

Swelling and Mechanical Properties of Cellulose Hydrogels. IV. Kinetics of Swelling in Liquid Water

LENNART WESTMAN and TOM LINDSTRÖM, *Swedish Forest Products Research Laboratory, Box 5604, S-114 86, Stockholm, Sweden*

Synopsis

The swelling kinetics of cellulose hydrogels have been studied in experiments where partially dried gels were reswollen to equilibrium in liquid water. The swelling interval studied was from the dry state to 3.6 g water/g dry gel, and the temperature range was from 15 to 65°C. The experimental arrangement and the theoretical analysis was based on the unidimensional, unsteady sorption of water into a swelling sheet. The effects of sheet thickness, temperature and the initial degree of swelling were investigated. The integral sorption curves obtained were sigmoid in shape when plotted as the sorbed amount of water versus the square root of time. These anomalous, non-Fickian sorption curves were analyzed under the assumption that the anomalous behavior is due to a slow establishment of concentration equilibrium at the boundary surfaces. Each sorption curve can then be described by a combination of a mutual diffusion coefficient and a surface relaxation rate. The sigmoidicity of the sorption curves is accordingly determined by the ratio of a characteristic diffusion time to a characteristic surface relaxation time. More classical, Fickian-type behavior is then explained by an increase in this ratio. The experimental sorption curves were found to become more nearly classical as the sheet thickness, the temperature and/or the initial degree of swelling was increased. The relaxation process was found to be associated with a higher apparent activation energy than the diffusion process.

INTRODUCTION

Diffusion of penetrants into polymers is a subject of great interest from both a technological and a fundamental point of view.

Knowledge relating to the transport of water in cellulose is needed for the analysis of many important cellulose processing steps. Examples of such processes are the wetting and drying of cellulose in the manufacture of paper. An understanding of the diffusion process is also essential in many applications of cellulose materials, since the physical properties of cellulose materials are highly dependent on the water content.

The kinetics of sorption of water into cellulose has only received limited attention in the literature and studies have usually been restricted to comparatively low water contents. A review of early papers on the transport and sorption of water in wood and cellulose has been published by Stamm.¹

Hermans² was apparently the first to note the influence of the initial water content on the sorption kinetics when cellulose filaments are brought into contact with liquid water. In carefully dried regenerated cellulose, a sharp, slowly moving boundary develops between a swollen outer part and an interior part. No clear boundary line is observed if the cellulose initially contains more than 6% water.

In a number of papers, News³ has reported on the sorption and desorption kinetics of regenerated cellulose films in moist air. If the change in relative

humidity is small (differential sorption), two-stage behavior is found for sorption curves in which the amount of sorbed water is plotted versus the square root of time. The first stage is linear in such a diagram while the second stage has an inflection point and gives sigmoid curves.

Stamm⁴ studied the steady-state permeation as well as the sorption of liquid water and water vapor into regenerated cellulose films containing 25% of glycerine plasticizer. The sorption curves for liquid water are initially linear and no inflection point is found.

Thus, different types of diffusion behavior have been reported in these studies. However, a common feature is that the calculated diffusion coefficients increase considerably with increasing concentration of water.^{3,4}

In earlier papers in this series,⁵ the preparation, swelling, and mechanical properties of cellulose hydrogels have been investigated. The object of the work presented in this paper was to study the kinetics of the process of reswelling of partially dried gels in liquid water. An attempt is made to analyze sigmoid sorption curves in terms of a combination of classical diffusion and relaxation effects. The results are also discussed in relation to the earlier investigations of the cellulose-water system.

THEORETICAL CONSIDERATIONS

The unsteady, unidimensional diffusion of a diluent, or a solvent, into a swelling plane sheet of infinite area is here considered. The sheet is assumed to be exposed to the diluent on both sides. In this analysis, two reference frames⁶ are used for diffusion fluxes and coefficients, namely the volume-fixed and the polymer-fixed frames.

The diffusion process in the volume-fixed reference frame is described by a single diffusion coefficient. This coefficient is unambiguously defined if there is no overall change of volume on mixing and is then called the mutual diffusion coefficient, D_m . Normal units of lengths are used in this frame. In the polymer-fixed frame, a reference frame is chosen which moves with the local velocity of the polymer.^{7,8} In this case, each section of unit length includes a constant amount of dry polymer. The corresponding diffusion coefficient is denoted D_A^B . By definition, the diffusion coefficient of the polymer, D_B^B , equals zero in this case. In order to derive a relation between D_m and D_A^B , the following considerations were made.

In the polymer-fixed reference frame, the thickness of a swelling sheet is constant and equal to its dry thickness $2l'$. If isotropic swelling is assumed, the volume element (dx', dy', dz') in this frame then equals $\gamma^{-1}(dx, dy, dz)$, where γ is a local expansion factor and unprimed coordinates refer to the volume-fixed frame.

If the flux of solvent per unit area in the thickness direction (the x axis) is denoted J in the volume-fixed frame of reference, then the flux in the polymer-fixed frame will be equal to $J' = \gamma^2 J$. If the concentration of solvent is given as the number of moles per unit total volume, c , then $c' = \gamma^3 c$ and is given as moles per unit dry volume. For each reference frame, Fick's first law can be written

$$J = -D_m \frac{\partial c}{\partial x} \quad (1)$$

$$J' = -D_A^B (\partial c' / \partial x') \quad (2)$$

By combining eqs. (1) and (2) and by use of the relations between the fluxes and concentrations in the two frames, it follows that

$$D_m = \phi_2^{-2/3} D_A^B \quad (3)$$

since γ^2 equals $\phi_2^{-2/3}$, where ϕ_2 denotes the volume fraction of polymer in the mixture. Note that eq. (3) refers to an isotropically swelling sheet. Buckley and Berger⁹ used the relation $D_m = \phi_2^{-2} D_A^B$ when studying the swelling kinetics of a gum butyl vulcanizate in organic solvents. This relation may be derived by analogous reasoning if the sheet is assumed to swell along the x direction only, i.e., if the swelling increase is anisotropic.

In the units defined for the polymer-fixed frame, the diffusion equation

$$\frac{\partial c'}{\partial t} = \frac{\partial}{\partial x'} \left(D_A^B \frac{\partial c'}{\partial x'} \right) \quad (4)$$

can be derived.⁸ Standard mathematical techniques can now be employed to solve this equation, since the coordinates of the boundaries of the sheet do not move with time in the polymer-fixed reference frame. The D_A^B values obtained by solving eq. (4) will give a kind of average value over the concentration interval if D_A^B is a function of the concentration. If the concentration changes from c'_i to c'_∞ , the average $\overline{D_A^B}$ can be assumed to be an integrated mean value,^{10a} i.e.,

$$\overline{D_A^B} = \frac{1}{c'_\infty - c'_i} \int_{c'_i}^{c'_\infty} D_A^B(c') dc' \quad (5)$$

A solution to eq. (4) can now be given that can describe both classical and anomalous diffusion. The term "classical diffusion" is taken to mean here that the boundary conditions are not time dependent and the diffusion coefficient depends only on concentration and temperature. This type of diffusion is also often referred to as Fickian or Case I diffusion. It will be assumed here that anomalous diffusion behavior is due to a change in the boundary conditions with time at a rate corresponding to a relaxation at the surface. This type of boundary condition has been used to explain both sigmoid sorption curves and two-stage behavior^{8,10b,11,12} and can be written

$$t = 0 \quad -l' \leq x' \leq l' \quad c' = c'_i \quad (6)$$

$$t > 0 \quad x' = \pm l' \quad c' = c'_i + (c'_\infty - c'_i)(1 - e^{-\beta' t}) \quad (7)$$

where β' is a surface relaxation rate. Equation (4) can be solved for this boundary condition, which yields⁸

$$\frac{M'_t}{M'_\infty} = \frac{c' - c'_i}{c'_\infty - c'_i} = 1 - a^{-1/2} \exp(-ab^2) \tan(a^{1/2}) - \frac{8}{\Pi^2} \sum_{n=0}^{\infty} \frac{\exp\{-0.25(2n+1)^2 \Pi^2 b^2\}}{(2n+1)^2 [1 - (2n+1)^2 \{0.25 \Pi^2 a^{-1}\}]} \quad (8)$$

where M'_t denotes the total amount of solvent that has diffused into the sheet at time t , c' is averaged over the sheet thickness, and the parameters a and b are given by

$$a = \frac{\beta'(l')^2}{D_A^B} \quad (9)$$

$$b = \left[\frac{D_A^B t}{(l')^2} \right]^{1/2} \quad (10)$$

When $a \rightarrow \infty$, i.e., $\beta' \rightarrow \infty$ or $l' \rightarrow \infty$, it follows from eq. (8) that the sorption curves M_t/M_∞ vs. $t^{1/2}/l'$ will show features characteristic of classical diffusion¹¹: (i) the sorption curves reduce to a single curve in experiments where l' is varied (ii) the curves are initially linear and later concave with respect to the $t^{1/2}/l'$ axis.

For finite values of the parameter a , the sorption curves have an inflection point and are thus sigmoid in shape.

In this context it is appropriate to consider the concept of the Deborah diffusion number $(DEB)_D$ recently introduced by Vrentas et al.^{13,14} for diffusion in amorphous polymers. The Deborah number is defined as the ratio between a mechanical relaxation time and a diffusion time of the system, and can be used to characterize the diffusion type.

A region can be established for $(DEB)_D$ where the diffusion and relaxation times are comparable in magnitude and which is experimentally demonstrated as anomalous diffusion behavior. This region of so called viscoelastic diffusion is located around the glass-transition temperature T_g in the polymer-solvent system¹⁴.

Well above T_g , where the mechanical relaxation time is much shorter than the diffusion time [$(DEB)_D \ll 1$], the diffusion type is classical and referred to as viscous diffusion. Also well below T_g , where $(DEB)_D \gg 1$, the diffusion type is classical and is referred to as elastic diffusion.

It is interesting to note here the similarity in definition between the Deborah diffusion number and the parameter a , which is defined as the ratio between a characteristic diffusion time, $(l')^2/D_A^B$, and a characteristic relaxation time, $(\beta')^{-1}$. Therefore the parameter a is related to $[(DEB)_D]^{-1}$, although differences in the definitions of the diffusion and relaxation times prevent a quantitative comparison between the two numbers.

EXPERIMENTAL

The gels were prepared by crosslinking sodium cellulose xanthate with different amounts of epichlorohydrin followed by regeneration of the cellulose. The preparation, crystallinity, and swelling behavior of these gels have been described in a previous communication.^{5a} The same notation for the gels is also used here, i.e., a figure denoting the amount of epichlorohydrin added (percent w/w on cellulose) and a letter denoting the preparation batch. The degree of swelling, determined by weighing the gels before and after oven drying at 105°C, is given as g water/g dry gel which is abbreviated g/g.

The gels were cut to cylindrical disks and then partially dried to a known degree of swelling over saturated salt solutions or P₂O₅ in desiccators. The gels were then polished with a fine abrasive and the edge surface was covered with a vacuum grease, Apiezon Grease N (Shell Chemicals).

The diameter of the gels was measured with a sliding caliper and the thickness of the disk was measured with the linear variable differential transformer (LVDT) in the viscoelastometer described earlier.^{5b} The dry thickness, $2l'$, was approximately 1 mm unless otherwise stated, and the diameter of completely dried gels was 4.5 mm.

The gels were mounted between two sintered glass filters as shown in Figure

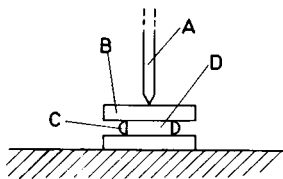


Fig. 1. Experimental method used to obtain swelling kinetic curves (A: rod (weight 41 g) connected to the linear variable differential transformer of the viscoelastometer (Ref. 5b); B: sintered glass filter; C: grease; D: gel disk).

1. Each experiment was started by putting this unit into a large, thermostated bath containing deionized water. The increase in the gel thickness with time was measured using the LVDT in the viscoelastometer.

The role of the grease is to make the edges hydrophobic, reducing the diffusion into the gel phase to the unidimensional case. A number of tests revealed that the grease possessed the desired properties. Partially dried gels did not increase their water content on immersion for 24 h in water if they were totally covered by the grease. In another experiment, the edge of a gel disk was covered and the gel was allowed to partially reswell after which the faces of the disk were also covered with grease. No continued reswelling could be detected when the gel was replaced in water. Thus, under normal experimental conditions the grease prevents water penetration through the edges even when the disk expands. Owing to the small dimensions of the gels and the sticky character of the grease, it was, however, difficult always to guarantee complete coverage of the edge.

In order to ensure that the glass filters contained no entrapped air, they were boiled in deionized water before use. The surfaces to be in contact with the gel were dried using an absorbent paper in order to prevent the swelling process from starting immediately. Glass-filter No. 2 was used with pore diameters of 40–90 μm . No significant change in the sorption behavior was found when filter No. 1 with pore diameters 90–150 μm was used instead.

The increase in the degree of swelling during the experiments was found to be isotropic when the final increases in thickness and diameter were compared. Thus the increase in thickness could be recalculated into a weight gain. The density of swelling water was set to 1.0 g/cm^3 at all temperatures. It has earlier been shown^{5a} that above 0.13 g/g and at 23°C, the partial specific volume of gel water is constant and equal to the specific volume of bulk water. The correctness of the calculated swelling values was checked by a comparison with the weight gain at equilibrium. Normally the values agreed to within $\pm 10\%$.

RESULTS

The ratio M'_t/M'_∞ in eq. (8) can be written

$$\frac{M'_t}{M'_\infty} = \frac{Q_t - Q_i}{Q_\infty - Q_i} \quad (11)$$

where Q denotes the degree of swelling in g/g . Since M'_t/M'_∞ is initially linear versus $t^{1/2}/l'$ if classical diffusion prevails, Q_t will then also be a linear function of $t^{1/2}/l'$.

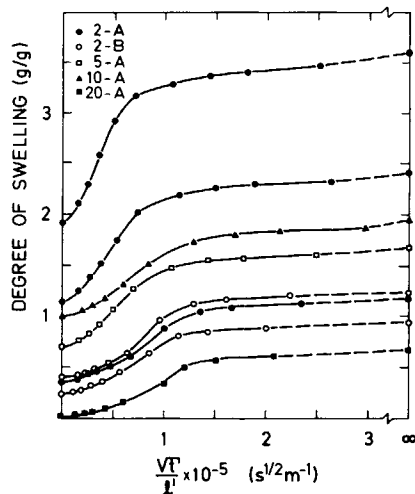


Fig. 2. Some typical sorption curves recorded at 20°C.

Figure 2 shows some representative integral sorption curves recorded at 20°C. The curve shape is obviously sigmoid in character and thus the diffusion type is not classical. The final degrees of swelling for the gels in the sorption curves are equilibrium swelling values, which are lower the drier the gels are when replaced in water. The swelling increment, $(Q_{\infty} - Q_i)$, increases with increasing initial degree of swelling. The equilibrium swelling values are determined by the irreversible drying effect discussed earlier.^{5a} From Figure 2 it can also be concluded that the initial part of the sorption curves gradually becomes more linear and classical in form the higher the initial degree of swelling.

It also appears from Figure 2 that there is no significant effect of the degree of chemical crosslinking (2–20% added epichlorohydrin) provided the sorption curves are compared at the same initial degree of swelling. A closer analysis of the curve shapes shown in Figure 2 and of other sorption curves not presented here confirmed this observation.

When the temperature is increased the sorption curves become more classical in form, as illustrated in Figure 3. At the highest temperature studied, 65°C,

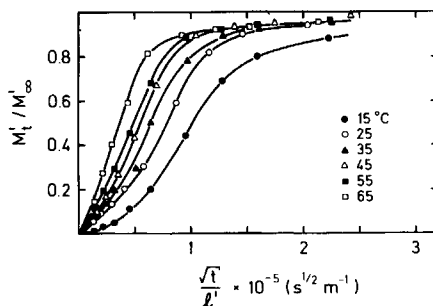


Fig. 3. M_t/M_{∞} as a function of $t^{1/2}/l'$ for gels 2-A at different temperatures. Q increased from 0.40 to 1.12 g/g during the experiments.

the deviation from linearity is very small. The increment ($Q_\infty - Q_i$) was found to be independent of the temperature within the experimental resolution.

The influence of the gel thickness was also investigated, and the results are given in Figure 4. The dry thickness ($2l'$) was varied from 1.08 to 3.6 mm and the curves became less sigmoid and more classical in shape as the thickness was increased.

It can thus be concluded since sigmoid curves are obtained in Figures 2-4 that the sorption behavior is of the anomalous type. However, as the initial degree of swelling, the temperature, and/or the sheet thickness is increased, the diffusion process approaches the classical type.

DISCUSSION

The experimental observations can be discussed in relation to the earlier investigations of the cellulose-water system. This discussion adopts the diffusion-terminology based on the Deborah diffusion number. In addition, the term "Case II diffusion"¹⁵ is useful since it denotes the limiting case of anomalous diffusion below T_g that gives linear curves in diagrams showing the sorbed amount versus time instead of versus the square root of time. The rate of Case II transport is controlled by relaxation processes and this diffusion type can be found if the concentration changes are large.¹⁶ A characteristic feature of case II transport is that a sharp boundary is observed that separates an inner glassy core from a swollen rubbery shell.

At very low water contents in cellulose, either case II diffusion² or elastic diffusion³ is observed, probably depending on the magnitude of the concentration change. At water contents exceeding approximately 6%,^{2,3} the diffusion type approaches the viscoelastic region. The diffusion type is viscoelastic at least up to a water content of 22% at 15°C.³ Stamm⁴ noted that glycerine added to cellulose as plasticizer can further change the diffusion behavior into the viscous type.

It was found for the sorption curves reported in this paper that in general they are not initially linear if plotted versus time. Since, in addition, the sorption curves are not linear versus $t^{1/2}$, it can be concluded that the curves are of the viscoelastic type. Thus the characteristic relaxation and diffusion times are of about the same order of magnitude. News³ also interpreted sigmoid sorption

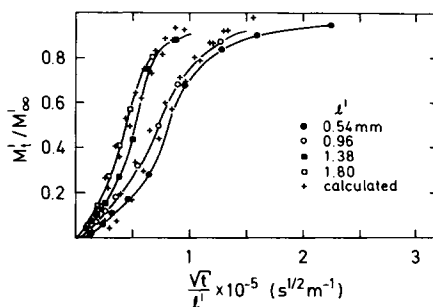


Fig. 4. Thickness dependence of the sorption curves obtained. Gels 2-B at 20°C; half the dry thickness is given in the figure; swelling interval from 0.36 to 1.15 g/g. The calculated points are based on the values given in Table I and the theory outlined in the section Theoretical Considerations.

curves as being related to mechanical creep or relaxation. The experimental data in Figure 2 and 3 on the effects of the initial degree of swelling and temperature on the shape of the sorption curves may thus be interpreted in terms of a gradual transition from viscoelastic to viscous diffusion in regenerated cellulose.

It can be noted here that in the case of semicrystalline polymers, anomalous diffusion behavior is often observed even well above T_g .^{10b,17,18} This is presumably due to the presence of ordered regions in the polymer, which restrict the segmental mobility near the interfaces of the crystallites. Fujita et al.¹⁹ have discussed this effect and concluded that for semicrystalline polymers, e.g., for cellulose, it is difficult to obtain purely viscous diffusion.

In order to analyze the sigmoid curves quantitatively, the approach with a time-dependent surface concentration was adopted. Long and Richman²⁰ have experimentally shown that for the sorption of methyl iodide vapor into polyvinylacetate and cellulose acetate the surface concentration actually slowly varies with time. They interpreted the surface relaxation rate to be a qualitative measure of the rate of stress relaxation.

It must be emphasized that β' is probably not characteristic of a well-defined physical stress relaxation process. If relaxation processes in the bulk of the gels also influence the swelling kinetics, β' can not be interpreted as purely a measure of surface relaxation rate. However, this approach represents a fairly straightforward way of including relaxation effects into the solution to the diffusion equation as was shown in the theoretical section.

As β' is determined in the polymer-fixed reference frame, the same type of relation for the surface concentration as that in eq. (7) does not strictly hold in the volume-fixed reference frame. The interpretation of β' as a surface relaxation rate is, however, not dependent on the frame of reference.

\bar{D}_A^B , β' , and D_m were thus determined from the sorption curves in the following way. Firstly, the experimental M'_t/M'_∞ values were plotted against $\log [t/(l')^2]^{1/2}$. The curve form obtained was then compared with theoretical curves [eq. (8)] showing M'_t/M'_∞ vs. $\log b$ with a as parameter. \bar{D}_A^B was obtained from the horizontal shift between curves agreeing in shape and β' was calculated from the parameter a , which characterizes the curve shape, and the known dry sheet thickness $2l'$.

From the assumption of a time-dependent surface concentration it follows that the curves are expected to become less sigmoid and more classical in form with increasing thickness of the gels since the characteristic diffusion time will then increase while the characteristic surface relaxation time is constant. This corresponds to an increase in the parameter a in eq. (9) and when the thickness of the gel is large, classical diffusion characterized solely by \bar{D}_A^B prevails.

In Figure 4, the sorption curves obtained when l' was varied are compared with the theoretical curves calculated for the \bar{D}_A^B and β' values given in Table I. According to the theory used, \bar{D}_A^B and β' are expected to be independent of l' . β' was also found to be independent of l' within the limits of experimental accuracy, whereas \bar{D}_A^B increased by a factor of 2 within the studied length interval. It can be concluded that the theory at least approximately can describe the change in sorption curves caused by the variation in gel thickness. However, successful curve fitting cannot alone be considered as a proof of the correctness of the assumption of a nonconstant surface concentration.

TABLE I
 Values Used for the Calculated Points in Figure 4

Dry Thickness (mm)	$\overline{D}_A^B \times 10^{10}$ (m ² /s)	$\beta' \times 10^3$ (s ⁻¹)
1.08	0.69	1.2
1.91	0.59	1.0
2.76	1.11	1.2
3.60	1.31	1.4

When the theoretically predicted and the experimentally determined curve shapes were compared, a systematic difference was found near equilibrium where M'_t/M'_∞ increased more slowly with time in the experimental curves than in the theoretical curves. This may be due to the elastic restraints from crosslinks, which probably become appreciable near swelling equilibrium. A two-stage behavior was also indicated, since M'_t/M'_∞ generally increased more rapidly than predicted by theory at shorter times. Due to the large concentration changes, it was difficult to make a clear distinction between the two stages, as was also noted by Newns³ for interval sorption. The difference in the curve shape between the experimental and theoretical curves led to an error in β' estimated to be at least $\pm 35\%$. However, the curve fitting was in general better than that depicted in Figure 4.

The sorption curves yield a \overline{D}_A^B value, which is an average value over the interval $(Q_\infty - Q_i)$ studied. Figure 5 shows that D_A^B varies in a linear fashion with the average $\overline{Q} = (Q_i + Q_\infty)/2$. It is then reasonable to assume that \overline{D}_A^B depends on \overline{Q} in a linear manner which by use of eq. (5) yields

$$\overline{D}_A^B = D_A^B(\overline{Q}) \quad (12)$$

The $\overline{\phi}_2$ value corresponding to \overline{Q} was obtained by assuming volume additivity, which yields

$$\overline{\phi}_2 = (\rho_d \rho_w^{-1} \overline{Q} + 1)^{-1} \quad (13)$$

where ρ_d denotes the density of dry gels,^{5a} which is approximately equal to 1.52 g/cm³, and ρ_w is the density of water.

The mutual diffusion coefficient D_m could then be calculated from \overline{D}_A^B and the corresponding ϕ_2 value by use of eq. (3) since the expansion due to swelling was found to be isotropic.

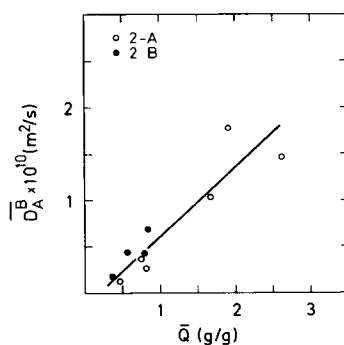


Fig. 5. \overline{D}_A^B as a function of $\overline{Q} = (Q_i + Q_\infty)/2$. Gels 2-A and 2-B at 20°C.

In Figure 6, the D_m and β' values determined from the sorption curves in Figure 3 are shown in an Arrhenius-type diagram. The apparent activation energy was found to be 22 kJ/mol for D_m and 58 kJ/mol for β' . As is also expected from the shape of the curves in Figure 3 and the definition of the parameter a , the relaxation process is thus associated with a higher apparent activation energy than the diffusion process.

In Figures 7 and 8, D_m and β' values determined from sorption curves recorded for gels 2-A and 2-B are shown as a function of $\bar{\phi}_2$. There is some scatter in the data, but it appears as though the dependence of both D_m and β' on $\bar{\phi}_2$ is of the exponential type. β' is more concentration dependent than D_m .

At 20°C and a mean degree of swelling of 1 g/g, β' equals 0.0065 s⁻¹ and D_m equals 1.15 × 10⁻¹⁰ m²/s. The β' value corresponds to a relaxation time of about

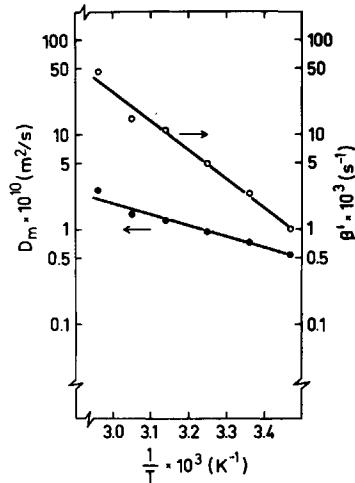


Fig. 6. D_m and β' values determined from the sorption curves in Figure 3 versus the reciprocal of the absolute temperature.

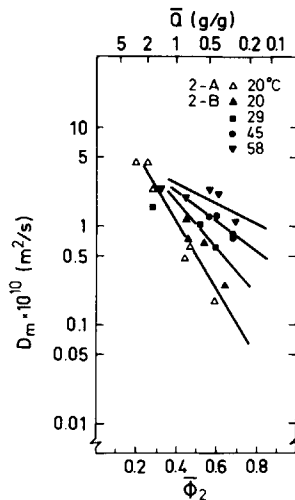


Fig. 7. Concentration dependence and temperature dependence of D_m determined for gels 2-A and 2-B.

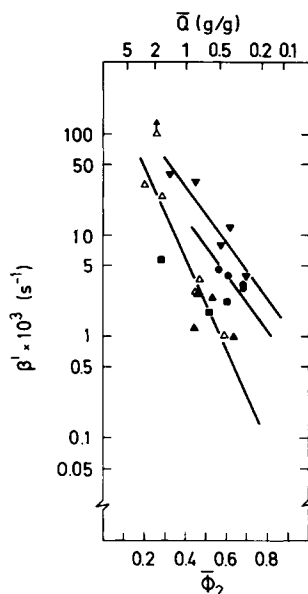


Fig. 8. Concentration dependence and temperature dependence of β' values obtained for gels 2-A and 2-B. The arrow indicates that β' was found to be infinite. Symbols are the same as in Figure 7.

150 s. As can be expected, this relaxation time is shorter the higher the degree of swelling.

D_m is also considerably concentration dependent, although the dependence is less marked at higher temperatures. Furthermore, it is clear from Figure 7 that the apparent activation energy for D_m decreases as the degree of swelling increases.

The point where the activation energy of the diffusion process corresponds to the activation energy of η^{-1} , where η is the viscosity of the penetrant, has been suggested by McGregor⁶ to mark the transfer from "small-pore" to "large-pore" transport. Pores are considered to be "large" if they are very much larger than the average jump distance for diffusion.

From viscosity data for water,²¹ an activation energy of 16 kJ/mol is obtained for η^{-1} as an average value in the temperature interval 15–65°C. From the data in Figure 7, the activation energy of D_m can be estimated to be 16 kJ/mol at a degree of swelling of 1 g/g.

In principle, the data in Figure 7 may be analysed in terms of the free-volume theory of diffusion.^{11,14,22} However, besides the basic problem of converting mutual diffusion coefficients to self diffusion coefficients^{6,22} (it is only in the limit $\phi_2 \rightarrow 1$ that these coefficients have identical values²²), there are other factors that complicate such an analysis. The gels are semicrystalline and the volume fraction of nonpermeable crystallites in the gels depends on the degree of swelling. Furthermore, the gels contain both chemical crosslinks and, probably more important, crosslinks due to secondary bonds which increase in number as the degree of swelling is decreased.^{5b}

The authors are indebted to Dr. Bo Nyström and Dr. Jaan Roots, University of Uppsala, Sweden, for valuable discussions of this paper and to Petter Kolseth at this laboratory for valuable comments on the manuscript.

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Received September 23, 1980

Accepted January 23, 1981