma < \Gamma_\mathrm{t}$, *i.e.*, in the region of linearity of the adsorption isotherm, Eq. (4) cannot be used, and the surface pressure should be calculated by the equation of state of the ideal two-dimensional gas $\varphi_\mathrm{id} = RT\Gamma$. All expressions presented hereinafter are valid only in the region described by the TI equation and lose the physical sense beyond its applicability.

Compare Eq. (4) with the equation of state of the ideal two-dimensional gas. This can conveniently be made examining the $\varphi/\varphi_\mathrm{id}$ ratio:

$$\varphi/\varphi_\mathrm{id} = (\Gamma_\mathrm{t}/\Gamma) + [f\Gamma/(2\Gamma_\mathrm{m})] - [f\Gamma_\mathrm{t}^2/(2\Gamma\Gamma_\mathrm{m})].$$

In the region described by the TI equation, $\Gamma_\mathrm{m} > \Gamma \geq \Gamma_\mathrm{t}$ and $\Gamma_\mathrm{t}^2/(\Gamma\Gamma_\mathrm{m}) < \Gamma/\Gamma_\mathrm{m} < 1$. Therefore, at low f and high Γ_m, $\varphi < \varphi_\mathrm{id}$. This relation characterizes the initial region of adsorption on sorbents with a relatively uniform and well-developed surface. At some f and Γ_m, we can imagine the situation where an increase in adsorption changes the sign in the inequality and $\varphi > \varphi_\mathrm{id}$. To provide the surface pressure higher than φ_id in the whole range of possible Γ values, the conditions $\Gamma_\mathrm{t}/\Gamma_\mathrm{m} > 2/f$ should be fulfilled. As a rule, the value of f ranges from 4 to 100. Then the $\Gamma_\mathrm{t}/\Gamma_\mathrm{m}$ ratio, which identifies the threshold coverage, should be >0.5—0.02, correspondingly. These values are real for the lower boundary of applicability of TI.

The equation of state and, hence, the properties of the adsorption layer differ substantially from the equation of state obtained previously[3] for FI ($\varphi = RTn\Gamma$, where n is constant and $n > 1$). At the same time, these isotherms are similar in shape and, in some cases, the TI and FI equations can describe the same array of experimental data with the same accuracy.[5] Therefore, to reveal the properties of the adsorption layer, the complete information about the thermodynamics of the adsorption process is needed in addition to the adsorption isotherm.[6]

To examine the thermodynamic parameters of adsorption as a function of Γ, use can be made of the following known equations[4]:

$$\bar{U}^\mathrm{s} = \tilde{U}^\mathrm{s} + \varphi\Gamma^{-1} - T\Gamma^{-1}\cdot(\partial\varphi/\partial T)_\Gamma, \quad (5)$$

$$\bar{S}^\mathrm{s} = \tilde{S}^\mathrm{s} - \Gamma^{-1}\cdot(\partial\varphi/\partial T)_\Gamma, \quad (6)$$

$$\bar{U}^\mathrm{s} = \tilde{U}^\mathrm{s} + \Gamma\cdot(\partial\tilde{U}^\mathrm{s}/\partial\Gamma)_T, \quad (7)$$

$$\bar{S}^\mathrm{s} = \tilde{S}^\mathrm{s} + \Gamma\cdot(\partial\tilde{S}^\mathrm{s}/\partial\Gamma)_T, \quad (8)$$

where U is the internal energy; S is the entropy, the superscript "s" indicates the excess quantity, and the signs "line" and "tilde" designate differential ($\bar{U}$, $\bar{S}$) and mean molar ($\tilde{U}$, $\tilde{S}$) quantities.

In the general case, $\Gamma_\mathrm{t} = f(T)$. However, we accept for simplicity that Γ_t is independent of T.

Since $(\partial\varphi/\partial T)_\Gamma = R\Gamma_\mathrm{t}$, then we have from Eq. (5)

$$\bar{U}^\mathrm{s} = \tilde{U}^\mathrm{s} + [\Delta/(2\Gamma_\mathrm{m})]\cdot(\Gamma - \Gamma_\mathrm{t}^2/\Gamma). \quad (9)$$

Inserting the $\bar{U}^\mathrm{s}$ value into Eq. (7), dividing variables, and integrating, we obtain

$$\tilde{U}^\mathrm{s} = [\Delta/(2\Gamma_\mathrm{m})]\cdot(\Gamma + \Gamma_\mathrm{t}^2/\Gamma) + \alpha(T), \quad (10)$$

here the integration constant $\alpha(T)$ is a function of temperature. The question about the functional relationship between $\alpha(T)$ and Γ_t remains yet unclear.

Combining Eqs. (9) and (10), we find

$$\bar{U}^\mathrm{s} = \alpha(T) + \Delta\Gamma/\Gamma_\mathrm{m}. \quad (11)$$

From the condition $\bar{U}^\mathrm{s} \to \bar{U}^{\mathrm{s}0}$ at $\Gamma \to 1$, we obtain

$$\alpha(T) = \bar{U}^{\mathrm{s}0} - \Delta\Gamma_0/\Gamma_\mathrm{m}, \quad (12)$$

where $\Gamma_0 = 1$ in the chosen units of measurement.

Except for Γ_0, all values in Eq. (12) depend on the nature of the adsorption phase, *i.e.*, on the properties of the adsorbent and adsorbate interacting with the field of adsorption forces. The $\alpha(T)$ value has a dimensionality of energy and, therefore, it can be considered as an indicator of the energy level of the adsorbate in the adsorption layer.

For the isosteric heat of adsorption $q_\mathrm{st} = \tilde{H}_\mathrm{g} - \bar{U}^\mathrm{s}$, we can write

$$q_\mathrm{st} = (\tilde{H}_\mathrm{g} - \alpha(T)) - \Delta\Gamma/\Gamma_\mathrm{m}, \quad (13)$$

where $\tilde{H}_\mathrm{g}$ is the enthalpy of the adsorbate in the gas phase.

The isosteric heat of adsorption is determined experimentally and independent of the method of determination of Γ_t. Therefore, $\alpha(T)$ and $\bar{U}^\mathrm{s}$ are independent and the mean molar value $\tilde{U}^\mathrm{s}$ depends on Γ_t.

Substituting the equation $q_{st} = RT^2 \cdot (\partial \ln p/\partial T)_\theta$ into the TI equation, Temkin arrived at the following equation:

$$q_{st} = q_0 - \Delta\theta,$$

which corresponds completely to Eq. (13) under the assumption that $q_0 = \tilde{H}_g - \alpha(T)$ and $\theta = \Gamma/\Gamma_m$.

The expressions for the mean molar and differential entropies of adsorption can similarly be obtained from Eqs. (4), (6), and (8)

$$\tilde{S}^s(\Gamma) = (\Gamma_t/\Gamma) \cdot [\tilde{S}(\Gamma_t) - \beta(T)] + \beta(T), \tag{14}$$

$$\bar{S}^s = \beta(T), \tag{15}$$

where $\beta(T)$ is the temperature-dependent constant.

The conclusion that $\bar{S}^s$ is independent of coverage corresponds to predictions of the molecular statistical theory, although this conclusion is valid only in the coverage interval described by the TI equation.

The mean molar entropy $\tilde{U}^s$ and the surface pressure depend on Γ_t. In fact, the Γ_t value is related to the lower limit of the region of moderate coverages and, hence, Eqs. (4), (10), and (14) reflect the relations of φ, $\tilde{U}^s$, and $\tilde{S}^s$ to the parameters determining the position of this boundary (f and a_0).

When we take into account the temperature function of Γ_t, the form of Eqs. (11), (13), and (15) remains unchanged, but the $\alpha(T)$ and $\beta(T)$ constants therein are replaced by $\alpha_1(T)$ and $\beta_1(T)$, The relationship between these groups of constant values is determined by the following equations:

$$[\alpha_1(T) - \alpha(T)] \cdot \Gamma_0 = -RT^2\Gamma_t' + \Delta T \Gamma_t \Gamma_t'/\Gamma_m,$$

$$[\beta_1(T) - \beta(T)] \cdot \Gamma_0 = -RT\Gamma_t' + \Delta \Gamma_t \Gamma_t'/\Gamma_m,$$

where $\Gamma_t' = \mathrm{d}\Gamma_t/\mathrm{d}T$. Since $\Gamma_t \ll \Gamma_m$ and Δ is the value of an order of RT, the second term in the right parts of the obtained equations can be neglected, and it is seen that the difference between the exact and approximate solutions increases with higher T and larger Γ_t' values.

The changes to be introduced into Eqs. (10) and (14) due to the temperature dependence of Γ_t are not of principal character.

It is of interest to compare restrictions imposed on the interval of applicability of the TI equation by the thermodynamic and statistical approaches. In the statistical approach, applicability of TI is limited by pressures, which satisfy the inequalities $a_1 p \ll 1$ and $a_0 p \gg 1$ [2] (the a_1 coefficient is determined similarly to a_0, but q_1 is used instead of the q_0 parameter). The region of coverages corresponding to these pressures is defined as the region of medium coverages. In the thermodynamic treatment of TI outlined above a poorly specified lower limit gives way to the condition $p > p_t$. The explicit restriction of TI applicability in the region of high coverages is related to the definition of Γ as excess adsorption. Evidently, when the pressure increases, the excess adsorption should increase, pass through a maximum, and then decrease to zero, as it occurs for adsorption from solutions. The TI equation does not describe the descending branch of the plot Γ *vs.* pressure and, hence, can be used only on the ascending branch. At the same time, high pressures at which this effect becomes discernible are virtually inaccessible[4] under conventional experimental conditions. Therefore, this restriction is of the theoretical character. Another, implicit restriction is of greater significance. It is due to the fact that the differential entropy is not independent of Γ for a compact monolayer. Therefore, the TI region can be interpreted from the thermodynamic point of view only until the adsorption quantity reaches the values above which effects appear that are characteristic of the saturated surface.

In conclusion it seems appropriate to consider another disadvantage of the molecular statistical treatment of TI. When the surface heterogeneity decreases and $f \to 0$, the equation of adsorption isotherm on the nonuniform surface would become the equation describing adsorption on the uniform surface, *i.e.*, Langmuir equation. In fact, the TI equation loses the physical sense in this case because $\Gamma \to \infty$ at any p.

This contradiction cannot be found in the thermodynamic approach because this approach is independent of the assumptions involved in a particular model, such as the nature of the surface heterogeneity.

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