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THERMOGRAVIMETRIC ANALYSIS OF THE DESORPTION OF IODINE FROM ION-EXCHANGE RESINS

B. A. Gorelik, K. M. Djumaev, A. P. Masljukov, G. A. Matiushin and *V. S. Nechitajlo*

ALL-UNION MEDICAL POLYMERS INSTITUTE, MOSCOW, U.S.S.R.

A method was developed for the evaluation of isothermal and dynamic thermogravimetric measurements of the desorption of low molecular weight compounds dissolved in polymers. The method is based on a solution of the non-linear equation for the diffusion of the low molecular weight compounds. Experimental data were analyzed for the desorption of alcohol from PMMA and of iodine from ion-exchange resins, the latter being strongly influenced by the degree of association of the polyiodide in the anions.

Numerous methods have been developed for determination of the permeabilities diffusion coefficients and solubilities of low molecular weight substances in polymers. Among these methods, thermogravimetry is most useful; and it is based on determination of the weight changes of a sample due to sorption or desorption. The data obtained during thermogravimetric measurements are usually represented for a plane sheet (thickness $2l$) using the graphical dependence of sample weight upon the value of $\tau^{1/2}/l$, where τ is the sorption (desorption) time. The slope of the curve (G) must be determined near the point where $\tau \to 0$. The diffusion coefficient D_o of a low molecular weight substance is calculated from the relation $D_o = \frac{\pi}{4} G^2$ [1].

The above method is based on the solution of the diffusion equation, with a constant value of D_o during sorption and a value of the Bio criterion (Bi) of more than 100, where $Bi = \frac{\alpha l}{D_o}$ and α is a parameter accounting for the evaporation of substance from the polymer surface [2].

However, in practice neither of these conditions is fulfilled. The diffusion coefficient is dependent on the concentration of the low molecular weight substance in the polymer (U) and the value of Bi is <100 (see below). Accordingly, in order to describe the desorption process and to determine the value of $D(U)$, it is necessary to solve the non-linear diffusion equation with a finite value of Bi.

This work is devoted to the method of solution of the non-linear diffusion equation in integral form, which allowed calculation of the values of α and $D(U)$ for low molecular weight substances in polymers from the desorption

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curves. It has been shown that the usual method for the determination of D_o, based on the solution of linear diffusion equations (here, $Bi \to \infty$ means that the rate of evaporation of the low molecular weight substance from the polymer surface is much greater than its transport rate in the polymer bulk), gives incorrect values for the initial stage of desorption. The theoretical conclusions have been proved experimentally during investigations of the desorption of (i) ethanol from polymethylmethacrylate and (ii) iodine from ion-exchange resins.

Theory

Let us consider the desorption of a low molecular weight substance from a plane sheet (thickness $2l$). The initial concentration of this substance is U_o. Introducing the dimensionless parameters $X = \frac{Z}{l}$ (the Z axis is perpendicular to the plane of the sheet, and the origin of the coordinates is at the centre of the sheet), $C = \frac{U}{U_o}$ and $t = \frac{D_o \tau}{l^2}$ $(D_o = D/U_o)$ one may obtain the diffusion equations as follows:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} (f(c) \frac{\partial c}{\partial x}) \tag{1}$$

where $f(c) = \frac{D(c)}{D_o}$.

The initial and boundary conditions are presented by the relations:

$$c(x,0) = 1; \ |x| \leqslant 1; \frac{\partial c}{\partial x}(0,t) = 0;$$

$$f(c) \frac{\partial c(l,t)}{\partial x} = -Bi \, C(l,t)$$

Let us introduce the new function

$$p(x,t) = 1 - \int_o^x c(y,t) \, dy \tag{2}$$

where

$$p(1,t) \equiv p_1(t) = \frac{M_o - M_t}{M_o} \tag{3}$$

is the relative mass loss of the sample (M_o = the initial mass of the low molecular weight substance in the polymer, and $M(t)$ = the mass at time t). It is easy to show that

$$\frac{dp_1}{dt} = Bi\, c\,(1,t) \equiv Bi\, c_1\,(t) \tag{4}$$

Returning to ordinary variables for small values of τ, we obtain

$$p_1\,(\tau) = \frac{\alpha}{l}\,\tau \tag{5}$$

At the same time, using the solution of the linear equation of diffusion (assuming $Bi \to \infty$), we obtain

$$p_1\,(\tau) = \frac{2}{\sqrt{\pi}}\,\frac{\sqrt{D_o\,\tau}}{l} \tag{6}$$

Thus, neglect of the non-infinite magnitude of Bi results in an incorrect description of the desorption process. Indeed, Eq. (5) indicates that the mass loss of the sample in the initial stage is related with parameter α, but not with D_o, as it would be in accordance with Eq. (6).

Analogous derivations for a polymer sample having a cylindrical (7) or spherical (8) form lead to

$$p_1\,(\tau) = 2\,\frac{\alpha}{\rho}\,\tau \tag{7}$$

$$p_1\,(\tau) = 3\,\frac{\alpha}{R}\,\tau \tag{8}$$

where ρ = radius of cylinder, and R = radius of sphere.

In order to determine the diffusion coefficient of a low molecular weight substance in a polymer, one has to perform double integration on Eq. (1), and to obtain the equivalent integral equation:

$$c(x,t) = c_1(t) + \int_1^x f^{-1}(c)\, dy \int_o^y \frac{\partial c}{\partial t}\, dz \tag{9}$$

Introducing Eq. (9) into Eq. (2), it is easy to obtain [3] the relation as follows:

$$p_1(\tau) = \frac{\alpha\tau}{l}\left\{1 - \frac{\sqrt{3}}{3}\left(\frac{\alpha}{D_o}\right)^{1/2}(\alpha\tau) + \frac{(16-9\gamma)^{\alpha}/D_o - \frac{20}{l}}{56}\alpha\tau\right\} \quad (10)$$

where γ is a parameter characterizing the dependence of D upon concentration U. For the case $\tau \to 0$, Eq. (10) results in Eq. (5). The same relation for $p_1(\tau)$ may be derived for cylindrical and spherical specimens.

Thus, using the experimentally obtained relation $p = p_1(\tau)$ for the initial time of desorption, one is able to calculate the values of α, γ and D_o for finite magnitudes of the Bio criterion.

In general, the values of α, γ and D_o depend on the temperature of the sample. Thus, during studies of the desorption of a low molecular weight substance in a polymer at various temperatures, it is possible to investigate the temperature relations for α, γ and D_o, to find the main parameters characterizing these relations (such as E and A in the Arrhenius equation).

Experimental

The non-linear diffusion of low molecular substances in polymers was investigated with PMMA samples containing about 20% of ethanol. The thickness $2l$ of the specimen was l+2 mm. The samples of PMMA were produced by means of radiation polymerization between plane glass sheets. We chose this model object of investigation since ethanol is a readily volatile plasticizer of PMMA and its relative loss during one hour of desorption is a few per cent.

The desorption process was followed with a Perkin-Elmer TgS–2 thermobalance at 353, 373 and 393 K (isothermal regimes), and at heating rates of 1 and 10 deg $\min^{-1}$ dynamic regimes. (The elevated temperatures were chosen because the weight loss at ambient temperature was too small for detection.)

The accuracy of mass determinations was not worse than $5 \cdot 10^{-6}$ g.

Results

It was shown experimentally, that in the initial stage of desorption the absolute loss of mass does not depend on the thickness of the sample, as consistent with Eq. (10). The theoretical curve of desorption calculated with the use of Eq. (10) is in good agreement with the experimental data for the period of desorption up to 3.10^3 s. It is to be emphasized that, even for such a readily volatile plasticizer as ethanol, the value of Bi is smaller than 100 ($Bi = 33.6$). The magnitude of D_0 calculated in accordance with method [1] is proved to be one-third of that arising from Eq. (10).

By means of thermogravimetry, we investigated iodine desorption from several ion-exchange resins containing polyhalogen anions I_n^- ($n = 3$, 5 or 7). The resins used were products of copolymerization of styrene with divinylbenzene.

Our experiments demonstrated that the stucture of the anion I_n^- in the ion-exchange resin significantly affects the kinetics of iodine desorption (Fig. 1). It is seen from Fig. 1 that the initial desorption is a linear function of the elapsed time as emerges from Eq. (8).

The experiments carried out at various temperatures on the desorption of iodine from polyhalogenated resins showed that the value of α increases with elevation of the temperature, and the activation energy of the evaporation of iodine from the resin surface (Ea) is about 3 kcal/mol. The data obtained may be used to predict the storage period of iodine-containing resins.

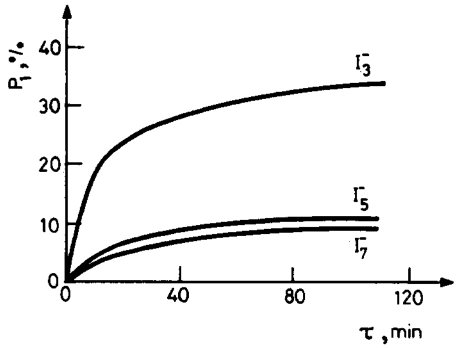

Fig. 1 Dependence of relative mass loss of iodine from ion-exchange resins on time for various polyiodide anions. $T = 373$ K

Conclusions

This work presents a method of solution of the problem of the non-linear diffusion of low molecular weight substances in polymers, taking into consideration a finite value of the Bio criterion. This solution gives a correct description of the desorption process during the initial stage. The method allows the high-accuracy determination of the parameter α, characterizing the evaporation of a low molecular weight substance through a polymer surface into the environment, and the diffusion coefficient D_o.

References

1 K. V. Rogers, Problems of Physics and Chemistry of Solubility of Organic Compounds, Mir, Moscow, 1968, p. 229.

2 A. V. Lykov, Heat Conduction of Nonstationary Processes, Gos. Energ. Isd., Moscow, 1948.

3 K. M. Dyumaev, A. P. Maslyukov, G. A. Matyushin and V. S. Nechitaylo, DAN USSR, 279 (1984) 130.

Zusammenfassung — Eine Methode zur Auswertung isothermer und temperatur-programmierter TG-Messungen der Desorption gelöster niedermolekularer Verbindungen aus Polymeren wurde entwickelt. Die Methode beruht auf der Lösung der nichtlinearen Differentialgleichung für die niedermolekularen Verbindungen. Experimentelle Ergebnisse für die Desorption von Alkohol aus PMMA und von Iod aus Ionenaustauscher-Harzen werden ausgewertet, die letztere wird vom Assoziationsgrad n des Polyiodid-Anions I_n^- erheblich beeinflußt.

РЕЗЮМЕ — Разработан метод оценки изотермических и температурных термогравиметрических измерений десорбции низкомолекулярных соединений, растворенных в полимерах. Метод основан на решении нелинейного уравнения диффузии для низкомолекулярных соединений. Анализ экспериментальных данных проведен на примере десорбции спирта из полиметилметакрилата и иода из ионнообменных смол. В последнем случае процесс сильно затрагивается степенью ассоциации (n) полийодиданионов I_n^-