Absorption and desorption of water in rubbers

A. G. Thomas and K. Muniandy*
Tun Abdul Razak Laboratory, MRPRA, Brickendonbury, Hertford, Herts SG13 8NL, England, UK

(Received 21 April 1986; revised 26 September 1986; accepted 13 October 1986)

It is believed that the presence of small amounts of hydrophilic impurities in vulcanized rubbers strongly influence their water absorption and desorption behaviour. These impurities are thought to be responsible for the high water uptake and low diffusion coefficient observed with these rubbers. To test this hypothesis, a model of the absorption and desorption process in such rubbers is proposed and a theory, which invokes the chemical potential gradient of the water as the driving force, is developed. The predictions of the theory are compared with experimental observations for the case of vulcanized *cis*-polyisoprene containing sodium chloride as impurity with satisfactory agreement.

(**Keywords: absorption; desorption; rubber; water; polyisoprene**)

INTRODUCTION

The absorption and desorption of water by vulcanized rubber is of considerable practical importance. Vulcanized rubber articles which are continually in contact with water will, in time, absorb several per cent by weight of water. This absorbed water may significantly alter its physical properties and the product could consequently fail in its application.

Numerous studies have been made on the subject of diffusion of water in polymers[1] and the basic mechanism of water absorption in rubber vulcanizates containing hydrophilic impurities is known[2,3]. For such vulcanizates, the diffusion coefficient D decreases with increasing concentration c[4-7].

A theoretical treatment of the water absorption process of such a vulcanizate has already been reported elsewhere[8]. This paper extends the earlier experimental work and includes experimental and theoretical studies of the desorption process. For the sake of completeness, the theory is presented here again in outline.

In order to study the mechanism of the processes, a model material whose rubber phase contains very little hydrophilic impurities is doped with a known amount of sodium chloride so that the thermodynamic characteristics are well defined.

THEORY OF WATER ABSORPTION AND DESORPTION

Equilibrium water absorption

It is assumed that the absorption of water by rubbers is due to the presence of hydrophilic impurities in them. Consider the case in which a vulcanized rubber sample containing a finely dispersed water soluble impurity is immersed in an aqueous solution of this impurity and allowed to equilibrate. This situation is equivalent thermodynamically to surrounding the sample with an unsaturated vapour at the appropriate pressure. Water diffuses through the rubber phase, in which it is slightly soluble, and forms droplets of solution at the impurity sites. This gives rise to an osmotic pressure gradient between the droplet solution and the external solution in which the rubber is immersed. As a result of this, more water diffuses through the rubber into the impurity droplets. These droplets, assumed spherical, consequently grow in size and deform the rubber surrounding them, the increase in the volume of the droplets being equal to the volume of water present in the droplet solution. Equilibrium water uptake is reached when the osmotic pressure difference between the droplet solution and the external solution in which the rubber is immersed balances the restraining elastic stresses acting on the droplet[3,4]. A schematic diagram of the model is shown in *Figure 1*. Effects due to the surface energy of the liquid/rubber interface will be neglected as the sizes of the droplets, which are usually greater than microns in dimension, are too large for the effects to be significant.

If π_0 is the osmotic pressure of the external salt solution in which the rubber is immersed, π_i the osmotic pressure of the impurity solution in the rubber and p the elastic pressure exerted by the rubber on the impurity droplet, then at equilibrium water uptake

$$\pi_i - \pi_0 = p \qquad (1)$$

This assumes that the rubber acts as a semipermeable membrane permitting the passage of water but not of the relevant dissolved impurities.

The osmotic pressures π_0 and π_i are given by

$$\pi_0 = \frac{c_0 RT}{M_0} \quad \text{and} \quad \pi_i = \frac{c_i RT \rho_w}{(c_w - s)M_i} \qquad (2)$$

---

* Rubber Research Institute of Malaysia, PO Box 10150, 50908 Kuala Lumpur, Malaysia.

0032-3861/87/030408-08$03.00

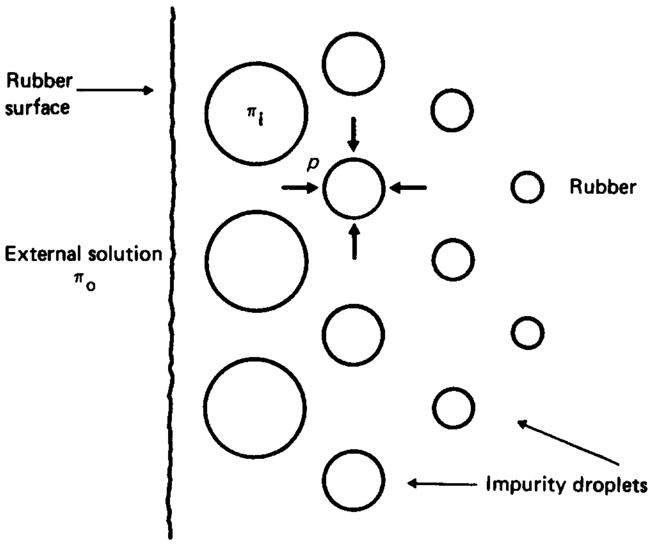

Figure 1 Schematic representation of the model used in the analysis of water absorption and desorption in vulcanized rubber. π_0 and π_i are the osmotic pressures of the external solution and the impurity droplet solution, respectively. p is the elastic stress

where c_0, M_0 are the concentration and molecular weight of the salt in the external solution and c_i, M_i of the impurity in the rubber. c_w is the total concentration of water in the rubber and s the concentration in the rubber phase itself. The concentrations are expressed as mass per unit volume. The molecular weight M_i must be the suitable average if an electrolyte is the impurity, viz. $\frac{1}{2}(M_1+M_2)$ where M_1 and M_2 are the weights of the two ions. The density of water is denoted by ρ_w, R is the gas constant and T the absolute temperature.

The concentration of water, s, present in the rubber phase is given by means of Raoult's and Henry's laws as

$$s=s_0\frac{1}{1+\frac{M_w\rho_i}{M_i\rho_w}\left(\frac{1}{(\lambda^3-1)}\right)} \tag{3}$$

where s_0 is the mass of water per unit volume that rubber containing no impurities will absorb when immersed in pure water and λ is the ratio of the radius of the deformed and undeformed droplet. M_w is the molecular weight of water and ρ_i the density of impurity.

If the vulcanizate is assumed to obey the statistical theory of rubberlike elasticity having an elastic stored energy function of the form,

$$W=(G/2)(\lambda_1^2+\lambda_2^2+\lambda_3^2-3)$$

where λ_1, λ_2 and λ_3 are the principal extension ratios and G the elastic shear modulus of the rubber, then the pressure p required to enlarge a spherical hole in an infinite block of rubber is given by[9]

$$p=\frac{G}{2}\left(5-\frac{4}{\lambda}-\frac{1}{\lambda^4}\right) \tag{4}$$

Substituting equations (2) and (4) into equation (1) and rearranging yields

$$\frac{c_0}{M_0}=\frac{c_i\rho_w}{(c_w-s)M_i}-\frac{G}{2RT}\left(5-\frac{4}{\lambda}-\frac{1}{\lambda^4}\right) \tag{5}$$

Equation (5) represents the condition that has to be satisfied when the rubber attains equilibrium water uptake. The total water concentration in the rubber, c_w, is given in terms of λ by

$$c_w=\frac{\rho_w}{\rho_i}(\lambda^3-1)c_i+s \tag{6}$$

Hence equation (5) can be rewritten in the form

$$\frac{c_0}{M_0}=\frac{\rho_i}{(\lambda^3-1)M_i}-\frac{G}{2RT}\left(5-\frac{4}{\lambda}-\frac{1}{\lambda^4}\right) \tag{7}$$

Apparent diffusion coefficient

As the diffusion progresses, the impurity droplets increase in size as a result of accumulation of water. This implies, therefore, that until equilibrium is reached, the droplets near the surface of the rubber sample will generally be larger and the solution within them generally more dilute than those deeper in the rubber sample. If we assume that the water dissolved in the rubber phase immediately adjacent to the impurity droplet is in local equilibrium with the water in the droplet solution, then a concentration gradient exists in the rubber phase favouring movement of water into the body of the rubber. In the usual statement of Fick's law, this concentration gradient is the driving force.

However, the calculation of the concentration of water dissolved in the rubber immediately adjacent to an impurity droplet is not straightforward. The rubber here will generally be stressed and there is a complex stress field in this region. Even if such a calculation were carried out, the flux of water would not simply be given by the concentration gradient as the strain gradient present in the rubber would lead to some concentration gradient even at equilibrium.

To overcome this difficulty, we use the concept of a thermodynamic diffusion coefficient[11] which assumes that the chemical potential gradient of the water rather than its concentration gradient, is the driving force. This approach was used by Nah and Thomas[10] to explain the blooming of waxes in rubber vulcanizates. The chemical potential of the water in the rubber phase can be readily formulated to take into account both the elastic and osmotic pressure contributions. The following two assumptions are necessary.

(1) The diffusion is assumed to take place only in the rubber phase. There is strong evidence for this from work by Barrie and Machin[5] who found that the presence of water at hydrophilic sites in elastomers did not significantly affect the steady state permeation flux of water through the material.

(2) The water dissolved in the rubber phase in the immediate neighbourhood of a droplet is in local thermodynamic equilibrium with water in the droplet solution, that is, they have the same chemical potential. Because of this assumption, we need only concern ourselves with the chemical potential changes of the water in the droplet solution, taking into account the elastic stress as well as the concentration of the impurity in the solution, in order to derive the driving force.

Using this approach, the flux F of the diffusing substance is given by[11]

$$F=-D_T\left(\frac{c}{RT}\right)\left(\frac{\partial\mu}{\partial x}\right) \tag{8}$$

where D_T is the thermodynamic diffusion coefficient, c is the concentration of water in the rubber phase measured in mass per unit volume of rubber and $(\partial\mu/\partial x)$ is the rate of change of chemical potential per mole of the water with distance x. As the concentration of water dissolved in the rubber is small, D_T can be taken as equal to the ordinary diffusion coefficient D, of water in the pure rubber. The problem now reduces to determining the dependence of μ on the total fraction of water present in the rubber, comprising both that truly dissolved in the rubber and that present in the droplets.

The chemical potential change of a mole of water when it is transferred into the droplet solution is given by

$$-\mu = PV \tag{9}$$

where $P = (\pi_i - \pi_0 - p)$, V is the molar volume of water, π_i and π_0 are the osmotic pressures of the impurity droplet solution and of the solution in which the sample is immersed and p is the pressure exerted on the droplet by the surrounding strained rubber. Assuming that there are a large number of impurity sites in the rubber where the droplets are formed, the gradient of average chemical potential per mole with distance x into the rubber will be given by

$$-\frac{\partial\mu}{\partial x} = V\frac{\partial P}{\partial x}$$

Hence from equation (8)

$$F = D_T\frac{cV}{RT}\frac{\partial P}{\partial x} \tag{10}$$

We shall now define an apparent diffusion coefficient D_a, such that the flux F is given by Fick's first law. Thus

$$F = -D_a\left(\frac{\partial c_w}{\partial x}\right) \tag{11}$$

and from equations (10) and (11)

$$D_a = -D_T\frac{cV}{RT}\frac{dP}{dc_w} = -D_T\frac{cV}{RT}\frac{dP}{d\lambda}\frac{d\lambda}{dc_w} \tag{12}$$

Substituting s from equation (3) into equation (6) and differentiating the resulting equation with respect to λ yields $(dc_w/d\lambda)$; $(dP/d\lambda)$, which is equal to $d(\pi_i - \pi_0 - p)/d\lambda$ is obtained from equations (2), (4) and (6). Substituting these into equation (12) gives

$$D_a = \frac{(\lambda^3 + A - 1)(\lambda^3 - 1)}{(\lambda^3 + A - 1)^2 + s_0A/kc_i}\left\{\frac{K_2}{(\lambda^3 - 1)^2} + K_1\left(\frac{1}{\lambda^4} + \frac{1}{\lambda^7}\right)\right\} \tag{13}$$

where

$$K_2 = D_T s_0 V\rho_w/M_i k^2 c_i; \quad K_1 = 2D_T G s_0 V/3kRTc_i;$$
$$A = M_w\rho_i/M_i\rho_w; \quad k = \rho_w/\rho_i$$

In the derivation of equation (13), the quantity c in equation (12) is replaced by s since the diffusion takes place in the rubber phase, s being given by equation (3). The constant K_1 governs the elastic pressure on the droplet and K_2 the osmotic pressure. Equation (13) shows that the apparent diffusion coefficient is dependent on λ and thus on the concentration of water.

A graphical representation of the concentration dependence of D_a is shown in *Figure 2* for a vulcanizate having a shear modulus of 0.37 MN m^{-2} and containing 1.50 kg m^{-3} sodium chloride as impurity. The value of D, which will be assumed to be equal to D_T, is taken as 1.32×10^{-10} m^2 s^{-1} and s_0 as 0.32 kg m^{-3}, from data by Barrie *et al.*[12]

When the concentration of water is below that which is present in the rubber at the vapour pressure of saturated salt solution ($0.75\,s_0$), the impurity will be completely dry and will not affect the diffusion process so that D_a has the value of D_T. At a slightly higher water concentration some of the salt will dissolve in the droplet that forms around it, and the diffusion coefficient drops by about three orders of magnitude. The resulting solution will be saturated. In this concentration range, i.e. the 'elastic only' region in *Figure 2*, there is thus no variation in the concentration of salt in the droplet solution. This means that the osmotic term, the K_2 term in equation (13), must be ignored and D_a is determined solely by the elastic term, governed by K_1.

At the concentration when all the salt in the impurity droplet solution has dissolved, further ingress of water into the droplet causes a dilution of the solution and therefore brings into effect the relatively larger osmotic term in the expression for D_a, given by equation (13). As a result of this, the diffusion coefficient rises sharply, by about two orders of magnitude. As the water

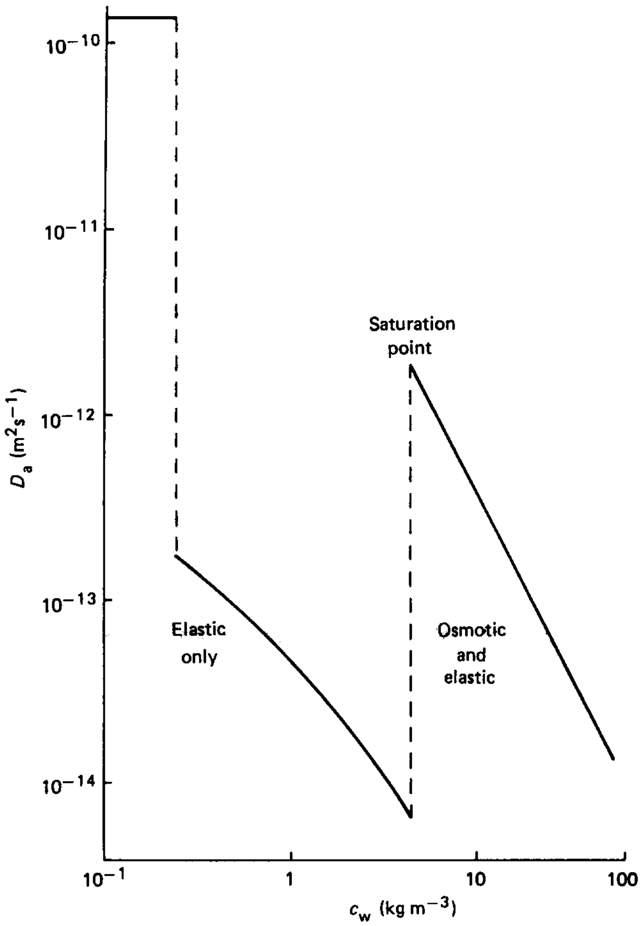

Figure 2 Theoretical concentration dependence of the diffusion coefficient

concentration in the rubber increases beyond this point, the saturation point in *Figure 2*, the diffusion coefficient decreases. This last region is usually the most important. Various workers have found that the diffusion coefficient of water in rubber does in fact decrease with increasing water concentration[4–7] as predicted by equation (13). Beyond the saturation point, it was found that the diffusion coefficient was approximately inversely proportional to the square of the total water concentration in the rubber. This particular dependence of the diffusion coefficient on concentration was derived, using a less rigorous approach, by Southern and Thomas[4], and was shown to be approximately in accord with their reported experiments.

Kinetics of water absorption

To calculate the initial rate of mass uptake when a sheet of rubber is immersed in an aqueous solution, or vapour, the diffusion equation that has to be solved with suitable initial and boundary conditions is

$$\frac{\partial c_w}{\partial t}=\frac{\partial}{\partial x}\left(D_a\frac{\partial c_w}{\partial x}\right) \tag{14}$$

As only the initial mass uptake rate is considered, the sheet may be treated as semi-infinite and, since the concentration is initially constant in the region $x>0$, this partial differential equation can be reduced to an ordinary differential equation by introducing a new variable y such that[13]

$$y=x/2(K_1t)^{1/2}$$

With this substitution, and using the relation for D_a given by equation (13), differentiating with respect to λ gives

$$\frac{d^2\lambda}{dy^2}=\frac{1}{\alpha\beta(\lambda^2+\gamma\beta^2K)}\left\{\left[3\lambda^4(\alpha+\beta)-2\lambda\alpha\beta-3\lambda^2AK\beta^2\gamma\right.\right.$$
$$\left.\left.-K\alpha\beta^3\frac{d\gamma}{d\lambda}\right]\left(\frac{d\lambda}{dy}\right)^2-2\alpha^2\beta^2y\lambda^2K\left(1+\frac{B}{\alpha^2}\right)\left(\frac{d\lambda}{dy}\right)\right\} \tag{15}$$

where

$$\alpha=(\lambda^3+A-1);\quad \beta=\lambda^3-1;\quad \gamma=\left(\frac{1}{\lambda^2}+\frac{1}{\lambda^5}\right);$$

$$B=s_0A/kc_i;\quad K=K_1/K_2=2GM_i/3RT\rho_i$$

Equation (15) has to be solved numerically. However, the numerical integration cannot be carried out to the value of λ corresponding to the initial state of the rubber when $\lambda=1.0$ because at some point the impurity droplet solution will become saturated, and a further reduction in the total water concentration will not of course produce any further change in the concentration of this saturated solution. As pointed out above, in this range only the term involving K_1 in equation (13) is applicable so that

$$D_a=\frac{cK_1}{s_0}\left(\frac{1}{\lambda^4}+\frac{1}{\lambda^7}\right)$$

where c is the amount of water truly dissolved in the rubber at the vapour pressure of saturated sodium chloride. For the present material (c/s_0) is approximately 0.75.

Numerically, the above value of D_a is much less than that for other concentrations (see *Figure 2*) as it derives solely from the elastic component and this, as will be seen later, is usually much smaller than the osmotic component. This means that the concentration profile shows an almost discontinuous drop in this region as in *Figure 3*. In the region beyond B, where the salt is dry, the diffusion process is of the usual nature with a constant value of D_T. As the amount of water in the material is now only that in true solution, and at most that in equilibrium with saturated salt solution, it is small compared with the other water concentrations. Under these circumstances, approximating the profile by a discontinuous step as indicated in *Figure 3*, the boundary condition at A for the concentration profile CA can be expressed as

$$\Delta c\frac{\partial X}{\partial t}=D_{a_1}\left(\frac{\partial c}{\partial x}\right)_1$$

where Δc, the concentration drop at the discontinuity, can be calculated from the solubility of the salt in water. For sodium chloride, for example, $\Delta c=(100/36)c_i\times10^3\ \text{kg m}^{-3}$. D_{a_1} is the apparent diffusion coefficient when the salt has completely dissolved and the solution saturated, i.e., at A, and $(\partial c/\partial x)_1$ is the concentration gradient at A. The partial differential $\partial X/\partial t$ is the velocity of the front AB. Expressing the equation above in terms of the parameter y gives

$$\left(\frac{dc_w}{dy}\right)_1=\frac{2y_1K_1\Delta c}{D_{a_1}} \tag{16}$$

where $(dc_w/dy)_1$ is the gradient of the concentration *versus* y curve at point A. Substituting for $(dc_w/dy)_1$ in terms of $(dc_w/d\lambda)_1$ and $(d\lambda/dy)_1$, equation (16) becomes

$$\frac{1}{y_1}\left(\frac{d\lambda}{dy}\right)_1=\frac{2K_1\Delta c}{3D_{a_1}kc_i\lambda_1^2}\left(\frac{(\lambda_1^2+A-1)^2}{(\lambda_1^3+A-1)^2+s_0A/kc_i}\right) \tag{17}$$

where λ_1 is the extension ratio when all the impurity in the droplet has completely dissolved and the salt solution is saturated and y_1 is the value of y at this point.

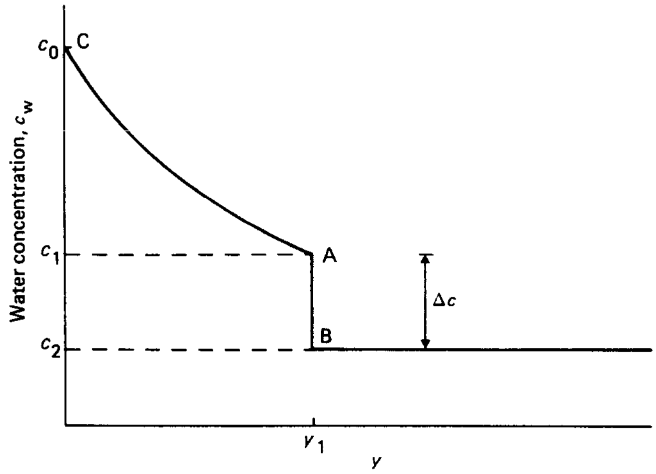

Figure 3 Water concentration profile in the rubber during absorption. c_2 is the initial water concentration in the rubber. c_1 is the concentration in the rubber when all the impurity has dissolved and the solution saturated and c_0 is the water concentration at the surface of the rubber

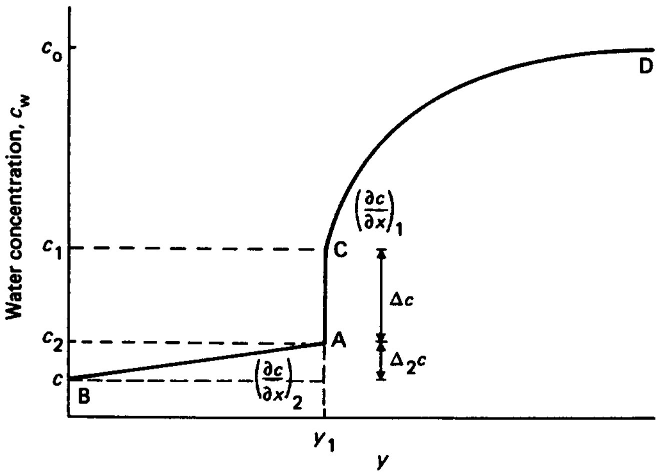

Figure 4 Water concentration profile in the rubber during desorption: c_0 is the initial water concentration in the rubber and c the concentration at the rubber surface. $(\partial c/\partial x)_1$ and $(\partial c/\partial x)_2$ are the concentration gradients at C along CD and at A along AB

The numerical integration of equation (15) has to be carried out beginning at $y=0$, assuming an initial value of $(\mathrm{d}\lambda/\mathrm{d}y)$, viz. $(\mathrm{d}\lambda/\mathrm{d}y)_0$, to $y=y_1$. The value of $(\mathrm{d}\lambda/\mathrm{d}y)_1/y_1$ at this point has to have the value given by equation (17). By trial and error the appropriate value of $(\mathrm{d}\lambda/\mathrm{d}y)_0$ can be found, and this may then be used to calculate the absorption rate required.

This absorption rate $(M_t/\sqrt{t})$, can be obtained from equation (11) by substitution of the relevant relations. It gives

$$\frac{M_t}{\sqrt{t}}=\frac{D_{\mathrm{a}_0}3k\lambda_0^2c_{\mathrm{i}}[(\lambda_0^3+A-1)^2+s_0A/kc_{\mathrm{i}}]}{\sqrt{K_1}(\lambda_0^3+A-1)^2}\left(\frac{\mathrm{d}\lambda}{\mathrm{d}y}\right)_0 \tag{18}$$

where λ_0 is the extension ratio around the droplet when in equilibrium with the surrounding salt solution given by equation (7), D_{a_0} is the apparent diffusion coefficient appropriate to the concentration of water at the surface of the rubber obtained from equation (13) and M_t is the mass uptake per unit surface area of the sample.

Kinetics of water desorption

The water concentration profile in a rubber sample which is drying out is shown in *Figure 4*. The sharp concentration drop of *Figure 3* is also present here for the same reasons. The concentration c, at the rubber surface B, is that which is present in the rubber when it is in equilibrium at the vapour pressure of the drying atmosphere. In the region AB, the diffusion coefficient of water will be assumed to be constant and since the water concentration in the rubber is low, the diffusion coefficient can be taken as equal to the ordinary diffusion coefficient, D.

In order to work out the desorption rate, we need to know the value of $(\mathrm{d}\lambda/\mathrm{d}y)_1$ at point C in *Figure 4* so that we can carry out the numerical integration of the concentration profile along CD. We can obtain the expression for $(\mathrm{d}\lambda/\mathrm{d}y)_1$ in the following manner.

The fluxes at points A and C are related to the velocity of the front AC, $\mathrm{d}X/\mathrm{d}t$, by the equation

$$\Delta c\frac{\mathrm{d}X}{\mathrm{d}t}=D\left(\frac{\partial c}{\partial x}\right)_2-D_{\mathrm{a}_1}\left(\frac{\partial c}{\partial x}\right)_1 \tag{19}$$

where Δc is the concentration drop along AC. $(\partial c/\partial x)_1$ and $(\partial c/\partial x)_2$ are the concentration gradients at C and A respectively and are indicated in *Figure 4*. D_{a_1} and D are the diffusion coefficients of water in the rubber at points C and A, respectively.

Introducing the Boltzmann variable $y=x/2\sqrt{K_1t}$ and expressing $(\partial c/\partial x)$ in terms of $(\mathrm{d}c/\mathrm{d}y)$, in equation (19), it can be shown that

$$\left(\frac{\mathrm{d}c}{\mathrm{d}y}\right)_1=\frac{1}{D_{\mathrm{a}_1}}\left[D\left(\frac{\mathrm{d}c}{\mathrm{d}y}\right)_2-2\Delta cK_1y_1\right] \tag{20}$$

Now the flux of water leaving the rubber surface at B is $D(\mathrm{d}c/\mathrm{d}x)_0$. The concentration gradient $(\mathrm{d}c/\mathrm{d}x)_0$ is equal to (Δ_2c/x) where Δ_2c is the difference between the water concentration in the rubber at the vapour pressure of saturated salt solution and the vapour pressure of the drying environment. If we express x in terms of y and integrate the flux equation we obtain an expression for y, i.e. the value of y at point C as shown in *Figure 4*, and this is given by

$$y_1=\frac{D\Delta_2c}{\sqrt{K_1}}\frac{1}{(M_t/\sqrt{t})} \tag{21}$$

where M_t is the amount of water lost per unit area of rubber surface. If we substitute this expression for y_1 into equation (20), noting that $(\mathrm{d}c/\mathrm{d}y)_2=\Delta_2c/y$, and expressing c in terms of λ, we obtain the following expression for $(\mathrm{d}\lambda/\mathrm{d}y)_1$:

$$\left(\frac{\mathrm{d}\lambda}{\mathrm{d}y}\right)_1=\frac{\sqrt{K_1}(\lambda_1^3+A-1)^2}{3D_{\mathrm{a}_1}k\lambda_1^2c_{\mathrm{i}}[(\lambda_1^3+A-1)^2+s_0A/kc_{\mathrm{i}}]}\left[\frac{M_t}{\sqrt{t}}-\frac{2\Delta cD\Delta_2c}{(M_t/\sqrt{t})}\right] \tag{22}$$

where $(M_t/\sqrt{t})$ is referred to as the desorption rate.

Equation (15) also holds for the case of desorption and to carry out the numerical integration for this case we proceed as follows. A value of $(M_t/\sqrt{t})$ is chosen and the values of y_1 and $(\mathrm{d}\lambda/\mathrm{d}y)_1$ are calculated from equations (21) and (22) respectively. All other quantities in these equations are known or can be calculated separately. The numerical integration of equation (15) is then carried out using the calculated values of y_1 and $(\mathrm{d}\lambda/\mathrm{d}y)_1$ until a constant value of λ, which is a function of c_w, is obtained. By trial and error, a suitable $(M_t/\sqrt{t})$ value can be found such that this value of λ corresponds to the initial uniform concentration of the water in the rubber, c_0, at the start of the desorption process. This value of $(M_t/\sqrt{t})$, the theoretical desorption rate, can then be compared with the experimentally determined value.

EXPERIMENTAL

The rubber used was synthetic *cis*-polyisoprene, which is chemically similar to natural rubber. Being a solution polymerized rubber, it is relatively free from hydrophilic impurities. Sodium chloride was chosen as the impurity to be introduced into the rubber because it is readily soluble in water and, furthermore, does not have any water of crystallization in the range 20°C–30°C.

Sodium chloride was incorporated into the rubber on a hot (60°C) two roll mill in the form of a 20% aqueous

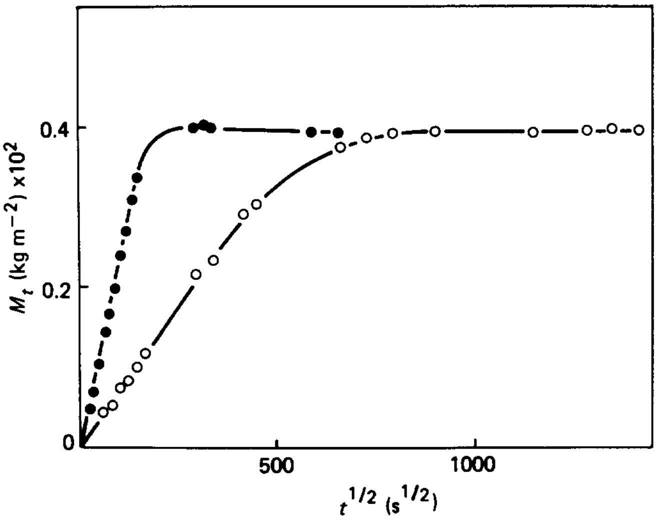

Figure 5 Typical absorption (○) and desorption (●) curves. (○) in a 20% salt solution at 23°C and (●) in oven containing silica gel at 30°C and 25% relative humidity

solution. Rubbers with different levels of impurity were prepared by dropping varying amounts of the salt solution from a pipette. The water in the sodium chloride solution quickly evaporated as the milling proceeded.

Rubbers containing between 0.05% to 0.52% by weight of salt were prepared and they were then cured with 2.0 parts of dicumyl peroxide (DCP) per 100 parts of rubber (pphr). The vulcanization time was 10 min at 100°C followed by 60 min at 160°C, the first being necessary to reduce anisotropy in the vulcanizate. The transparent vulcanizates prepared were acetone extracted for 48 h and subsequently dried before use. Both the extraction and drying were carried out in darkened vessels to minimize degradation of the rubber.

The absorption experiments were carried out at an ambient temperature of (23 ± 1)°C. The rubber samples were flat sheets of approximate dimensions $50 \times 50 \times 0.6$ mm. They were immersed in 10% and 20% sodium chloride solutions (500 ml). Darkened bottles were used to contain the solutions and samples in order to minimize degradation of the rubber samples due to light.

The rubber samples were periodically removed from the bottles, firmly dried using filter paper, weighed and finally replaced in their respective bottles containing the salt solutions. The bottles were always tightly recapped to minimize evaporation losses of water and thus prevent any variation in the concentration of the solution. The solution was kept well stirred. Since the time a sample spent outside the solution was very short, typically 45 s, 'drying-out' effects during the weighing operation could be neglected.

The desorption measurements were carried out in a well circulated thermostated oven which was maintained at (30 ± 0.2)°C and contained freshly prepared silica gel which acted as the drying agent. Samples of the vulcanizate which had previously attained equilibrium absorption in 10% and 20% salt solutions at 23°C were used. They were removed from the containers, dried, weighed and then suspended in the oven. The loss in weight was monitored as a function of time. All weighings, subsequent to the initial one, were made with the sample in the oven.

The relative humidity of the air in the oven was measured by a wet and dry bulb hygrometer arrangement. This had been previously calibrated by weighing the amount of water vapour in a known volume of air aspirated from the oven. Fresh silica gel was introduced into the oven when the relative humidity in the oven begins to rise. In this way, the relative humidity could be controlled to within $\pm 2\%$.

The shear modulus of the vulcanizate is required by the theory and this was determined from the stress–strain relation in simple extension of small dumbbell testpieces. The results were plotted as suggested by the statistical theory of rubber elasticity as stress *versus* $(\lambda - \lambda^{-2})$. Although a linear relation, as required by this theory[14], is not strictly found, the best straight line fit up to about 200% strain was used to give the slope, which could be taken as G, the parameter required by the theory presented here. The value found in this way was 0.50 MN m^{-2}.

Since there was a possibility that some of the salt introduced may have been lost during the mixing process, the amount of sodium chloride present in the vulcanizate after acetone extraction as quantitatively determined by atomic absorption spectrum analysis.

RESULTS AND DISCUSSION

Figure 5 shows typical absorption and desorption curves where M_t, the weight of water gained or lost by the sample per unit area is plotted against the square root of time t. As would be expected from a diffusion controlled process, both the curves show an initial linear dependence of M_t with $\sqrt{t}$. The slope of this linear region, $(M_t/\sqrt{t})$, is usually referred to as the initial absorption or desorption rate and has units of kg m^{-2} s$^{-1/2}$.

It is clear from *Figure 5* that the desorption rate is several times greater than the absorption rate even allowing for differences in temperatures of test. The reason for this is the particular dependence of the diffusion coefficient with concentration given by equation (13), the diffusion coefficient D_a decreasing strongly with increasing water concentration.

Chemical analysis of the amount of sodium chloride in the model vulcanizate showed that, ignoring extreme values, only between (73–87%), or an average of 80% of the nominal amount of salt introduced during mixing was present in it after vulcanization and acetone extraction. Since the method of salt incorporation for these samples were almost identical to that used for samples whose results were published elsewhere[8], we can therefore assume that the latter samples also contained only 80% of the nominal salt content. We can thus analyse the equilibrium aspects of the absorption process since we now know quantitatively the amount of salt present in the vulcanizates.

Such an analysis was carried out with the new samples described in this publication as well as those used in the previous publication[8] and a comparison between theory and experiment is shown in *Figure 6*. The value of λ at equilibrium was calculated using equation (7) and this value was then substituted into equation (6) together with the corrected experimental value of c_i to evaluate c_w (the equilibrium water content in this case). If we take all the data points in *Figure 6*, on average, the experimental values are about 8% higher than the theoretical values.

Figure 7 shows a comparison between the experimental

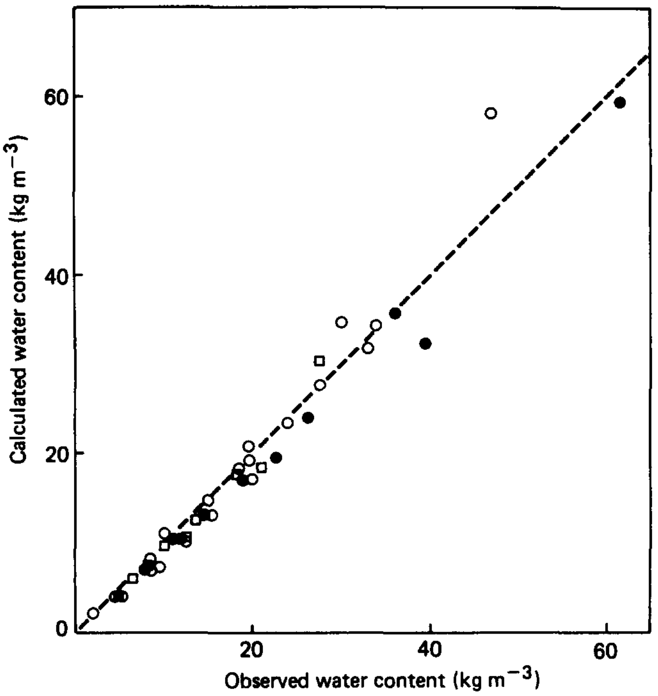

Figure 6 Comparison of the equilibrium water uptake obtained from theory and experiment. Vulcanizates containing 1.6 (●), 2.0 (○) and 3.0 (□) pphr of dicumyl peroxide are shown, (-----) line for equality between theory and experiment

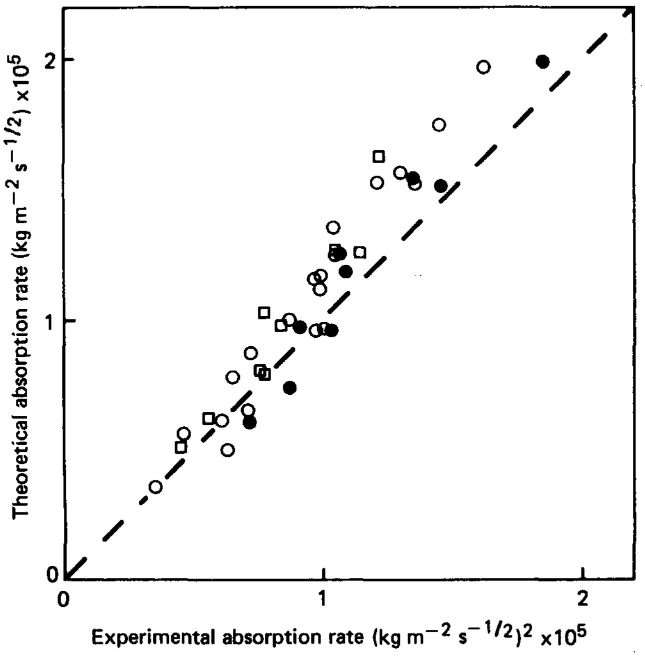

Figure 7 Comparison of the initial absorption rate obtained from theory and experiment. (●) contains 1.6, (○) 2.0 and (□) 3.0 pphr of dicumyl peroxide. (-----) line for equality between theory and experiment

and theoretical initial absorption rates. The latter values were calculated using the corrected experimental value of c_i. The values of D and s_0 were obtained by linear extrapolation of data by Barrie *et al.*[12] On average, the theoretical values are about 12% higher than the experimental values.

A comparison between the experimental and theoretical initial desorption rates is shown in *Figure 8*. It shows that the theoretical values are again somewhat higher than the experimental. However, in view of the fact that all the parameters used in the theory are determined independently, the observed discrepancies are probably little more than would be expected from the cumulative uncertainties in their values.

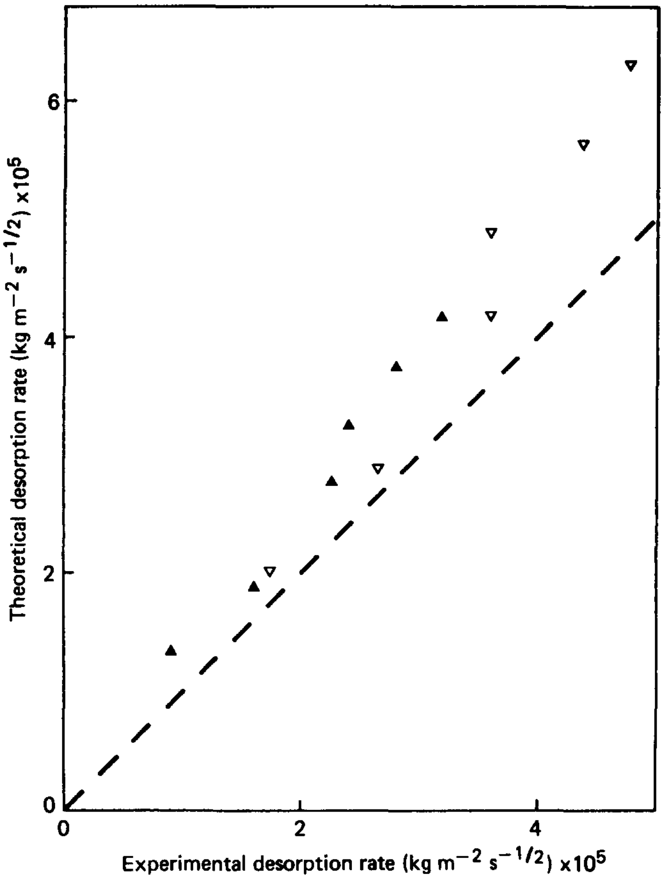

Figure 8 Comparison of the initial desorption rate obtained from theory and experiment for a vulcanizate containing 2.0 pphr of dicumyl peroxide. Temperature 30°C. Relative humidity for (▲) was 25% and 19% for (▽). (-----) line for equality between theory and experiment

CONCLUSIONS

The theory formulated in this paper, which makes use of the concept of the chemical potential gradient of water in the rubber as the driving force for diffusion, satisfactorily predicts the equilibrium uptake, and the initial absorption and desorption rates of water in rubbers containing hydrophilic impurities. It predicts that the diffusion coefficient decreases strongly as the water content increases, in agreement with published results[4].

The very marked effect of quite small amounts of hydrophilic impurity in an otherwise hydrophobic material suggests that the purity of such materials has to be carefully controlled when diffusion measurements are being considered.

REFERENCES

1 Barrie, J. A. in 'Diffusion in Polymers', (Eds. J. Crank and G. Park), Academic Press, New York, 1967, Ch. 8
2 Briggs, G. T., Edwards, D. C. and Storey, E. B. *Rubb. Chem. Technol.* 1963, **36**, 621
3 Fedors, R. F. *Polymer* 1980, **21**, 207

4 Southern, E. and Thomas, A. G. ACS Symposium Series No. 127, 1980, 375
5 Barrie, J. A. and Machin, D. J. *Macromol. Sci.* (*B*) 1969, **3**, 673
6 Barrer, R. M. and Barrie, J. A. *J. Polym. Sci.* 1958, **28**, 377
7 Rouse, P. E. *J. Am. Chem. Soc.* 1947, **69**, 1068
8 Muniandy, K. and Thomas, A. G. *Trans. Inst. Mar. Eng.* (*C*) 1984, **97**, Conf. 2, paper 13
9 Gent, A. N. and Lindley, P. B. *Proc. Roy. Soc. A* 1958, **249**, 195
10 Nah, S. H. and Thomas, A. G. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **21**, 207
11 Park, G. S. *Trans. Faraday Soc.* 1950, **46**, 684
12 Barrie, J. A., Machin, D. and Nunn, A. *Polymer* 1975, **16**, 811
13 Crank, J. 'The Mathematics of Diffusion', Oxford University Press, London, 1975
14 Treloar, L. R. G. 'The Physics of Rubber Elasticity', Clarendon Press, Oxford, 1958