

The Uptake of Solvent in Blymeric Thin Membranes By a Relaxation-Sorption Coupled Mechanism

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1. Introduction

The diffusion behavior of liquid into polymer has been described by Fick's law, but the departure from Fickian diffusion is frequently found. In this study, 'noble' expressions for the rates of relaxation and sorption are introduced to eliminate these limitations. The relaxation-sorption coupled mechanism model are based on the possibility of contacting liquid molecule and the active site which has the numerical concept of free volume. The concept has an analogy of reaction rate expressed by the possibility of collision with molecules and used in adsorption and reactive extraction etc. The new model simulated by Runge-Kutta method for initial-value problem and Fickian diffusion is caompared with experimental data. The results show that the relaxation-sorption coupled mechanism is able to account well for Fickian and non-Fickian sorption behavior including sigmoid and two-stage. In addition, this model has a chance of expansion to multi-component sorption with ease.

2. Modelling

We assume that the sorption rate is expressed by the product of function of time and the number of activateed site unoccupied by any molecules. The the sorption rate of pure solvent can be expressed as follow:

$$\frac{dn_i}{dt} = K_i(t) (n_i^s - n_i) \quad (1)$$

where n_i is the number of i-component sorbed in polymer. The mole number of activated site in polymer, n_i^s , is determined by the relaxation rate and a initial condition of polymer. $K_i(t)$ is dependent on time and expressed as a function of square root of time by the comparison with Fickian diffusion in the case of rapid relaxation. On the other hand, we assume that the relaxation rate is proportional to the number of occupied site and the number of activatable site. The number of occupied site indicates the possibility to make any sites active. Thus relaxation rate could be expressed by

$$\frac{dn_i^s}{dt} = r_i n_i (n_i^* - n_i^s) \quad (2)$$

where r_i is a proportional constant and n_i^* is mole number of i-component sorbed at equilibrium.

3. Results and Discussion

In case of the rapid relaxation, since the number of activated site instantly reaches the value at equilibrium, n_i^s equals n_i^* and eq. (1) yields

$$\frac{n_i}{n_i^*} = 1 - e^{-k_i t^{1/2}} \quad (3)$$

It can be shown that the sorption amount of solvent must be proportional to the square root of time from Fickian diffusion and in the case of a plane sheet we have

$$k_i \approx \frac{4}{l} \left(\frac{D}{\pi} \right)^{1/2} \quad (4)$$

The diffusivity of benzene in polyurethane determined from Fickian is 8.01×10^{-7} cm²/sec and that from the proposed model is 13.9×10^{-7} cm²/sec. The relaxation-sorption coupled mechanism model has a good agreement in these systems.

In the case of comparable rate of relaxation with that of sorption, eq. (1) and (2) are coupled. This case can be solved by Runge-Kutta method for initial-value problem. The sorption curve obtained from the results is obviously sigmoid in shape. It can be shown by the proposed model that the boundary condition at equilibrium is satisfied and the sigmoid sorption can be explained by the numerical calculation. Diffusivity of pure water in cellulose acetate can be calculated better by relaxation-sorption coupled mechanism model than Fickian diffusion.

References

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