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The equation of vapor-phase sorption on heterogeneous surfaces with local Guggenheim–Anderson–De Boer model

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Abstract

Recently, we proposed a new four-parametric MGAB equation (modified Guggenheim–Anderson–De Boer equation, GAB) for fitting of experimental isotherms of vapor-phase sorption on geosorbents. In the present study, the theoretical meaning of MGAB equation was elucidated. For this purpose, the properties of the equation of multilayer adsorption on a heterogeneous surface with local characteristics described by GAB model and Zeldovitch–Roginskiy energy distribution function $\rho(\varepsilon)$ were derived and the satisfaction of MGAB equation with these properties was shown. MGAB model has two parameters connected with GAB model: v_m is the monolayer sorption capacity and k is the constant of the multilayer sorption, as well as two parameters of sorption energy distribution function $\rho(\varepsilon)$: α , characterizing heterogeneity of $\rho(\varepsilon)$ and C_0 , reflecting energy baseline. The influence of parameters α and C_0 on the shape of both $\rho(\varepsilon)$ and model sorption isotherm was established. The applicability of MGAB model for the description of surface heterogeneity of a natural sorbent by example of 13 different sorbate–sorbent systems dried and moistened has been discussed. For these systems equilibrium sorption isotherms were measured, corresponding energy distribution functions $\rho(\varepsilon)$ were calculated, and obtained α values were compared. On the whole, the differences in α values responded to the real tendencies of heterogeneity changes in these systems.

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1. Introduction

The surface of natural adsorbents, such as soils, clays and other minerals, is energetically heterogeneous due to complex chemical composition and structural irregularities [1]. Moreover, surface heterogeneity is a fundamental feature of almost all solid surfaces [2]. This fact is now generally recognized by scientists investigating adsorption at gas–solid interface [3–9].

The problem of description of gas-phase sorption in heterogeneous systems has been actively discussed [6,10–14]. For solids having heterogeneous surfaces it is not possible to describe sorption precisely using simple models. Such models derived for homogeneous surfaces can be employed to the experimental data of a heterogeneous sorbent only over a limited surface coverage

range [15]. For the description of experimental isotherms the mathematical models are usually proposed to understand the nature of adsorption equilibrium between gases (vapors) and solids [16–21]. Some of such models are semi-empirical and others are derived from a fundamental adsorption theory. An advantage of a theoretical equation over a semi-empirical one is the definite physical meaning of its parameters. But sometimes theoretical models lose the simplicity in form and fail to explain highly complicated practical cases [21]. An ideal sorption model should simultaneously satisfy two conditions: it should describe well an isotherm in a whole range of concentrations and have parameters with a physical meaning. However for heterogeneous sorbents, it is difficult to combine both these requirements. Thus, an approximation equation usually satisfies only one of two these conditions.

Recently [22], we have proposed the four-parametric empirical MGAB equation (modified Guggenheim–Anderson–De Boer equation, GAB) for the approximation of vapor-phase

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