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Thermodynamic quantities of adsorption described by Freundlich isotherm

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Thermodynamic analysis of the Freundlich adsorption isotherm was performed. Equations describing the thermodynamic characteristics of adsorption as a function of the adsorbed quantity are presented, and relationships between the excess differential and average molar thermodynamic adsorption quantities were obtained. It was shown that the thermodynamic approach does not contradict the molecular statistical theory and provides more general equations. A model of adsorption described by the Freundlich isotherm is discussed.

Key words: adsorption, Freundlich adsorption isotherm, thermodynamic quantities.

The Freundlich isotherm (FI) equation describing adsorption on a solid surface has a simple analytical form and is applicable to any convex adsorption isotherm.[1] In studies of adsorption at a solid—gas interface, the FI equation is mainly used only as a convenient approximation formula. At the same time, any isotherm exactly describing experimental data should reflect the thermodynamic properties of the adsorption system. Therefore, it is of interest to consider the FI from the viewpoint of the thermodynamic theory of adsorption.[2]

Thermodynamic analysis can substantially be simplified on going from the adsorption isotherm to the equation of state of the adsorption phase. For this purpose, let us write the FI equation in the form $\Gamma = Cp^{1/n(T)}$, where Γ is the excess adsorbed quantity, p is the partial pressure of the adsorbate, C and $n(T)$ are constants independent of Γ but dependent on temperature (T), and $n(T) > 1$. It is known[2] that

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

where φ is the surface pressure. Inserting the Γ value from the FI equation into this expression and integrating it, we obtain the equation of state

$$\varphi = RT\Gamma n(T). \qquad (1)$$

This expression differs from the equation of state of the ideal two-dimensional gas only by the $n(T)$ factor. It follows from it that the surface pressure in the adsorption layer is always higher than that in the case of the ideal two-dimensional gas ($n(T) > 1$). Since $n(T)$ is independent of Γ, we can conclude that an increase in the surface pressure is related only to enhancement of the adsorbate—adsorbent interaction as compared to the ideal adsorption layer.

To study the dependence of the thermodynamic quantities of Γ, let us use the following equations[2]:

$$\overline{U}^s = \tilde{U}^s + \varphi\Gamma^{-1} - T\Gamma^{-1}\cdot(\partial\varphi/\partial T)_\Gamma, \qquad (2)$$

$$\overline{S}^s = \tilde{S}^s - \Gamma^{-1}\cdot(\partial\varphi/\partial T)_\Gamma, \qquad (3)$$

$$\overline{U}^s(\overline{S}^s) = \tilde{U}^s(\tilde{S}^s) + \Gamma\cdot(\partial\tilde{U}^s(\partial\tilde{S}^s)/\partial\Gamma)_T. \qquad (4)$$

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where U is the internal energy, S is the entropy, the index "s" implies an excess quantity, and the diacritics "dash" and "tilde" refer to the differential ($\bar{U}$, $\bar{S}$) and average molar ($\tilde{U}$, $\tilde{S}$) quantities, respectively.

Since $(\partial\varphi/\partial T)_\Gamma = R\Gamma n(T) + RT\Gamma n'(T)$, where $n'(T) = \mathrm{d}n(T)/\mathrm{d}T$, from Eq. (2) we obtain

$$\bar{U}^s = \tilde{U}^s - RT^2n'(T). \qquad (5)$$

Inserting $\bar{U}^s$ into Eq. (4), dividing variables, and integrating, we obtain

$$\tilde{U}^s = -RT^2n'(T)\ln\Gamma + \alpha(T), \qquad (6)$$

where the integration constant $\alpha(T)$ is a function of temperature.

From the condition $\tilde{U}^s \to \tilde{U}^{s^0}$ at $\Gamma \to 1$, we find that $\alpha(T) = \tilde{U}^{s^0}(T)$. Then, inserting the expression for $\tilde{U}^s$ from Eq. (6) into Eq. (5), we have

$$\bar{U}^s = \tilde{U}^{s^0}(T) - RT^2n'(T)\cdot(\ln\Gamma + 1). \qquad (7)$$

If it is accepted that $\bar{U}^{s^0}(T) = \tilde{U}^{s^0}(T) - RT^2n'(T)$, then

$$\bar{U}^s = \bar{U}^{s^0}(T) - RT^2n'(T)\ln\Gamma. \qquad (8)$$

The correlations obtained differ from similar equations for the ideal adsorption layer corresponding to Henry's isotherm, where $\bar{U}^s = \tilde{U}^s$ and $\tilde{U}^s \neq f(\Gamma)$. It is usually accepted that $n(T) = K/(RT)$, where K is a constant. When the temperature increases, $n(T) \to 1$, and $n'(T) \to 0$, hence, $\bar{U}^s \to \tilde{U}^s$, *i.e.*, the FI degenerates into Henry's isotherm.

An important quantity of the adsorption interaction is the isosteric adsorption heat $q_{st} = \tilde{H}_g - \bar{U}^s$, where $\tilde{H}_g$ is the enthalpy of the adsorbate in the gas phase. Inserting $\bar{U}^s$ from Eq. (8), we obtain

$$q_{st} = \tilde{H}_g - \bar{U}^{s^0}(T) + RT^2n'(T)\ln\Gamma, \qquad (9)$$

i.e., q_{st} decreases linearly with an increase in $\ln\Gamma$ (because $n'(T) < 0$). This dependence corresponds to the exponentially heterogeneous surface.[3] Thus, the thermodynamic treatment of the FI does not contradict the molecular statistical description given by Zel'dovich.[4]

By analogy, from Eqs. (3) and (4) we can obtain the expressions for the excess differential and average molar entropies:

$$\tilde{S}^s = \tilde{S}^{s^0}(T) - R[n(T) + Tn'(T)]\ln\Gamma, \qquad (10)$$

$$\bar{S}^s = \bar{S}^{s^0}(T) - R[n(T) + Tn'(T)]\ln\Gamma, \qquad (11)$$

$$\bar{S}^s = \tilde{S}^s(T) - R[n(T) + Tn'(T)].$$

Equations (10) and (11) differ from those corresponding to Henry's isotherm by the factor in brackets. The closer the FI to Henry's isotherm (when $n(T) \to 1$, $n'(T) \to 0$), the closer the factor to 1.

Analysis of the equations obtained by Zel'dovich has shown[3] that if the FI is valid, the entropy of the adsorption phase is independent of filling. Inserting $n(T) = K/(RT)$ and its derivative into Eqs. (10) and (11), we obtain expressions $\bar{S}^s = \bar{S}^{s^0}(T)$ and $\tilde{S}^s = \tilde{S}^{s^0}(T)$, which correspond to the conclusions of the molecular statistical theory. At the same time, the thermodynamic approach is more general because it does not require *a priori* knowledge of the form of the $n(T)$ function. Since we have no experimental data, to consider the formula $n(T) = K/(RT)$ versatile, in the general case, the entropy should depend on filling. Taking into account that in Eqs. (10) and (11), the term $[n(T) + Tn'(T)] < 1$ ($n(T)$ is the descending function and $n(T)_{T\to\infty} = 1$), the dependence of the entropy on filling when the FI is used should not be as pronounced as that in the case when Henry's isotherm is fulfilled.

One of the statements of the model of gas adsorption on a solid surface described by the FI follows from the above considerations and from the equation of state (1). According to this statement, the adsorbed substance is in a state similar to that of the ideal adsorption phase, but adsorbed particles are less mobile than those in the ideal two-dimensional gas.

For a sufficient measurement accuracy, a weak dependence of the entropy on filling can be used as a criterion of feasibility of the FI equation for the problem of choosing the approximating equation from the great number of them proposed in the adsorption theory. In fact, in a narrow interval of filling, experimental data can be described with a high accuracy by the majority of known isotherms with two and more fitting parameters; different isotherms can follow from opposite adsorption models. However, for all isotherms that either directly follow from lattice adsorption models or suppose the interaction of particles in the adsorption layer, the entropy depends on filling more strongly than it follows from the FI.

In conclusion let us enlarge on the limitations associated with the feasibility of the FI equation. According to the opinion in Ref. 3, the FI is valid only in the region of average fillings because of the approximate character of the molecular statistical consideration. The thermodynamic approach is not based on simplifying assumptions; however, from this viewpoint, extrapolation of the FI equation to the region of extremely low filling is intolerable, because by Eqs. (8)—(11) at $\Gamma \to 0$, q_{st}, U, and $S \to \infty$, which has no physical sense. Thus, restriction of the applicability of the FI to the region of extremely low filling is rigorous and follows from the form of the isotherm. Restriction of the FI applicability in the region of high filling has no explicit grounds. At the same time, a weaker (than for Henry's isotherm) dependence of the entropy on Γ cannot be observed when a compact monolayer is formed. Therefore, the region of "thermodynamic interpretation" of the FI is restricted by the low adsorbed quantities in which the effects characteristic of the saturated surface are not manifested.

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Reaction of sulfenamides with *N*,*N*-dimethylaniline in the presence of phosphorus(v) oxochloride

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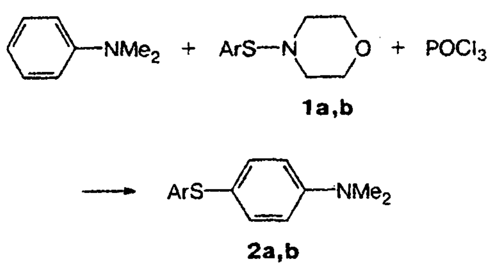
Reaction of arylsulfenamides with *N*,*N*-dimethylaniline in the presence of $POCl_3$ at room temperature affords unsymmetrical diaryl sulfide, only *para*-substituted *N*,*N*-dimethylanilines being formed.

Key words: sulfenamides, phosphorus(v) oxochloride, diaryl sulfides.

Sulfenylation of aromatic compounds with sulfenyl chlorides in the presence of Friedel—Crafts catalysts such as $AlCl_3$, $TiCl_4$, BF_3, and $FeCl_3$ was first described at the beginning of the 20th century and studied more extensively in the 1960s.[1–5] Later, sulfenamides activated with SO_3[6] and sulfenyl acetates activated with $AlBr_3$[6] were proposed as sulfenylating reagents. However, such reactions usually afford low yields, involving only reactive aromatic substrates. Recently, we found that arylsulfenamides in electrophilic sulfenylation of alkenes can be activated with phosphorus oxohalides.[7] It was promising to try this sulfenylating system in reactions with arenes.

We studied reactions of *p*-nitrophenylthiomorpholine (**1a**) and *o*-nitrophenylthiomorpholine (**1b**), both activated with $POCl_3$, with a number of aromatic substrates, *viz.*, *N*,*N*-dimethylaniline, phenetole, anthracene, *p*-xylene, and toluene. The reaction with *N*,*N*-dimethylaniline (Scheme 1) yielded diphenyl sulfides monosubstituted at the *para*-position with respect to the dimethylamino group.

Scheme 1



Ar = 4-$NO_2C_6H_4$ (**a**), 2-$NO_2C_6H_4$ (**b**)

In the other cases, no substitution occurred; we recovered the starting aromatic compounds, yet disulfide, a product of sulfenamide decomposition, was formed. In all probability, the benzene ring activated with one or even two methyl groups still remains unreactive. The sulfenylation of phenetole seems to be hindered by the reaction of $POCl_3$ with the phenetole O atom rather than with the sulfenamide N atom.

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