

# Water Absorption Isotherms for Cured Bisphenol A Type Epoxy Resins: Effects of Isotherm Temperature and Resin Hardener

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## Synopsis

Water-sorption isotherms have been determined for some bisphenol-A-type epoxy resins cured with either 4,4'-diamino diphenyl methane (DDM), phthalic anhydride, or polyamide, Versamid 115. The absorption isotherms for the diamine-cured resin are reversible and that at 0.2°C is linear for the whole accessible range of relative pressures ( $0 \leq h \leq 1$ ). With increase in temperature deviations from Henry's law occur at successively lower relative pressures. It is shown that these deviations from Henry's law are related to a concentration dependence of the isosteric heat of absorption. Sorption by both the polyamide and phthalic-anhydride-cured resins is not reversible; there are weight increases following an absorption-desorption cycle.

## INTRODUCTION

Water absorption by polymers depends on their chemical structure; in general, the more "polar" the polymer the larger the amount of water sorbed. Some polymers are water-soluble, but for the majority there is limited miscibility.<sup>1</sup> Cured epoxy resins when immersed in liquid water sorb several weight percent, the amount being a function of the structure of the resin and the type of hardener used to effect cure.<sup>2</sup> The importance of absorbed water is due to its effect on the properties of the resin; its glass transition temperature is lowered,<sup>3-5</sup> and elastic moduli and compressive strength are reduced. Over recent years there have been a number of reports of the water sorption by cured epoxy resins,<sup>6</sup> their composites,<sup>7</sup> and the effects of thermal cycling.<sup>8</sup> However, there is still the need for a systematic study of the equilibrium water sorption by cured epoxy resins as a function of the relative pressure or activity of the water and sorption temperature. The purpose of the present paper is to present data on the absorption of water by a bisphenol-A-type epoxy resin cured with 4,4'-diamino diphenyl methane (DDM), a commonly used hardener. Other variables investigated were the effects of under and post cure, primary initial molecular weight of the epoxy resin prepolymer, and type of hardener. From the temperature dependence of the sorption, the isosteric heats and entropy of absorption were determined.

## EXPERIMENTAL

Commercial samples of bisphenol-A type epoxy resins, I, were used as received: their molecular weights and epoxy equivalents are given in Table I, together with

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the hardener type, ratio, and curing schedule. The water sorption by a cured resin prepared from a specially purified sample of prepolymer was essentially identical to that prepared from the commercial sample. The "standard" cure(S) used for the diamine cured resins (D series) is the optimum cure required to attain a limiting glass transition temperature.<sup>9</sup> The films of cured resin were prepared by pressing the liquid resin-hardener mixture at a suitable temperature between aluminum foil and then heating for the specified times at the required temperatures. After the cure treatment, the aluminum foil was peeled from the thin films with great care because they were very fragile. Thin films or powdered samples are required in order to attain equilibrium sorption within convenient time periods. Measurements were continued for sufficient time to ensure that equilibrium had been attained.

Films from resins cured with phthalic anhydride could not be prepared because the adhesion to the aluminum foil was too high. Preparation of films by cutting and then polishing was completely unsatisfactory. The absorption isotherms were anomalous, and the water uptake was very much larger than when measured using finely powdered samples. Powdered samples with particle sizes ranging

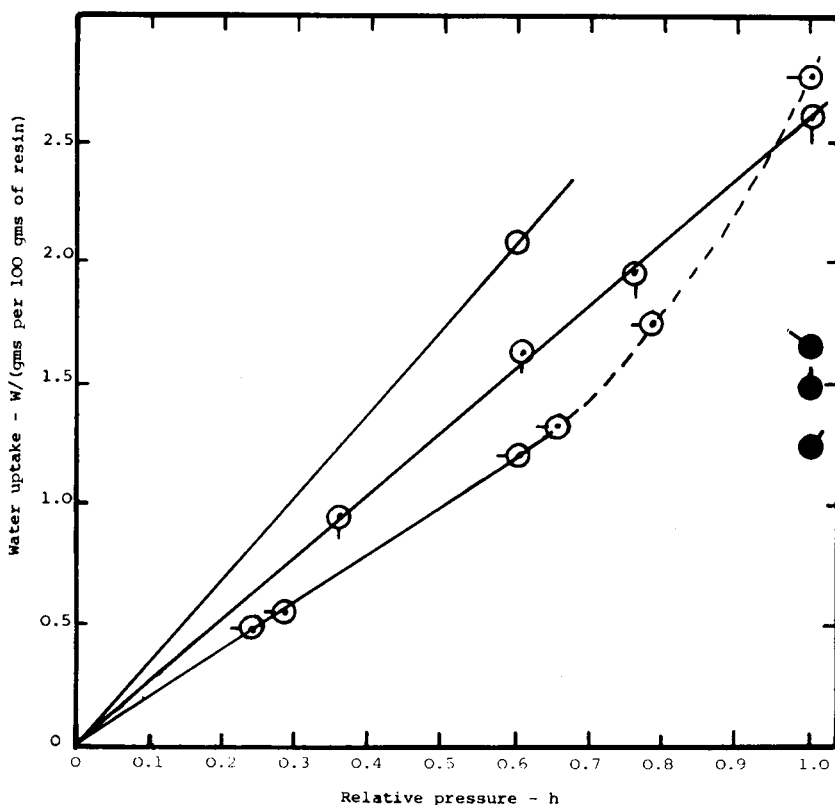


Fig. 1. Water absorption isotherms for cured epoxy resins. Diamine-cured resin: D.1.S: (○) 0.2°C; (◌) 90°C. (○) from Kwei<sup>17</sup>: isotherm temperature 60°C, similar prepolymer to resin 1 but cured with the stoichiometric amount of 1,6-hexane diamine. Data of Moy and Karasz<sup>4</sup>: 73 wt % tetraglycidyl-4,4'-diaminodiphenyl methane cured with 27 wt % of 4,4'-diaminodiphenyl sulfone: (●) 25°C; (●) 35°C; (●) 75°C.

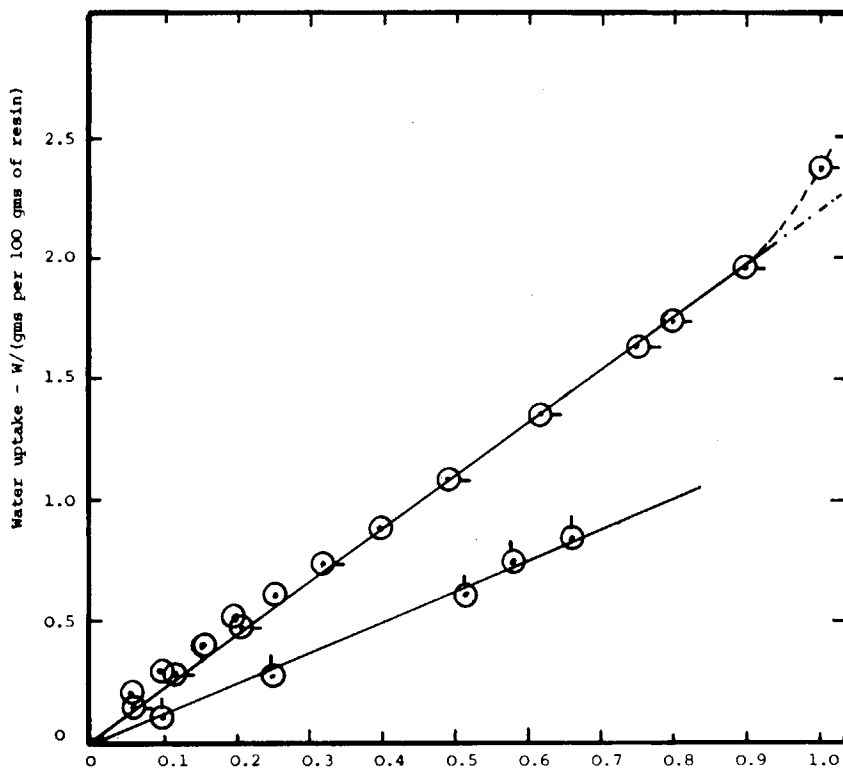


Fig. 2. Water absorption isotherms for epoxy resins. Diamine-cured resin: D.1.S (O) 37°C. Data of Eley, Goodchild, and Rudham<sup>18</sup>: (⊙) 38°C. Resin 2, uncured: (—) 25°C.

from 0.03 to 0.4 mm in diameter were used for measurements with phthalic anhydride cured resins.

Prior to a water sorption measurement the thin films, or powdered resin, was conditioned to constant weight by storage in a desiccator at room temperature. The equilibrium sorption in the dry resin was measured using either a vacuum system incorporating a Beckman RHIC L.M. microbalance<sup>10</sup> or individual sorption cells such as in the technique described by Kantra et al.<sup>11</sup> except that each specimen was isolated within its own sample cell. Satisfactory agreement was attained when sorptions were measured by both methods. Saturated salt solutions were used to ensure that relative pressures remained constant. Individual sample cells were evacuated so that the specimen was surrounded only by water vapor, and the temperature was controlled by immersion of the sorption cells in a water bath with the temperature controlled to  $\pm 0.1^\circ\text{C}$ . For the microbalance-vacuum system the sample tube was immersed in a modified large glass beaker through which thermostatically controlled water was circulated using a small rotary pump.

Desorption measurements were carried out in a similar way to the absorption procedure except that the sample was surrounded by a vacuum. For the diamine-cured resins (D systems) an adsorption-desorption cycle was reversible,<sup>10</sup> the final weight of the sample was essentially identical to its initial weight, even for samples which had been immersed in liquid water (change in weight  $< \pm 0.0002$

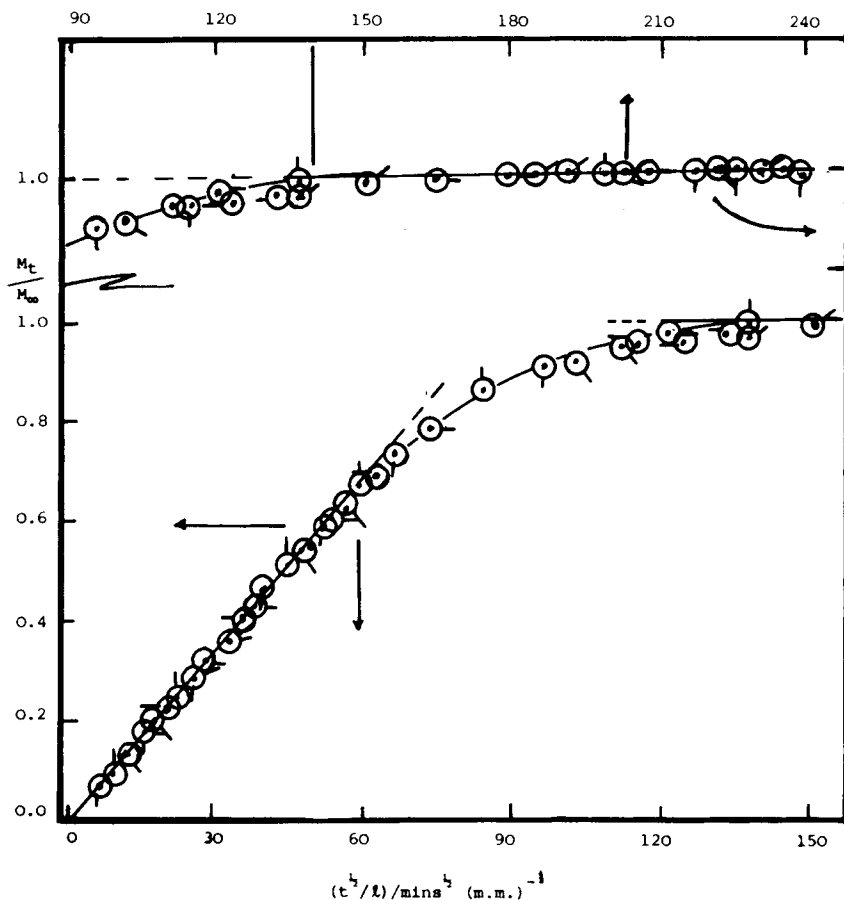


Fig. 3. Diffusion of water into and out of thin epoxy resin films.  $M_{\infty}$  is total water uptake due to absorption or loss due to desorption;  $M_t$  is water uptake due to absorption or loss due to desorption at time  $t$ . Temperature 37°C: lower graph,  $0 \leq (t^{1/2}/l) \leq 150 \text{ min}^{1/2}\text{-mm}^{-1}$ ; upper graph,  $90 \leq (t^{1/2}/l) \leq 240 \text{ min}^{1/2}\text{-mm}^{-1}$ . Resin D.I.S. absorption: relative pressure  $h = 0.75$ ; film thickness  $l$  (mm) ( $\odot$ ) 0.285; ( $\ominus$ ) 0.319; ( $\odot$ ) 0.384. Desorption: ( $h = 0$ ) film thickness  $l$  (mm): ( $\odot$ ) 0.285; ( $\ominus$ ) 0.319; ( $\odot$ ) 0.384. Vertical line at  $(t^{1/2}/l)_{0.99} = 139.4 \text{ min}^{1/2}\text{-mm}^{-1} = 3.03 (t^{1/2}/l)_{0.5}$ .

g, i.e.,  $\sim 0.02\%$ ). For the polyamide (PA)- and anhydride (A)-cured resins there was a net gain in weight following a sorption-desorption cycle. Only the reversible sorption data for the diamine-cured resins was used for the thermodynamic analysis and the computation of isosteric heats of absorption.

## RESULTS AND DISCUSSION

### Equilibrium Sorption by Diamine-Cured Resins

Typical absorption isotherms are given in Figures 1 and 2 in which the equilibrium water uptake  $W$  (%) (g absorbed water/100 g resin) is plotted vs. relative pressure or humidity,  $h = p/p_0$ , where  $p$  is the pressure and  $p_0$  is the saturation vapor pressure of water at the isotherm temperature. The water sorption data is listed in Table II. Diffusion of water into these resins is slow and hence long

TABLE II  
 Water Sorption by Resin D.I.S

Temp	$h$	$p$ (mm Hg)	$W$ (g/100 g resin)
0.2°C	0.35	1.63	0.95
	0.60	2.79	1.62
	0.76	3.53	1.93
	1.00	4.65	2.59
25°C	0.08	1.9	0.24
	0.22	5.23	0.52
	0.33	7.84	0.69
	0.53	12.59	1.17
	0.75	17.82	1.68
	0.90	21.38	2.06
	1.00	23.76	2.51
37°C	0.06	2.82	0.13
	0.115	5.41	0.26
	0.21	9.88	0.45
	0.32	15.06	0.72
	0.491	23.11	1.08
	0.62	29.18	1.35
	0.75	35.30	1.63
	0.80	37.65	1.73
	0.90	42.36	1.96
	1.00	47.07	2.36
	50°C	0.31	28.86
0.46		42.55	0.88
0.75		69.38	1.53
1.00		92.51	2.47
60°C	0.30	44.81	0.60
	0.43	64.23	0.85
	0.75	112.03	1.62
70°C	1.00	149.38	2.44
	0.29	67.77	0.49
	0.40	93.48	0.75
	0.75	175.27	1.46
80°C	1.00	233.70	2.45
	0.29	102.98	0.53
	0.38	134.94	0.69
	0.74	262.77	1.63
90°C	1.00	355.1	2.57
	0.24	126.18	0.47
	0.28	147.21	0.54
	0.60	315.46	1.26
	0.65	341.74	1.32
	0.78	410.09	1.73
	1.00	525.76	2.77

sorption times are required to ensure that equilibrium was attained (Fig. 3). For the film 0.285 mm thick sorption was almost complete within 1.25 days, but, to ensure that equilibrium had been attained, measurements were continued for 4.9 days. For this resin hardener system all the absorbed water diffused out at  $h = 0$ ; hence the water sorption behavior is reversible, and Figures 1 and 2 are equilibrium isotherms.

For a thermodynamic analysis of absorption isotherms it is essential that equilibrium sorption be measured. There are several types of effects which may

lead to nonequilibrium effects, and several of these were discussed by Park,<sup>12</sup> and more recently other anomalies have been observed.<sup>13</sup> These include viscoelastic relaxation<sup>14</sup> and chemical changes due to reaction between the penetrant molecule and some species present in the resin.<sup>15</sup> Sorption into the resins cured with phthalic anhydride and the polyamide were not reversible, there was a net weight gain after water sorption, as will be discussed subsequently, and hence the sorption data for resins cured with these hardeners was not included in the thermodynamic analysis.

The reversibility for the DDM cured resin is shown by the common curve for absorption and desorption data points in Figure 3. Thus, the behavior of this resin system is different from that studied by Moy and Karasz,<sup>16</sup> who found that not all the water desorbed at the sorption temperature, but could be removed by heating the polymer above 100°C. Also from the long-term measurements (upper curve in Fig. 3), it can be seen that within this period there is not an increase in water sorption due to either viscoelastic relaxation, chemical changes, or a combination of such effects.

From an examination of Figure 1 it can be seen that for the whole range  $0 \leq h \leq 1$  the absorption isotherm at 0.2°C is linear and obeys an apparent Henry's law in the form

$$W = K'_H \cdot h \quad (1a)$$

where  $W$  is the concentration of absorbed water (g water/100 g resin),  $h$  is the relative pressure  $p/p_0$ , and  $K'_H$  is the equivalent reciprocal of Henry's law constant. At higher absorption temperatures there is a deviation from the linear isotherm and that at 90°C is linear in the region  $0 < h < 0.65$ . Kwei<sup>17</sup> also found a linear isotherm in the same relative pressure range for a resin cured with another type of diamine hardener (Fig. 1), but the amount of water absorbed is higher.

All the sorption measurements were made at temperatures lower than the glass transition temperature of the resin containing absorbed water. From broadline proton NMR measurements<sup>3</sup> it may be concluded that the extent of molecular motion of the resin matrix is constant over the temperature range of these sorption measurements. At 90°C the line width of a sample containing 2.5 wt % water is essentially identical with that of the dry resin.<sup>3</sup> Also, there is a linear Arrhenius type plot of  $\ln D$  vs.  $1/T$  for the region 0.2–90°C, and hence the rate controlling diffusional processes are the same at 90°C as at lower temperatures. Hence this change in shape of the absorption isotherm with temperature cannot be attributed to increased mobility of the resin which might increase the availability of sorption sites. In any case the amount absorbed decreases slightly with increase in sorption temperature except in the region where  $h \rightarrow 1$ .

The effect of hardener is also illustrated by the amount of water absorbed in the resin studied by Moy and Karasz<sup>4</sup> (see Fig. 1); for the amount absorbed when  $h = 1$ , but the isotherms were not linear, those at 25°C, 35°C, and 75°C were sigmoidal, while at higher temperature the amount of water absorbed was lower and the isotherms were of the saturation or Langmuir type.<sup>4</sup> At 37°C, Figure 2, the isotherm is linear up to a relative pressure of at least  $h = 0.9$ . The data point for the amount absorbed from liquid water,  $h = 1.0$ , is about 8% higher than would be predicted from a linear isotherm. It is important to note that agreement is poor with recently reported data<sup>6</sup> for this system but is in excellent

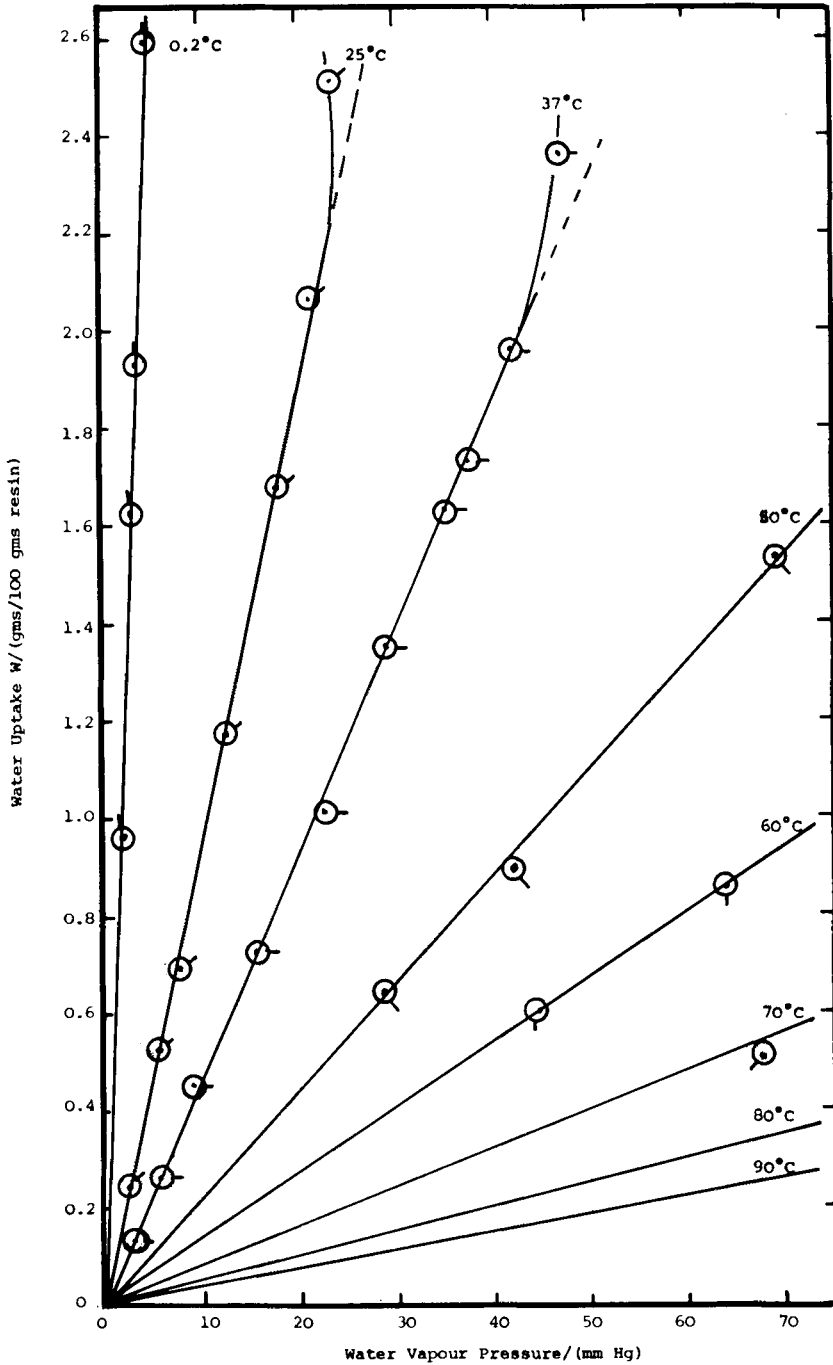


Fig. 4. Water uptake vs. water vapor pressure for resin D.1.S. in the temperature range  $0.2^{\circ}\text{C} \leq T \leq 60^{\circ}\text{C}$ : ( $\odot$ )  $0.2^{\circ}\text{C}$ ; ( $\ominus$ )  $25^{\circ}\text{C}$ ; ( $\oplus$ )  $37^{\circ}\text{C}$ ; ( $\otimes$ )  $50^{\circ}\text{C}$ ; ( $\phi$ )  $60^{\circ}\text{C}$ ; ( $\rho$ )  $70^{\circ}\text{C}$ . Data points at higher temperatures are given in Figure 5; the graphs for  $70^{\circ}\text{C}$ ,  $80^{\circ}\text{C}$ , and  $90^{\circ}\text{C}$  are drawn with the same slope as in Figure 5.



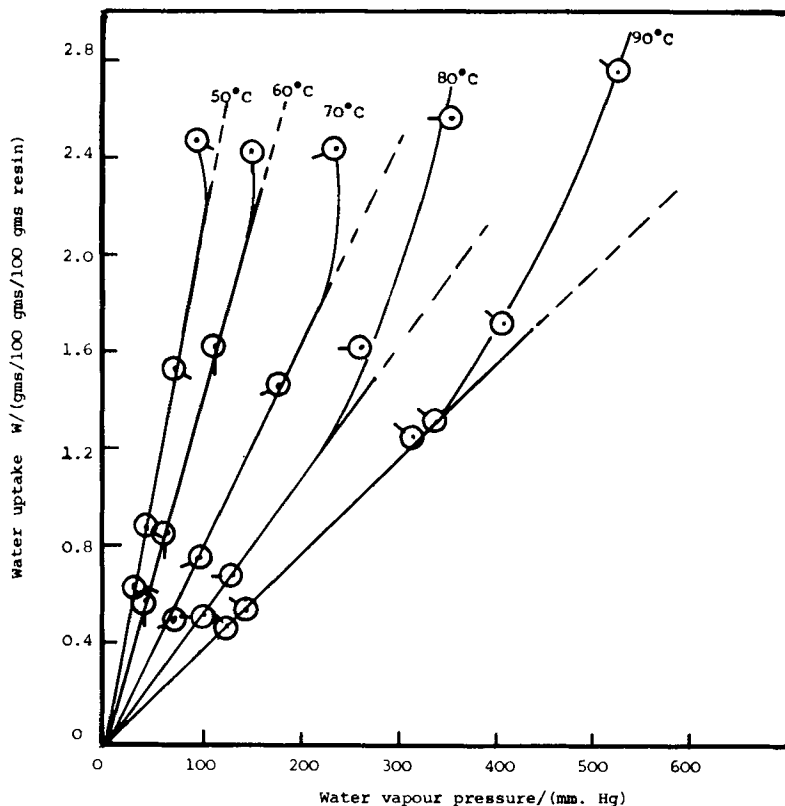


Fig. 5. Water uptake vs. water vapor pressure for resin D.1.S in the temperature range  $50^{\circ}\text{C} \leq T' \leq 90^{\circ}\text{C}$ : (Q)  $50^{\circ}\text{C}$ ; ( $\phi$ )  $60^{\circ}\text{C}$ ; ( $\rho$ )  $70^{\circ}\text{C}$ ; ( $\ominus$ )  $80^{\circ}\text{C}$ ; ( $\odot$ )  $90^{\circ}\text{C}$ .

agreement with that of Eley, Goodchild, and Rudham<sup>18</sup> as may be seen from an inspection of Figure 2.

To assess the effect of resin cure on water uptake a higher molecular weight precursor resin which is solid at ambient temperatures had to be used. The water sorption for such an uncured resin is also shown in Figure 2, and is only about half that of the resin cured with DDM. (The data points for water sorption by D.2.S at  $25^{\circ}\text{C}$  are omitted from Figure 2 for clarity, but the isotherm is essentially identical with that shown for D.1.S at  $37^{\circ}\text{C}$ ). With cure the water sorption increases due to the formation of hydroxyl groups which provide sorption sites for the water due to hydrogen bonding. For example, when  $h = 0.33$  the water uptake by the cured resin (D.2.S) is only 0.78 wt % while that of the uncured resin 2 is 0.42 wt %.

Higher temperature isotherms differ little in the temperature range  $50\text{--}90^{\circ}\text{C}$ , but deviations from linearity occur at lower relative pressures the higher the isotherm temperature. The effect of temperature is more clearly illustrated by plotting water uptake versus pressure as in Figures 4 and 5, a form of plot required for the thermodynamic analysis which will be discussed later. It can be seen that in general  $W = W(p)$  is linear except at pressures close to the saturation

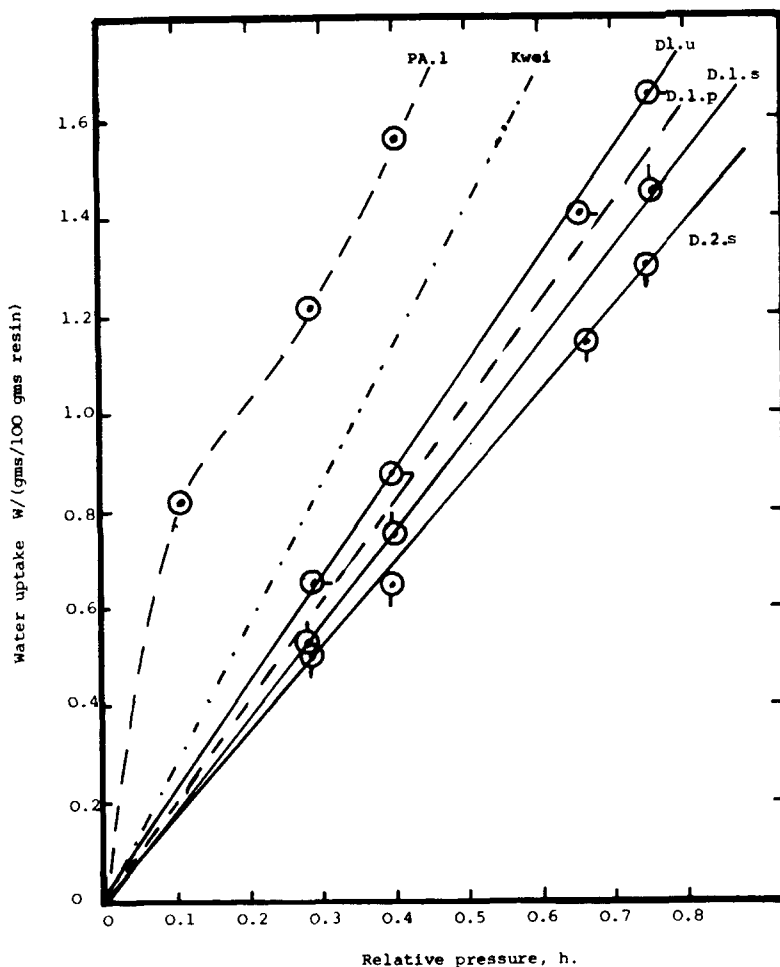


Fig. 6. Water absorption isotherms at 70°C: effect of cure treatment: (- - ○ - -) polyamide cured resin PA.1; for measurements at higher relative pressures, see Figure 9; (- . - .) Data of Kwei<sup>17</sup> at 70°C. Similar prepolymer to resin 1 cured with the stoichiometric amount of 1,6-hexane diamine; (○) diamine-cured resin, D.1.S, standard cure; (⊕) diamine-cured resin, D.1.u, under cure, (- - -) diamine-cured D.1.pa and D.1.p.b—post-cured—data points omitted for clarity; (⊙) diamine-cured resin D.2.S—higher molecular weight prepolymer—standard cure.

vapor pressure, that is, as  $p \rightarrow p_0$ . These curves also demonstrate that deviations from Henry's law in the form

$$W = K_{HP} \quad (1b)$$

occur at lower water uptakes at higher temperatures.

The effect of resin cure treatment on the sorption isotherms at 70°C can be seen to be small (Fig. 6), but the differences are real. For the postcured resins there was not any significant difference in sorption behavior between samples which had been heated at 160°C for 24 h or alternatively at 200°C for 1 h. The sample prepared with a standard cure treatment absorbs slightly less water than either the under- or postcured resins.

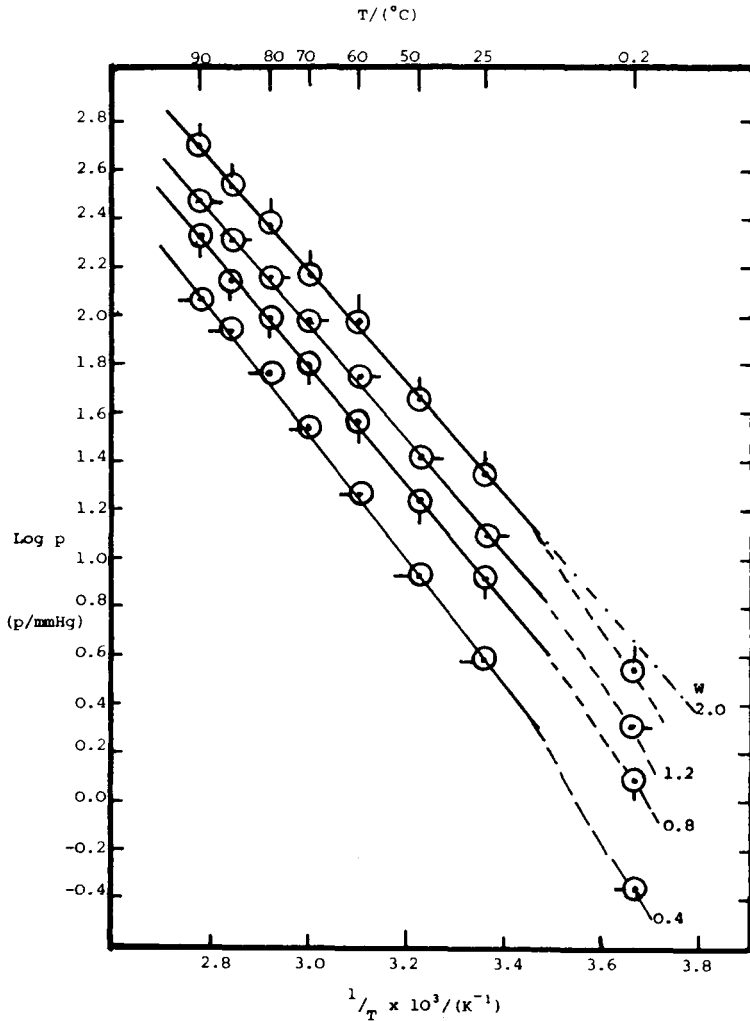


Fig. 7. Water absorption isotherms for resin D.1.S. Water uptake  $W$  (g/100 g resin);  $W \equiv$  (◐) 2.0; (◑) 1.2; (◒) 0.8; (◓) 0.4. Data for  $W = 1.6$  (omitted for clarity) is linear in the range  $2.76 \times 10^{-3} \leq 1/T \leq 3.36 \times 10^{-3}$  ( $90^\circ\text{C} \geq T' \geq 25^\circ\text{C}$ ).

### Thermodynamic Analysis

The isosteric heat of absorption,  $q_{st}$ , can be calculated from

$$q_{st} = -R \left[ \frac{\partial \ln p}{\partial (1/T)} \right]_W \tag{2}$$

and its application has been discussed by Skirrow and Young.<sup>19</sup> Data in the form of sets of  $\log p$  and  $1/T$  values at constant amount of absorbed water are obtained from the linear regions of the plots of  $W$  vs.  $p$  (Figs. 4 and 5) and are plotted as isotherms in Figure 7. It can be seen that the isotherms are linear for all water concentrations in the range  $0.4 \leq W \leq 2.0$  and in the temperature range  $25^\circ\text{C} < T < 90^\circ\text{C}$  ( $298 \text{ K} \leq T \leq 363 \text{ K}$ ). A condition for the direct applicability of

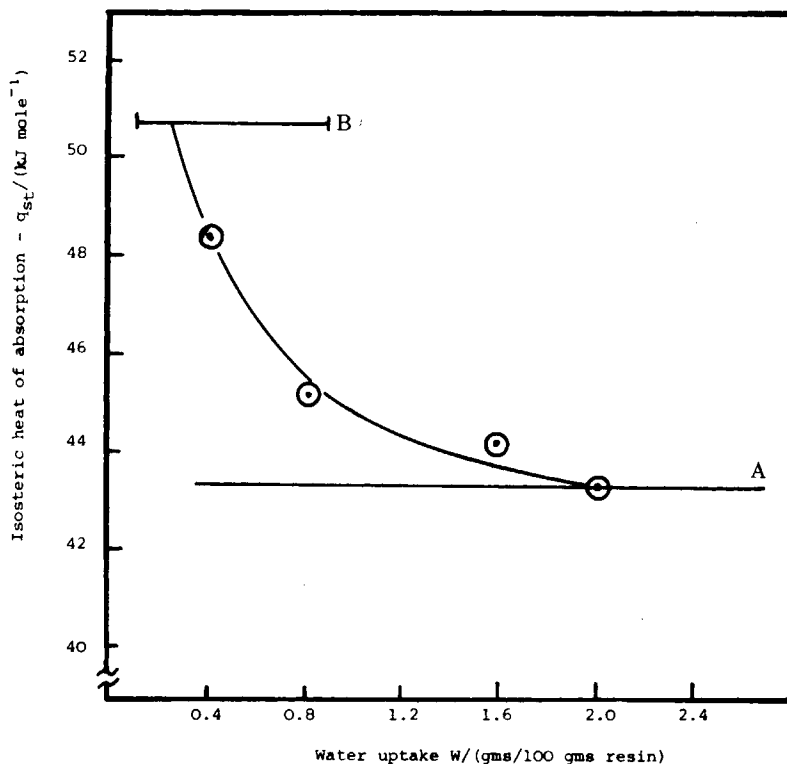


Fig. 8. Isosteric heat of absorption for diamine cured resin D.1.S: (A) heat of vaporization of water at 37°C; (B) data of Eley, Goodchild, and Rudham<sup>18</sup> for a resin similar to D.1.S.

eq. (2) is that the isosteric heat of absorption should be essentially constant over the temperature range of the data used for the calculation of  $q_{st}$ . This condition is satisfied in temperature range 25–90°C, and the only data in that range were used for the calculation of  $q_{st}$ . It is not clear why there is a slight deviation (see Fig. 7), for the absorption at 0.2°C, especially as both the absorption isotherm Figure 1 and the plots of  $W$  vs.  $p$  (Fig. 4) are linear as required by eqs. (1a) and (1b) for sorption which obeys Henry's law.

For the lower amounts of water uptake the isosteric heat of absorption is similar to that obtained by Goodchild,<sup>18</sup> who did not find any significant change with the amount absorbed. From the present measurements it was found that  $q_{st}$  decreases with increase in the amount of water absorbed (Fig. 8). Similar effects have been observed for the absorption of water by nylon-6<sup>19</sup> and also by several poly(alkyl methacrylate)s.<sup>20</sup> The absolute amounts of water absorbed in the poly(alkyl methacrylate)s are similar to the water uptake by the diamine-cured epoxy resins but the water sorption by the nylon-6 is much higher. The interpretation of the heat of absorption has been discussed by Skirrow and Young,<sup>19</sup> and the similarity of the heats of absorption in these systems indicates that the interaction of the water molecules with the sorption sites will be similar. More specifically, the water is hydrogen bonded to the sorption sites as may be seen in some cases by the infrared spectra of epoxy resins in which deuterium exchange, using  $D_2O$ , allows separation of the isolated —OD and “hydrogen”

TABLE III  
Concentration Dependence of Thermodynamic Data at 37°C for Diamine-Cured Resin D.1.S

$h$	$W$ (g/100 g)	$-\Delta G$ (kJ·mol <sup>-1</sup> )	$-\Delta H$ (kJ·mol <sup>-1</sup> )	$\Delta S$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )
0.18	0.4	4.42	4.93	-1.66
0.315	0.8	2.98	1.71	4.08
0.546	1.20	1.56	0.79	2.48
0.73	1.60	0.81	0.247	1.81
0.912	2.0	0.24	-0.213	1.45

Note:  $\Delta H_A = q_{st} - \Delta H_c$ , where  $\Delta H_c$  is the molar heat of condensation of water.

bonded —O—D—O— infrared absorption bands.<sup>10</sup> These effects were also observed by Fuller and co-workers.<sup>21</sup>

The entropy of dilution was calculated using

$$\Delta S = - \left[ \frac{\Delta H_A - \Delta G}{T} \right] \quad (3)$$

where  $\Delta H_A = q_{st} - \Delta H_c$ ,  $\Delta G = RT \ln h$ , and  $\Delta H_c$  is the molar enthalpy of condensation of water as discussed by Skirrow and Young,<sup>19</sup> who also point out that caution must be used when interpreting such calculations. The calculated free energies, enthalpies, and entropies of absorption at 37°C are given in Table III. It may be seen that the entropies of dilution are of similar magnitude to those for water absorption by nylon-6<sup>19</sup> but are less than those for water absorption by poly(alkyl methacrylate)s.<sup>20</sup> The decrease in both heat and entropy of dilution with increase in the concentration of absorbed water has been regarded by Barrie and Machin<sup>20</sup> as consistent with progressive association of water molecules with increased uptake. This association is often analyzed in terms of a clustering function. Brewis and co-workers<sup>6</sup> have calculated the cluster function for water sorption by a resin similar to the present resin 1 but cured with di(1-aminopropyl-3-ethoxy) ether in which the amount of water absorbed is more than twice that by the present diamine-cured system. Also the absorption isotherm is not linear, and they found that the nature of the cluster function indicates that clustering of water molecules occurs. Lundberg<sup>22</sup> has calculated the cluster function for a mixture which obeys Henry's law and concluded that clustering of solute molecules does not occur. Therefore, because the water sorption isotherms for the diamine cured resin (D.1.S) are linear over most of the accessible concentration range, clustering of water molecules will be excluded in the region where Henry's equation (1a) [or (1b)] is obeyed.

### Effect of Hardener

Water absorption isotherms for the resin cured with a polyamide PA.1 are given in Figure 9 and differ from those cured with a diamine (D.1.S). They are sigmoidal, type II, isotherms in the BDDT classification,<sup>23</sup> but there is another important difference: the isotherms are irreversible. After a sorption-desorption cycle the weight of the sample is *higher* than its initial weight. Not all of the absorbed water could be removed even after evacuation at a temperature of 90°C. Of course, raising the temperature may increase the rate of reaction

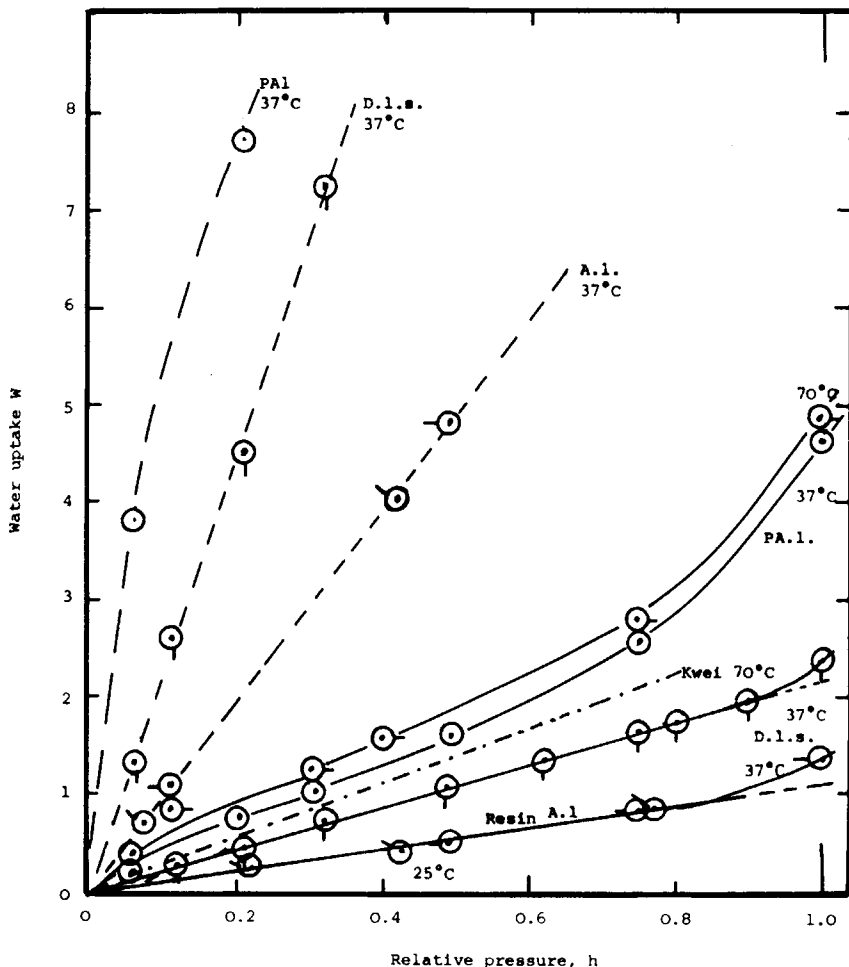


Fig. 9. Water absorption isotherms; the effect of curing agent. (—) ordinate scale 1  $\equiv$  1 g/100 g resin; (---) ordinate scale 1  $\equiv$  0.1 g/100 g resin. Versamid-cured resin PA.1, isotherm temperature: ( $\odot$ ) 37°C; ( $\ominus$ ) 70°C. Diamine-cured resin D.1.S., isotherm temperature ( $\oplus$ ) 37°C. Phthalic anhydride cured resin A.1, isotherm temperature: ( $\ominus$ ) 37°C; ( $\odot$ ) 25°C. Resin prepolymer similar to resin 1 cured with 1,6-hexane diamine—data of Kwei<sup>17</sup>—isotherm temperature 70°C (---) (ordinate scale 1  $\equiv$  1 g/100 g resin).

of water with the resin; but sorption-desorption cycles for water absorbed by the diamine-cured resin were reversible even at 90°C.

At present it is not possible to be specific regarding the possible reactions between water and the polyamide or the anhydride cured resin. Kaebel and Dynes<sup>15</sup> have concluded that there is chemical reaction between water and the crosslinking site in a dicyandiamide-cured epoxy resin. But the specific reaction which they postulate could not occur with the present resins because of the different chemical species involved in the crosslinking site. Thus the elucidation of the retention of water by the polyamide- and anhydride-cured resins requires further study. However, it is established that for the polyamide- and anhydride-cured resins not all the water can be removed even after desorption at 90°C

TABLE IV  
 Retention of Water

$h$	$W$ (g/100 g resin)	$\Delta W^a$	$\Delta W/W \times 100\%$
A. Resin PA.1			
Sorption at 37°C			
0.313	1.035	0.45	43.5
0.491	1.573	0.53	33.7
0.748	2.51	0.59	23.5
Sorption at 70°C			
0.29	1.21	0.63	52.1
0.75	2.78	0.767	27.6
B. Resin A.1			
Sorption at 37°C			
1.0	1.35	0.35	25.9

<sup>a</sup>  $\Delta W = W_d - W_i$ , where  $W_d$  is the weight of the test piece after a sorption-desorption cycle with desorption for 16 h at 90°C.  $W_i$  is its initial weight.

for 16 h (Table IV). In this respect the behavior of these resin systems is different from those with a sulphone hardener studied by Moy and Karasz,<sup>16</sup> who found that all water could be desorbed at 100°C in a dry atmosphere.

The *amount* of water which reacted with the polyamide-cured resin increased with the amount of water absorbed and also with increase of sorption temperature, as is shown in Table IV. However, the percentage of sorbed water that reacted decreased with concentration of sorbed water but increased with sorption temperature. From this it would appear that it is the concentration of reactive groups in the resin which determines the amount of water which reacts. However, the limited data presented here shows that a systematic investigation of this effect is required. Water sorption by the phthalic-anhydride-cured resin, A.1, was also irreversible and the amount of water retained in the resin after a sorption-desorption cycle is given in Table IV.

### General Observations

From the results presented in this paper it is clearly established that the amount of water absorbed by these epoxy resins depends on the type of hardener used to effect cure, that is, the chemical nature of the crosslinks determines the water sorption behavior. The polyamide cured resin, PA.1, absorbs at  $h = 1$  nearly four times as much water as the anhydride-cured resin, A.1 (see Fig. 9). It should also be noted that for the resins cured with the polyamide or phthalic anhydride the water sorption even at modest sorption temperatures was not reversible (see Table IV). Water sorption by the diamine-cured resins was reversible, and the uptake at  $h = 1$  intermediate between that of the polyamide and phthalic anhydride systems.

Models for water sorption by polymers may be classified as either "site" or solution theories.<sup>1</sup> Initially, solution models would appear inappropriate for sorption when only relatively small amounts of water are absorbed ( $W < 5\%$ ), but some systems have been analyzed in terms of the Flory-Huggins theory of polymer solutions, as discussed by Barrie.<sup>1</sup> By suitable graphical plots it was established that such a theory is unsatisfactory for the absorption of water by

these epoxy resins. The value of the polymer-solute interaction parameter,  $\chi$ , is not constant, and its value is too high for conformity with the Flory-Huggins theory.

Since a solution model is unsatisfactory, it is appropriate to consider site models for water sorption by these epoxy resins. In its simplest form site models are based on the postulate that there are specific sites, that is, chemical groups in the resin onto which the water molecules are strongly bound. At lower relative pressures these sites are singly occupied, but the behavior at higher relative pressures will depend on the details of the particular site theory. In this general form the type of bonding in singly occupied sites is not specified, but with a sorbate such as water it is obvious to postulate hydrogen bonding between the water molecules and these specific absorption sites in the resin. This has been confirmed for resin D.1.S by the change in the infrared spectrum with absorption of heavy water,  $D_2O$ , from which it may be seen that deuterium exchange of the resin hydroxyl groups occurs.<sup>10</sup> Goodchild<sup>18</sup> was unable to observe changes of the infrared spectrum due to the presence of ordinary water, and our results were similar. However, by effecting deuterium exchange, it can be concluded that the resin hydroxyl groups are accessible to heavy water since exchange occurs hydrogen bonds must be formed between the absorbed  $D_2O$  and the resin hydroxyl groups.

For the present isotherms for the diamine-cured resin, D.1.S, it is appropriate to regard them as essentially conforming to Henry's law but with a specification for each temperature of an upper limit for the relative pressure  $h$ , for which eq. (1) is applicable. Alternative isotherms equations such as the BET equation<sup>24</sup> gave an inferior "fit," and those suggested by Dent,<sup>25</sup> Barnes et al.,<sup>26</sup> and Burghoff and Pusch<sup>27</sup> offered no advantage compared with Henry's law [eq. (1)].

Also, a better fit would not be obtained by application of the dual sorption theory,<sup>28,29</sup> which is based on the postulate that in addition to a solution, Henry's law, sorption there is also a Langmuir-type sorption, such as would be due to "hole" filling. The combined isotherm is a simple sum of these two contributions. Such a combined isotherm is *concave* to the pressure axis at lower relative pressures. There is no evidence of such concavity in the isotherms for water sorption into these resins (Figs. 1 and 2), and in fact the isotherms at higher temperatures become *convex* to the pressure axis. Thus the slight deviation from Henry's law at higher temperatures cannot be attributed to a Langmuir-type contribution.

For Henry's law to apply to all temperatures the isosteric heat of absorption should be independent of the amount absorbed as may be shown by the following argument. Linear isosteres such as those in Figure 7 may be represented by

$$\ln p = \ln A + B \cdot (1/T) \quad (4)$$

with  $A = f(W)$ ,  $B \neq g(W)$ , and  $B = -q_{st}/R$  in conformity with eq. (2), when the isosteric heat is independent of the amount absorbed. Then the relationship between the pressure and the amount absorbed is

$$p = \kappa_H W \quad (5)$$

with  $A = \alpha W$  and the Henry's law constant

$$\kappa_H = \alpha \exp(B/T) \quad (6)$$



When  $A = \alpha W^n$  the relationship between pressure and the amount absorbed is then

$$p = \kappa_F W^n \quad (7)$$

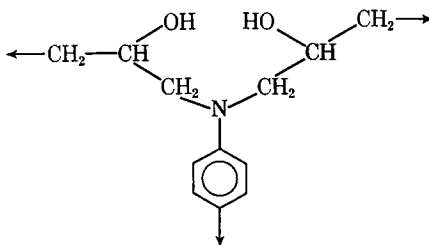
which is the equation for a Freundlich isotherm. However, if  $B = g(W)$ , then

$$p = \alpha W^n \exp[g(W)/T] \quad (8)$$

and Henry's law is not strictly correct even when  $n = 1$ , since there are two concentration-dependent terms; the deviation from eq. (1) will depend on the function  $g(W)$ . When  $B = g(W)$ , the isosteric heat of absorption will be concentration-dependent. Thus, deviations from Henry's law and the concentration dependence of the heat of absorption are interrelated.

Over recent years the Freundlich isotherms, eq. (7), has been used to represent the water absorption of epoxy resins and their composites with considerable discussion concerning the most appropriate value of  $n$ <sup>5</sup>. A plot of the present isotherm data at 37°C in the form  $\log W$  vs.  $\log h$  was linear with  $n = 1$ , as required by conformity with Henry's law. However, with this plot the absorption at  $h = 1$  in excess of that predicted by Henry's law is obscured, and it is not advisable to use the Freundlich equation (7) to predict the water sorption at high relative pressures and when these resins are immersed in liquid water.

From the structure of the cured resin it may be inferred that a primary candidate for the absorption site in the diamine cured resin, D.1.S, is a junction point which has the structure



From broad-line proton NMR measurements,<sup>3</sup> there is unambiguous evidence that the absorbed water molecules are reorienting isotropically at a frequency greater than  $10^5$  Hz. This is shown by the presence of a motionally narrowed line, which is absent from the dry resin but present in a resin containing absorbed water. This motionally narrowed line broadens and merges with that for the resin at about 0°C the lowest temperature at which a water isotherm was measured. Hence for the whole of the temperature range studied the water molecules must be jumping on and off the absorption sites, and the residence time of a water molecule at a junction point will on average be less than  $10^{-5}$  s. From the number of such sites present, which may be calculated from the stoichiometry given in Table I, and the amount of water absorbed at  $h = 1$  and 25°C of 2.51 wt %, it can be calculated that the ratio of number of water molecules to the number of junction point sites is about 2/3 (0.63). Barrie<sup>1</sup> gives a table from which the ratio of the moles of water sorbed to moles of polar groups per 100 g of polymer may be calculated for a range of polymers, and for this epoxy resin this ratio is approximately in the middle of the range.

However, further evidence that the junction points are primary sites for absorbed water molecules is provided by lower water uptake by the anhydride cured resins, while that cured with the polyamide, which has many potential hydrogen bonding sites, is more than double that of the diamine cured resin (Fig. 9). Thus, it is clear that the hardener has a major effect on the water sorption by epoxy resins. Therefore, in discussion of the behavior of epoxy resins exposed to either liquid water or environments containing water vapor, it is essential that the type of hardener, the stoichiometry, and cure treatment are specified.

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