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Abstract

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PRECALCULATION OF ADSORPTION-EQUILIBRIUM PARAMETERS FOR THE SYSTEM ADSORBENT–BINARY VAPOR MIXTURE

(Presented by Academician M. M. Dubinin on 16 V 1963)

There is no doubt that the possibility of precalculating the parameters of adsorption equilibrium for the system adsorbent–gas mixture is one of the most important practical problems in the theory of physical adsorption. In the present work we shall attempt to give at least an approximate solution of this problem within the framework of the potential theory of adsorption (in what follows, instead of the term "potential theory" we shall use the term "theory of volume filling of micropores," in order to emphasize that the basic function in this theory,

$$\varepsilon = RT \ln \frac{p_s}{p},$$

should be interpreted not as an adsorption potential, but as a change in free energy). Attempts to solve such a problem are known ([1,2]); however, the solution proposed below differs favorably from them in the accuracy of the results, the simplicity of the calculations, and the physical clarity of the assumptions.

Let us specify the formulation of the problem, restricting ourselves to binary gas mixtures. It is required to determine the functions

$$a_1 = f_1(p_1, p_2), \qquad a_2 = f_2(p_1, p_2) \tag{1}$$

(a_i is adsorption, p_i is the equilibrium partial pressure of the i-th component), if it is known that the functions

$$a_1^0 = f_1(p_1, 0), \qquad a_2^0 = f_2(0, p_2), \tag{2}$$

i.e., the adsorption isotherms of the individual components of the mixture on the same adsorbent, are described by the Dubinin—Radushkevich equations (^{3}) for adsorbents of the first structural type:

$$a_i^0 = \frac{W_0}{v_i^0} \exp\left[-\frac{BT^2}{\beta_i^{0\,2}} \lg^2\left(\frac{p_{s_i}^0}{p_i^0}\right)\right] \tag{3}$$

(B and W_0 are structural characteristics of the adsorbent; v_i^0, β_i^0, and $p_{s_i}^0$ are, respectively, the molar volume, the affinity coefficient of the characteristic curve, and the saturated-vapor pressure of the i-th component; the superscript zero indicates that the corresponding quantity refers to the individual component). In addition, the dependences of the molar volume, surface tension, and partial pressures of saturated vapor of the components over normal-volume solutions of these components on the composition of the solution are assumed to be known.

To solve the stated problem, we shall proceed from the natural generalization of equation (3) to the case of a gas mixture:

$$a_\Sigma = \sum a_i = \frac{W_0}{\sum N_i v_i} \exp\left[-\frac{BT^2}{\left(\sum N_i \beta_i\right)^2}\left(\sum N_i \lg\frac{p_{s_i}}{p_i}\right)^2\right]. \tag{4}$$

In this equation N_i is the mole fraction of the i-th component in the surface solution at the equilibrium partial pressure p_i; v_i and β_i are, respectively, the partial molar quantities of the volume and of the affinity coefficient of the characteristic curve for a volume solution with the same values of N_i.

Recall that the coefficient β in the theory of volume filling of pores is taken to be equal to the ratio of the parachor of the given substance to the parachor of the substance conventionally taken as standard. The quantities B and W_0 in equation (4) have not only the same meaning, but also the same numerical values as in equation (3).

As is known, in the case of adsorption of an individual substance, the state of the normal liquid at the given temperature is taken as the standard state in the theory of volume filling of pores. Therefore the quantity $p_{s_i}^0$ is determined uniquely—this is the saturated-vapor pressure over the liquid at temperature T. The situation is different in the case of adsorption of a mixture. It is not clear a priori which state of the bulk solution should be taken as standard: one having the same composition as the given surface solution, or one for which the saturated vapor above it has the same composition as the equilibrium vapor above the surface solution, or, finally, one having the same composition as the surface solution that is in equilibrium with saturated vapor of the same composition as the equilibrium vapor above the given surface solution. Only experiment can answer the question of the correct choice of the standard state. However, as the experimental material obtained by us shows (see below), equation (4) is equally well satisfied for the first two methods of choosing the standard state. We had no material for checking the third method, but since equation (4) is apparently in general little sensitive to the composition of the bulk solution (within known limits) taken as standard, it may be assumed that in this case as well equation (4) will be well satisfied. We therefore leave the question of the choice of the standard state open for the time being. In the present paper we shall stop, somewhat arbitrarily, at the first method, i.e., we take as the standard state a bulk solution for which the saturated vapor above it has the same composition as the equilibrium vapor above the given surface solution.

In this case, evidently, $p_{s_1}/p_1 = p_{s_2}/p_2$, and, consequently,

$$\left(\sum N_i \lg \frac{p_{s_i}}{p_i}\right)^2 = \lg^2 \left[(p_{s_1} + p_{s_2})/(p_1 + p_2)\right] = \lg^2 \frac{p_{s_{12}}}{p_{12}}. \tag{5}$$

For a binary vapor mixture, introducing the notation $\sum a_i = a_{12}$, $\sum N_i v_i = v_{12}(N_2)$ and $\sum N_i \beta_i = \beta_{12}(N_2)$, we may write equation (4) in the form

$$\lg[a_{12} v_{12}(N_2)] = W_0 - 0.434\, BT^2 \frac{\lg^2 \dfrac{p_{s_{12}}}{p_{12}}}{\beta_{12}^2(N_2)}. \tag{6}$$

Thus, in the coordinates $\lg[a_{12} v_{12}(N_2)] - \left(\lg^2 \dfrac{p_{s_{12}}}{p_{12}}\right) / \beta_{12}^2(N_2)$, the experimental data must lie on a straight line cutting off on the ordinate axis the intercept W_0 and having the slope $0.434\, BT^2$. It will be shown below how well equation (6) is fulfilled for the systems studied by us.

To describe the adsorption equilibrium for a binary gas mixture we have 4 variable quantities p_1, p_2, a_1, and a_2, or, what is the same, p_1, p_2, a_{12}, and N_2. If we consider that two of them, namely p_1 and p_2, are independent variables and can be assigned by us arbitrarily, then to solve the problem, in addition to equation (6), one more must be found. As such we shall use the semiempirical relation of Lewis known in the literature (^{1}), which for a binary gas mixture may be written in the form

$$\frac{a_1}{a_1^0} + \frac{a_2}{a_2^0} = 1. \tag{7}$$

Here a_1^0 and a_2^0 are the adsorption quantities of the pure components at pressures $p_1^0 = p_2^0 = p_1 + p_2$. In other words, equation (7) means that at constant total pressure the adsorption of one component depends linearly on

adsorption of the other. Choosing a_{12} and N_2 as variables, we can rewrite equation (7) in the form

$$a_{12}\left(\frac{1 - N_2}{a_1^0(p_1, p_2)} + \frac{N_2}{a_2^0(p_1, p_2)}\right) = 1. \tag{8}$$

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

The set of equations (6) and (8) represents the solution of the problem formulated above.

For an experimental verification of the proposed method for precalculating the parameters of the adsorption equilibrium of a binary gas mixture, we studied the joint adsorption of the ethyl chloride—diethyl ether mixture on activated carbon at 50 and 71°, and of the diethyl ether—chloroform mixture on the same carbon at 60°. The study was carried out by the volumetric-weight method (4). The experiment is described in detail in (5).

Fig. 1. Adsorption isotherms of the individual components: 1 –$(C_2H_5)_2O$, 2 –$CHCl_3$, 3 –C_2H_5Cl; *a* –50°, *b* –60°, *v* –71°.

In Fig. 1 data on the adsorption of the individual components are presented. Measurements for all three vapors at all studied temperatures lead to values of the constants B and W_0 for our carbon equal to $W_0 = 0.465 \pm 0.001$ cm^3/g and $B = 0.674 \pm 0.001$ deg^{-2}. Thus, the assumption made regarding the validity of equation (3) is well justified for our case.

Fig. 2. Isotherms of the total adsorption of binary vapor mixtures C_2H_5Cl–$(C_2H_5)_2O$ at 50° (upper curve) and $(C_2H_5)_2O$–$CHCl_3$ at 60° (lower curve).

Figure 2 illustrates how well equation (6) is satisfied for the systems studied. In the calculations, the quantities $v_{12}(N_2)$ and $p_{s12}(p_1, p_2)$ were found from the phase diagrams of the corresponding bulk solutions, while the quantity $\beta_{12}(N_2)$ was calculated by the additive scheme, since it is known (6) that the parachor of a solution depends linearly on its composition if the surface tensions of the components differ by no more than ~ 17 dyn/cm.

It should be emphasized that the straight lines in Fig. 2 are drawn not through the experimental points, but according to the values of the constants W_0 and B, as well as the temperature T. The constants W_0 and B were determined from the individual adsorption isotherms of the components.

When equation (8) was checked against our experimental data, it turned out that it is satisfied with an accuracy of up to 2–2.5%, and only at some points does the discrepancy amount to $\sim 4\%$.

In Fig. 3 the curved lines depict some of the data obtained on the joint adsorption of vapors. These curves correspond to adsorption isotherms of one of the components at constant values of the adsorption of the other.

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Fig. 3

Figure 3: Fig. 3

component; they are the projection onto the plane $p_j = 0$ of the intersection of the surfaces $a_i = f(p_1, p_2)$ and $a_j = \text{const}$.

Taking pairs of values p_1 and p_2 as independent variables, and solving equations (6) and (8) jointly, we find the corresponding pairs of values a_{12} and N_2, or, equivalently, a_1 and a_2. The values obtained are shown in Fig. 3 as circles. To judge the accuracy of the proposed method for precomputing the parameters of adsorption equilibrium, we also give Table 1, in which the experimental and calculated values of a_{12} and N_2, corresponding to pairs of values p_1 and p_2 for the system C_2H_5Cl—$(C_2H_5)_2O$ at 50°, are compared. In this table, to save space, we have included only part of the material available to us; the selection was made on an entirely random basis (experimental points having an odd ordinal number were taken). Index 1 in the table refers to C_2H_5Cl, index 2 to $(C_2H_5)_2O$.

Fig. 3. Adsorption isotherms of one component of a binary mixture at a constant value of adsorption of the other component. **A** —adsorption of $(C_2H_5)_2O$ at 50° during adsorption of C_2H_5Cl, equal to: 1—0, 2—1 mmol/g, 3—2 mmol/g. **B** —adsorption of C_2H_5Cl at 50° during adsorption of $(C_2H_5)_2O$, equal to: 1—0, 2—2 mmol/g, 3—3 mmol/g.

Analysis of Fig. 3 and Table 1 makes it possible to draw the following conclusion. If the adsorption of the individual components on the given adsorbent can be satisfactorily expressed by equation (3), then the joint adsorption of a binary vapor mixture on the same adsorbent can be described just as satisfactorily by the system of equations (6) and (8). It is assumed here that the state diagrams (partial pressures of saturated vapor, molar vapor volume) of the volumetric binary solutions of the same components are known.

Table 1

Partial pressures, mm Hg	Partial pressures, mm Hg	Experimental values	Experimental values	Calculated values	Calculated values	$\frac{\Delta a_{12}}{a_{12}^{\text{op}}}$, %	$\frac{\Delta N_2}{N_2^{\text{op}}}$, %
p_1	p_2	a_{12}, mmol/g	N_2	a_{12}, mmol/g	N_2		
17.4	36.9	3.75	0.870	3.79	0.885	1.0	1.7
17.8	12.9	3.54	0.794	3.58	0.790	1.1	0.5
31.5	104.6	4.02	0.861	4.07	0.875	1.2	1.7
32.5	14.2	3.72	0.737	3.73	0.750	0.3	1.7
49.3	18.1	3.90	0.675	3.92	0.650	2.0	3.9

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Partial pressures, mm Hg	Partial pressures, mm Hg	Experimental values	Experimental values	Calculated values	Calculated values	$\frac{\Delta a_{12}}{a_{12}^{\text{op}}}$, %	$\frac{\Delta N_2}{N_2^{\text{op}}}$, %
68.0	24.8	4.07	0.625	4.10	0.610	0.8	2.5
70.2	50.7	4.19	0.690	4.19	0.695	0.0	0.7
83.0	115.0	4.25	0.735	4.31	0.730	1.6	0.8
118.6	31.6	4.34	0.519	4.40	0.520	1.4	0.2
129.3	63.7	4.38	0.564	4.50	0.565	2.7	0.2
137.6	77.0	4.42	0.452	4.50	0.455	1.8	1.5
149.0	88.4	4.49	0.451	4.75	0.475	0.9	5.6
274.5	33.9	4.87	0.323	4.87	0.350	0.9	8.4
				Average		1.1	2.2

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