Introduction

In a number of papers describing equilibrium properties of gas mixtures on solids, the adsorption isotherms were not expressed analytically. The adsorption equilibria were calculated rather numerically using thermodynamic relations. The best known and frequently used method is that of Myers and Prausnitz (1) based on the ideal adsorbed solution theory. Comparing this method to experimental data, in Myers and Prausnitz (1) and Fredrich and Mulins (2, 3) papers, favorable results were shown. Hoory and Prausnitz (4) extended this method to non-ideal adsorbed solutions on homogeneous and heterogeneous surfaces. Similar treatment of mixed-gas adsorption was used by Bering and Serpinsky, and the thermodynamic relations for isosteric heats of adsorption in the case of gas mixtures were discussed in details by them, as well (5, 6). A summarizing description of applications of thermodynamics in studies of mixed-gas adsorption was excellently presented by Van Ness (7), Bering and Serpinsky (6), and Sircar and Myers (8).

The best known analytical form of an adsorption isotherm is the Langmuir equation, extended by Markham and Benton (9) to mixed-gas adsorption. As well-known, this equation describes the localized adsorption without molecular interactions in the adsorbed phase. Similar equation to Markham and Benton’s one has been proposed by Schay et al. (10), assuming the mobile adsorption. Recently, the Jovanović isotherm has been used to describe of mixed-gas adsorption (11).

Interesting treatments of mobile adsorption of gas mixtures were presented by Kemball et al. (12), and Ivanov and Martinov (13). Kemball et al. (12) discussed Volmer’s adsorption model for binary gas mixtures on homogeneous surfaces. However, Ivanov and Martinov (13) presented a general description of localized and non-localized adsorption taking into account the molecular interactions between adsorbed molecules. They derived general expressions for mixed-gas adsorption isotherms, which examined experimentally have not yet been. From these equations, as the most interesting result become the extension of Fowler and Guggenheim adsorption isotherm for binary gas mixtures. Recently, Lee and O’Connell (14) proposed an adsorption model, slightly differing from that of mentioned above, however, having assumed partially mobile adsorption, very complicated equations describing adsorption equilibria of binary gas mixtures on homogeneous surfaces have been got.

Considerable difficulties have to be faced in the description of multilayer adsorption of gas mixtures. The exact extension of BET equation to mixed-gas adsorption leads to very complicated equation of adsorption isotherm (15–17). Exceptionally simple equation for bilayer adsorption of binary gas mixtures on homogeneous surfaces has been recently proposed by Gonzalez and Holland (18, 19). An additional
assumption to the BET model was made by them, which led to a simple form of adsorption isotherm. This isotherm will be discussed later.

Recent studies of the author concerned the adsorption of gas mixtures on heterogeneous surfaces (20-27), when the adsorption isotherms could be derived by means of the well-known integral equation (20, 21). Assumption of surface heterogeneity in description of mixed-gas adsorption give better agreement of theoretical isotherms with experimental ones (26).

It follows from the papers cited that considerable difficulties appear in the description of multilayer adsorption of gas mixtures and mixed-gas adsorption taking into account the molecular interactions between adsorbed molecules. The adsorption model detailedly discussed by Kiselev et al. (28-32), assuming the adsorbate-adsorbate associations on the adsorbent surface (AA model), seems to be useful in studies of mixed-gas adsorption. The analytical adsorption isotherms obtained on the basis of this model, satisfactorily describe the experimental data for adsorption of pure gases (33). The AA model is a natural extension of Langmuir and BET models. In this paper the possibilities of extension of AA model to adsorption of binary gas mixtures on homogeneous solid surfaces will be shown. In the case of binary gas mixtures, the most useful equations can be obtained by assuming the formation of double associates on the adsorbent surface. Similarly to Berezin and Kiselev (30) the associations of molecules, parallel and normal to the surface, will be considered.

Association parallel to the surface

Let us consider the behaviour of a mixture of gases A and B on a homogeneous surface. Next, assume that single and double localized associates can be formed on a homogeneous surface, whose links all intersect with the surface (see fig. 1a). The formation of such associates on the adsorbent surface could be considered as series of successive reactions of gas molecules with free positions of the surface. In the case of binary gas mixture A-B, this model considers the following reactions:

\[ A + S \rightleftharpoons A_1 \; K_{A1} \]
\[ B + S \rightleftharpoons B_1 \; K_{B1} \]

for single associates, and

\[ A_1 + A_1 \rightleftharpoons A_2 \; K_{A2} \]
\[ B_1 + B_1 \rightleftharpoons B_2 \; K_{B2} \]
\[ A_1 + B_1 \rightleftharpoons A_1B_1 \; K_{A1B1} \]

\[ A \; \text{for double parallel associates, where } A \text{ and } B \text{ denote molecules of gases } A \text{ and } B, \text{ respectively; } A_i, B_j \text{ and } A_iB_j \text{ denote associates parallel to the surface; } S \text{ is the free place on an adsorbent surface; } K_{A\alpha}, K_{B\beta} \text{ and } K_{A\alpha B\beta} \text{ are equilibrium constants characterizing the reactions [1] and [2]. Eqs. [1] and [2] lead to the following expressions for equilibrium constants:} \]

\[ K_{A1} = \frac{\theta_{A1}}{p_A(1 - \theta)} \]
\[ K_{B1} = \frac{\theta_{B1}}{p_B(1 - \theta)} \]

\[ K_{A2} = \frac{\theta_{A2}}{2(\theta_{A1})^2} \]
\[ K_{B2} = \frac{\theta_{B2}}{2(\theta_{B1})^2} \]

\[ K_{A1B1} = \frac{\theta_{A1B1}}{2\theta_{A1}\theta_{B1}} \]