Interaction of Weak Organic Acids with Insoluble Polyamides II

Study of Sorption of Selected Weak Organic Acids by Nylon 610

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Sorption studies were conducted at several different temperatures for a group of compounds having or behaving as weak organic acids using nylon 610 as the substrate. Six compounds were included in the investigation—benzoic acid, o-hydroxybenzoic acid, m-hydroxybenzoic acid, p-hydroxybenzoic acid, methyl p-hydroxybenzoate, and propyl p-hydroxybenzoate. The collected data permitted the evaluation for each compound of (a) the saturation value of solute in the nylon, (b) the affinity of the solute toward the plastic, (c) the standard heat of sorption, (d) the apparent diffusion coefficient and (e) the activation energy of diffusion. With the Rotinyan and Drozdov equation, it was possible to confirm that the diffusion of the solute in the plastic was the rate-determining step in the sorption process.

GREATER USE is being found for insoluble polymeric materials in pharmacy and medicine. Such diverse uses as packaging material, administration devices, prosthetic devices, and vehicles for prolonged action medication emphasize the versatility of plastic materials and suggest even greater applications in the future for plastics in the various facets of pharmacy and medicine.

One particular phase of plastics which deserves special attention is the possible interaction of drugs with plastics. A knowledge of such reactions may be helpful to the industrial pharmacist and other investigators interested in solute-polymer interactions.

A previous paper (1) presented results from a sorption study of salicylic acid by nylon 66 and showed the influence of concentration, solvent system, temperature, and pH on the uptake of the drug by the nylon. It was assumed that the salicylic acid was adsorbed on the surface of the nylon followed by penetration and diffusion of the drug into the plastic. The rate-determining step, it was deduced, was the diffusion process.

This paper reports a sorption study of six agents by nylon 610. From the data it has been possible to derive some thermodynamic constants which may be used to compare the six agents. Kinetic treatment of the data also makes possible the calculation of apparent diffusion coefficients. Finally, the data may be treated in a manner to justify the assumption that the rate controlling step in the sorption process is one of diffusion in the plastic.

EXPERIMENTAL

Equipment and Supplies.—Beckman DB spectrophotometer, Fullerton, Calif.; pH meter, Leeds and Northrup Co., Philadelphia, Pa.; benzoic acid, A.R., J. T. Baker Chemical Co., Phillipsburg, N. J.; o-hydroxybenzoic acid, A. R., Mallinckrodt Chemical Works, St. Louis, Mo.; m-hydroxybenzoic acid, A. R., K & K Laboratories, Inc., Jamaica, N. Y.; p-hydroxybenzoic acid, A. R., Eastman Organic Chemicals, Rochester, N. Y.; methyl p-hydroxybenzoate, A. R., Eastman Organic Chemicals, Rochester, N. Y.; propyl p-hydroxybenzoate, A. R., Eastman Organic Chemicals, Rochester, N. Y.; Nylon 610, (Zytel Fe-2419 NC-10) E. I. du Pont de Nemours & Co., Wilmington, Del., were employed.

Treatment of Nylon 610 Samples.—It was necessary to devise a washing procedure which would ensure the purity of samples needed for the experiments to remove contaminates or other components from the samples of nylon used throughout this investigation. The exact method of cleaning is described below.

Strips of nylon, measuring 1 × 13 in. were cut using a paper cutter and placed (approximately 200 strips) into a glass jar with 3500 ml. of solvent ether. The jar was capped and set aside (with intermittent shaking) for 2 hours at which time the solvent was decanted and acetone (3500 ml.) added. After 2 hours this solvent was decanted and the strips rinsed with distilled water, followed by the addition of 50% (v/v) ethyl alcohol. After 12 hours of contact, the alcoholic eluate was decanted and once again the strips rinsed with distilled water. The final step of washing consisted of exposing the strips to absolute ethyl alcohol for 2 hours, followed by repeated rinsings with distilled water. The strips were placed into a constant temperature oven at 65 ±1.0° for 8 hours to dry, then transferred into a desiccator for further use.

General Procedure for Studying Equilibrium Sorption Isotherms.—Exactly 150 ml. of each solution, prepared to a known concentration, was pipeted into the specially prepared glass tubes.

These tubes were closed by using ground glass stoppers and placed into a constant temperature water bath at a temperature slightly above the temperature which was to be used in the experiment. After an equilibrium temperature was reached inside the tube, the tubes were withdrawn, the stoppers removed, and a single strip of nylon (prepared as described earlier), previously weighed,[1] was immersed into the solution. The ground-glass stoppers were securely inserted to prevent leakage and the tubes placed back into the water bath at a specified temperature for a time period sufficient to ensure that equilibrium had been reached. Each experiment was done in duplicate. A control solution of each agent, without the nylon, was also included in each experiment.

Aliquots were drawn from each tube after equilibrium had been reached and the concentration of compound remaining in the solution determined. The difference between the amount of compound in the control solution and the amount left in the solution was considered as the quantity of agent sorbed by the nylon.

Method of Analysis.—In the experiments to be reported, six agents were employed. The assay for each agent was based upon a spectrophotometric method, using a Beckman spectrophotometer employing matched 1-cm. silica absorption cells. To determine the wavelength of maximum absorption, ultraviolet absorption spectra for methyl *p*-hydroxybenzoate and propyl *p*-hydroxybenzoate were carried out using distilled water as the solvent, while benzoic acid, *o*-hydroxybenzoic acid, *m*-hydroxybenzoic acid, and *p*-hydroxybenzoic acid were run in a 0.1 *N* hydrochloric acid solution. Appropriate blanks were used in all cases. From the absorption curves of each agent, the maximum wavelengths found were: benzoic acid, 229 mμ; *o*-hydroxybenzoic acid, 303 mμ; *m*-hydroxybenzoic acid, 236 mμ; *p*-hydroxybenzoic acid, 255 mμ; methyl *p*-hydroxybenzoate, 255 mμ; and propyl *p*-hydroxybenzoate, 255 mμ. Each of the solutions obeyed the Beer-Lambert relationship in the concentration range employed.

During the actual experiments, concentrations of the agents in each solution were determined by removing an aliquot sample from the test solution, bringing it to room temperature, diluting with the appropriate solvent or solution until the concentration was in a range suitable for determination of the optical density in the spectrophotometer. In each instance, methyl *p*-hydroxybenzoate and propyl *p*-hydroxybenzoate were diluted with distilled water while the other four compounds were diluted with 0.1 *N* hydrochloric acid. Suitable blanks were run simultaneously with each compound. The optical density was converted to an equivalent concentration unit based upon standard solutions of each drug.

Effect of Concentration on Sorption.—An experiment was conducted at a temperature of 50±0.02° to determine the equilibrium concentration of each agent sorbed by nylon 610 at different original concentrations. The data was then fitted to a Langmuir relationship

$$\frac{1}{q} = \frac{1}{KS\bar{C}} + \frac{1}{S} \qquad \text{(Eq. 1)}$$

where q is the amount of solute sorbed at equilibrium in moles per kilogram, K is a constant, S the saturation concentration when all sites in the nylon are occupied, and C is the equilibrium concentration of the agent in the solution in moles per liter. When $1/q$ is plotted against $1/C$, a linear relationship exists. From the intercept $(1/S)$, it is possible to calculate S or the saturation value for each agent.

Table I summarizes $1/q$ and $1/C$ values for all of the six agents and the calculated S values. Figure 1 represents a Langmuir plot of one of the agents. The intercepts for the six compounds were computed by least square methods, using only those points which fell on the linear portion of the line.

Affinity and Heat of Sorption.—To accumulate useful data on the interaction of solute molecules with polymeric materials, it was necessary to find a way of describing the magnitude of the interaction in the form of an affinity value. The standard molar free energy or standard chemical potential ($-\Delta\mu°$) has been used in dyeing as a means of quantitizing the interaction of a dye with a particular fiber at steady state conditions, and this same value ($-\Delta\mu°$) has been called the "standard affinity" of the solute for the polymeric material. If it is assumed that the solute molecules are in the unionized state in both the liquid phase and the solid phase, an appropriate equation may be written for the affinity as

$$-\Delta\mu° = RT \ln a_s/a_1 \qquad \text{(Eq. 2)}$$

where $-\Delta\mu°$ is the difference in standard chemical potential between the solute in the liquid phase and the solute in the solid phase, a_s is the activity of the solute in the solid phase, a_1 is the activity of the solute in the liquid phase, and RT the usual gas constant and absolute temperature, respectively. In dilute solution, the activities may be replaced by concentration terms or

$$-\Delta\mu° = RT \ln C_s/C_1 \qquad \text{(Eq. 3)}$$

where C_s is in moles/Kg. in plastic and C_1 is the concentration of the solute in the liquid phase expressed in the same units (moles/Kg.)

A series of experiments, whereby the concentration of the solute in the liquid phase and the solid phase were determined after equilibrium had been reached, were conducted at several temperatures. Calculated values for $-\Delta\mu°$ are recorded in Table II and have been rounded off to three significant places since the accuracy of these constants are probably no greater than to the third significant figure.

The standard affinity and the standard heat of sorption ($\Delta H°$) are related by

$$\frac{-\Delta\mu°}{T} = \frac{\Delta H°}{T} + C \qquad \text{(Eq. 4)}$$

where $-\Delta\mu°$ and $-\Delta H°$ are as already defined, T the absolute temperature, and C a constant. A plot of $-\Delta\mu°/T$ *versus* $1/T$ will give a linear relationship with a slope equal to $\Delta H°$ A representative plot for methyl *p*-hydroxybenzoate is shown in Fig. 2; the $\Delta H°$ values for all the agents are included in Table II. The negative sign indicates that the sorption process is an exothermic reaction.

Diffusion and Activation Energy of Diffusion.—Experiments were conducted to evaluate the apparent diffusion coefficient of each of the six

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[1] Average weight of strips of nylon was approximately 2.0 Gm.

TABLE I.—EFFECT OF CONCENTRATION ON SORPTION OF SIX AGENTS BY NYLON 610 AT 50 ± 0.02° C.

Benzoic Acid		o-Hydroxybenzoic Acid		m-Hydroxybenzoic Acid	
$1/C^b$	$1/q^a$	$1/C$	$1/q$	$1/C$	$1/q$
961.5^d	35.36^d	1191.0	27.05	1191.0^d	27.01^d
386.5	13.77	587.9	14.15	586.2^d	14.31^d
289.1	10.50	391.5	9.4607	385.1	10.09
109.6	7.463	294.0	7.072	288.4	7.609
142.7	5.637	234.5^d	5.718^d	229.3	6.241
113.5	4.682	...	...	188.6	5.495
94.07	4.045	...	...	140.3	4.270
...	...			110.1	3.740
S^c = 1.05 moles/Kg.		S = 1.25 moles/Kg.		S = 0.934 moles/Kg.	

p-Hydroxybenzoic Acid		Methyl p-Hydroxybenzoate		Propyl p-Hydroxybenzoate	
$1/C$	$1/q$	$1/C$	$1/q$	$1/C$	$1/q$
1115.0^d	25.65^d	1609.0^d	33.36^d	2057.0	9.285
591.37^d	13.87^d	592.4^d	14.87^d	1634.0	7.557
350.9^d	8.658^d	394.8	8.850	1372.0	6.116
287.9	7.645	260.2	6.135	1168.0	5.383
228.6	6.315	194.0	4.700	811.0	3.865
189.4	5.394	153.0	3.965	...	...
140.1	4.300	...	...	...	...
110.4	3.708				
S = 0.837 moles/Kg.		S = 1.22 moles/Kg.		S = 3.81 moles/Kg.	

[a] q = Amount of solute sorbed at equilibrium in moles/Kg.   [b] C = Equilibrium concentration of solute in solution (moles/L.).   [c] Saturation concentration of solute in nylon.   [d] Points which did not fall on the linear portion of curve.

agents in nylon 610 at various temperatures. Solutions and samples were prepared as described earlier and the uptake of solute by the plastic determined at different time periods until equilibrium was reached. The apparent diffusion coefficient was calculated for each solute at each temperature by using Berthier's method as reported in a previous paper (1). In general, this procedure involves the plotting of two curves: (a) the experimental data is plotted as fractional uptake ($M_t/M\infty$) of the solute by plastic *versus* the square root of time, and (b) a theoretical curve based upon Berthier's work where fractional uptake (at a final per cent uptake) is plotted against the square root of a constant, K. The constant K is equal to Dt/l^2, D being the apparent diffusion coefficient (in cm.²/sec.), t the time at any fractional uptake, and l the thickness of the plastic. Since the solution has contact with both surfaces of the plastic, the thickness is divided by 2. It can be seen that a comparison of one curve with the other will permit the calculation of D. An experimental curve of fractional uptake ($M_t/M\infty$) *versus* square root of time is shown in Fig. 3 for one compound. Table III presents the apparent diffusion coefficient for each of the agents at each temperature.

By the use of the Arrhenius relationship

$$\log D = \log D_0 - \Delta E/2.303\ RT \quad (Eq.\ 5)$$

the activation energy of diffusion ($-\Delta E$) may be computed from the slope of the line when $\log D$ is plotted against $1/T$. Figure 4 demonstrates one such plot for one agent. Table III contains the calculated activation energies of the six agents studied.

Diffusion versus Rate of Interaction.—It has been assumed that the rate-determining step in the sorption of solute molecules by nylon is the diffusion process in the plastic in the experiments so far described. Much information from the dye industry lends support to this thesis, but it was felt that added proof of this fact with the six agents used in this investigation with nylon 610 would serve a useful purpose.
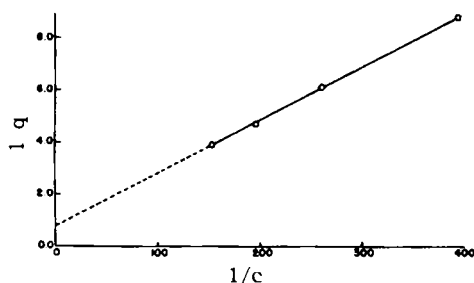

Fig. 1.—Sorption of methyl p-hydroxybenzoate by nylon 610 as a Langmuir plot at 50 ± 0.02°C.

Rotinyan and Drozdov (2) developed a basic mathematical formula which could be used to evaluate both the diffusion coefficient and the rate constant for a chemical reaction (first order) which could be applied to such diverse processes as roasting, leaching, washing, and cementation. The equation may be stated

$$\frac{1}{t} \ln \frac{a}{a-x} - \beta \frac{x}{t} = M \quad (Eq.\ 6)$$

where a is the initial concentration of solute in the liquid phase, x is the concentration of the solute reacting in time, t, and β and M are constants further defined as

$$\beta = \frac{vk}{kva + DSB\mu} \quad (Eq.\ 7)$$

$$M = \frac{kDSB\mu}{kva + DSB\mu} \quad (Eq.\ 8)$$

where v is the volume of solution in contact with the solid phase, k is the first-order rate constant, D is the diffusion coefficient, S is the surface area of the solid phase, and μ is a coefficient allowing for the transition from surface to volume concentration. The term β in the above two equations is equal to $xv/S\lambda$, where x and v are as previously defined, and λ is the thickness of the growing diffusion zone in the solid.

Equation 6 appears to be a very general equation

TABLE II.—AFFINITIES AND HEATS OF SORPTION OF
SIX AGENTS BY NYLON 610

—Benzoic Acid—		*o*-Hydroxybenzoic Acid		*m*-Hydroxybenzoic Acid	
Temp., °C.	$-\Delta\mu^{ob}$	Temp., °C.	$-\Delta\mu^\circ$	Temp., °C.	$-\Delta\mu^\circ$
65.0	1.96	65.0	2.17	67.0	2.20
60.0	2.04	55.0	2.20	55.0	2.22
55.2	2.07	50.0	2.22	50.0	2.22
50.0	2.08	...	...	45.0	2.24
45.0	2.10	...	...	...	...
$\Delta H^{\circ c} = -3.19$		$\Delta H^\circ = -3.39$		$\Delta H^\circ = -2.78$	
(75 mg./ 150 ml.)[a]		(225 mg./ 150 ml.)		(75 mg./150 ml.)	

p-Hydroxybenzoic Acid		Methyl *p*-Hydroxybenzoate		Propyl *p*-Hydroxybenzoate	
Temp., °C.	$-\Delta\mu^\circ$	Temp., °C.	$-\Delta\mu^\circ$	Temp., °C.	$-\Delta\mu^\circ$
65.0	2.24	69.7	2.16	65.0	3.06
60.0	2.25	65.0	2.19	60.0	3.04
55.0	2.27	55.0	2.23	55.2	3.04
50.0	2.24	50.0	2.26	50.0	3.04
45.0	2.28	45.0	2.28	45.0	3.03
$\Delta H^\circ = -2.75$		$\Delta H^\circ = -3.63$		$\Delta H^\circ = -2.60$	
(75 mg./ 150 ml.)		(150 mg./ 150 ml.)		(45 mg./150 ml.)	

[a] Original solution concentration. [b] $-\Delta\mu^\circ$ = Difference in standard chemical potential between the solute in the liquid phase and the solute in the solid phase (in Kcal./mole) or *affinity*. [c] $-\Delta H^\circ$ = Standard heat of sorption (in Kcal./mole).
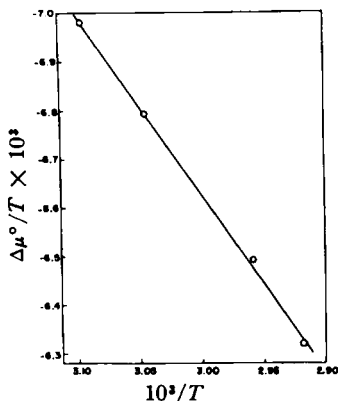

Fig. 2.—Relationship between standard affinity of methyl *p*-hydroxybenzoate toward nylon 610 as a function of temperature.

which may be applied to a process where molecules from one phase react at the surface of a second phase, then penetrate and diffuse into the second phase interacting at various sites as diffusion continues. If $1/t \ln(a/a - x)$ is plotted against x/t, a straight line should result with a slope of β and an intercept of M. To test the validity of Eq. 6, a plot was made of all six agents sorbed by the nylon; in each instance a linear relationship was noted. Figure 5 shows one such plot for methyl *p*-hydroxybenzoate. The values for β and M (by least squares) are shown in Table IV for each of the six agents at each temperature.

If we now assume that the diffusion process is the determining step in the sorption, then

$$DSB\mu \ll kva; \quad \beta \rightarrow 1/a; \quad M \rightarrow DSB\mu/va$$

Table IV shows that the calculated values for $1/a$ do approach the β values, hence the assumption of diffusion being the rate-determining step is justified. If $1/a$ were exactly equal to β, the diffusion coefficient would be zero, and the reaction would take place only at the surface of the plastic.

Effect of pH on Sorption.—To determine the effect of pH on the sorption of certain acidic compounds, benzoic acid, *o*-hydroxybenzoic acid, *m*-hydroxybenzoic acid, and *p*-hydroxybenzoic acid were prepared as aqueous solutions at different pH values using hydrochloric acid at very low pH values and sodium hydroxide at the higher pH values. The other two agents (methyl *p*-hydroxybenzoate and propyl *p*-hydroxybenzoate) were not included in this experiment since degradation was taking place in the alkaline pH range. These solutions were placed in contact with samples of nylon 610 in glass tubes, stoppered, and stored in a constant temperature water bath at a temperature of $50 \pm 0.02°$ for a period of time sufficient for equilibrium to have been reached. The amount of agent sorbed by the nylon for each compound at each pH was determined. At the same time the pH of each solution was measured. Plots of uptake *versus* final pH for each of the agents were made and in each instance appeared as shown for benzoic acid in Fig. 6.

DISCUSSION

Nylon 610 is a condensation polymer prepared from hexamethylenediamine and sebacic acid. In general, these polyamides have a number average molecular weight of around 25,000. The polymer, as with all nylons, has three polar sites in the chain (3): (*a*) terminal carboxylic end groups, (*b*) terminal amino groups (at other end), and (*c*) repeated amide groups. It is believed that interactions of certain ionic compounds are with the end amino groups, while those unionized compounds having acidic hydrogens will interact primarily at the amide linkages (3–5). In the sorption process solute molecules will penetrate into the nylon and diffuse through the amorphous zone. The crystalline regions in the nylon prevent the passage of solute molecules due to the extremely high degree of polymer chain orientation.

Samples of nylon 610 used in the experiments reported here were taken from the same lot of nylon to
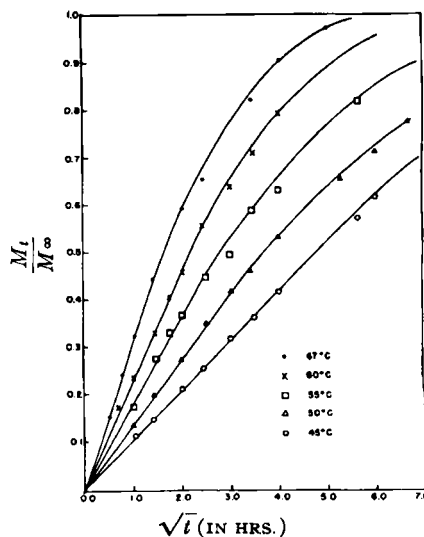

Fig. 3.—Fractional uptake of methyl *p*-hydroxybenzoate by nylon 610 *vs.* square root of time at a number of temperatures.

Table III.—Apparent Diffusion Coefficients of Six Agents in Nylon 610 and Activation Energies of Diffusion

Compd. Name	Temp., °C.	Diffusion Coefficient, cm.²/sec.	Activation Energy, Kcal./ mole
Benzoic acid (75 mg./150 ml.)[a]	65.0	3.32 × 10⁻⁹	12.9
	60.0	1.46	
	55.2	1.04	
	50.0	0.693	
	45.0	0.305	
o-Hydroxybenzoic acid (225 mg./150 ml.)	65.0	3.06 × 10⁻⁹	19.9
	60.0	1.99	
	55.0	1.35	
	50.0	0.770	
m-Hydroxybenzoic acid (75 mg./150 ml.)	60.0	9.15 × 10⁻¹⁰	18.9
	55.0	5.61	
	50.0	3.93	
	45.0	2.34	
p-Hydroxybenzoic acid (75 mg./150 ml.)	65.0	9.40 × 10⁻¹⁰	17.9
	60.0	7.44	
	55.0	4.74	
	50.0	3.07	
Methyl p-hydroxy-benzoate (150 mg./-150 ml.)	67.0	3.54 × 10⁻⁹	20.9
	60.0	1.81	
	55.2	1.16	
	50.0	0.720	
	45.0	0.372	
Propyl p-hydroxy-benzoate (45 mg./150 ml.)	65.0	3.93 × 10⁻⁹	14.5
	60.0	2.98	
	55.2	1.73	
	45.0	1.01	

[a] Original concentration in solution.

ensure a uniform sample. In our own laboratory it has been found that there may be significant differences in certain physical properties of nylon when samples are taken from different lots. In these experiments, as well as others, it was necessary to wash the nylon thoroughly with selected solvents to remove any contaminates. Inadequate or improper washing led to erratic results.

Effect of Concentration.—An increase in the original concentration for each compound resulted in an increase in the equilibrium sorption of the compound by the nylon at isothermal conditions. A Langmuir plot (Fig. 1) made possible the calculation of the theoretical amount of solute which would be sorbed by the nylon if all the sites in the nylon were filled. Table I presents these values. In general the S values approached 1.0 moles/Kg. In the hydroxybenzoic acid group, the S value decreased as the hydroxyl group moved from the *ortho* to the *meta* to the *para* position. The highest value for S was seen with propyl p-hydroxybenzoate.

One must be careful in taking these saturation values as more than they are—approximate values. Slight changes in the slope of the line in the Langmuir plot (Fig. 1) will give different intercepts which can lead to significant changes in S values. Even

though theoretically it is assumed that the extrapolated portion of the curve is to continue in a linear fashion, this may not actually be the case. Certain solute molecules (*i.e.*, phenol), when they reach a critical concentration in the solution, may alter the morphology of the nylon, creating more sites for interactions. In other words, for compounds of the phenolic type, data used from dilute solutions will give an S value which will be much less than S values taken from the more concentrated solutions. With the compounds used in these studies in the concentration range employed, no dramatic break was noted in the curves, even though five of the agents were phenolic in nature. However, there may have been a break in the curve if a much broader concentration range had been used.

The S value for propyl p-hydroxybenzoate was much higher than for the other compounds. The reason for this result may be attributed to the increase in hydrophobic character of the propyl p-hydroxybenzoate, which would tend to push this compound from the aqueous phase into the solid phase (plastic).

The saturation value may be used to compare different compounds sorbed by nylon and may be helpful in predicting if changes have occurred in nylon when stored under various conditions. For example, if the saturation value changes appreciably for the same nylon after storage, it should be evident that the plastic has been altered in some way.

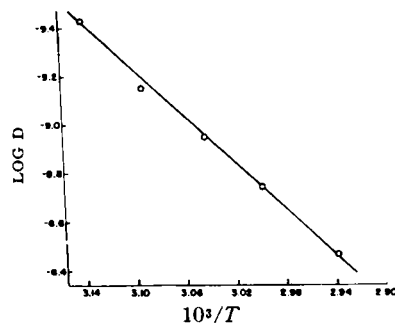**Affinity and Heat of Sorption.**—The affinity values for each of the compounds (except one in Table II)

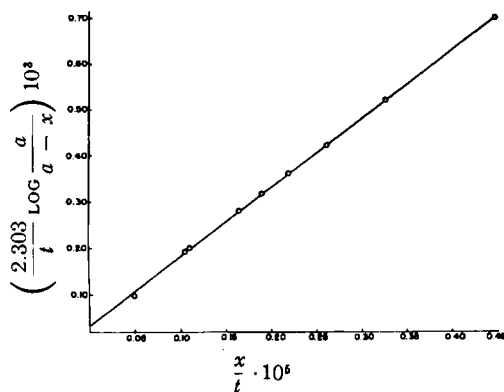Fig. 4.—An Arrhenius plot of methyl p-hydroxy-benzoate as log D vs. $1/T$.

Fig. 5.—A plot of Rotinyan and Drozdov equation from kinetic data for methyl p-hydroxybenzoate. (See text for explanation).

TABLE IV.—VALUES OF SLOPE (β) AND INTERCEPT (M) FROM PLOTS OF KINETIC DATA USING THE ROTINYAN AND DROZDOV EQUATION

Compd. Name	Temp., °C.	$\beta \cdot 10^{-2}$	$M \cdot 10^{3}$	Theoretical[a] $1/a \cdot 10^{-2}$
Benzoic acid	65.0	2.498	0.07219	2.442
	60.0	2.487	0.05382	
	55.2	2.386	0.04370	
	50.0	2.462	0.03104	
o-Hydroxybenzoic acid	65.0	0.9211	0.1291	0.9207
	60.0	0.9175	0.09138	
	55.0	0.9305	0.06259	
	50.0	0.9216	0.04496	
m-Hydroxybenzoic acid	60.0	2.754	0.04874	2.762
	55.0	2.748	0.03258	
	50.0	2.784	0.01933	
	45.0	2.722	0.01577	
p-Hydroxybenzoic acid	65.0	2.881	0.04524	2.762
	60.0	2.842	0.03672	
	55.0	2.781	0.02605	
	50.0	2.819	0.01629	
Methyl *p*-hydroxybenzoate	60.0	1.580	0.07427	1.521
	55.2	1.585	0.05374	
	50.0	1.556	0.03981	
	45.0	1.539	0.02966	
Propyl *p*-hydroxybenzoate	65.0	6.708	0.4428	6.006
	60.0	6.580	0.3880	
	50.0	6.606	0.2497	

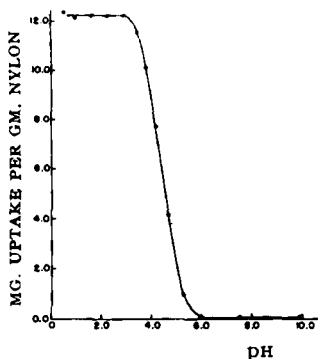[a] a = Initial concentration of solution.

Fig. 6.—The effect of pH on sorption of benzoic acid by nylon 610.

reveal that as the temperature is decreased the affinity increases. This is expected since the distribution of solute molecules between the plastic and the solution will tend to move toward the solid phase with a decrease in temperature. No suitable explanation could be given for the reverse of this tendency in regard to propyl *p*-hydroxybenzoate. As may be noted from the table, at the same temperature, the $-\Delta\mu°$ values for most of the compounds fell into a relatively narrow range. For example, for all of the compounds except propyl *p*-hydroxybenzoate at 50°, $-\Delta\mu°$ was around 2.2 Kcal./mole, indicating that the affinity for these compounds toward nylon was approximately equal. The standard chemical potential ($-\Delta\mu°$) of the propyl *p*-hydroxybenzoate at the same temperature (50°) was slightly above 3.0 Kcal./mole, indicating that this compound has the greatest affinity for the nylon 610 in the series of compounds studied.

Heats of sorption for the six compounds shown in Table II range from a value of -2.60 Kcal./mole for propyl *p*-hydroxybenzoate to -3.63 Kcal./ mole for methyl *p*-hydroxybenzoate. Even though heats of sorption values should not be equated directly to intermolecular forces existing between solute molecules and the nylon, some generalization may be made. Low values of $\Delta H°$ for the six compounds suggest that these compounds are bound to the nylon by weak molecular forces, probably of the van der Waals' type. Browne and Steele (6) have found that heat of sorption for benzoic acid by nylon 610 is approximately -2.2 Kcal./mole and have interpreted their experimental results on a number of organic acids sorbed by nylon as essentially a physical mixture where the intermolecular forces approach van der Waals' forces. Chipalkatti, Giles, and Vallance (3) have reported that molecules of the type studied in this investigation are probably bound to the nylon by hydrogen bonding and report that phenol has a heat of sorption of around -4.5 Kcal./mole. For large molecules, such as dyes, Meggy (7) and Derbyshire and Peters (8) have found even for those molecules having polar functional groups, the interaction forces can be dependent on the hydrophobic portion of the molecule. Even though the compounds studied here fell into a heat of sorption range below that which might be considered as due to hydrogen bonding, physical forces alone cannot account for the bonding energy between these solute molecules and the nylon. If this were the case, pyridine (a molecule of approximately the same size as phenol) would be sorbed. The absence of an acidic hydrogen in pyridine prevents the interaction, while with phenol and similar compounds, acidic hydrogens confer binding ability to the amide linkages. On the other hand, hydrogen bonding is not sufficient to hold the solute molecules to the nylon as may be surmised if one considers the overwhelming number of water molecules, which on the basis of the law of mass action, would compete for the same sites, dislodging the bound solute molecules. The intermolecular forces involved in the interaction of the solute molecules with the nylon reported here must be due to both hydrogen bonding which attracts the solute molecules and to van der Waals' forces which stabilize the interaction.

Diffusion and Activation Energy.—The data shown in Table III indicate that diffusion coefficients

for all of the compounds in the temperature range studied were of the order of magnitude of 10^{-9} to 10^{-10} cm.^{2}/sec. It can be further seen that as the temperature increased, the diffusion coefficient increased, as would be expected from theory. The activation energy for diffusion varied from a low of 12.9 Kcal./mole (for benzoic acid) to a high of 20.9 Kcal./mole (for methyl p-hydroxybenzoic acid). In a previous paper on nylon 66, the activation energy for diffusion for o-hydroxybenzoic acid was found to be 20.5 Kcal./mole. This compares to 19.9 Kcal./mole for the same compound in nylon 610 found in this study.

Activation energies for diffusion do indicate that structural changes in the molecule can alter the rate of diffusion. For example, the addition of a hydroxy group *ortho* to the carboxylic acid in benzoic acid increases the activation energy by 7 Kcal./mole. Unfortunately, since diffusion was not studied at the same original concentration for all of the compounds, it would be difficult to postulate exact effects of structure on the diffusion rate. It would also seem that many more compounds would have to be studied to get a general picture concerning the importance of structure on the diffusion rate.

Diffusion versus Rate of Interaction.—The use of the Rotinyan and Drozdov equation (Eq. 6) helped to support the accepted theory that solute molecules penetrate and diffuse through a plastic material and that the rate-determining step is the diffusion process. For all the compounds investigated in this paper, β approached $1/a$ which verified that the diffusion in the plastic was the determining step in the sorption process.

pH and Sorption.—Figure 6 shows that above pH 6.0 there is very little sorption taking place, but from pH 6.0 down to 3.8 a sudden increase in sorption takes place, leveling off after the pH is reduced below 3.8. This indicates that the four acidic compounds included in this particular experiment are sorbed in their unionized form.

SUMMARY

1. Sorption experiments were conducted on six compounds having similar functional groups. These compounds were benzoic acid, o-hydroxybenzoic acid, m-hydroxybenzoic acid, p-hydroxybenzoic acid, methyl p-hydroxybenzoate, and propyl p-hydroxybenzoate. Nylon 610 was employed as the substrate.

2. Experiments were conducted at both steady state conditions and nonsteady state conditions and at a number of temperatures. From the accumulated data, the following constants were evaluated for each compound: saturation value (S), standard affinity ($-\Delta\mu^\circ$), standard heat of sorption (ΔH°), apparent diffusion coefficient (D), and activation energy of diffusion (ΔE).

3. The results suggested that the compounds employed in the study were bound to the nylon 610 by hydrogen bonding with secondary valence forces stabilizing the interaction. In this series of compounds, propyl p-hydroxybenzoate had the greatest affinity for the nylon which was explained on the basis of the greater hydrophobic character of the molecule.

4. Apparent diffusion coefficients for all of the compounds in nylon 610 were found to be of the order of 10^{-9} to 10^{-10} cm.^{2}/sec. The diffusion coefficients were related to temperature by the usual Arrhenius equation from which activation energies were calculated. Application of the Rotinyan and Drozdov equation to the kinetic data confirmed that the diffusion process in the nylon was the rate-determining step.

5. Changes in hydrogen ion concentration in the solutions revealed that the four acidic compounds were sorbed in the unionized state.

6. Methods employed in this study and the treatment of data help to generate information on drug-plastic interactions of a more fundamental nature. As more drugs or compounds are studied with one or more substrates, valuable information will become available concerning the most suitable plastic material to use in a specific pharmaceutical or medical application.

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