Mutual and self-diffusion of water in gelatin: experimental measurement and predictive test of free-volume theory

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Self-diffusion of water in unhardened photographic gelatin is measured by pulsed-gradient n.m.r. spectroscopy. Mutual diffusion and activity of water in hardened and unhardened gelatin is measured by step-change gravimetric sorption methods. Predictions of mutual diffusion from the self-diffusion data and published thermodynamic data by using the Vrentas–Duda theory are in agreement with the measured mutual diffusivities. Hardening (i.e. crosslinking) of the gelatin reduces the diffusivity as predicted by an extension to the Vrentas–Duda theory. The water activity increases with crosslinking.

(Keywords: gelatin; self-diffusion; free volume)

INTRODUCTION

The drying of thin film coatings is a key stage in the production of products ranging from adhesive tapes to photographic film. Because of the large expense associated with industrial dryers, optimization of the dryer design and its utilization is imperative, and a simulation of the drying process by computer-aided numerical methods is required. To utilize such computational methods, a complete understanding of the thermodynamic and transport properties of the system of interest is necessary. The most important coating solution system for photographic and graphic arts production is gelatin and water.

Measurements were made on an inert ossein gelatin. The self-diffusion coefficient as a function of concentration and temperature is determined by the pulse-gradient n.m.r. spectroscopic method, while the mutual diffusivity and vapour–liquid equilibria are determined by gravimetric sorption methods. The self-diffusion data, along with known physical property data for water and gelatin, were used to successfully correlate the gelatin–water data with the well-known Vrentas–Duda free-volume diffusion theory. Using known thermodynamic data for water in gelatin, the mutual diffusivity as a function of concentration and temperature is predicted from the self-diffusion data alone. The mutual diffusivities measured by the sorption methods are in agreement with the predictions from the self-diffusion data, confirming the predictive capabilities of the Vrentas–Duda theory, even for a thermodynamically complex system such as water and gelatin.

The mutual diffusivity of water was determined in a formalin-hardened or crosslinked gelatin, in addition to the unhardened gelatin. As expected from diffusion theory, the crosslinking hindered the diffusion of the water in gelatin.

EXPERIMENTAL

Materials

Samples for the experimental determination of the self-diffusivity and mutual diffusivity were prepared using inert ossein photographic gelatin, type 669, manufactured by Croda Colloids Ltd, Widnes, UK. The weight-average molecular weight, as measured by low-angle laser light scattering (l.a.l.l.s.), for this material is 2.13×10^4 ($\pm 8\%$). The polydispersity (M_w/M_n) of the gelatin measured by gel permeation chromatography (g.p.c.) with poly(ethylene oxide) and poly(ethylene glycol) standards (Polymer Laboratories, Shrewsbury, UK), is 1.82.

The hardened samples were prepared from the type 669 gelatin granules by first dispersing a 5 wt% solution of the granules in distilled water and soaking overnight. The soaked granules were then stirred and heated at 40°C until they melted into solution. A 10 wt% dilution of formalin (i.e. a 40% aqueous solution of formaldehyde) was prepared and 30 g of this were added to 1000 g of the 5 wt% gelatin solution. The hardened samples that

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were prepared from this solution were dried and then allowed to stand for 1 week at room temperature to permit them to cure fully.

N.m.r./p.g.s.e. diffusion measurements

Pulsed-gradient spin echo (p.g.s.e.) measurements of the diffusion of the solvent (water) were performed. This method is an elaboration of the nuclear magnetic resonance (n.m.r.) spin–spin relaxation experiment in which the amplitude of the spin echo of a diffusing species at resonance is decreased in the presence of a pair of calibrated magnetic-field-gradient pulses. The diffusion coefficient is obtained from the echo attenuation as a joint function of the magnitude, duration, and separation of the gradient pulses, as described in the literature[1]. This method has been in use by the Akron group since 1977 and was employed here as described earlier, with continuous refinements[2–4]. The resonance frequency was 33 MHz, the time between the 90 and 180 deg r.f. pulses, and also between the gradient pulses, was 25 ms, and the magnitude of the gradient pulses was $1.25\,\mathrm{T\,m^{-1}}$; echo attenuation by a factor of at least 15 was obtained with gradient pulses of up to 3 ms in duration. All measurements were made in the proton resonance without Fourier transform, at 15.2 and 40.2°C. Data acquisition required signal averaging, typically of 8 echoes per data point, with 10–15 data points constituting a complete echo attenuation measurement. Primary interpretation of the echo attenuation data was performed by off-line computer programs, as described elsewhere[5,6].

The precision of our p.g.s.e. diffusion measurements in any single-component liquid is approximately 2–4%. Most of this uncertainty originates in the calibration of the applied pulsed field gradient; the reproducibility may be made arbitrarily small, e.g. by signal averaging.

Step-change sorption experiment

The mutual diffusivity, D, of the water in the gelatin was determined by a step-change sorption experiment, utilizing an experimental apparatus similar to that described by Duda *et al.*[7]. The experimental procedures and analyses are as described in detail by Vrentas *et al.*[8]. Experiments were conducted at 40°C and consequently the saturation pressure of water is 7.407×10^{3} Pa (55.56 mmHg). The tables presented below show the initial weight fraction of water and the final weight fraction after the experiment. The mutual binary diffusion coefficient is determined from the slope of the curve of the weight gain *versus* the square root of the time. The weight fraction of solvent (water) is known at the beginning and end of each step change in solvent vapour pressure, so the activity of the water, a_1, which is the ratio of the solvent vapour pressure, P_1, to the pure solvent saturation pressure at the system temperature, $P_{1,\mathrm{sat}}$, is obtained directly as a consequence of the diffusivity measurement itself.

RESULTS AND DISCUSSION

The self-diffusion coefficients, D_1, were first measured by the p.g.s.e. n.m.r. technique as described above. The measured values of D_1 at 15.2 and 40.2°C are shown in *Table 1*.

At these temperatures it was impossible to measure the self-diffusion coefficient in samples below ~35 wt% water. The reason for this is not because of a particular low diffusion coefficient, but in fact a very short spin–spin relaxation time for water, which prevented a spin-echo from being observed and hence precluded any diffusion measurement from being attempted.

Table 1 Values of the self diffusivities measured by the p.g.s.e. n.m.r. technique

Water content (weight fraction) w_1	Self-diffusion coefficient, D_1 ($\mathrm{cm^2\,s^{-1}}$) 15.2°C	40.2°C
0.374	1.122×10^{-6}	2.951×10^{-6}
0.574	4.074×10^{-6}	8.912×10^{-6}
0.654	5.888×10^{-6}	1.230×10^{-5}
0.676	6.607×10^{-6}	1.349×10^{-5}
0.822	1.023×10^{-5}	1.950×10^{-5}
0.920	1.318×10^{-5}	2.511×10^{-5}

Because the discrete self-diffusion data points over the limited range of weight fraction (0.374–0.920) and temperature (15.2–40.2°C) are of limited utility in computational or other analysis, it is best to fit the data to a suitable theoretical framework to allow not only interpolation, but also extrapolation and prediction beyond the measurement range that is available. The well-known Vrentas–Duda free-volume theory has been used extensively to successfully describe the self-diffusion of solvents in polymers, and also allows a prediction of the mutual diffusivity, D, that is actually needed in the analysis of transport phenomenon, from the self-diffusivity, D_1, and a knowledge of the solvent activity. This theory and its development has been extensively described elsewhere by Vrentas, Duda and their collaborators[9–12] and others. For a binary system of one solvent (component 1), in this case water, and one polymer (component 2), in this case gelatin, the Vrentas–Duda theory describes the self-diffusivity in terms of the free-volume parameters by the following equation:

$$D_1 = D_{01}\exp\left(\frac{-(w_1\hat{V}_1^* + w_2\xi\hat{V}_2^*)}{\hat{V}_{\mathrm{FH}}/\gamma}\right) \tag{1}$$

where γ is the so-called overlap factor for free-volume, w_1 is the mass fraction of solvent, w_2 is the mass fraction of polymer, ξ is the ratio of critical volumes of the jumping units of solvent and polymer, $\hat{V}_{\mathrm{FH}}$ is the average hole free-volume per gram of mixture, and $\hat{V}_1^*$ and $\hat{V}_2^*$ are the specific critical hole free-volumes required for a jump of solvent and polymer, respectively. The pre-exponential term, D_{01}, is in general temperature dependent but in this case we will assume it is a constant. The free-volume expression for the ratio of the average hole free-volume per gram to the free-volume overlap factor is

$$\frac{\hat{V}_{\mathrm{FH}}}{\gamma} = \frac{K_{11}}{\gamma}w_1(K_{21} - T_{g1} + T) + \frac{K_{12}}{\gamma}w_2(K_{22} - T_{g2} + T) \tag{2}$$

where K_{11} and K_{21} are the free-volume parameters for the solvent, K_{12} and K_{22} are the free-volume parameters for the polymer, T_{g1} is the glass transition temperature of the solvent, and T_{g2} is the glass transition temperature of the polymer.

One of the strengths of the Vrentas–Duda theory is that all of the parameters are not 'fitted' from the diffusion data, but are independently determined, based on other

Table 2 Parameters used in self-diffusion correlation and mutual prediction for the water/gelatin system

Parameter (units)	Value	Note
$\frac{K_{11}}{\gamma}$ (cm^3 g^{-1} K^{-1})	2.33×10^{-3}	Ref. 13
$K_{21}-T_{g1}$ (K)	-156.9	Ref. 13
$\hat{V}_1^*$ (cm^3 g^{-1})	1.071	Ref. 13
D_{01} (cm^2 s^{-1})	5.354×10^{-4}	$w_1=1$, average value
$\frac{K_{12}}{\gamma}$ (cm^3 g^{-1} K^{-1})	3.8185x10^{-4}	By 3-parameter regression
$K_{22}-T_{g2}$ (K)	-145.036	By 3-parameter regression
$\xi\hat{V}_2^*$ (cm^3 g^{-1})	0.8256	By 3-parameter regression
$\hat{V}_2$ (cm^3 g^{-1})	$(1/1.42)=0.7042$	Ref. 18
χ		Polynomial fit in water volume fraction, with equation (9)
c_0	-2.795	
c_1	31.422	
c_2	-107.331	
c_3	176.995	
c_4	-143.09	
c_5	45.379	

information. For the case of water in gelatin, we already knew the free volume parameters for water, namely K_{11}/γ, $(K_{21}-T_{g1})$, and $\hat{V}_1^*$ (Ni[13]) (see *Table 2*). At the limit for pure water where $w_1\rightarrow1$ the expressions above simplify to

$$D_1=D_{01}\exp\left(\frac{-\gamma\hat{V}_1^*/K_{11}}{K_{21}-T_{g1}+T}\right) \quad (3)$$

Extrapolating from the p.g.s.e. data, we find that at 15.2°C, $D_1(w_1\rightarrow1)\approx1.579\times10^{-5}$ cm^2 s^{-1} and at 40.2°C, $D_1(w_1\rightarrow1)\approx2.897\times10^{-5}$ cm^2 s^{-1} ($\pm5\%$). Thus, we calculate from the above equation that $D_{01}=5.240\times10^{-4}$ and 5.469×10^{-4} cm^2 s^{-1} at 15.2 and 40.2°C, respectively. In the correlation an average value for this temperature range, namely $D_{01}=5.354\times10^{-4}$ cm^2 s^{-1}, was used (see *Table 2*).

Finally, all that remains to be determined for the self-diffusion correlation are three parameters, namely K_{12}/γ, $(K_{22}-T_{g2})$, and $\xi\hat{V}_2^*$. Three-parameter regression yields values of 3.8185×10^{-4} cm^3 g^{-1} K^{-1}, -145.036 K, and 0.8256 cm^3 g^{-1}, respectively. The curves generated from this correlation of the Vrentas–Duda theory at 15.2°C and 40.2°C are plotted, using the p.g.s.e. measured values, in *Figure 1*. Not only is the correlation quite good, but the numerical values of the parameters seem quite reasonable from a physical point of view.

The Vrentas–Duda theory relates the mutual diffusion coefficient, D, to the self-diffusion coefficient, D_1, according to the following equation[14,15]:

$$D=D_1\frac{\rho_2\hat{V}_2\rho_1}{RT}\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_{T,P} \quad (4)$$

where ρ_1 and ρ_2 are the mass concentrations of the solvent and polymer respectively, μ_1 is the chemical potential of the solvent, $\hat{V}_2$ is the partial specific volume of the polymer, and R is the gas constant. This is a general expression and is not restricted to any thermodynamic theory in particular. For many systems previously studied with the Vrentas–Duda theory, the thermodynamics can be adequately described by the Flory–Huggins theory using the polymer solvent interaction parameter, χ, (i.e. the Flory–Huggins parameter). In these cases and when the polymer molecule is much larger than the solvent molecule, the chemical potential and activity of the solvent are defined by

$$\ln a_1=\ln\left(\frac{p_1}{p_{1,\mathrm{sat}}}\right)=\frac{\mu_1-\mu_{1,0}}{RT}=\ln\phi_1+\phi_2+\chi\phi_2^2 \quad (5)$$

where ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively. It is clear that

$$\phi_1+\phi_2=1$$

and

$$\phi_i=\rho_i\hat{V}_i \quad (6)$$

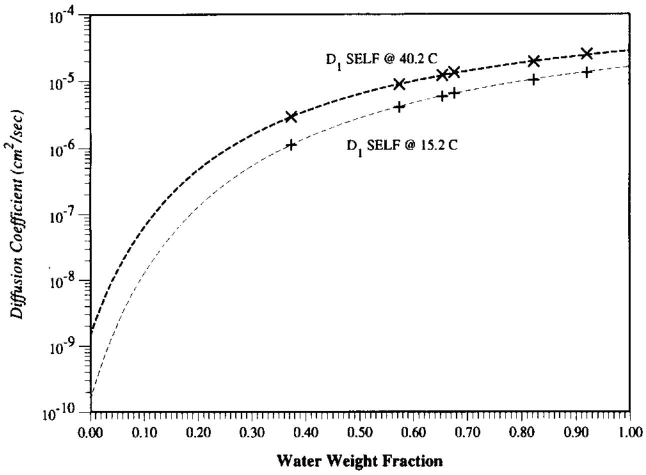

Figure 1 Variation of the self-diffusion coefficient in the water/gelatin system as a function of the water weight fraction: (×) 40.2°C and; (+) 15.2°C

For systems with simple thermodynamics, such as toluene and polystyrene, it is adequate to assume that χ is a constant. In this case, equation (4) simplifies to

$$D=D_1(1-\phi_1)^2(1-2\chi\phi_1) \quad (7)$$

Unfortunately, in the case of water in gelatin, the thermodynamics is considerably more complex due to the highly associative interactions of water with the amino acids that make up the gelatin protein structure. Previously, Bull[16] measured the activity of water in concentrated gelatin samples at 25 and 40°C by sorption methods. Busk[17] measured the Flory–Huggins parameter, χ, for dilute solutions of gelatin in water at 6°C, by a suction-pressure method. The density of the gelatin is 1.42 g cm^{-3} (see *Table 2*)[18], so the Busk activity can be converted to Flory–Huggins parameter values and plotted with the Busk data, as shown in *Figure 2*. Clearly, χ is not a constant parameter for the water/gelatin system. In fact, the strong binding interaction of the water to the gelatin is reflected in the large negative values of χ at low concentrations of water. Simple Flory–Huggins theory does not describe the complex thermodynamics of the water/gelatin system, so the results obtained from equation (7) above cannot be used directly in this case.

Although the Flory–Huggins theory itself does not explain the thermodynamics of the water/gelatin system, *Figure 2* shows that we can use a modified version of this theory to correlate the thermodynamics of this system. As can be seen in this figure, χ has a very strong dependence on concentration but is independent of temperature, with the data measured at 40, 25, and 6°C clearly lying on the same curve. Therefore, we have

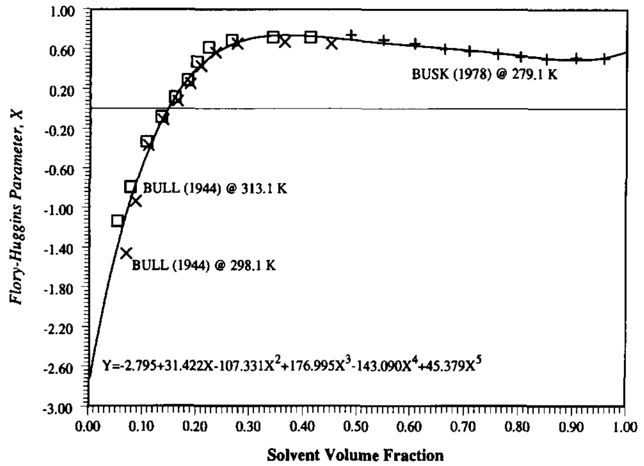

Figure 2 Variation of the Flory–Huggins interaction parameter of the water/gelatin system as a function of the solvent volume fraction: (+) 279.1 K (ref. 17); (×) 298.1 K (ref. 16) and; (□) 313.1 K (ref.16). The fitting of a fifth-order polynomial to the χ data is shown as a continuous line (see text)

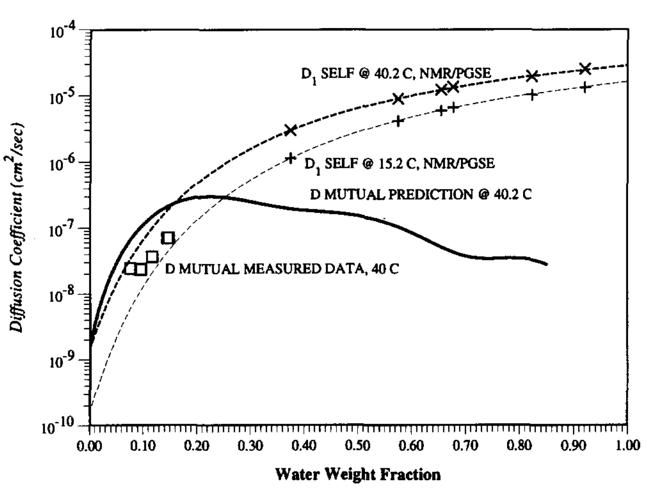

Figure 3 Comparison of mutual and self-diffusion coefficients in the water/gelatin system as a function of the water weight fraction: (×) self, 40.2°C; (+) self, 15.2°C and; (□) mutual measured data, 40°C. The mutual predicted values are shown by the continuous line

correlated the water activity by fitting a fifth-order polynomial in the water volume fraction to the χ data in *Figure 2*. From this correlation we know the chemical potential and activity of the water as a function of concentration and temperature (see *Table 2*).

Now, using the Vrentas–Duda theory of mutual diffusion as in equation (4), and the Flory–Huggins expression of equation (5), but assuming that χ is now a function of concentration, we get the new result:

$$D=D_1(1-\phi_1)^2\left(1-2\phi_1+\phi_1(1-\phi_1)\frac{\partial\chi}{\partial\phi_1}\right) \tag{8}$$

and

$$\chi=\sum_{n=0}^{5} c_n\phi_1^n \tag{9}$$

$$\frac{\partial\chi}{\partial\phi_1}=\sum_{n=1}^{5} c_n n\phi_1^{(n-1)} \tag{10}$$

With the correlated thermodynamic data, and the Vrentas–Duda correlation of the self-diffusion data measured by the p.g.s.e. n.m.r. technique, it is possible to predict the mutual diffusion coefficient using the results from equations (8)–(10). The resulting prediction is the continuous curve shown in *Figure 3* (measured at 40°C). Equation (4), which presents the inner relationship between self diffusion and mutual diffusion, is a very approximate relationship which is, at best, valid only for the range of low solvent concentration. Unfortunately, the concentration region for which this relationship represents a reasonable approximation has never been ascertained. In some cases, this seems to be a reasonable approximation for concentrations up to 80 wt% solvent, while in other cases it seems to break down at concentrations as low as 10 wt% solvent. The derivation of equation (4) incorporates several approximations, including the assumption that the self-diffusion coefficient of the solvent is much greater than the self-diffusion coefficient of the polymer. Although the utilization of this relationship is somewhat precarious, it is the best relationship available in the literature at the present time[19–21].

Because the self-diffusion data obtained from the n.m.r. method did not cover the whole concentration range, and because the thermodynamics for the water/gelatin system is more complex than other solvent/polymer systems studied using the Vrentas–Duda theory, a direct measurement of the mutual diffusion coefficient of the water in the gelatin by the step-change sorption method was performed over the concentration range which was unavailable to the n.m.r. method. The measured mutual diffusivities of water in unhardened gelatin are shown in *Table 3* and are plotted in *Figure 3*. The measured mutual diffusivities are in reasonable agreement with the mutual diffusion curve predicted by the Vrentas–Duda theory using only the limited self-diffusion data and the previously published activity data for water in gelatin. This is an important example of the predictive capability of the Vrentas–Duda theory, because it not only involves an extrapolation in concentration from the measured self-diffusion range, but also the relationship of self-diffusion to mutual diffusion of equation (4) with the complicated thermodynamics of water in gelatin. There are several approximations incorporated in this procedure for prediction of the mutual binary diffusion coefficient from the solvent self-diffusion and the thermodynamics of the system. First of all, as discussed earlier, the relationship relating the mutual and self diffusion coefficients is an approximation which is limited to the region of low water concentration. In addition, the extension of the Flory–Huggins theory to include an interaction parameter which is a function of concentration is a strictly empirical modification of that theory.

Table 3 Values of the mutual diffusivities obtained by step-change sorption measurements for unhardened Croda type 669 gelatin at a sample temperature of 40.2°C

$w_{1,\text{init}}$, mass fr.	$P_{1,\text{init}}$ (mmHg)[a]	$w_{1,\text{final}}$, mass fr.	$P_{1,\text{final}}$ (mmHg)[a]	$w_{1,\text{average}}$ $=w_{1,\text{i}}+0.7$ $(w_{1,\text{f}}-w_{1,\text{i}})$	$D\times10^{-8}$ ($\text{cm}^2\,\text{s}^{-1}$)
0.0632	5.905	0.0834	13.69	0.0773	2.4357
0.0893	5.699	0.0987	17.6	0.0959	2.3542
0.0987	17.6	0.1254	30.17	0.1174	3.6845
0.1352	31.96	0.151	40.07	0.1463	7.0960
0.1254	30.17	0.1583	40.07	0.1484	7.0924

[a] 1 mmHg = 133.322 Pa

Considering these approximations and the precarious procedure of differentiating the polynomial correlation of the interaction parameter with concentration, it is surprising that agreement between the experimental data and the prediction is as good as that shown in *Figure 3*.

The activity data measured in the sorption experiments are presented in *Table 4* and are plotted with the activity data of Bull[16] and Busk[17] in *Figure 4*. The activity of the water when measured here using the Croda type 669 gelatin is in reasonable agreement with the previously measured activity data taken from the literature.

Finally, we used the step-change sorption method to determine the mutual diffusion of water in a hardened gelatin. Hardening is a means of crosslinking the gelatin to increase the toughness and stability of the gelatin layers and is commonly used in the photographic industry[22]. In this study, the Croda type 669 gelatin was hardened using formalin, one of many possible crosslinkers that are commonly used. Vrentas and Vrentas[23] extended the Vrentas–Duda free-volume theory to include the effects of crosslinking on diffusion. They predicted, based on theoretical arguments, that since crosslinking generally decreases the specific volume of the polymer, the diffusion coefficient will decrease with crosslinking (i.e. hardening).

Table 4 Measured activities of water in unhardened Croda type 669 gelatin at a sample temperature of 40°C[a]

T_{DewPoint} (°C)	P_1 (mmHg)[b]	w_1, mass fr.	ϕ_1, vol. fr.	$a_1 = P_1/P_{1,\mathrm{sat}}$
3	5.699	0.0893	0.1186	0.1026
3.5	5.905	0.0632	0.085	0.106
16	13.69	0.0834	0.111	0.246
20	17.6	0.0987	0.1306	0.3168
25	23.86	0.1089	0.144	0.429
29	30.17	0.1254	0.1643	0.543
30	31.96	0.1352	0.177	0.575
34	40.07	0.151	0.186	0.721
34	40.07	0.1583	0.2052	0.7212

[a] $P_{1,\mathrm{sat}}$ for pure water at 40°C = 55.56 mmHg (7.407 × 10^3 Pa)
[b] 1 mmHg = 133.322 Pa

Table 5 Values of the mutual diffusivities obtained by step-change sorption measurements for hardened gelatin at a sample temperature of 40°C

$w_{1,\mathrm{init}}$, mass fr.	$P_{1,\mathrm{init}}$ (mmHg)[a]	$w_{1,\mathrm{final}}$, mass fr.	$P_{1,\mathrm{final}}$ (mmHg)[a]	$w_{1,\mathrm{average}} = w_{1,\mathrm{i}} + 0.7\,(w_{1,\mathrm{f}} - w_{1,\mathrm{i}})$	$D \times 10^{-9}$ ($\mathrm{cm^2\,s^{-1}}$)
0	0	0.0748	18.04	0.0524	1.3397
0.0748	18.04	0.1069	31.96	0.0973	3.9226
0.1069	31.96	0.1554	47.27	0.1409	8.9536

[a] 1 mmHg = 133.322 Pa

Table 6 Measured activities of water in hardened gelatin at a sample temperature of 40°C[a]

T_{DewPoint} (°C)	P_1 (mmHg)[b]	w_1, mass fr.	ϕ_1, vol. fr.	$a_1 = P_1/P_{1,\mathrm{sat}}$
20.6	18.04	0.0748	0.0999	0.325
30	31.96	0.1069	0.141	0.575
37	47.27	0.1554	0.2016	0.851

[a] $P_{1,\mathrm{sat}}$ for pure water at 40°C = 55.56 mmHg (7.407 × 10^3 Pa)
[b] 1 mmHg = 133.322 Pa

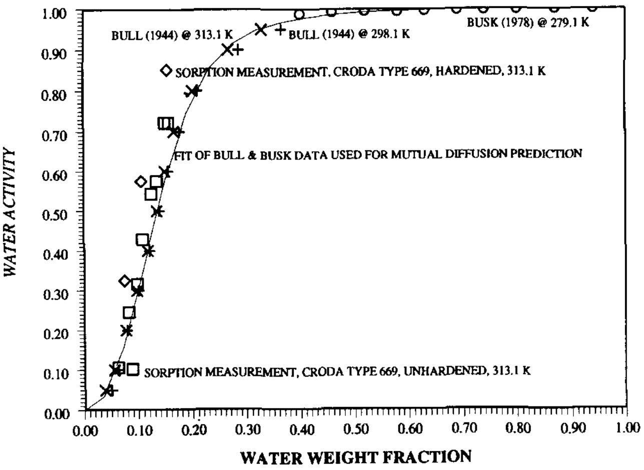

Figure 4 Variation of the water activity parameter of the water/gelatin system as a function of the water weight fraction. The continuous line represents a fourth-order polynomial

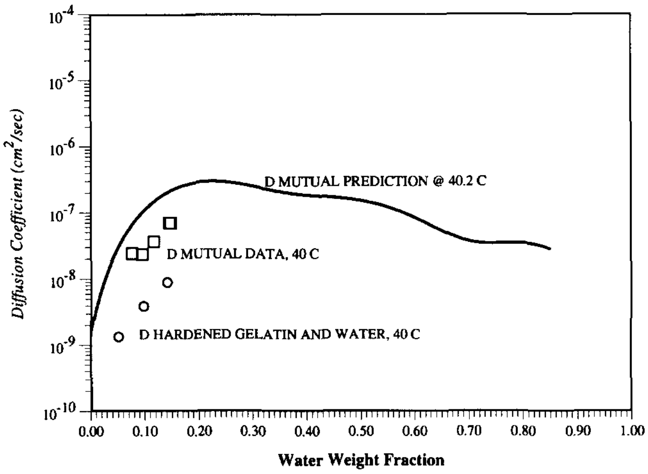

Figure 5 Comparison of the mutual diffusion coefficients in the water/gelatin system, for hardened and unhardened gelatin, as a function of the water weight fraction. The mutual predicted values for *D* at 40.2°C are shown by the continuous line

The measured mutual diffusion coefficients for water in the hardened gelatin are given in *Table 5* and plotted, along with the unhardened data in *Figure 5*, while the corresponding activity data is presented in *Table 6* and shown in *Figure 4*. As the theory predicts, the measured values of the mutual diffusion coefficient in the case of hardened material are less than those for the unhardened gelatin, again, lending credence to the free-volume theory of diffusion. The Flory–Rehner theory[24] for the swelling of crosslinked polymers indicates that the free energy change associated with the swelling of a polymer network consists of two contributions. The first contribution is the ordinary free energy of mixing represented by the Flory–Huggins equation. The second contribution is the elastic free energy change associated with the expansion of the network structure. Consequently, the Flory–Rehner theory predicts that crosslinking will increase the vapour pressure, or the activity, of a water–gelatin solution of a fixed concentration, as observed in this study. An alternative way of viewing this behaviour is that, at a given activity or water vapour pressure, less water will be absorbed into the crosslinked gelatin since it takes energy to swell the network.

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REFERENCES

1 Stejskal, E. O. and Tanner, J. I. *J. Chem. Phys.* 1965, **42**, 288

2 von Meerwall, E. and Ferguson, R. D. *J. Appl. Polym. Sci.* 1979, **23**, 877

3 von Meerwall, E., Burgan, R. D. and Ferguson, R. D. *J. Magn. Reson.* 1979, **34**, 339

4 von Meerwall, E. D., Grigsby, J., Tomich, D. and Van Antwerp, R. *J. Polym. Sci., Polym. Phys. Edn* 1982, **20**, 1037

5 von Meerwall, E. *Comput. Phys. Commun.* 1979, **17**, 309

6 von Meerwall, E. and Ferguson, R. D. *Comput. Phys. Commun.* 1981, **21**, 421. This program has since been substantially enhanced and now operates on MS/DOS and UNIX computers.

7 Duda, J. L., Kimmerly, G. K., Sigelko, W. L. and Vrentas, J. S. *Ind. Eng. Fundament.* 1973, **12**, 133

8 Vrentas, J. S., Duda, J. L. and Ni, Y. C. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 2039

9 Duda, J. L. in 'Devolatilization of Polymers' (Ed. J. A. Biesenberger), Hanser, Munich, 1983, Sect. III, p. 348

10 Vrentas, J. S., Duda, J. L. and Ling, H. C. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 459

11 Vrentas, J. S., Duda, J. L. and Ling, H. C. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 275

12 Vrentas, J. S., Duda, J. L. and Ling, H. C. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 289

13 Ni, L. W. *PhD Thesis* Pennsylvania State University, 1984

14 Duda, J. L. *Pure Appl. Chem.* 1985, **57**, 1681

15 Vrentas, J. S. and Duda, J. L. in 'Encyclopedia of Polymer Science and Engineering' (Eds H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges), Vol. 5, 2nd Edn, Wiley, New York, 1986

16 Bull, H. B. *J. Am. Chem. Soc.* 1944, **66**, 1499

17 Busk, G. C. *PhD Thesis* University of Minnesota, 1978

18 Gelfax, A. 'Series of Useful Facts on all Aspects of Gelatin Quality', Croda Colloids Ltd, Widnes, UK, Sect. 19

19 Vrentas, J. S. and Duda, J. L. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 403

20 Vrentas, J. S. and Duda, J. L. *AIChE J.* 1979, **25**, 1

21 Duda, J. L., Ni, Y. C. and Vrentas, J. S., *Macromolecules* 1979, **12**, 459

22 Burness, D. M. and Pouradier, J. in 'The Theory of the Photographic Process' (Ed. T. H. James), 4th Edn, Macmillan, New York, 1977

23 Vrentas, J. S. and Vrentas, C. M. *J. Appl. Polym. Sci.* 1991, **42**, 1931

24 Flory, P. J. and Rehner, J. R. *J. Phys. Chem.* 1943, **11**, 521