Mathematical modeling of adsorption isotherms of water vapour on polymeric ionites used in agrochemical practice

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Abstract. Polymeric ion-exchange materials (ionites) are used in agriculture to make substrates for complete and long-term plant nutrition. The main nutrients in bound form are contained on the ion-exchange groups of the ionite. The degree of dissociation of these groups, and thus the release of ions into the soil, depends on the moisture content. In case of heavy rainfall and during drought, the exchange properties of the ionite will be different. Therefore, the study of water adsorption in such ionites is a rather urgent problem. In this work, the water vapour adsorption by ionites is studied using a thermodynamic model that incorporates the interplay between changes in the energy of dissociation of ion-exchange groups and the osmotic effect. Within the framework of this approach adsorption isotherms are built in the range of air humidity from 0,1 to 1 at physically reasonable values of system parameters. Isotherms have a characteristic inflection point in the area of medium humidity, which allows them to be attributed to isotherms of the fifth type. The obtained model isotherms describe adsorption in mesoporous and microporous materials, which are ionites, and fully correspond to experimental adsorption isotherms of this type.

1 Introduction

At present, there is no single general equation adequately describing the physical adsorption isotherm of a substance from a gas phase to a solid surface with certain properties in the entire range of relative pressures of the sorbed gas; i.e., from 0 to 1. To describe the isotherms of multilayer adsorption of gases by nonporous, mesoporous and microporous solids, different equations are used, and for different ranges of relative pressures the equations can also differ [1].

Since water vapour adsorption isotherms are usually cited for ion-exchange materials in the literature, this work considers this particular process. A reasonable description of water vapour adsorption by ionites is possible only with models that allow for the interrelationship between the amount of absorbed water and the dissociation of ion-

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exchange groups, which is a specific feature of ionites [2-12]. On the one hand, raising the content of water increases hydration and thus ion-exchange groups dissociation. On the other, the content of water depends on the degree of dissociation (an osmotic effect). This mutual dependence determines the type of adsorption isotherms (the dependence of the amount of absorbed water on the relative air humidity). As noted in works [12-14] at some parameters of the system jumping areas appear on adsorption isotherms (a sharp increase in the moisture content of ionite). These critical phenomena in the experimental adsorption-desorption isotherms appear in the form of hysteresis loops, and in these works they are explained on the basis of a model that take into account the mutual influence of changing the dissociation energy of ion-exchange groups and the osmotic effect.

In the present work within the framework of thermodynamic approach described in detail in [14] adsorption isotherms are built in the range of air humidity from 0,1 to 1 at physically reasonable values of system parameters. The adequacy of these parameters is confirmed by comparing theoretical dependences of the resistance of polymer cation-exchange membranes on relative air humidity with corresponding experimental dependences. This approach makes it possible to model adsorption isotherms for different samples at different temperatures.

2 Theoretical Analysis

Mathematical model of the water vapour sorption in ion-exchange materials was built by minimizing the total thermodynamic potential of the system. This potential consists of the thermodynamic potential of the ionite in the standard state, which was defined as the state in which the ionite contains only the water entering into the hydration shells; the change in the thermodynamic potential caused by the subsequent condensation of water; the ionic subsystem potential, more specifically, this associated with the dissociation of ion-exchange groups, the formation of their hydration shells, and the formation of a solution composed of a hydrated ions and free water, as well as the entropy contribution associated with the different configurations in the positioning of dissociated and nondissociated ion-exchange groups in the polymer matrix; and finally the potential associated with elastic deformation of the polymer chains during moisture sorption. In comparison with previous models, this model calculates the ion-exchange groups dissociation energy more precisely. In addition to the effects of the surface charge and the Debye screening, the ion-dipole interaction during the sorption of polarized molecules is taken into account. The contribution of these factors is most significant at low humidity.

Without going into details of calculation described in work [14], we present the system of equations describing water vapour sorption on the surface of ionite:

\[
\begin{align*}
\frac{P}{P_s} &= \frac{\beta - \beta_0 - \alpha n}{1 + \beta - \beta_0 - \alpha (n-1)} \exp\left(\frac{\alpha}{T} \frac{\partial E_D}{\partial \beta} + U\beta\right), \\
\frac{\alpha^2}{1 - \alpha} \frac{(1 + \beta - \beta_0 - \alpha (n-1))^{n-1}}{(\beta - \beta_0 - \alpha n)^n} &= \exp\left(- \frac{1}{T} \frac{\partial (\alpha E_D)}{\partial \alpha}\right).
\end{align*}
\]

The system includes the following parameters: \(P/P_s\) is the relative air humidity, \(P\) is the water vapour pressure and \(P_s\) is the saturation vapour pressure; \(\beta = N_W/N\) is the relative moisture content, \(\beta_0 = N_{W_0}/N\) is the conventional number of hydration of ion-exchange groups, were \(N\) is the number of ion-exchange groups bonded to the polymer matrix, \(N_{W_0}\) is
the number of water molecules entering into the primary hydration shells of the ion-exchange groups, and \( N_W \) is the total number of water molecules in the system; \( \alpha \) is the degree of dissociation of ion-exchange groups; \( n \) is the conventional number of hydration of ions in a single-component solution; \( T \) is the absolute temperature expressed in energy units; \( E_D = E_0 + E_{EL} \) is the dissociation energy, which consists of the energy of abstraction of the ion from the polymer chain (\( E_0 \)) and the change in its electrostatic energy (\( E_{EL} \)); \( U_\beta = 1/2 \partial(\alpha E_D)/\partial\alpha \to E_0, \partial E_D/\partial\beta \to 0 \), and, therefore, formula (1) transforms into the standard expression for the concentration dependence of the vapour pressure over solution [15], while formula (2) takes the form of the law of mass action [16]. Formulas (1) and (2) make it possible not only to determine the values of \( \alpha \) and \( P/P_s \) for the bulk phase, but also to examine how they change in the case of sorbed thin water films.

As shown in work [14], the dependence of the energy \( E_D \) on the degree of dissociation \( \alpha \) and the water content \( \beta \) takes the form:

\[
E_D = E_0 - \frac{CT}{\beta} \left( \frac{\xi \sqrt{\alpha \beta}}{2} + \ln \left( 1 - f \exp(-\xi \sqrt{\alpha \beta}) \right) \right) - \frac{\xi T \sqrt{\alpha \beta} \exp(-\xi \sqrt{\alpha \beta}/2)}{1 - \exp(-\xi \sqrt{\alpha \beta})} - \frac{n\delta}{12T} (C\xi)^{2/3} T, \tag{3}
\]

Where \( C = \frac{2q^2 s}{\epsilon T W} \) and \( \xi = \frac{4\pi q^2 V_w}{\epsilon T s^2} \) are dimensionless quantities that include the following parameters: \( q \) is the ion charge, \( s \) is the surface area per ion-exchange group, \( \epsilon \) is the dielectric permittivity of the solution; \( f = (\epsilon - \epsilon_1)/(\epsilon + \epsilon_1) \), \( \epsilon_1 \) is the dielectric permittivity of the polymer matrix; \( \delta q \) is effective charge of dipole edges (polarized water molecule \( \delta \sim 0.1 \)).

Fig. 1. The \( \beta(P/P_s) \) dependence at non-critical parameters.
The terms in (3), starting from the second, correspond to the contributions to the electrostatic energy from the bulk of the screening cloud and the charges induced in the solid dielectric layers due to the finite thickness of the liquid layer, the charge of the surface, and the ion-dipole interaction respectively.

The expression (3) is valid at all physically reasonable values of system parameters (water content and degree of dissociation), even at lowest humidity, when hydration shells of ions are not formed completely (the dependence \( n(\beta) \) is needed). For this reason, this expression can be used over the full relative humidity range.

### 3 Results and Discussion

The numerical solution of equation system (1), (2) taking into account (3) allows us to construct water vapour adsorption isotherms on the ionite surface – dependence \( \beta(P/P_s) \), Figure 1 and also to find the dependence \( \alpha(P/P_s) \), Figure 2. These dependences were calculated using the following values of the model parameters: \( q = 4.8 \cdot 10^{-10} \) esu, \( \varepsilon = 79 \), \( \varepsilon_1 = 4 \), \( V_w = 3 \cdot 10^{-23} \) cm\(^3\), \( s = 1.2 \cdot 10^{-15} \) cm\(^2\), \( n = 4 \), \( \beta_0 = 2 \), \( U = 0.6 \), and the dissociation constant is \( K_0 = \exp(-E_0/T) = 0.3 \) at \( t = t_0 = 15 \) °C. The elastic deformation energy parameter \( U \) was assumed to be temperature-independent.

The isotherm shown in Figure 1 has an inflection point in the area of medium humidity values and belongs to the fifth type characteristic of adsorption in mesoporous and microporous materials [1] which, in fact, are ionites.

As indicated in [2], hysteresis was experimentally detected for isotherms of this type both in the range of high and low values of sorbed molecules activity. The resulting model isotherm also “admits” such a critical phenomenon. Indeed, by changing the parameters of polymer matrix, for example, \( s \) and \( \beta_0 \), it’s possible to obtain characteristic jumping areas on the isotherm at high, as well as at low values of relative air humidity, Figure 3. Such situations can appear in ionites with a small number of hydration of surface ion-exchange groups (\( \beta_0 = 1 \), Figure 3, curve 1) or with rarely placed ion-exchange groups (\( s = 2.1 \cdot 10^{-15} \) sm\(^2\), Figure 3, curve 2).

![Fig. 2. The \( \alpha(P/P_s) \) dependence.](image-url)
Fig. 3. The $\beta(P/P_s)$ dependences at critical parameters.

In the proposed model hysteresis on adsorption isotherms can be explained by the relationship between the amount of absorbed water and the dissociation of ion-exchange groups. On the one hand, an increase in water content enhances hydration and, consequently, dissociation of ion-exchange groups. On the other hand, an osmotic effect takes place, i.e. the dependence of the moisture content on the degree of dissociation. In the presence of such a mutual dependence, a situation is possible when a fluctuating increase in moisture content enhances the dissociation of ion-exchange groups, which, due to the osmotic effect, leads to the condensation of additional water molecules into the ionite phase. As a result, under certain conditions, fluctuations greater than a certain value will not decay, but grow until the system enters a new state. This state is characterized by a moisture content and degree of dissociation significantly different from the initial ones, so this transition can be considered as a phase transition of the first kind, similar to the phase transitions of a thin film – a thick film of an adsorbed substance [17] or a strong electrolyte – a weak electrolyte [18].

Obviously, in order to obtain more accurate quantitative results for real systems, the proposed calculation method can be somewhat refined or modified. For this purpose it is possible to consider details of adsorption of water molecules specifically interacting with active centers [11], dependence of dissociation energy on geometry of growing clusters [19], effect of self-dissociation of electrolyte [16, 18]. However, these effects will slightly change the quantitative parameters of adsorption and will not fundamentally affect the type of isotherm.

4 Conclusion

The results of this work indicate that in the theoretical interpretation of the available experimental data on water adsorption in polymer ionites, within the framework of the proposed approach, it is fundamentally important to take into account the electrostatic energy of charges in the sorbed film as accurately as possible, as well as the elastic energy of the polymer matrix.
The numerical solution of the equations system describing the adsorption of water molecules on the surface of the ionite made it possible to construct adsorption isotherms with a characteristic inflection point in the area of medium humidity close to isothermals of the fifth type, having a hysteresis loop at certain values of the system parameters. The obtained model isotherms describe adsorption in mesoporous and microporous materials, which are ionites, and fully correspond to experimental adsorption isotherms of this type.

References