Thermochimica Acta, 68 (1983) 113–119
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

AN APPROACH TO THE KINETICS OF WATER DESORPTION FROM A-ZEOLITES. PART III. THERMODESORPTION OF COMPLEXES WITH NON-UNIFORM ACTIVATION ENERGIES *

VERA DONDUR and DUŠAN VUČELIĆ

Institute of General and Physical Chemistry, Institute of Physical Chemistry, Faculty of Sciences and Mathematics, Belgrade University, P.O. Box 551, Belgrade (Yugoslavia)

(Received 5 April 1983)

ABSTRACT

The distribution of activation energy within corresponding complexes was used in integral methods of non-isothermal kinetics. Qualitatively satisfactory agreement was obtained between the theoretical and experimental DTG results for exponential energy activation distribution.

INTRODUCTION

In previous papers [1,2], the impossibility of direct application of various thermokinetic methods on complex systems such as water–zeolite was presented. In this case it is necessary to establish the real model with all elementary complexes and all existing inter-equilibrium states. On the basis of experimental results, it is evident that water on zeolites can be described as three or four independent water–zeolite complexes depending on the valency of the counterions. It was possible to obtain theoretical values for the kinetic parameters, by applying integral thermokinetic methods (Satava–Sestak [3]) to the thermodesorption of every particular complex. Agreement with experimental values was not very high.

Improvement of theoretical kinetics calculation

It has already been mentioned in a previous paper [2] that the independence of the energy of activation on the degree of coverage [$E_i(\theta) = \text{const.}$] can be a source of discrepancy between theoretical and experimental results.

---

* This paper was presented in part at The Second European Symposium on Thermal Analysis, Aberdeen, 1981.

0040-6031/83/$03.00

It is logical to assume that during thermodesorption, changes in the number of molecules within the complex are followed by energy interaction changes which correspond to an activation energy dependence on the degree of coverage $[E_i(\theta) = f_i(\theta)]$. Due to the small number of molecules in corresponding complexes, $E_i(\theta)$ can vary significantly with θ.

The form of $E_i(\theta)$ is not known. The most commonly used forms are: linear, exponential, hyperbolic and logarithmic [4,5]. All these functions were added to the computer program described in a previous paper [2]. Numerical coefficients were chosen to give the best fit between experimental and theoretical DTG or DSC curves. Computer plotting of the exponential and hyperbolic distribution for a hypothetical model with a pre-exponential factor of 10^5 s^{-1} are presented in Fig. 1. The shape of the peak depends

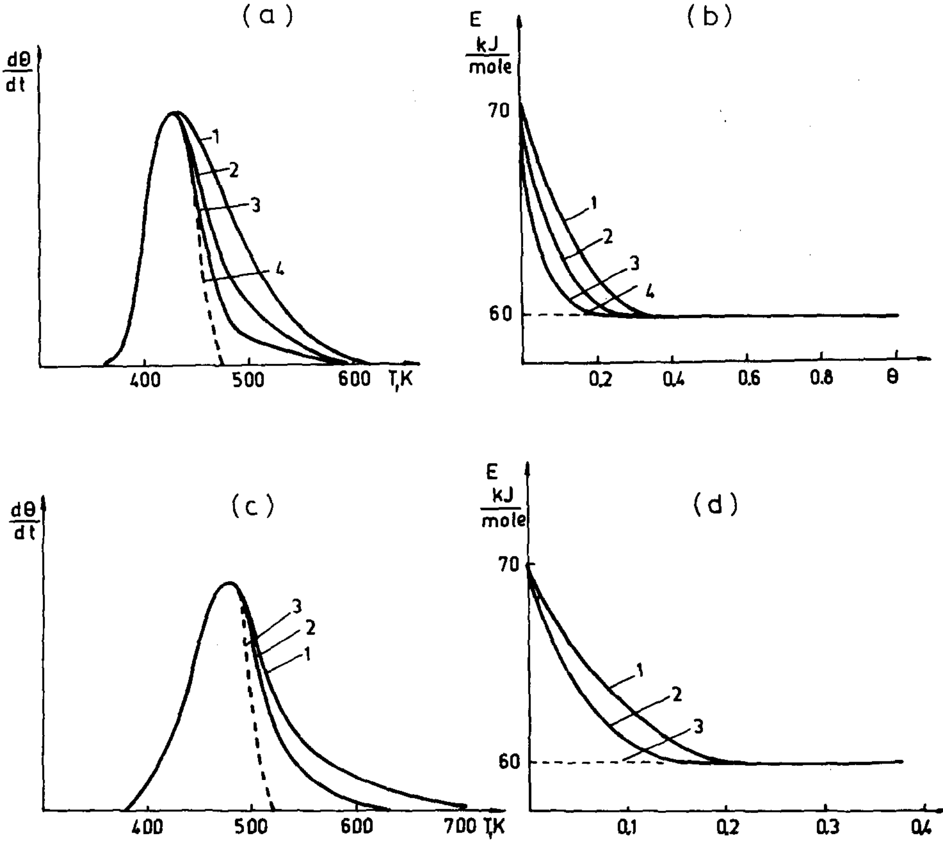

Fig. 1. Influence of the numerical coefficients in the function $E(\theta)$ on the peak shape in thermodesorption. (a) and (b), Exponential form, $E(\theta) = \bar{E} + a\exp(-b\theta)$: 1, $E_1(\theta) = 59.5 + 12.5\exp(-10\theta)$; 2, $E_2(\theta) = 59.5 + 12.5\exp(-30\theta)$; 3, $E_3(\theta) = 59.5 + 12.5\exp(-40\theta)$; 4, $E(\theta)$ = const. = 59.5 kJ mole^{-1}. (c) and (d), Hyperbolic form $E(\theta) = \bar{E} + a/b + \theta$: 1, $E_1(\theta)$ = const. = 59.7 kJ mole^{-1}; 2, $E_2(\theta) = 59.7 + 15/\theta + 10^{-3}$; 3, $E_3(\theta) = 59 + 50/\theta + 10^{-3}$. - - - - - -, Homogeneous surface.

significantly on the parameters of the function. It is obvious that the peaks that correspond to a heterogeneous surface are always wider than the one corresponding to a homogeneous surface as shown in Fig. 1. Similar changes in the shape of the thermodesorption peak occur if the activation energy is a linear function of the degree of coverage.

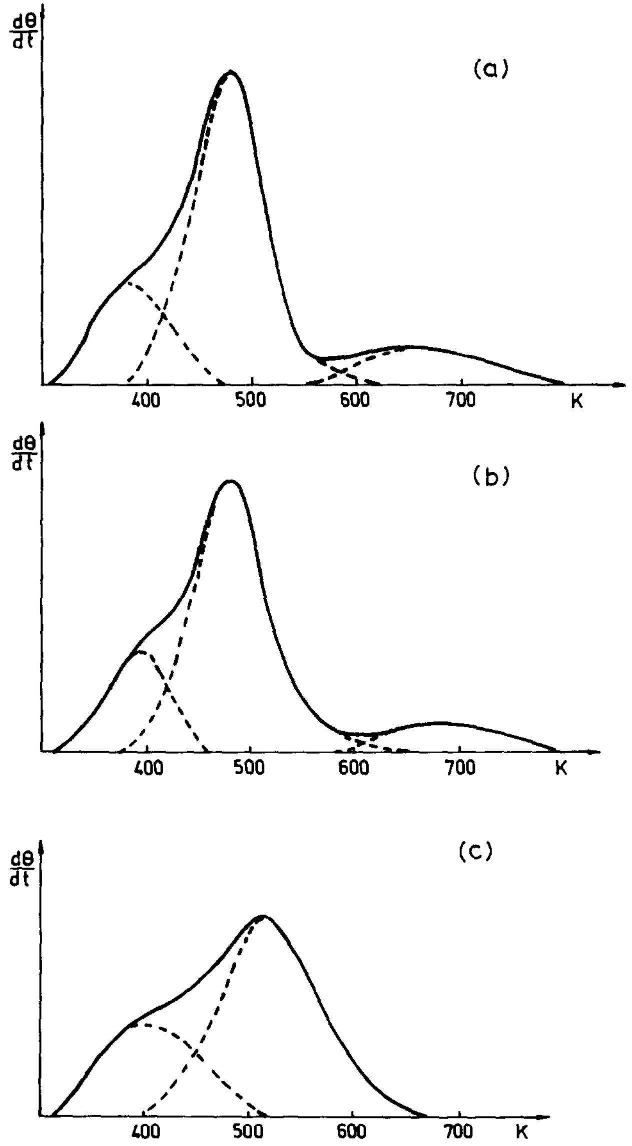

Fig. 2. Resolution of the complex desorption process for A-zeolites with monovalent counterions into elementary reactions. (a) LiA; (b) NaA; (c) KA. - - - - - -, Elementary desorption processes, $E_i(\theta) = \bar{E}_i + a\exp(-b_i\theta_i)$. ————, Experimentally obtained curves.

EXPERIMENTAL

All experimental details have been described in previous papers [2]. Additional changes concerning the dependence of $E_i(\theta)$ on the degree of coverage were only made in the computer program.

RESULTS AND DISCUSSION

The best computer fittings were obtained with the exponential function $E(\theta)$. In that way the thermal desorption of water from A-zeolites with various counterions can be expressed in the form

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = \sum \frac{A_i}{\beta} \exp\left[-\frac{E_i + a_i \exp(b_i \theta_i)}{RT} \right] \theta_i \qquad (1)$$

where θ is the degree of coverage; θ_i is the degree of coverage of the ith complex; A_i is the pre-exponential factor of the ith complex; E_i is the mean

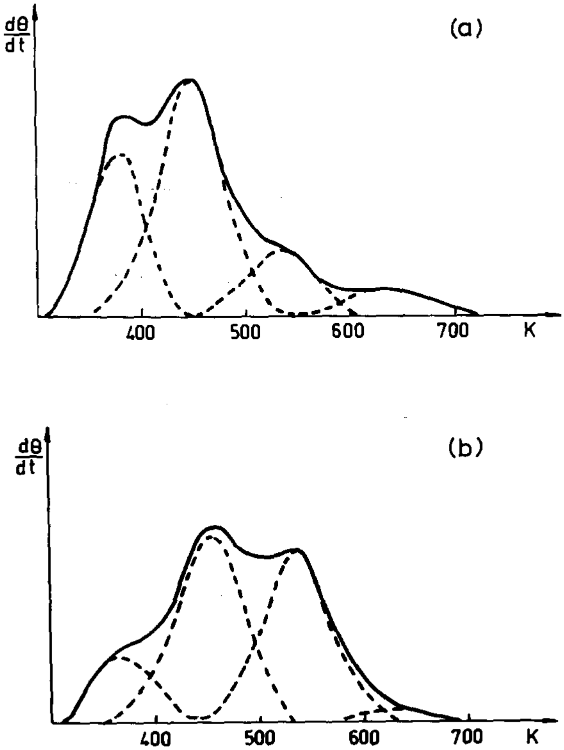

Fig. 3. Resolution of the complex desorption process for A-zeolites with bivalent counterions into elementary reactions. (a) MgA; (b) CaA. ------, Calculated results of elementary desorption processes, $E_i(\theta) = \overline{E}_i + a_i \exp(-b_i \theta_i)$. ———, Experimentally obtained curves.

TABLE 1

Kinetic parameters obtained from computer fitting of eqn. (1)

Zeolite	Elementary process															
	I				II				II′				III			
	$\bar{E}$ (kJ mole^{-1})	a	b	Z (s^{-1})	$\bar{E}$ (kJ mole^{-1})	a	b	Z (s^{-1})	$\bar{E}$ (kJ mole^{-1})	a	b	Z (s^{-1})	$\bar{E}$ (kJ mole^{-1})	a	b	Z (s^{-1})
LiA	43.4	4.2	40	3.2×10^4	60.6	12.6	80	6×10^5					87.8	8.4	10	1.8×10^6
NaA	45.6	4.2	40	3.2×10^4	59.8	12.6	50	6×10^5					90.0	8.4	15	1.8×10^6
KA	43.9	4.2	40	3.2×10^4	56.0	12.6	15	6×10^4								
MgA	43.4	4.2	40	3.2×10^4	56.0	12.6	30	6×10^5	74.8	4.2	40	6×10^5	79.4	8.4	10	2.0×10^6
CaA	43.4	4.2	40	3.2×10^4	56.8	12.6	40	6×10^5	76.0	4.6	40	6×10^5	77.3	8.4	10	1.9×10^6

activation energy of the ith complex; n is the number of complexes, $n = 3$ for zeolites with monovalent counterions, $n = 4$ for bivalent counterions; β is the heating rate.

The agreement between the experimental and theoretical DTG or DSC curves is exceptionally good, see Figs. 2 and 3. The error does not exceed 1%. The application of other functions results in an error increase of up to 5%.

Table 1 presents the values obtained for the elementary desorption kinetic parameters. The parameters are much more realistic. The mean activation energies have reasonable values in comparison with the published heat of desorption. All coefficients have the same values within the corresponding complexes. In all cases dehydration occurs by a first-order reaction.

Unfortunately, although some improvement was accomplished, some disagreements still exist. First, as can be seen from Table 1, the pre-exponential factors are much lower than those predicted by transition-state theory. Second, agreement between the calculated activation energies and differential sorption heats in the whole range of coverage is still not satisfactory, see Fig. 4. Contrary to the middle range of coverage where disagreement does not exceed 5%, for low ($\theta = 0.2$) and high coverages ($\theta = 0.7$) differences can be as much as 15–30%.

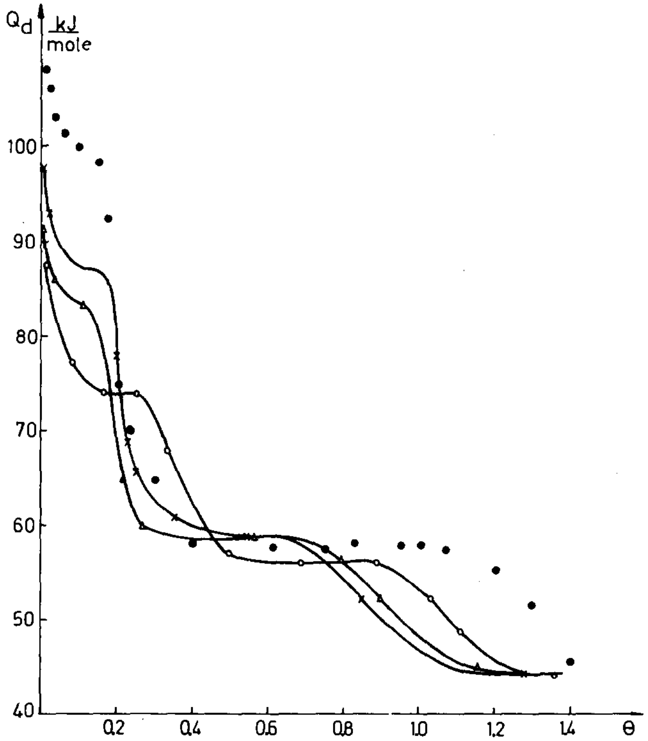

Fig. 4. Desorption heat obtained by calculation for LiA, NaA and MgA zeolites. ●, Experimentally obtained differential heat of adsorption [6]. △, LiA; ×, NaA; ○, MgA.

From Fig. 4 it is obvious that even the best published functions $E(\theta)$, instead of giving excellent resolution (Figs. 2 and 3), cannot lead to complete agreement between theoretical and experimental results.

CONCLUSION

Only the non-isothermal method can be applied in the calculation of kinetic parameters of water desorption from zeolites. However, at present, the best approach can only lead to a qualitative description of the kinetics of water desorption. For a final solution it is necessary to find the right form of the function $E_i(\theta)$ and to solve the problem of the low pre-exponential factor.

REFERENCES

1 V. Dondur and D. Vučelić, Thermochim. Acta, 68 (1983) 91.
2 V. Dondur and D. Vučelić, Thermochim. Acta, 68 (1983) 101.
3 V. Satava and J. Šesták, Anal. Chem., 45 (1973) 154.
4 V.I. Yakerson and V.V. Rozanov, Fiz. Hem. Kinet., Vol. 3, Nauk Dum., Moscow, 1974.
5 V.I. Yakerson, V.V. Rozanov and M.A. Rubinstein, Surf. Sci., 12 (1968) 221.
6 M.M. Dubinin, A.A. Isirikin, G.U. Rahmatkeriev and V.V. Serpinski, Izv. Akad. Nauk SSSR, Ser. Khim., 10 (1972) 1269.