

The sorption and diffusion of water in halogen-containing epoxy resins

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(Received 2 October 1984)

The effect of halogen containing substituents on the sorption and transport of water in the epoxy system, tetraglycidyl 4,4' diaminodiphenyl methane cured with 4,4' diaminodiphenyl sulphone, has been studied at 40°C, 50°C and 60°C. The introduction of halogen containing groups reduces the sorption over the whole of the activity range, the effect being greatest for the fluorine-containing sample. Sorption-desorption kinetics exhibit many of the features observed for the unsubstituted network including some element of non-Fickian behaviour. Diffusion coefficients are greatest for the fluorine-containing sample and have a relatively weak concentration dependence for all the samples.

(Keywords: sorption; diffusion; water; epoxies; halogenation; curing)

INTRODUCTION

The interaction of water with epoxy resins used in fibre-reinforced composites and its effect on their physical properties is a problem of some technological importance¹. Accurate determination of the isotherm shape at lower activities indicates a degree of localization of the penetrant². Spectroscopic and dielectric studies indicate interaction of the water molecules and various groups in these resins, and physical states for the sorbed water with different degrees of mobility have been postulated³⁻⁹. It has also been shown that the introduction of halogen groups into epoxy resins reduces their affinity for water¹⁰⁻¹⁵. As part of an investigation into the interaction of water with epoxy networks, the effect of chemical substitution on both sorption and diffusion over the entire activity range is examined for a series of halogen-containing MY720 resins.

EXPERIMENTAL

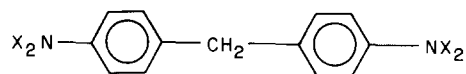
Materials

The base resin MY720 (Ciba Geigy Ltd.) had an epoxide equivalent of ~115 (theoretical value 105.5) and was ~92% pure; the main constituent is tetraglycidyl 4,4' diaminodiphenyl methane (TGDDM) (Resin E of Figure 1). The preparation scheme for the halogen-containing resins has been given¹⁵. These materials were of high purity (>98%) and the chemical structure of the main constituent is shown in Figure 1. For the halogen-containing networks 0.83 mol 4,4' diaminodiphenyl sulphone (DDS) per mole of resin was employed, and for the unsubstituted network 0.91 mol DDS per mol TGDDM was used (assuming 92% purity). The appropriate mix of resin and DDS was cured between glass plates to give thin films; the compositions of the networks are given in Table 1. Also included in Table 1 are

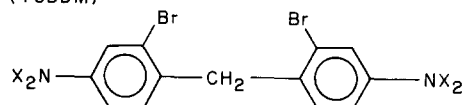
the glass transition temperature T_g^{15} , typical film thickness l and density ρ estimated from the weight and dimensions of the sample.

Technique

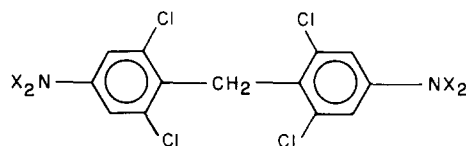
Sorption isotherms and conjugate integral sorption-desorption rate curves were determined using McBain-Bakr sorption balances and an electronic vacuum micro-



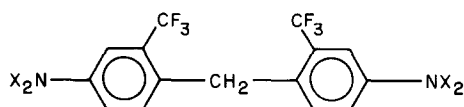
Resin E : 4,4'-methylene bis [*N,N*-bis(2,3-epoxy propyl)aniline] (TGDDM)



Resin BR : 4,4'-methylene bis [*N,N*-bis(2,3-epoxy propyl)-3-bromoaniline]



Resin CL : 4,4'-methylene bis [*N,N*-bis(2,3-epoxy propyl)-3,5-dichloroaniline]



Resin CF : 4,4'-methylene bis [*N,N*-bis(2,3-epoxy propyl)-3-trifluoromethylaniline]

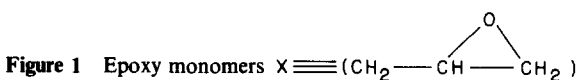


Figure 1 Epoxy monomers $X \equiv (\text{CH}_2-\text{CH}(\text{O})-\text{CH}_2)$

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Table 1 Compositions of cured epoxy films

Sample	Composition (parts DDS/100 parts resin by wt)	T_g ($^{\circ}\text{C}$)	$l \cdot 10^2$ (m)	$\rho \cdot 10^{-3}$ (kg m^{-3})
E	49	274	0.0149	1.25
BR	35.6	238	0.0140	1.42
CL	36.9	240	0.0153	1.37
CF	36.9	217	0.0150	1.32

balance (Sartorius Instruments Ltd.) as described earlier².

A few immersion measurements were made with selected samples at 40°C only. After outgassing under high vacuum for ~5 days, the samples were immersed in liquid water or solutions of sodium chloride to cover the activity range 0.75 to 1. The water regain was estimated by rapid weighing after removal of excess liquid so as to minimize loss of water sorbed by the sheet.

RESULTS AND DISCUSSION

Sorption

It has been established that the sorption isotherm for water in the MY720 resin is a function of hygrothermal history^{2,15} and, in common with vapour-glassy polymer systems in general, truly equilibrium states are often not realized on normal time scales because of slow relaxation processes. With this in mind sorption isotherms were determined in the order 40°C, 50°C, 60°C for each of the virgin samples, that is as prepared, and are shown in *Figures 2* and *3*. The isotherm points, unless stated otherwise, are 'first' sorptions² and were determined in the order of increasing pressure at any one temperature. On completion of the 'first' sorption isotherm at 60°C the sample was outgassed and a 'second' sorption isotherm measured at 40°C, followed in some instances by a 'third' sorption again at 40°C. Isotherms for all samples but E were obtained with the microbalance with desorption after each point. For sample E, the McBain-Bakr balance was used with desorption generally after 3 to 4 sorptions. As shown in *Figures 2* and *3* good agreement was obtained with regains obtained from immersion in solutions of known activity.

For all samples there is a distinct Langmuir-type curvature to the sorption isotherm at the lower activities consistent with some degree of localization of the sorbed water at specific sites in the network. The 'first' sorption isotherms are virtually independent of temperature but the presence of hysteresis, albeit on a relatively small scale, precludes an exact analysis of heats of sorption. However, it appears likely that the heat of sorption is close to the heat of condensation, lending further support to localized water-network interactions at the lower activities. Although the detailed nature of these interactions requires further study it is suggested that polar groups relatively exposed in microvoids in the glassy matrix may offer preferred sites for sorption.

The introduction of halogen-containing groups into TGDDM reduces the sorption over the whole of the activity range; similar sized reductions were observed in the regain from liquid water for identical and related systems^{13,15}. The effect, however, is not as marked as would at first appear as the regain is expressed relative to a given weight of network rather than to a given number of resin units in a network of fixed stoichiometry. Replacing

the halogen-containing groups in the substituted resins by hydrogen atoms yields the equivalent unsubstituted network; the 'corrected' isotherms in *Figure 4* refer to 100 g of the equivalent unsubstituted network. Because of the differences in stoichiometry and in impurity level between the halogen-containing and unsubstituted networks a strict comparison of the sorptions is not possible. The effect of these factors on the water sorption is under study and preliminary measurements suggest that it is relatively weak. It is also noted that the reaction mechanism for network formation in these systems is not sufficiently well established to conclude that identical stoichiometries will follow the same reaction paths and form equivalent networks. Studies on model compounds indicate that meta substituents have a marginal effect in reducing the rates of the reactivity of secondary to primary hydrogen atoms¹⁶. Samples BR and CF contain the same number of substituted groups and assuming identical extents of reaction a direct comparison can be made indicating that CF_3 is the more effective in reducing the water sorption.

The second sorptions show a significant increase in regain over most of the activity range for all samples. A feature of the 'second' isotherm is the extended linear region following on the Langmuir-type curvature at the

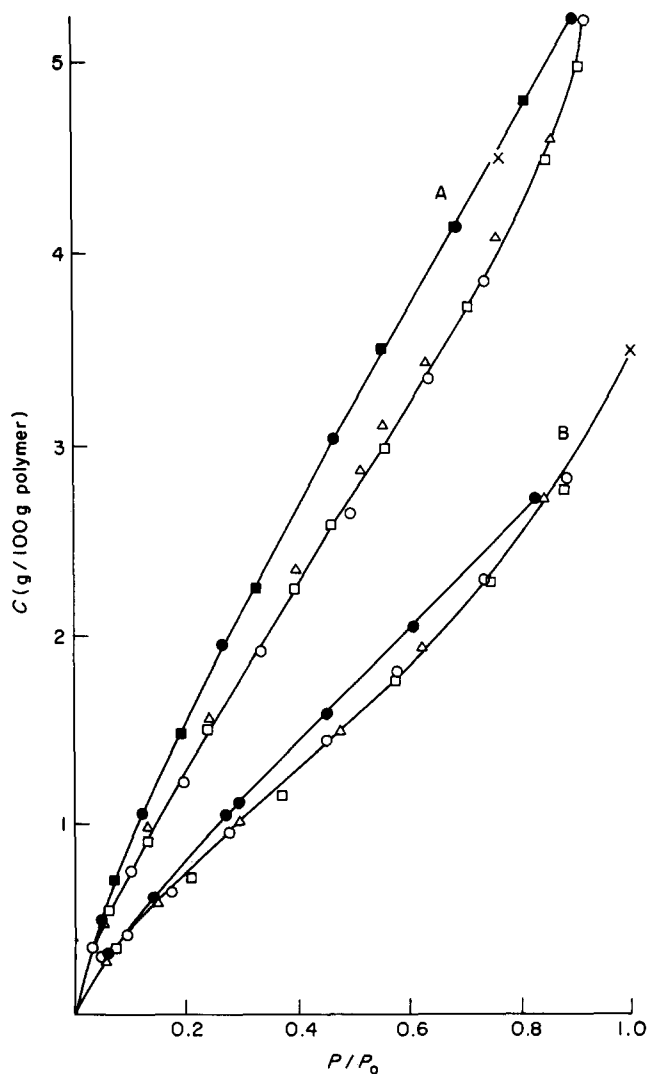


Figure 2 Sorption isotherms. (A) sample E, (B) sample CF: (○, △, □) first sorptions at 40°C, 50°C, 60°C respectively; (●, ■) second and third sorptions respectively at 40°C; (×) immersion in aqueous solution

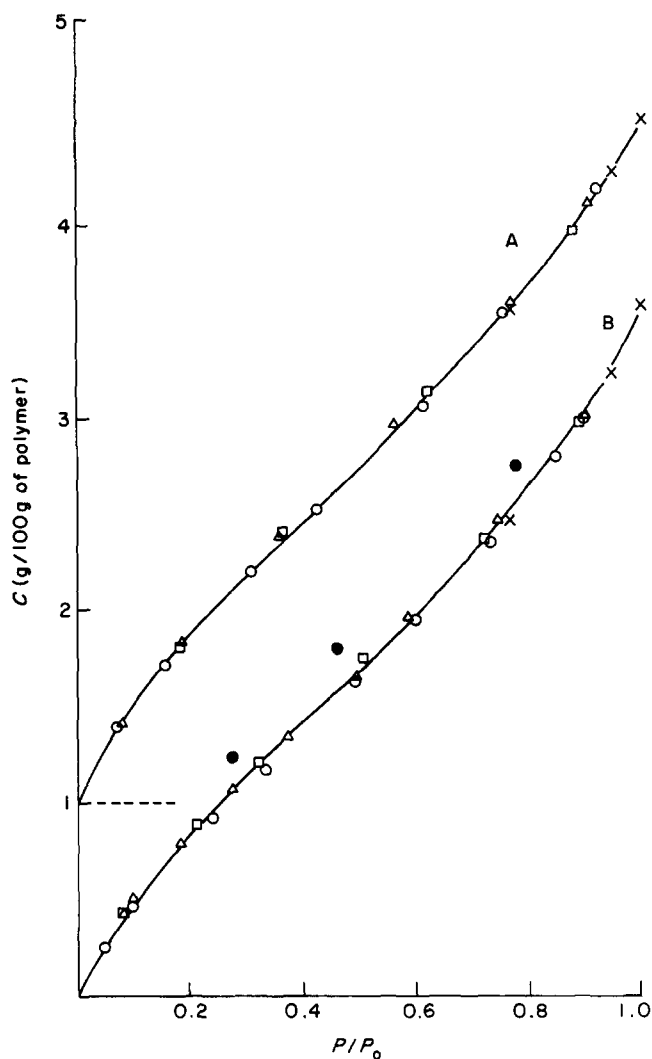


Figure 3 Sorption isotherms. (A) sample BR. (B) sample CL: symbols as for Figure 1. Note that the origin for (A) has been displaced 1 unit along the ordinate

lower activities. The removal of the curvature observed in the 'first' isotherms at high activities suggests that this may be attributed, at least in part, to an irreversible component to the expansion of the network on water sorption; on relatively rapid desorption of the water the expanded structure is frozen in as network relaxation is slow. Hysteresis of this type is a feature of vapour sorption in glassy polymers and natural fibres^{17,18}.

The shape of the 'second' sorption isotherm resembles that for vapours in glassy polymers and superficially may be represented by the dual-sorption model^{17,19}. Values of k_D , the Henry's-law constant for the dissolution mode and C'_H , the amount of vapour required to saturate the sites in the Langmuir mode are given for samples E and CF in Table 2.

As indicated earlier the values of k_D are relatively high compared with gases in glassy polymers and it was suggested that it is unlikely that this amount of water is dissolved ideally according to Henry's law and that compensating factors such as site sorption and restricted cluster growth might lead to isotherms of a similar shape². It is of interest that isotherms resembling the 'second' isotherms can be obtained from the BET model with multilayer formation restricted to a comparatively small number of layers²⁰. A plausible interpretation is that

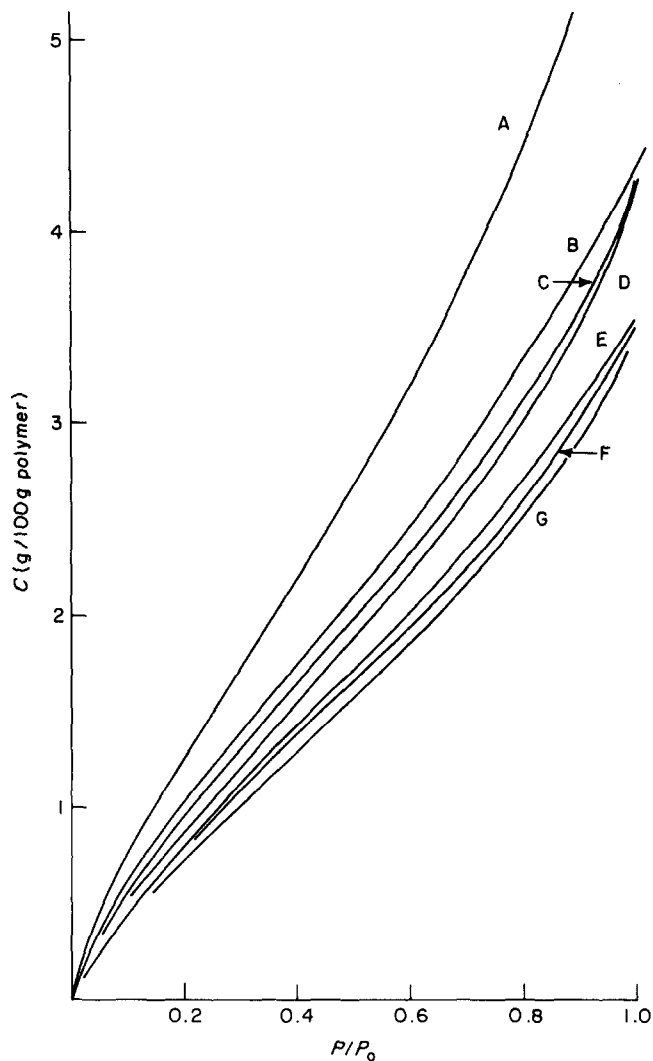


Figure 4 First sorption isotherms at 40°C. (A) sample E; (B), (C), (D), corrected isotherms for samples BR, CL and CF respectively; (E), (F), (G), uncorrected isotherms for samples BR, CL and CF, respectively

sorption occurs preferentially at polar sites relatively exposed in microcavities and that the initial sorbed water provides centres for association or development of clusters the growth of which is restricted to the microcavity; in addition there will be some dissolution component to the sorption.

The mechanism whereby the halogen-containing groups reduce the sorption affinity for water is not clear. The nitrogen on the phenyl ring would appear to be more prone to direct inductive effects. The apparent heats of sorption are practically identical for both substituted and unsubstituted resins suggesting that if any particular site is effectively removed by induction its energy differs little from that of remaining sites. A decrease in sorption with little change in the heat of sorption could also arise through a reduction in the effective microvoid volume

Table 2 Dual-mode sorption parameters for 'second' isotherms at 40°C

Sample	C'_H ($\text{cm}^3 \text{stp cm}^{-3}$)	b (cmHg^{-1})	k_D ($\text{cm}^3 \text{stp cm}^{-3} \text{cmHg}^{-1}$)
E	$16.2 \pm 52\%$	$1.03 \pm 71\%$	$13.7 \pm 8\%$
CF	$5.6 \pm 11\%$	$2.49 \pm 29\%$	$8.54 \pm 1\%$
CF (corrected)	$6.4 \pm 14\%$	$2.79 \pm 37\%$	$10.3 \pm 2\%$

available for sorption; the bulkier halogen substituents may restrict access to some sites and also effectively reduce the microvoid volume available for sorption.

Diffusion

Conjugate sorption-desorption rate curves were determined in the relative pressure range 0 to 0.9 at 40°C, 50°C and 60°C for all samples except E (40°C only). Typical curves at 40°C are shown in Figure 5; the solid lines were computed as discussed below. The behaviour of the halogen-containing networks is similar to that of the unsubstituted epoxy discussed earlier². Thus at lower activities sorption is generally faster than desorption whilst at higher activities the curves converge in the early stages and eventually cross at the higher activities. In addition there was an indication of a weak inflexion in the \sqrt{t} curves at higher activities and of a small but persistent increase in regain over extended time scales.

The results are first analysed assuming a purely Fickian behaviour. Average coefficients \bar{D}_s were obtained from the initial slopes of the sorption rate curves and are shown in Figures 6 and 8; the solid lines are second order best fit polynomials except that for sample E which is third order. The smoothed \bar{D}_s data were used as a first approximation to

$$\frac{1}{C_0} \int_0^{C_0} D dC$$

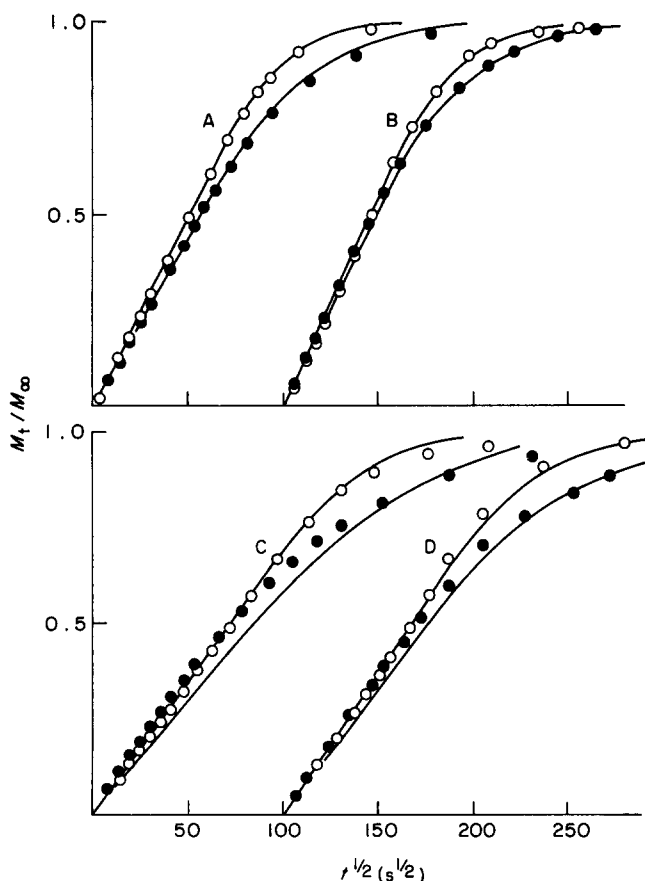


Figure 5 Conjugate sorption-desorption rate curves at 40°C. (A) sample CF, $M_\infty=0.976$ wt%; (B) sample CF, $M_\infty=2.85$ wt%; (C) sample BR, $M_\infty=3.19$ wt%; (D) sample CL, $M_\infty=3.0$ wt%; (○, ●), sorption and desorption points respectively; (—), computed rate curves

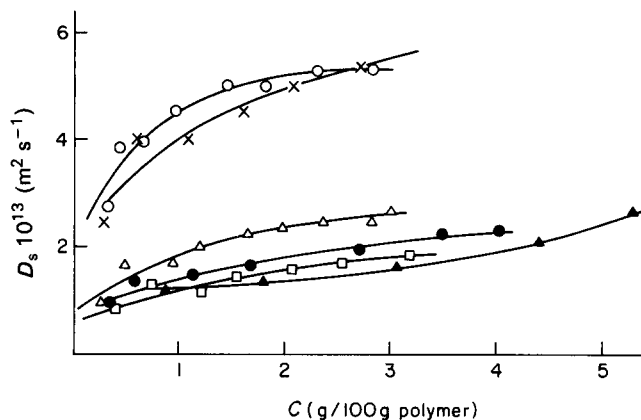


Figure 6 Concentration dependence of \bar{D}_s at 40°C. (○, △, □) and (▲), samples CF, CL, BR and E, respectively; (●), unsubstituted resin (ref. 2). (×), second sorptions for sample CF

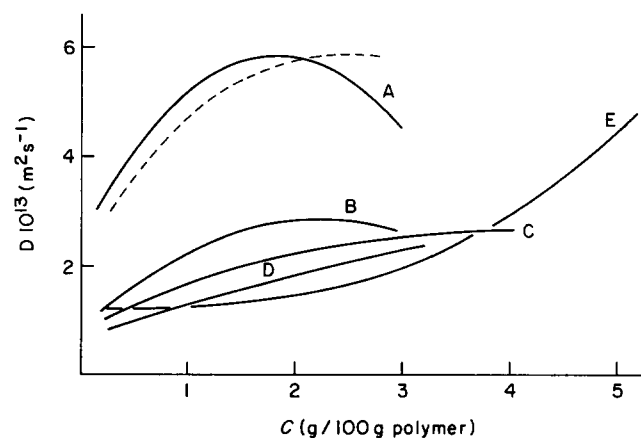


Figure 7 Concentration dependence of D at 40°C. (A), (B), (D), (E), samples CF, CL, BR and E, respectively; (C), unsubstituted resin (ref. 2). (---), second sorptions for sample CF

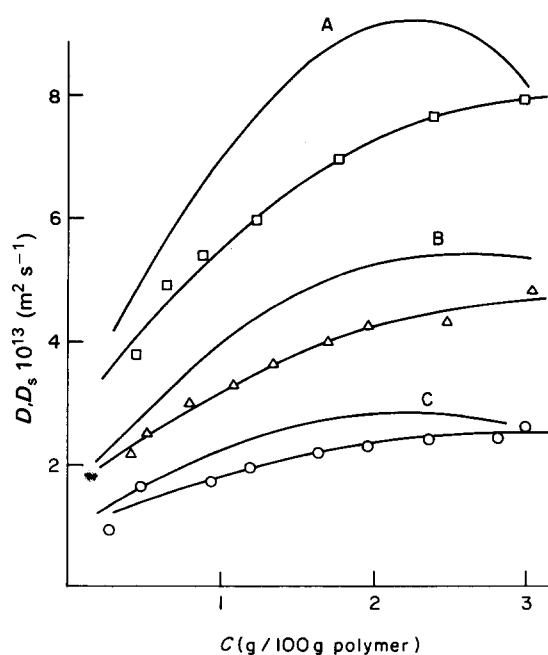


Figure 8 Concentration dependence of \bar{D}_s and D for sample CL at several temperatures. (A), (B), (C), D at 60°C, 50°C and 40°C, respectively; (□, △, ○), \bar{D}_s at 60°C, 50°C and 40°C, respectively

in a successive approximation procedure to obtain the differential coefficient D , typical values of which are shown in Figures 7 and 8²¹. The scatter in \bar{D}_s values is greatest at the lower activities where it proved more difficult to maintain constant boundary conditions; also the concentration dependence of \bar{D}_s is relatively weak. Consequently the shape or curvature of the \bar{D}_s -concentration profile is difficult to define accurately and the derived D - c profiles should be treated with some caution. With these limitations the D - c profiles were used to generate by numerical procedures the solid lines in Figure 5.

At the lower activities the agreement between computed and experimental rate curves is generally good but at the higher activities initial desorption rates are underestimated. Crossing of the computed conjugate rate curves was not observed even for those D - c profiles exhibiting a maximum; the conditions for crossing of conjugate rate curves in a purely Fickian process have been discussed²¹. These observations are indicative of some non-Fickian element which was discussed earlier in relation to hysteresis effects². Changes in surface temperature accompanying the sorption of vapour can also induce non-Fickian behaviour. Comparison with an earlier analysis²¹ suggests that this effect is likely to be small although it cannot be eliminated with certainty; such heating effects, however, would not account for the long time drift in the 'equilibrium' sorption.

Accepting some degree of uncertainty in the values of D and the exact shape of the D - c profiles the results indicate that for all samples the diffusion coefficient increases with concentration, albeit rather weakly and with indications of a maximum in the D - c profile. The order of decreasing D is CF > CL > BR ~ E which is the order of increasing affinity for water. Assuming that only a fraction of the sorbed water is free to diffuse, the effective diffusion coefficient of the system may be represented by $D_m \frac{\partial C_m}{\partial C}$ where the subscript m refers to mobile species¹⁸. In the absence of further information it is not possible to separate the effect of halogen substitution on D_m and C_m/C although the larger D for the fluorine-containing epoxy is consistent with the reduced localized component to the sorption leading to a larger C_m/C .

On the same basis the concentration dependence of D will be governed by that of D_m and $\partial C_m/\partial C$. The coefficient D_m is expected to increase with concentration on plasticization of the network and the term $\partial C_m/\partial C$ may increase with concentration for localized sorption and decrease for association or clustering of the sorbed water¹⁸. These competing factors could lead to a maximum

in the D - c profile although as indicated the concentration dependence is not strong. There is little significant variation of the activation energy for diffusion either with concentration or between samples as shown in Table 3.

'Second' sorptions lead to a small reduction in \bar{D}_s and D at the lower concentrations as shown in Figures 6 and 7 consistent with an increased localized component associated with a larger microvoid content for the expanded network.

CONCLUSIONS

The water isotherms for the halogen-containing epoxies are similar in shape to that for the unsubstituted TGDDM/DDS epoxy system and exhibit Langmuir-type curvature at the lower activities. The introduction of halogen-containing groups reduces the sorption over the whole of the activity range and the effect is greatest for the fluorine-containing sample. Sorption-desorption rate curves exhibit many of the features observed for the unsubstituted network² and there is some indication of non-Fickian behaviour.

ACKNOWLEDGEMENTS

The authors would like to thank Dr N. Shah and Dr A. Chakravarty for their assistance with the numerical analysis programme.

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Table 3 Activation energies of diffusion

C (g/100 g)	E_D (kJ mol ⁻¹)		
	BR	CL	CF
0.5	53	48	48
1.5	53	50	46
2.0	54	50	49
3.0	55	49	62