MODELING OF THE SORPTION DEFORMATION OF GLASSY POLYMER SORBENTS IN INTERACTION WITH GASES IN A HIGH-PRESSURE REGION

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UDC 541.183

Based on the phenomenological-thermodynamics method, a model of sorption deformation of a glassy polymer sorbent — polycarbonate — in interaction with carbon dioxide in a high-pressure region has been proposed. The possibility of describing sorption equilibrium for this system has been analyzed.

The thermodynamic behavior of glassy polymers in contact with gases at elevated pressures has attracted considerable recent attention as an important factor in considering the processes of removal of low-molecular-weight compounds from polymers, impregnation of polymers with different chemical substances, in the production of polymer foams, and in the separation of gas mixtures using polymer membranes. Many of these processes use carbon dioxide (having a high solubility in glassy polymers even at moderate pressures) as a penetrating gas. Such a high solubility may bring about a substantial swelling of the polymers and a significant reduction in the devitrification temperature. Quantitative description of sorption, swelling, and devitrification is, consequently, quite important for modeling of such processes and for using of polymers under these peculiar conditions. Experimental data for the glassy polymers in contact with gases at elevated pressures are very scarce or limited to narrow intervals [1].

The problem indicated must be attacked in a complex manner using sorption equations and the currently available experimental methods of investigation.

In this work, we have considered the general regularities of the physical sorption of carbon dioxide by a swelling polymer — polycarbonate — in a wide range of pressures (to 6 MPa). The sorption deformation of the above sorbent has been investigated.

The interest shown in polycarbonate is due to the unique properties of the latter. Polycarbonate belongs to the class of synthetic polymers and is a linear polyester of carbonic acid and phenols. Polycarbonate resembling acrylic glass in appearance has no analogs among the polymer materials used in mechanical properties. Polycarbonate is distinguished by a combination of high heat resistance, unique shock resistance, and high transparency at the same time. Its properties are affected by a change in the temperature only slightly. Polycarbonate possesses a high chemical stability to most substances noninert to polymers, which makes it possible to use it in aggressive media without changing the chemical composition and properties. Among these substances are mineral acids, even of high concentrations, salts, saturated hydrocarbons, and alcohols, including methanol [2].

Consideration of the physics of the process of sorption by microporous sorbents provides that a number of factors, e.g., change in the dimensions of a solid body in interaction with gases or a vapor, be allowed for. However, at the present time, there are no equations adequately describing the sorption deformation of sorbents.

The pressure deforming a sorbent is determined by internal and external factors [3]. The internal factor associated with the interaction between the sorbate molecules and the interior sorbent surface is, clearly, basic here. This is shown by simple evaluations performed, e.g., according to experimental data [4] (Fig. 1) and by the elastic-deformation modulus corresponding to this system.

The pressure may be represented in the form of the algebraic sum
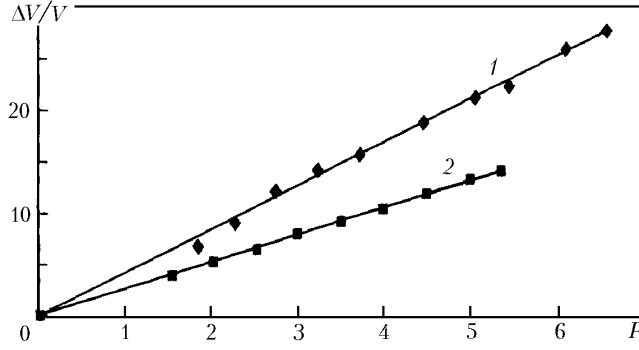
$$P = -P_1 + P_2,\qquad(1)$$

Fig. 1. Experimental isotherms of relative volume deformation of polycarbonate (PC) in sorption of CO_2: 1) $T = 308$; 2) 318 K. P, MPa; $\Delta V/V$, %.

where P_1 is the pressure compressing the sorbent due to the effect of decrease in the surface tension of the latter upon the penetration of the sorbate molecules into the solid body (it is related to the interaction between the substance sorbed and the opposite walls of the micropores comparable to the dimensions of the sorbate molecules) and P_2 is the pressure produced by the collisions of the sorbed molecules with the pore walls and determined by the molecular concentration per free volume and by the kinetic energy. The pressure P_1 may be represented as follows:

$$P_1 = \frac{f}{S} N = \frac{fN m_{\text{mol}} m_{\text{ads}}}{S m_{\text{mol}} m_{\text{ads}}} = \frac{fa}{S_{\text{sp}} m_{\text{mol}}} .$$ (2)

To write an expression for the pressure P_2 we introduce the assumption that the sorbed molecules, penetrating into the pores, behave similarly to an ideal gas there. As a result, a molecular-statistical analysis yields the formula [5]

$$P_2^{\text{id}} = \frac{2}{3} n \bar{\varepsilon} .$$ (3)

Expression (3) may also be written as follows:

$$P_2^{\text{id}} = \frac{2}{3} n \frac{ikT}{2} .$$ (4)

Since the collisions of molecules with each other and with the sorbent walls are inelastic, in an actual situation, we must introduce into consideration the coefficient A characterizing the inelasticity of the impacts. Also, we must allow for the concentration of the sorbed molecules per free volume. As a result, we take into account the geometric dimensions of the molecules and use n_* computed in accordance with the Boltzmann distribution [5] instead of the value of n in formula (4):

$$n_* = n_{\text{gas}} \exp\left(\frac{-(\varepsilon_p^{\text{ad}} - \varepsilon_p^{\text{gas}})}{RT}\right).$$ (5)

The physical meaning of the value of n_* is the concentration of the sorbed molecules in the sorbent field and in the natural-interaction field per free volume. Consequently, expression (4) will take the form

$$P_2^{\text{id}} = A \frac{2}{3} n_* \frac{ikT}{2} = A \frac{2}{3} \frac{ikT}{2} n_{\text{gas}} \exp\left(\frac{-(\varepsilon_p^{\text{ad}} - \varepsilon_p^{\text{gas}})}{RT}\right).$$ (6)

If the gas phase is ideal, we have $\varepsilon_p^{\text{gas}} = 0$ and (6) is reduced to the following expression:

$$P_2^{\text{id}} = A \frac{i}{3} \exp\left(\frac{-\varepsilon_p^{\text{ad}}}{RT}\right) P_{\text{gas}}^{\text{id}} ,$$ (7)

where $P_{gas}^{id} = n_{gas}kT$. For a nonideal equilibrium gas phase, we have $P_{gas}^{real} = zP_{gas}^{id}$, and as a result we obtain

$$P_2 = \frac{A}{z}\frac{i}{3}\exp\left(\frac{-\varepsilon_p^{ad}}{RT}\right)P_{gas}^{id}. \tag{8}$$

Thus, assuming that the deformation of the sorbent is elastic, with account for expressions (2) and (8), we may write

$$\frac{\Delta V}{V} = \frac{P}{M} = \frac{-P_1 + P_2}{M} = -\frac{fa}{MS_{sp}m_{mol}} + \frac{A}{Mz}\frac{i}{3}\exp\left(-\frac{\varepsilon_p^{ad}}{RT}\right)P_{gas} = -Ca + D\exp\left(-\frac{\varepsilon_p^{ad}}{RT}\right)P_{gas}, \tag{9}$$

where $\frac{\Delta V}{V}$ is the relative volume deformation of the sorbent, $C = \frac{f}{MS_{sp}m_{mol}}$, and $D = \frac{A}{Mz}\frac{i}{3}$.

In connection with the fact that the glassy polymer sorbent (polycarbonate) considered here possesses a specific intermacromolecular nature [6], we may disregard the component P_1 in expression (9). Then, finally, we obtain following expression:

$$\frac{\Delta V}{V} = D\exp\left(\frac{-\varepsilon_p^{ad}}{RT}\right)P_{gas}. \tag{10}$$

Clearly, consideration of the experimental isotherms (presented in Fig. 1) of relative deformation of polycarbonate in sorption of CO_2 [4] and of expression (10) makes it possible to calculate the most important characteristic of the sorption process, i.e., $-\varepsilon_p^{ad}$. Indeed, finding the values of the parameters of the correlation function from the isotherms of relative deformation of polycarbonate in sorption of CO_2 for two temperatures, we may determine the $-\varepsilon_p^{ad}$ values:

$$-\varepsilon_p^{ad} = \frac{R\ln\dfrac{k_1}{k_2}}{T_1^{-1} - T_2^{-1}}, \tag{11}$$

where k_i is the slope of the relative deformation of polycarbonate as a function of the gas-phase pressure at the temperature T_i.

Processing of experimental data has made it possible to calculate the value of $-\varepsilon_p^{ad}$ and thereby to check the adequacy of the model used. As a result, we obtained a value of $-\varepsilon_p^{ad} = 40.4$ kJ/mole = 9.67 kcal/mole. This result is quite consistent with the ideas of the physical nature of the process of sorption of carbon dioxide by polycarbonate.

Thus, to describe the relative volume deformation of polycarbonate in CO_2 sorption as a function of the pressure of the equilibrium gas phase we may use the following equation:

$$\frac{\Delta V}{V} = 5.76 \cdot 10^{-15}\exp\left(\frac{40.4 \cdot 10^3}{RT}\right)P_{gas}. \tag{12}$$

Figure 2 shows experimental isotherms of sorption of CO_2 by polycarbonate [4]. These curves are similar to the so-called Langmuir dependences in shape. The latter are characterized by virtually constant heats for different values of sorption.

Using the experimental isotherms, we may independently calculate the isosteric heats of CO_2 sorption by polycarbonate for any value of sorption from the formula [5]

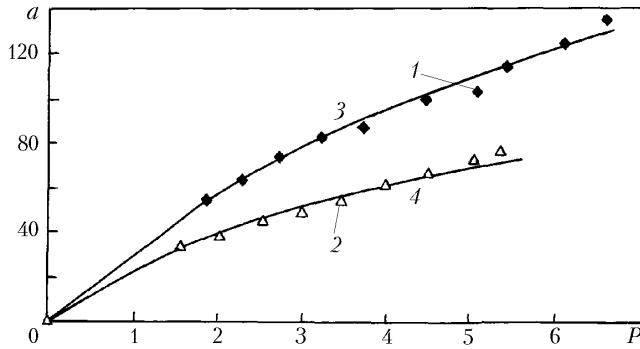$$q_{st} = -\frac{R\Delta\ln P}{\Delta(T^{-1})}. \tag{13}$$

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Fig. 2. Experimental data and theoretical isotherms of CO_2 sorption by a polycarbonate polymer sorbent: 1) experimental data for $T = 308$ K; 2) the same, 318 K; 3) theoretical isotherm for $T = 308$ K; 4) the same, 318 K. a, mg/g; P, MPa.
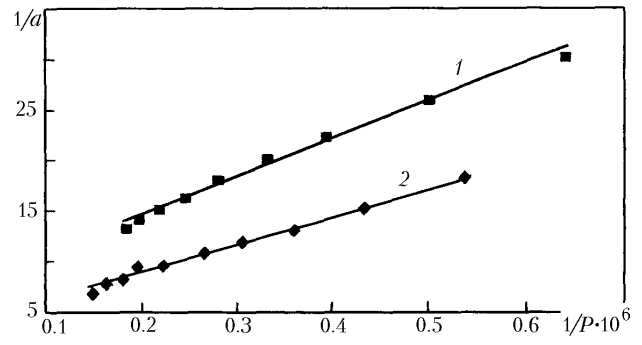
Fig. 3. Results of processing of experimental data in inverse coordinates: 1) $T = 318$; 2) 308 K. $1/a$, $(g/g)^{-1}$; $1/P \cdot 10^6$, Pa^{-1}.

Thus, the calculations have shown that, for sorptions of $a = 24$ and 50 mg/g, the isosteric heats are equal to 10.0 and 10.5 kcal/mole respectively. Taking into account that $-\varepsilon_p^{ad} = q_{st} - RT$, we have $-\varepsilon_p^{ad} = 9.39$ kcal/mole (for $a = 24$ mg/g) and $-\varepsilon_p^{ad} = 9.87$ kcal/mole (for $a = 50$ mg/g). It is clear that, within the computational error (~5%), these values correspond to a value of 9.67 kcal/mole for $-\varepsilon_p^{ad}$, which has been determined on the basis of the above model of elastic sorption deformation of sorbents.

The use of the general thermodynamic approach to description of ad- and absorption equilibria [7] has made it possible to obtain, for this sorption system, an equation similar to the Langmuir one but with the Henry constant having a clear physical definition:

$$P = \frac{K_a \Theta}{1 - \Theta}, \tag{14}$$

where $K_a = K a_{mon}$,

$$K = RT \left(\frac{V^{mon} \mu}{m_{ads}} \right)^{-1} \exp \left(-\frac{q_{st}}{RT} \right). \tag{15}$$

It was taken into account that sorption inside the polycarbonate occurs predominantly in amorphous regions, i.e., on energy-homogeneous active centers which are at a considerable distance from each other. Since Θ is equal to a/a_{mon}, we reduce (14) to the form

$$a = \frac{P a_{mon} K_*}{1 + K_* P}, \tag{16}$$

where $K_* = K_a^{-1}$. In inverse coordinates expression (16) may be whitten as follows:

$$\frac{1}{a} = \frac{B}{P} + \frac{1}{a_{mon}}, \tag{17}$$

where $B = (a_{mon} K_*)^{-1}$. Employing statistical-analysis methods, we may calculate the most important characteristics — the limiting value of sorption and the value of the coefficient K_* — necessary for theoretical calculations of the sorption isotherm using linear regression. Figure 3 gives results of processing experimental data on the interaction between

polycarbonate and carbon dioxide for temperatures of 308 and 318 K. The calculations have shown that we have a_{mon} = 280 mg/g and $K_* = 1.22 \cdot 10^{-7}$ for T = 308 K and a_{mon} = 144 mg/g and $K_* = 1.83 \cdot 10^{-7}$ for T = 318 K.

It follows from Fig. 2 that the calculations carried out from Eq. (16) and from the characteristics a_{mon} and K_* found fairly well correlate with the experimental isotherms, which makes it possible to confidently use the model employed in practice.

NOTATION

A, coefficient characterizing the inelasticity of a molecular collision; a, value of sorption, kg/kg; a_{mon}, limiting value of sorption for a given temperature T, kg/kg; C and D, parameters of the elastic-deformation model, Pa^{-1}; f, force causing compression (contraction) upon the penetration of one sorbate molecule into the micropores, N; i, number of degrees of freedom of a molecule; K_a and K_*, constants, Pa and Pa^{-1}; K, Henry constant, Pa; k, Boltzmann constant, J/K; k_1 and k_2, slopes of the relative deformation of polycarbonate as a function of the gas-phase pressure at different temperatures, Pa; M, modulus of volume deformation of the sorbent, Pa; m_{ads}, sorbent mass, kg; m_{mol}, sorbate–molecule mass, kg; N, running number of sorbed molecules; n, molecular concentration, m^{-3}; n_*, concentration of the sorbed molecules in the sorbent field and in the natural-interaction field per free volume, m^{-3}; n_{gas}, molecular concentration in a gas, m^{-3}; P, pressure deforming a sorbent, Pa; P_2^{id}, ideal-gas pressure produced by the collisions of the sorbed molecules with the pore walls, Pa; P_{gas}^{id} and P_{gas}^{real}, pressure of the ideal and real gas respectively, Pa; q_{st}, isosteric heat of sorption, J/mole; R, universal gas constant, J·K/mole; S, interior sorbent surface, m^2; S_{sp}, specific sorbent surface, m^2/kg; T, temperature, K; V, sorbent volume, m^3; V^{mon}/m_{ads}, specific volume of the porous sorbent space for the limiting value of sorption a_{mon}, m^3/kg; z, compressibility factor of the gas phase; ΔV, change in the sorbent volume due to swelling, m^3; $\bar{\varepsilon}$, average kinetic energy of one molecule, J; ε_p^{ad} and ε_p^{gas}, molar potential energies of interaction of molecules in the sorbed state and in the equilibrium gas phase, J/mole; μ, molar sorbate mass, kg/mole; Θ = a/a_{mon}, degree of filling (coverage). Subscripts and superscripts: ads, adsorbent; ad, adsorbate; gas, gas phase; id, ideal; mol, molecule; mon, monolayer; real, real; sp, specific; p, potential energy; st, isosteric heat of adsorption.

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