Title	KINETICS OF ADSORPTION FROM LIQUID MIXTURES ON HETEROGENEOUS SOLID SURFACES
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 26(3), 155-162
Issue Date	1979-02
Doc URL	https://hdl.handle.net/2115/25051
Type	departmental bulletin paper
File Information	26(3)_P155-162.pdf

J. Res. Inst. Catalysis Hokkasdo Univ., Vol. 26 No. 2, pp. 155 to 162 (1978)

KINETICS OF ADSORPTION FROM LIQUID MIXTURES ON HETEROGENEOUS SOLID SURFACES

By

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(Received August 31, 1978)

Abstract

A new approach to the kinetics of adsorption from ideal and non-ideal binary and multicomponent liquid mixtures on heterogeneous solid surfaces is proposed. The equilibrium adsorption isotherms, obtained from the rate equations, are discussed in detail. The adsorption isotherm obtained for ideal binary liquid mixtures and heterogeneous solid surfaces is compared with experimental data.

Introduction

The fundamental law of adsorption kinetics, defining the sorption rate $\mathrm{d}n/\mathrm{d}t$ (n is the number of adsorbed molecules at the time t), is a sum of three contributions deriving from adsorption, desorption and diffusion.[1~3] After a long enough time the diffusion contribution in the sorption rate equations becomes negligible.[2] Then, at the boundary case, when $\mathrm{d}n/\mathrm{d}t=0$, the equations of equilibrium adsorption isotherms may be derived. These equations permitting us to verify the kinetic results.

The present paper deals with the kinetics of adsorption from liquid mixtures on solid surfaces, and especially with the equations of equilibrium adsorption isotherms for heterogeneous surfaces resulting from the kinetic formulation. Throughout it is assumed that adsorption and desorption are slow compared to diffusion. This approach may be considered as a first step towards a theory of the adsorption kinetics from liquid mixtures on heterogeneous solid surfaces, which has not been yet considered. In the first section of this paper the adsorption kinetics on homogeneous solid surfaces will be discussed, and in the second, the energetic heterogeneity of the adsorbent surface will be taken into account. In the two last sections this approach will be generalized to non-ideal liquid mixtures and multicom-

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ponent liquid mixtures. All considerations concern liquid mixtures of non-electrolytes.

The generalization of our kinetic equations to that taking into account the diffusion effects is straight forward. The effect of diffusion on sorption kinetics can be introduced by considering that the concentration of a given component in the solution zone immediately next to the interface changes with time. Thus, the concentration of a given component in the bulk phase, appearing in our kinetic relationships, should be replaced by the actual concentration of this component. The analytical and integral equations for the actual concentration of a given component have been already discussed.[1,2,4]

Kinetics of adsorption from ideal binary liquid mixtures on homogeneous surfaces

Let us consider monolayer adsorption of a mixture "1–2" on a homogeneous solid surface and neglect the interactions in the adsorbed and bulk phases. Each molecule adsorbs on a well-defined site in which the molecular area is assumed to be identical for both types of molecules. This assumption occurs frequently in the adsorption theory of liquid mixtures.[5,6] In the case of adsorption from liquid mixtures on solids, the monolayer is always complete. Thus, if one molecule of the 1-*st* component adsorbs, then simultaneously one molecule of the 2-*nd* component desorbs. For such processes the differential equations of adsorption kinetics may be written as follows:

$$\frac{\mathrm{d}y_1}{\mathrm{d}t}=k^{\mathrm{a}}_{12}x_1y_2-k^{\mathrm{d}}_{12}x_2y_1\,, \tag{1 a}$$

$$\frac{\mathrm{d}y_2}{\mathrm{d}t}=k^{\mathrm{a}}_{21}x_2y_1-k^{\mathrm{d}}_{21}x_1y_2\,. \tag{1 b}$$

In the above x_i and y_i $(i=1,2)$ are the mole fractions of the i-th component in the bulk phase and adsorbed phase, respectively; $x_1+x_2=1$ and $y_1+y_2=1$. From (1 a) and (1 b) it follows that

$$k^{\mathrm{a}}_{12}=k^{\mathrm{d}}_{21} \tag{2}$$

and

$$k^{\mathrm{a}}_{21}=k^{\mathrm{d}}_{12}\,. \tag{3}$$

For the rate constants we write

$$k^{\mathrm{a}}_{ij}=K^{\mathrm{a}}_{ij}\exp\left(-E^{\mathrm{a}}_{ij}/RT\right) \tag{4 a}$$

and

$$k^{\mathrm{d}}_{ij}=K^{\mathrm{d}}_{ij}\exp\left(-E^{\mathrm{d}}_{ij}/RT\right) \qquad \text{for} \quad i\neq j\,. \tag{4 b}$$

E^{a}_{ij} is the difference between the activation energies of component i and of component j. E^{d}_{ij} is defined analogously. At equilibrium, *i. e.*, when $\mathrm{d}y_1/\mathrm{d}t = 0$, Eq. (1 a) becomes

$$\frac{y_1 x_2}{y_2 x_1} = k^{\mathrm{a}}_{12}/k^{\mathrm{d}}_{12} \tag{5}$$

From (5) one obtains

$$y_1 = \frac{k_{12} x_{12}}{1 + k_{12} x_{12}}, \tag{6}$$

where

$$k_{12} = k^{\mathrm{a}}_{12}/k^{\mathrm{d}}_{12} = (K^{\mathrm{a}}_{12}/K^{\mathrm{d}}_{12}) \exp{(E_{12}/RT)} \tag{7}$$

and $x_{12} = x_1/x_2$. In Eq. (7) E_{12} denotes the difference between the adsorption energies of the components "1" and "2". For the component "2" and adsorption isotherm, analogous to Eq. (6), may be derived:

$$y_2 = \frac{k_{21} x_{21}}{1 + k_{21} x_{21}}, \tag{8}$$

where $x_{21} = 1/x_{12}$ and $k_{21} = 1/k_{12}$.

Thus, Eq. (1) generates Eqs. (6) and (8), which are well-known in the theory of adsorption from ideal liquid mixtures.[5,6]

Kinetics of adsorption from ideal binary liquid mixtures on heterogeneous surfaces

Let us consider the adsorption of component "1" from an ideal liquid mixture "1-2" on an energetically heterogeneous surface. Let Y_1 denote the mole fraction of component "1" in the adsorbed phase. Then

$$Y_1 = \sum_{l=1}^{L} h_l y_{1l} \tag{9}$$

where y_{1l} denotes the mole fraction of component "1" on the l-th surface patch. If M_l denotes the number of adsorption sites on the l-th surface patch and $M = \sum_{l=1}^{L} M_l$, then $h_l = M_l/M$. For an energetically heterogeneous solid surface Eq. (1 a) assumes the form

$$\frac{\mathrm{d}Y_1}{\mathrm{d}t} = \sum_{l=1}^{L} h_l \frac{\mathrm{d}y_{1l}}{\mathrm{d}t} = x_1 \sum_{l=1}^{L} k^{\mathrm{a}}_{12,l} y_{2l} h_l - x_2 \sum_{l=1}^{L} k^{\mathrm{d}}_{12,l} y_{1l} h_l\,. \tag{10}$$

Using an approximation, which has been introduced by Wojciechowski *et al.*[7,8] in the adsorption kinetics of gases on solids, *i. e.*,

$$\sum_{l=1}^{L} k^{\mathrm{a}}_{12,l}\, y_{2l}\, h_l = \bar{k}^{\mathrm{a}}_{12}\, Y_2^{m_1+1} \tag{11 a}$$

$$\sum_{l=1}^{L} k^{\mathrm{d}}_{12,l}\, y_{1l}\, h_l = \bar{k}^{\mathrm{d}}_{12}\, Y_1^{m_1+1} \tag{11 b}$$

where $m_1 \geqslant 0$ is a free parameter, we get

$$\frac{\mathrm{d}Y_1}{\mathrm{d}t} = \bar{k}^{\mathrm{a}}_{12}\, x_1\, Y_2^{m_1+1} - \bar{k}^{\mathrm{d}}_{12}\, x_2\, Y_1^{m_1+1} \tag{12}$$

In the above

$$\bar{k}^{\mathrm{a}}_{12} = K^{\mathrm{a}}_{12} \exp\left(-\bar{E}^{\mathrm{a}}_{12}/RT\right) \tag{13 a}$$

and

$$\bar{k}^{\mathrm{d}}_{12} = K^{\mathrm{d}}_{12} \exp\left(-\bar{E}^{\mathrm{d}}_{12}/RT\right) \tag{13 b}$$

where $\bar{E}^{\mathrm{a}}_{12}$ and $\bar{E}^{\mathrm{d}}_{12}$ are some complex type of average values of E^{a}_{12} and E^{d}_{12}. Eq. (12) generates the following relationship

$$(Y_1/Y_2)^{m_1+1} = \bar{k}_{12}\, x_{12} \tag{14}$$

with $\bar{k}_{12} = \bar{k}^{\mathrm{a}}_{12}/\bar{k}^{\mathrm{d}}_{12}$, which gives a new adsorption isotherm:

$$Y_1 = \frac{c_{12}(x_{12})^{r_1}}{1 + c_{12}(x_{12})^{r_1}} \tag{15}$$

In the above $r_1 = (m_1+1)^{-1}$ and $c_{12} = (\bar{k}_{12})^{r_1}$. Eq. (15) may be considered as a combination of the Langmuir and Freundich adsorption isotherms. This type of isotherm has been proposed to describe the adsorption of gases on solids by Sips[9] and recently by Bering and Serpinsky.[10]

Kinetics of adsorption from non-ideal binary liquid mixtures

Assuming non-ideality of the bulk phase and ideality of the adsorbed phase, the differential equations (1 a) and (10) may be expressed by:

$$\frac{\mathrm{d}y_1}{\mathrm{d}t} = k^{\mathrm{a}}_{12}\, a_1 y_2 - k^{\mathrm{d}}_{12}\, a_2 y_1 \tag{16}$$

and

$$\frac{\mathrm{d}Y_1}{\mathrm{d}t} = a_1 \sum_{l=1}^{L} k^{\mathrm{a}}_{12,l}\, y_{2l}\, h_l - a_2 \sum_{l=1}^{L} k^{\mathrm{d}}_{12,l}\, y_{1l}\, h_l \tag{17}$$

where a_i $(i=1, 2)$ is the activity of the i-th component in the bulk phase. Applying similar transformations as in the preceding sections, from Eqs. (16) and (17) we have

$$y_1=\frac{k_{12}a_{12}}{1+k_{12}a_{12}} \tag{18}$$

and

$$Y_1=\frac{c_{12}(a_{12})^{r_1}}{1+c_{12}(a_{12})^{r_1}} \tag{19}$$

In the above $a_{12}=a_1/a_2$ and $a_i=f_i\cdot x_i$ $(i=1, 2)$, where f_i is the activity coefficient of the i-th component. In the case of regular solution, we have

$$\ln(f_1/f_2)=\beta(1-2x_1) \quad \text{where} \quad \beta<2 \text{ is a constant.} \tag{20}$$

Combination of Eqs. (19) and (20) gives

$$Y_1=\frac{c_{12}(x_{12})^{r_1}\exp[\beta r_1(1-2x_1)]}{1+c_{12}(x_{12})^{r_1}\exp[\beta r_1(1-2x_1)]} \tag{21}$$

or

$$\ln\frac{Y_1}{1-Y_1}=\ln c_{12}+r_1\ln x_{12}+\beta r_1(1-2x_1) \tag{22}$$

Eq. (21) contains three unknown parameters: c_{12}, r_1 and β, which may be evaluated from experimental data by means of Eq. (22).

Kinetics of adsorption from multicomponent liquid mixtures

Let us consider an n-component ideal liquid mixture. Let the adsorption ehergy of the n-th component is smallest. Then, the adsorption mechanism may be represented by the series of quasichemical reactions between a molecule of the i-th component $(i=1, 2, \cdots, n-1)$ and a molecule of the n-th component, *i. e.*

$$(i)_\mathrm{b}+(n)_\mathrm{a} \rightleftharpoons (i)_\mathrm{a}+(n)_\mathrm{b} \tag{23}$$

where the symbols (i) and (n) denote molecules of the components "i" and "n", respectively; the subscript "b" and "a" refer to the bulk and adsorbed phases, respectively. The kinetic equations describing rates of these reactions may be written in the form:

$$\frac{\mathrm{d}y_i}{\mathrm{d}t}=k_{in}^{\mathrm{a}}x_iy_n-k_{in}^{\mathrm{d}}x_ny_i \qquad \text{for} \quad i=1, 2, \cdots, n-1 \tag{24}$$

At the equilibrium, *i. e.*, $\mathrm{d}y_i/\mathrm{d}t=0$ we have

$$y_{in}=k_{in}\cdot x_{in} \qquad \text{for} \quad i=1, 2, \cdots, n-1 \tag{25}$$

and

$$y_n^{-1}\sum_{i=1}^{n-1} y_i = (1-y_n)/y_n = \sum_{i=1}^{n-1} k_{in}\,x_{in} \tag{26}$$

Eq. (26) gives

$$y_n = \frac{1}{1+\sum_{i=1}^{n-1} k_{in}\,x_{in}} \tag{27}$$

Combining Eqs. (27) and (25) we obtain

$$y_i = \frac{k_{in}\,x_{in}}{1+\sum_{j=1}^{n-1} k_{jn}\,x_{jn}} \qquad \text{for} \quad i=1,2,\cdots,n-1 \tag{28}$$

In the case of kinetics of adsorption from multicomponent liquid mixtures on heterogeneous solid surfaces we will use the approximation analogous as in Eq. (11) (see Appendix). Then,

$$\frac{\mathrm{d}Y_i}{\mathrm{d}t} = \bar{k}^{\mathrm{a}}_{in}\,x_i\,Y_n^{m_i+1} - \bar{k}^{\mathrm{d}}_{in}\,x_n\,Y_i^{m_i+1}$$

$$\text{for} \quad i=1,2,\cdots,n-1 \text{ and } m_i \geqslant 0 \tag{29}$$

Eq. (29) generates the important relationship:

$$(Y_{in})^{m_i+1} = \bar{k}_{in}\,x_{in} \tag{30}$$

or

$$Y_{in} = c_{in}(x_{in})^{r_i} \tag{31}$$

For similar components "*i*" and "*j*", the exponents $r_i = r_j = r$, and the ratio of Y_i and Y_j is equal to:

$$Y_{ij} = c_{ij}\,x_{ij}^{\,r} \qquad \text{for} \quad i \neq j \tag{32}$$

or

$$\ln Y_{ij} = \ln c_{ij} + r \ln x_{ij} \tag{33}$$

However, the mole fraction Y_i is given by

$$Y_i = \frac{c_{in}(x_{in})^{r_i}}{1+\sum_{j=1}^{n-1} c_{jn}(x_{jn})^{r_j}} \tag{34}$$

Eq. (15) is the special case of Eq. (34). Replacing in the above equations the ratio x_{in} by a_{in} we obtain the analogous expression for adsorption kinetics from non-ideal liquid mixtures.

Applications

The adsorption isotherm (15) has been applied to describe three adsorption systems: benzene-1, 2-dichloroethane (system "1"), benzene-cyclohexane (system "2") and acetone-1, 2-dichloroethane (system "3") on glass beads at 299.5 K; the first compound in these systems denotes the component "1". The experimental isotherms N_1, measured for small values of x_1 ($x_1 < 0.01$), were approximated by the following linear form of Eq. (15):

$$\ln \frac{N_1}{N_m - N_1} = \ln c_{12} + r_1 \ln x_{12} \tag{35}$$

where $N_1 = N_m \cdot Y_1$ and N_m is the total number of molecules in the monolayer. The parameters of Eq. (35) were calculated numerically applying the best-fit procedure. In Table 1 the parameters r_1, c_{12}, N_m and the sum of squares of deviations of experimental isotherms from theoretical ones are summarized. In Table 1 the average values of $\bar{E}_{12}$ are also given; they have been calculated from the following equation:

$$\bar{E}_{12} = (RT/r_1) \ln c_{12} - \ln (K^{d}_{12}/K^{a}_{12}) = (RT/r_1) \ln c_{12} \tag{36}$$

Summing up, it can be seen from Table 1 that Eq. (35) well approximates the investigated experimental data. This equation has been obtained from Eq. (12); for that reason Eq. (12) should also give good agreement with the experimental data.

TABLE 1. Parameters of adsorption calculated according to Eq. (35)

Adsorption system	r_1	c_{12}	$N_m \cdot 10^4$ mol/g	E_{12} kcal/mol	Sum of squares of deviations$\cdot 10^2$
1	0.911	26.25	1.6	2.12	1.16
2	0.774	20.74	2.9	2.32	2.72
3	0.822	22.54	1.9	2.24	0.88

Appendix

In equations (9) and (10) the summation may be replaced by integration. Then, the distribution function of differences of adsorption energies, $E_{12} = E^{d}_{12} - E^{a}_{12}$, may be introduced; this function is normalized to unity. Such approach to the equilibrium adsorption from binary liquid mixtures has been also used.[11,12] However, the generalization of Eq. (24) to heterogeneous solid surfaces is possible by means of $(n-1)$-dimensional distribution function, which depends upon $(n-1)$ variables : E_{1n}, E_{2n}, $\cdots$, $E_{n-1,n}$. The mathematical considerations are formally identical with that for adsorption of $(n-1)$-component gas mixtures on heterogeneous solid surfaces.13~17)

Acknowledgement

This research was supported by Polish Academy of Sciences, Problem No. 03.10.

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