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Equilibrium Kinetic Analysis of a Model Mixture of Anthracene and Benzothiophene

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Abstract—The kinetic and thermodynamic parameters of the hydrogenation of an anthracene–benzothiophene model mixture were calculated. The rate constants of forward and reverse reactions, the equilibrium constant, the activation energies, and the heat effects of hydrogenation reactions were determined by equilibrium kinetic analysis for second-order reactions in a model mixture of anthracene and benzothiophene in the presence of an iron-containing catalyst over a temperature range of 648–698 K at a pressure of 6 MPa.

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Data on the values of thermodynamic functions, such as heat capacity, enthalpy, entropy, and Gibbs free energy, and kinetic parameters are necessary for studying coal chemistry processes. Corresponding experimental data on polycyclic hydrocarbons and their derivatives are currently not available; therefore, attention has been focused on the development of theoretical and practical methods for their calculation [1, 2].

Methods based on a combination of equilibrium (thermodynamic) and kinetic approaches are used for the more precise and rapid determination of these values. The equilibrium kinetic analysis (EKA) developed by Malyshev makes it possible to directly relate equilibrium and kinetic characteristics and to obtain additional information from a usual set of experimental data [3]. The equilibrium kinetic analysis does not require the equilibration of concentrations in a process; the equilibrium concentration is found from a mathematical model of the reaction with the use of a random-search procedure. In this case, the accuracy of this procedure is sufficient with the use of initial data with a standard error of ±5 rel %.

Previously, Gagarin et al. [4] obtained the results of a study on the phenomenological kinetics of hydrogenation of polynuclear aromatic hydrocarbons (PAHs) over an alumina–cobalt–molybdenum catalyst using pseudo-first-order equations with respect to the hydrocarbons. However, under the conditions of the hydrogenation processing of coal, it does not always happen that coal is completely converted into liquid products. The liquefaction products almost always contain solid organic residue. In the context of current kinetic studies, it would be desirable to note that the reaction of coal decomposition can have a second order [5]. Haley et al. [6] constructed empirical models for the liquefaction of lignite in Tetralin. The models in which the reaction of lignite conversion was of second order with respect to lignite were found most adequate to experimental data.

Malyshev [7] considered in detail the EKA of a second-order reactions, which can be of general interest in terms of methodology because of the use of optimum procedures for the construction of a mathematical model and the processing of experimental data based on experience in the application of this method. In accordance with the above concepts, the aim of this work was to determine the thermodynamic and kinetic parameters of the hydrogenation of a model mixture of anthracene and benzothiophene by the EKA method for second-order reactions.

The integral equilibrium kinetic model (IEKM) of the hydrogenation of the model mixture of anthracene and benzothiophene takes the form [8]

$$\frac{3aD}{A-B}\left[-\frac{1}{6A^{2/3}}\ln\frac{(A^{1/3}-x)^2}{A^{2/3}+A^{1/3}x+x^2}\right.$$
$$+\frac{1}{A^{2/3}\sqrt{3}}\arctan\frac{2x+A^{1/3}}{A^{1/3}\sqrt{3}}+\frac{1}{6A^{2/3}}\ln\frac{(A^{1/3}-1)^2}{A^{2/3}+A^{1/3}x+1}$$
$$-\frac{1}{A^{2/3}\sqrt{3}}\arctan\frac{2+A^{1/3}}{A^{1/3}\sqrt{3}}+\frac{1}{6B^{2/3}}\ln\frac{(B^{1/3}-x)^2}{B^{2/3}+B^{1/3}x+x^2} \quad (1)$$
$$-\frac{1}{B^{2/3}\sqrt{3}}\arctan\frac{2x+B^{2/3}}{B^{2/3}\sqrt{3}}-\frac{1}{6B^{2/3}}\ln\frac{(B^{1/3}-1)^2}{B^{2/3}+B^{1/3}x+1}$$
$$\left.-\frac{1}{B^{2/3}\sqrt{3}}\arctan\frac{2+B^{2/3}}{B^{2/3}\sqrt{3}}\right] = q\tau.$$

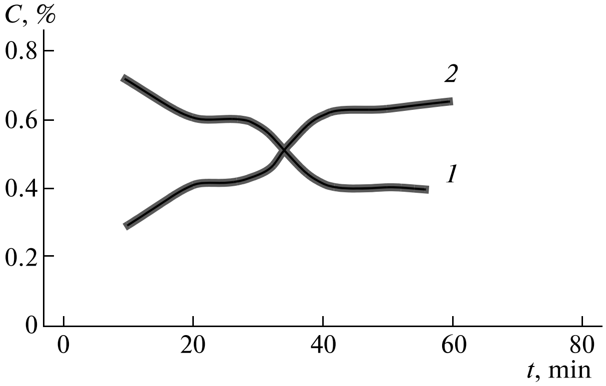

Fig. 1. Total degree of conversion of the model mixture of anthracene and benzothiophene at a temperature of 698 K: (*1*) the model mixture of anthracene and benzothiophene and (*2*) the total degree of conversion of the model mixture into dihydroanthracene and dihydrobenzothiophene.

In the left-hand side, all of the designations contain one unknown constant C_p and one variable C, which is measured experimentally; therefore, the entire left-hand side is functionally related to only the current concentration, and so it can be designated as the single variable Z. In the right-hand side, the unknown quantity k_2—the rate constant of reverse reaction—occurs as a constituent of qq in addition to the variable τ. As a result, we obtain the straight-line equation

$$Z = q\tau, \tag{2}$$

which contains the two unknowns C_p and k_2, for the determination of which the pairwise processing of the experimental data is used:

$$\frac{Z_i}{Z_j} = \frac{\tau_i}{\tau_j}. \tag{3}$$

After the substitution of the corresponding values of C_i and C_j into Z_i and Z_j, the Z_i/Z_j ratio is fit using a numerical method by varying the common value of C_p starting with an arbitrary value in the region of the upper values of current concentration or immediately after the upper value and, in any case, far from equilibrium, as provided by any EKA model. The procedure is repeated for all pairs with the subsequent calculation of the average value of C_p and the determination of its representativeness according to a test for homogeneity of a set. Next, the average value of q is found from inverted Eq. (1) by substituting the found value of C_p for all pairs of the set according to Eq. (4) with the subsequent calculation of k_2 from Eq. (5):

$$q = \sum_{i=1}^{n} Z_i \Big/ \sum_{i=1}^{n} \tau_i, \tag{4}$$

$$k_2 = \frac{\sum Z_i}{\sum \tau_i} \Big/ \frac{m_0}{r_0 \rho_{C_p}}. \tag{5}$$

Then, the equilibrium constant K_p is calculated through C_p using Eq. (6); next, the rate constant of the forward reaction k_1 is calculated with the use of k_2:

$$K_p = \frac{C_p^2}{(C_0 - C_p)^2}. \tag{6}$$

Calculations were repeated for all isotherms; this made it possible to calculate the average enthalpy and entropy of the process with the aid of the Gibbs–Helmholtz equation based on C_p. Correspondingly, the activation energies of forward and reverse reactions can be calculated based on k_1 and k_2 at different temperatures using the Arrhenius equation; thus, the use of the EKA method is completed.

For testing model (1), we performed experiments on the hydrogenation of a model mixture of anthracene and benzothiophene in the presence of a catalyst of Fe_2O_3 + S at a pressure of 6 MPa with a duration of 3600 s and used the experimental results (Fig. 1) for studying kinetic and thermodynamic characteristics with the use of the EKA method.

For solving Eq. (1) with respect to equilibrium concentration, the experimental data were processed with the use of a random-search procedure based on paired experimental points by searching all of their combinations according to formula (2) with the aid of the EKA program system (Delphi 7) with data output in Microsoft Excel.

The found equilibrium values of concentrations were tested for uniformity based on the Nalimov criterion. The average value of equilibrium concentration was considered as a calculated experimental value for the entire set of processed points. Table 1 summarizes the search values of equilibrium concentrations at temperatures of 648, 678, and 698 K.

To confirm the adequacy the developed model, it is necessary to compare its linear forms in the experimental and calculated versions. Because it is extremely difficult to calculate concentration through duration according to Eq. (1) because of the conversion of Z into C, the goal to be sought can be accomplished by calculating the duration through the experimental values of concentration and the equilibrium concentration by substituting them into Z with the subsequent determination of t_{calcd} from the inverted formula

$$t_{\text{calcd}} = Z/q. \tag{7}$$

Figure 2 illustrates the results of the calculations.

First of all, according to Fig. 2, we are convinced that the developed model is actually reduced to the

Table 1. Results of the calculations of equilibrium concentrations at temperatures of 648, 678, and 698 K (*i* and *j* are the numbers of coupled experimental points)

C_p at i/j at a temperature of 648 K															C_p, average
1/2	1/3	1/4	1/5	1/6	2/3	2/4	2/5	2/6	3/4	3/5	3/6	4/5	4/6	5/6	
648 K															
0.0415	0.0479	0.0752	0.0768	0.0781	0.0474	0759	0767	0781	0749	0.077	0.0779	0.077	076	0.0781	0.07752
678 K															
0.5802	0.06306	0.09234	0.10018	0.098	0.06306	092	0949	0979	092	0.091	0.097	0.939	097	0.0979	0.1799799
698 K															
0.08325	0.0892	0.1183	0.1191	0.12085	0.082	0.1209	0.1686	0.1708	0.1299	0.12094	0.12321	0.12913	0.1309	0.119353	0.1138217

form of a straight line that emerges from the origin of coordinates. For the IEKM developed for the hydrogenation of the model mixture of anthracene and benzothiophene, the correlation coefficients were $R(648\ \text{K}) = 0.961$, $t_R = 2.7 > 2$; $R(673\ \text{K}) = 0.9788$, $t_R = 2.6 > 2$; $R(698\ \text{K}) = 0.9846$, $t_R = 116.5 > 2$.

Consequently, it is possible to consider that the proposed EKA for the second-order reaction is sufficiently correct for the process of the hydrogenation of the model mixture of anthracene and benzothiophene.

Next, the average value of q is found by inverted dependence (1) upon substituting the obtained value of C_p for all pairs of the set according to Eq. (3). The results of the calculations of q at temperatures of 648, 678, and 698 K are the following: $q_1 = 0.0102$; $q_2 = 0.0028$; and $q_3 = 0.0182$.

Figures 3 and 4 show that the dependences of the rate constant of forward reaction and the equilibrium constant are adequately described by the Arrhenius and van't Hoff equations, respectively. Table 2 summarizes the kinetic and thermodynamic parameters of the hydrogenation of the model mixture of anthracene and benzothiophene in a range of 648–698 K.

According to the activation energies found from the Arrhenius equation at temperatures of 648–698 K, the hydrogenation reaction of the model mixture of anthracene and benzothiophene occurs in the kinetic regime. The activation energy of forward and reverse reaction is related to the heat effect ΔH by the relationship $E_1 - E_2 = \Delta H$ [9]. It is well known that the heat effect of a hydrogen transfer reaction is the sum of the heat effects ΔH_d and ΔH_a of dehydrogenation and acceptor hydrogenation reactions, respectively.

Consequently, the effectiveness of donors is determined only by the value of ΔH_d; moreover, an optimum donor of hydrogen should exhibit a minimum value of ΔH_d [10]. According to the data of Table 2, $\Delta H_d = 10.2$ kJ/mol; hence, it follows that dihydroanthracene and dihydrobenzothiophene are more reac-

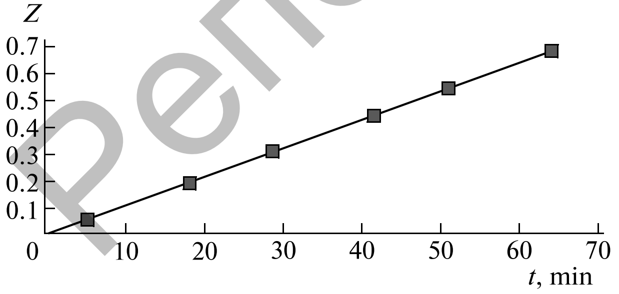

Fig. 2. Fig. 2. The time dependence of Z at a temperature of 648 K: the points and line refer to experimental data and the equation $Z = qt$, respectively.

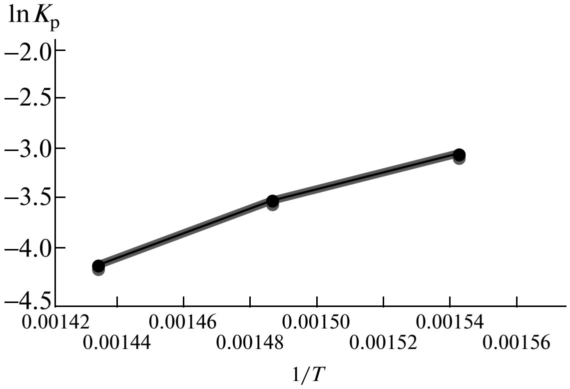

Fig. 3. Dependence of the equilibrium constant on the reciprocal of temperature.

Table 2. Kinetic and thermodynamic parameters of the hydrogenation reaction of the model mixture of anthracene and benzothiophene

T, K	Forward		Reverse		K_p, MPa^{-1}	$-\Delta H$, kJ/mol	$-\Delta S$, J mol^{-1} K^{-1}
	k_1, min^{-1}	E_a, kJ/mol	k_2, min^{-1}	E_a, kJ/mol			
648	$1.07 \cdot 10^{-6}$	128.6	$5.07 \cdot 10^{-8}$	138.8	0.047	10.2	62.4
678	$2.40 \cdot 10^{-6}$		$7.10 \cdot 10^{-8}$		0.029		
698	$5.39 \cdot 10^{-6}$		$8.24 \cdot 10^{-8}$		0.015		

tive donors of hydrogen than the more saturated derivatives of anthracene and benzothiophene because these products predominate in the equilibrium composition of the hydrogenation products of the model mixture of anthracene and benzothiophene. These data are indicative of a predominant shift of reaction equilibrium toward the formation of initial products and a corresponding increase in the concentration of an optimum donor of hydrogen.

Thus, we determined the rate constants of forward and reverse reactions, the equilibrium constant, the activation energies, and the heat effects of the reactions of the hydrogenation of the model mixture of anthracene and benzothiophene in the presence of a catalyst of Fe_2O_3 + S in a temperature range of 648–698 K at a pressure of 6 MPa; they are as follows: $k_1 = 1.07 \times 10^{-6}$ min^{-1}, $k_2 = 5.07 \times 10^{-8}$ min^{-1}, and K_p = 0.0473 MPa (648 K); $k_1 = 2.40 \times 10^{-6}$ min^{-1}, $k_2 = 7.10 \times 10^{-8}$ min^{-1}, and K_p = 0.0293 MPa (678 K); $k_1 = 5.39 \times 10^{-6}$ min^{-1}, $k_2 = 8.24 \times 10^{-8}$ min^{-1}, and K_p = 0.0153 MPa (698 K); E_a of forward reaction, 128.6 kJ/mol; E_a of reverse reaction, 138.8 kJ/mol; and ΔH = 10.2 kJ/mol. The data obtained are indicative of the adequacy of the EKA model used for second-order reactions.

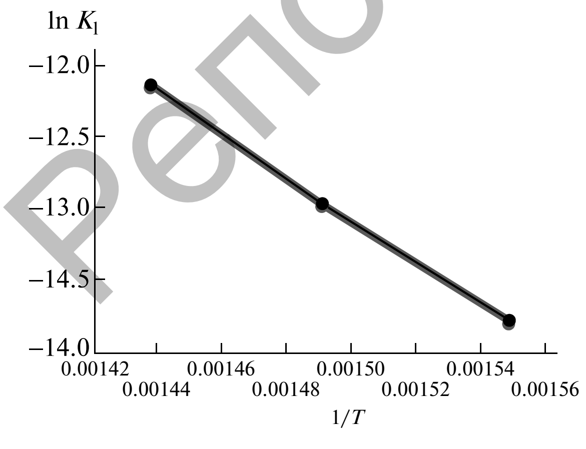

Fig. 4. Dependence of the rate constant on the reciprocal of temperature.

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