General Approach to Processing of Kinetic Adsorption Data

But-1-ene + Zeolite NaH-Y System

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The isothermal rate equation of adsorption has been modified and solved numerically. Its three parameters were evaluated from the nonlinear regression using the CERN-library programs. The kinetic data for the but-1-ene + zeolite NaH-Y system, which caused discontinuities in the Elovich plots, were successfully fitted to the proposed equation. The physical meaning of this equation and its parameters are discussed on the basis of the same experimental data. Some suggestions about the but-1-ene transformation mechanism are made.

The Elovich equation is the most successful way of presenting kinetic data in surface chemistry. Therefore, when in some systems the Elovich plot was closely approximated by two or even more linear segments, such discontinuities caused great interest in the literature. " Attempts [1] to explain the presence of discontinuities in terms of surface heterogeneity, anisotropy, formation of surface complexes, *etc.*, have proved unsuccessful ".[2] The hypothesis that such discontinuities are caused by the presence of surface contaminants [2] also seems less likely. In our previous paper it was shown that the breaks in the Elovich plot can be caused by either improperly chosen experimental conditions [3] or by application of the Elovich equation to experimental data which are beyond the limits of its range of application.[4] In the latter case the Elovich equation was converted into a new form of the kinetic equation based on a more general set of assumptions:

$$\ln (1-\theta) - \gamma(1-\theta) = -\frac{K}{e^{\gamma}}t - \gamma \qquad (1)$$

where $(1-\theta)$ denotes the bare surface fraction at time t, and K and γ are constants. Applying this equation to experimental data which cannot be satisfactorily described by the Elovich equation, linear plots have been obtained.[4]

In this paper, on the basis of kinetic data for the but-1-ene + zeolite NaH-Y system,[5] another reason for the appearance of breaks in the Elovich plot will be discussed and a way of eliminating them will be shown.

MODIFIED APPROACH TO ISOTHERMAL RATE EQUATION OF ADSORPTION

An isothermal rate equation of adsorption for the case of a homogeneous surface can be expressed as follows:[7]

$$\frac{d\theta}{dt} = K'(p)f(\theta) \exp - [E(\theta)/RT] \qquad (2)$$

where at constant temperature T, $K'(p)$ is a pressure-dependent constant comprising the collision frequency and a condensation coefficient; θ is the surface coverage fraction at time t and $E(\theta)$ is the activation energy for adsorption which is a function of θ. The term $f(\theta)$ expresses the probability that a molecule collides with a vacant surface site. Generally the probability function can be expressed as $(1-\theta)^n$. In the case of single site adsorption the rate of adsorption is simply proportional to $(1-\theta)$. For more complex cases the probability is lower or greater than $(1-\theta)$ and it is reflected by the value of parameter n. Now, if we assume that the activation energy of adsorption varies linearly with θ according to the relationship

$$E = E_0 + \gamma'\theta \tag{3}$$

where E_0 and γ' are constants, eqn (2) can be expressed as follows

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = K'(p)(1-\theta)^n \exp\left[-(E_0+\gamma'\theta)/RT\right]. \tag{4}$$

Putting $K'(p) \exp\left(-E_0/RT\right) = K$ and $\gamma'/RT = \gamma$ we obtain

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = K(1-\theta)^n \, \mathrm{e}^{-\gamma\theta}. \tag{5}$$

For small values of θ eqn (5) can be easily converted into a form of the Elovich equation since the variation in $(1-\theta)^n$ is negligible with respect to that of the exponential term when $\theta \ll 1$. Integration of eqn (5) over the whole variability range of θ values from 0 to θ results in the following equation:

$$t = \frac{1}{K} \int_0^\theta \frac{\mathrm{e}^{\gamma\theta}}{(1-\theta)^n} \, \mathrm{d}\theta. \tag{6}$$

It is difficult to determine the exact solution of the above integral. In a previous paper [4] the integral in eqn (6) was calculated approximately by expanding in the series. As a result a new kinetic equation of adsorption was obtained in the form already mentioned in the introduction [eqn (1)].

In this paper a numerical evaluation of the above integral is proposed. Three parameters K, γ and n, the knowledge of which is necessary to solve eqn (6), can be calculated from the non-linear regression by searching for such values of K, γ and n for which the expression

$$\sum (t_{\text{calc}} - t_{\text{exp}})^2$$

is a minimum. [Where t_{calc} is the time calculated from eqn (6) and t_{exp} is the experimental value of the time].

KINETICS OF CHEMISORPTION IN BUT-1-ENE+ZEOLITE NaH-Y SYSTEM

ELOVICHIAN PICTURE

In a previous paper [5] the plots of q against t for the but-1-ene + zeolite NaH-Y system were presented. It is a matter of speculation whether they should be drawn as smooth curves or not.[6] However, as can be seen from fig. 1 plots of q against $\log t$ show the presence of distinct discontinuities. As Low [1] stated " the Elovich plot is thus more sensitive and reveals irregularities ordinarily overlooked ".

NUMERICAL APPROACH

Application of eqn (1) to the experimental data taken from ref. (5) concerning the system but-1-ene+zeolite NaH-Y has also been a failure. Therefore, it is interesting to test the more general equation of adsorption in a form of eqn (6) for these experimental data. The calculations were executed using the " Cyber 72 " computer.
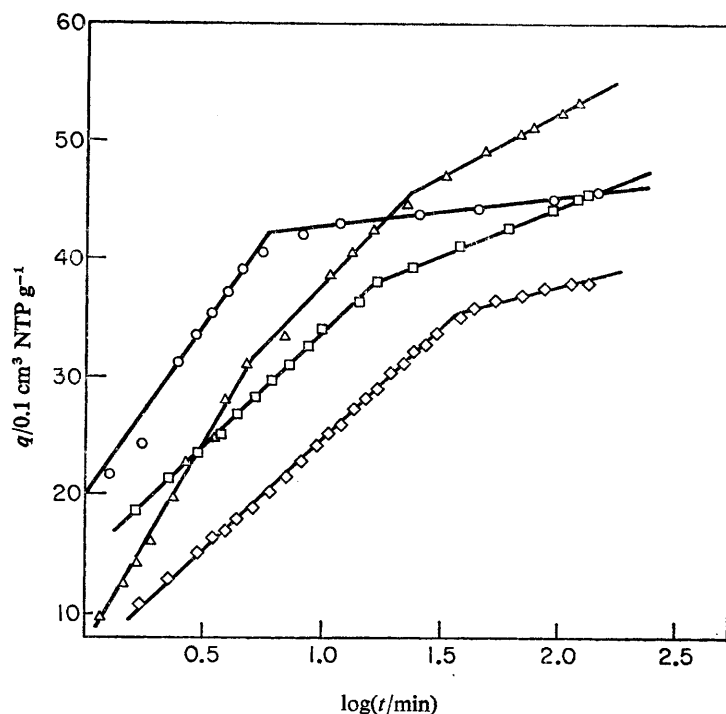

FIG. 1.—Elovich plots for selected experimental data for the but-1-ene+zeolite NaH-Y system. Percentage of exchanged cations △, 59; □, 43; ○, 0; ◇, 82.

TABLE 1.—CALCULATED VALUES OF PARAMETERS OF EQN (6) FOR BUT-1-ENE+ZEOLITE NaH-Y SYSTEM

percentage of exchanged cations	γ	K/min^{-1}	n	standard error in estimate for t_{cal}/min
0	3.0	46.9	2.5	2.1
9.5	lack of correlation			
12	lack of correlation			
23	5.9	6.4	0.9	3.4
43	8.7	11.4	0.3	2.8
59	5.1	1.3	0.7	1.9
68	7.8	3.2	0.1	3.6
77	4.9	0.6	0.3	2.5
82	2.0	0.2	0.9	0.7

The Minuit-Simplex and the Minuit-Migrad programs [8] were used. As the starting data, arbitrary but reasonable values of the parameters were assumed. The values of the integral in eqn (6) were evaluated numerically with the GAUSS method using the CERN library program.[9] The results obtained are collected in table 1. As examples several plots of t_{calc} against t_{exp} are shown in fig. 2.
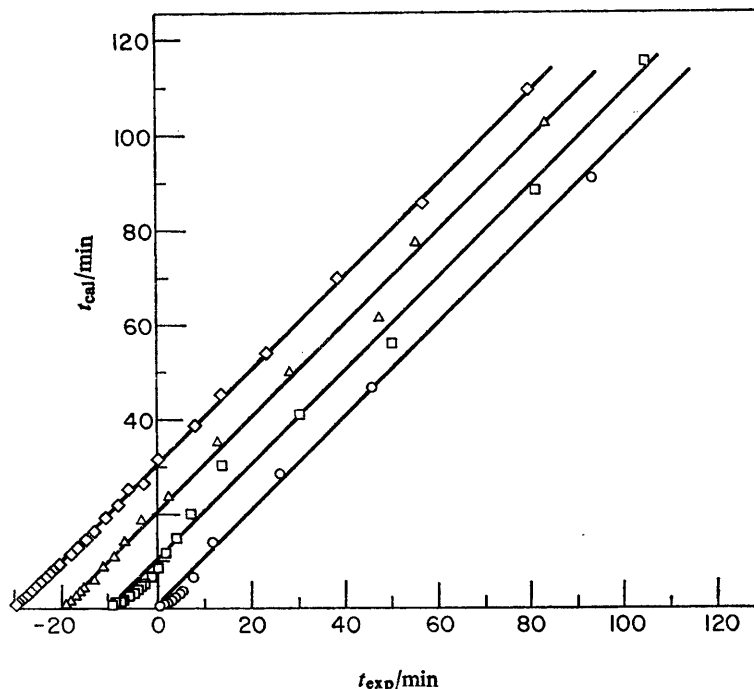
FIG. 2.—Results of fitting selected kinetic data (see fig. 1) by the proposed kinetic equation. In order to distinguish amongst the plots, the experimental points for samples exchanged in 43, 59 and 82 % are shifted by 10, 20 and 30 min, respectively. Percentage of exchanged cations $\diamondsuit$, 82; $\triangle$, 59; $\square$, 43; $\bigcirc$, 0.

DISCUSSION

PHYSICAL MEANING OF PROPOSED KINETIC EQUATION

Let us consider the physical meaning of eqn (6) and its particular parameters. According to the assumptions under which this equation has been derived, it is valid for a uniform surface model with induced heterogeneity. In reality, it is difficult to assess the origins of surface heterogeneity. Thus, the proposed equation can satisfactorily describe even the adsorption processes occurring on a heterogeneous surface. A good illustration of such a situation is the Elovich equation, derivation of which can be based either on the homogeneous surface model or on the heterogeneous surface model.[7]

The surface coverage fraction θ, knowledge of which is necessary to test this equation, was estimated by finding the ratio of the adsorbate amount on the surface at a given moment (q) to the maximum adsorbate amount which was adsorbed on the surface under the given experimental conditions after a long period (q_m).[1] The usefulness of such a defined surface coverage fraction was shown previously.[4]

The parameter γ indicates the degree to which the activation energy of adsorption increases in the course of adsorption. Thus, the physical sense of this parameter can be interpreted as a definite measure of the heterogeneous character of the surface.

The parameter K is a pressure dependent rate constant for the adsorption process comprising the collision frequency, condensation coefficient and activation energy of adsorption for a bare surface. The numerical value of K is difficult to interpret because many different factors have influence on it. This parameter, therefore, can be treated only relatively and does not give much information about the adsorption mechanism.

The parameter n taken together with the term $(1-\theta)$ denotes the probability of attaining a vacant surface site, or a group of surface sites, by a gas molecule when it is being adsorbed. The numerical value of this parameter, in a simple conception, gives information about how many active sites are involved in a single act of adsorption.[7, 13] When one molecule of adsorbate eliminates only one active site the rate of adsorption is proportional to $(1-\theta)$. Therefore, n is equal to unity. When a single act of adsorption incapacitates several adjacent sites, the probability function is lower than $(1-\theta)$. Although the chance of any site being vacant is $(1-\theta)$, the chance that sites next to an unoccupied site are themselves unoccupied is effectively equal to $(1-\theta)^n$, where n denotes the average number of sites involved in the act of adsorption. Such a picture of adsorption might be expected either when several parts of the dissociated molecule remain on adjacent sites or several molecules are being adsorbed on adjacent sites with simultaneous association. When n is lower than unity the probability function is $>(1-\theta)$. This case can be explained by assuming that the site creation takes place during adsorption or that the adsorption is accompanied by surface chemical processes which set free the sites previously incapacitated by the adsorbed molecules. The case when n has only a figurative meaning obviously cannot be excluded.

APPLICATION OF PROPOSED KINETIC EQUATION

In this paper the application of a general form of isothermal rate equation of adsorption and its particular case in a form of the Elovich equation has been shown on the base of kinetic data concerning the but-1-ene+zeolite NaH-Y system. These data cannot be satisfactorily described by either the Elovich equation, considering the presence of discontinuities in the q against $\log t$ plots, or by eqn (1). Eqn (1) fits the experimental data considered in ref. (3) and (4) perfectly, despite the fact that these data cause discontinuities in the Elovich plots. The inapplicability of eqn (1) to the experimental data discussed here, suggests that the origin of breaks in the Elovich plots for these data are different from those described in ref. (3) and (4).

In our previous series of papers [5, 10-12] the but-1-ene+zeolite NaH-Y system was discussed thoroughly. As a result, there is no doubt that different chemical processes take place in this system while but-1-ene is in contact with zeolite. The occurrence of surface chemical processes in the gas–solid system might be yet another reason for the appearance of breaks in the Elovich plots.

The results collected in table 1 and shown in fig. 2 prove that the proposed rate equation is in a form, [eqn. (6)], which satisfactorily describes, in most cases, the discussed experimental data. The less satisfactory results obtained for samples ion exchanged at 9.5 and 12 % will be discussed later.

The most interesting information results from analysis of the values of parameter n collected in table 1. As can be seen, n decreases with the degree of exchange from 2.5, for unexchanged zeolite, to ~ 0.1, for 68 % exchanged zeolite, and after that increases

to ~1 for 82 % exchanged zeolite. According to the previous observations for parameter n it is expected that on unexchanged zeolite associative adsorption of but-1-ene takes place (dissociative adsorption is experimentally excluded),[5] on 68 % exchanged zeolite chemical processes should occur effectively and on zeolite with a higher extent of exchange the rate of adsorption is proportional to $(1-\theta)$.

Several authors [14-16] agree that oligomerization of but-1-ene take place on unexchanged zeolite. In our previous paper the oligomerization of but-1-ene was confirmed experimentally.[11] The value 2.5 for parameter n for unexchanged zeolite agrees, therefore, with the concept of oligomerization and allows one to expect mostly dimers [14] and trimers of but-1-ene on the NaH-Y zeolite.

In ref. (5) it was shown that the chemical transformations of but-1-ene occurred with maximum yield on 68 % exchanged NaH-Y zeolite. The minimum value of parameter n for this sample agrees well with this. The increase in parameter n for samples exchanged to a higher extent reflects the decrease in the catalytic activity of these samples.[5]

The values of pressure dependent rate constant K changes almost regularly with the exchange degree. Consider the expression $K = K'(p)\exp(-E_0/RT)$ presented earlier, and assume that the variation in $K'(p)$ is negligible with respect to that of the exponential term, one should expect that the character of the rate constant changes reflect the activation energy of adsorption (E_0) variations for a bare surface.

Let us evaluate quantitatively E_0 changes by comparing the highest and lowest values of parameter K. Inserting the proper values we obtain:

$$\frac{K_1}{K_2} = \frac{K'(p)\exp-(E_{01}/RT)}{K'(p)\exp-(E_{02}/RT)} = \frac{46.9}{0.2}. \tag{7}$$

From this equation it is easy to show that $E_{0_2}-E_{0_1} \simeq 13 \text{ kJ mol}^{-1}$ at room temperature.

From the well known relationship between activation energy of desorption (E_d) and activation energy of adsorption (E_a); $E_d = E_a+q$, where q denotes heat of adsorption, one can see that the highest possible value of E_a in an exothermic process is equal to E_d. In our previous paper [10] it was shown that all surface species formed during the adsorption had activation energy of desorption values falling into the interval ~29 to ~79 kJ mol^{-1} for a highly covered surface. Therefore, the difference between the lowest and highest activation energies of adsorption (E_a) should be ~50 kJ mol^{-1} in a crude approximation. If we take into account that, on unexchanged zeolite, only species with the lowest activation energy of desorption exist and on the 82 % exchanged zeolite there is a mixture of all surface species with various activation energies of desorption,[5, 10] then the variation in the activation energy of adsorption evaluated from eqn (7) seems reasonable.

The parameter γ reflects changes in activation energy of adsorption during adsorption. The low value of γ for unexchanged zeolite indicates the weak heterogeneity of this sample. This agrees with the previous suggestion [5] that only one kind of active centre should be expected on Na-Y zeolite. The values of γ for the other samples are nearly the same except for the 82 % exchanged sample, which is interesting in the light of earlier considerations.[5] In ref. (5) a sudden decrease in catalytic activity of the high exchanged samples was observed. The explanation for this assumed a limitation of active centres involved in the process of adsorption for these samples. An alternative explanation assuming a great energy barrier cannot be fully excluded. Since the value of the γ parameter is low, arguments based on a high energy barrier would not be appropriate; hence, the formerly proposed [5] limitation of active centres would seem more applicable.

Finally, we discuss the less satisfactory results obtained for some samples, namely with 9.5 and 12 % exchanged cations. This might be due to a sudden change in catalytic property of the zeolite samples [5] with these degrees of exchange. This makes the system very complicated from the kinetic point of view, and as a result eqn (6) is useless in these cases.

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