Interaction of a Group of Low Molecular Weight Organic Acids with Insoluble Polyamides I

Sorption and Diffusion of Formic, Acetic, Propionic, and Butyric Acids into Nylon 66

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Insoluble polyamides are being used more in pharmacy and medicine as containers and parts of devices for the storage and administration of drugs and drug-like compounds. In previous reports, results have been presented which indicate that nylon will attract and sorb solute molecules which have acidic functional groups. The purpose of this study was to investigate the sorption of formic, acetic, propionic, and butyric acids by nylon 66 at a number of temperatures and concentrations. Equilibrium sorption isotherms were prepared from the data to evaluate the degree of sorption. Apparent diffusion coefficients of each of the acids were evaluated by kinetic sorption studies; these values were compared to results obtained by the use of diffusion cells. Results of these experiments revealed that the affinity of the aliphatic acids for the nylon discussed here were less than those having higher molecular weights and/or those weak organic acids having a phenyl group.

IN THE PAST, several papers have dealt with the interaction of a group of weak organic acids with several types of insoluble polyamides. Kapadia *et al.* studied the sorption and diffusion of benzoic acid, *o*-hydroxybenzoic acid, *m*-hydroxybenzoic acid, *p*-hydroxybenzoic acid, methyl *p*-hydroxybenzoate, and propyl *p*-hydroxybenzoate into nylon 610 as well as interaction studies on *o*-hydroxybenzoic acid with nylon 66 (1, 2). In general, the standard affinities, $\Delta\mu°$ (or standard chemical potential), for these compounds in the two nylons were in a narrow range of approximately -2 to -3 Kcal./mole within a temperature range of 40 to 70°. Standard heats of sorption ($\Delta H°$) for these same agents ranged from -2 to -4 Kcal./mole, an indication of a possible hydrogen bonding between the acid and the polymer. The various diffusion studies for the above compounds in the two nylons permitted the evaluation of apparent diffusion coefficients of the order of 10^{-9} to 10^{-10} cm.^{2}/second, with activation energies ranging from 13.0 to 21.0 Kcal./mole.

Rodell *et al.* investigated the interaction of sorbic acid (a 6-carbon unsaturated aliphatic acid) with nylon 66 and noted a standard heat of sorption approaching a value of -10.0 Kcal./mole, from which they deduced a possible double hydrogen bond formation between the acid and the polyamide chains (3). Further studies with this

system supported the double hydrogen bond thesis (4).

This paper reviews a sorption and diffusion study with a group of low molecular weight aliphatic acids (formic, acetic, propionic, and butyric) in nylon 66 in order to compare their behavior in nylon to those compounds already studied (1–3).

EXPERIMENTAL

Supplies.—Formic acid (97%) Eastman Organic Chemicals, Rochester, N. Y., glacial acetic acid, reagent ACS, Allied Chemical and Dye Corp., New York, N. Y., propionic acid, Eastman Organic Chemicals, Rochester, N. Y., butyric acid, Eastman Organic Chemicals, Rochester, N. Y., and nylon 66 (as sheets 0.012 in. thick), Zytel 42NCI0, E. I. du Pont de Nemours and Co., Wilmington, Del., were used.

Treatment of Nylon.—The nylon samples used in this study were from one lot, cut into strips measuring 1 × 4 in. To prevent erratic results in the sorption and diffusion studies, all samples were washed following an exact procedure described in another paper (2). All samples were dried in an oven at 60° for 24 hours, then placed into desiccators until needed for an experiment.

Sorption Equilibrium Studies.—Solutions of each of the acids were prepared with distilled water at the following concentrations: 1.0, 0.5, 0.2, 0.1, and 0.05% w/v. Each of these solutions was then pipeted into specially constructed glass tubes and stoppered with ground-glass plugs (3). All of the tubes were then placed into a water bath at a specified temperature and permitted to equilibrate to the temperature of the bath at which time the tubes were lifted from the bath, the plugs removed, and exactly 10.0 Gm. of nylon strips added. All tubes were then restoppered and placed back into the bath. After sufficient time had elapsed for sorption equilibrium to be attained (usually within

TABLE I.—SORPTION OF ALIPHATIC ACIDS BY NYLON 66

| Acid	40° C.,[a] moles/Kg.	50° C.,[a] moles/Kg.	60° C.,[a] moles/Kg.	70° C.,[a] moles/Kg.
Formic, %				
1.0	0.1508	0.1677	0.1753	0.1936
0.5	0.08500	0.09090	0.09810	0.09680
0.2	0.04990	0.05160	0.04980	0.05220
0.1	0.03310	0.03300	0.03380	0.03560
0.05	0.02400	0.02610	0.02670	0.02680
Acetic, %				
1.0	0.08607	0.09158	0.09088	0.08842
0.5	0.05167	0.05478	0.04891	0.04829
0.2	0.02531	0.02293	0.02250	0.02152
0.1	0.01965	0.01469	0.01283	0.01214
0.05	0.01150	0.008230	0.005900	0.004660
Propionic, %				
1.0	0.1218	0.1207	0.1190	0.1204
0.5	0.07030	0.06430	0.06350	0.06450
0.2	0.03480	0.03330	0.03050	0.02990
0.1	0.01750	0.01530	0.01530	0.01600
0.05	0.01140	0.01130	0.008900	0.008900
Butyric, %				
1.0	0.1924	0.1859	0.1806	0.1723
0.5	0.1051	0.1019	0.1000	0.09178
0.2	0.04818	0.04603	0.04314	0.04015
0.1	0.02611	0.02453	0.02305	0.02055
0.05	0.01491	0.01332	0.01172	0.008974

[a] ±0.02° C.
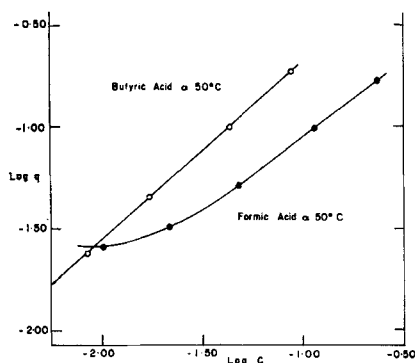
Fig. 1.—Freundlich sorption isotherms of butyric acid and formic acid (nylon 66).

a few days), the tubes were removed and aliquots of each solution assayed for remaining acid by a titration method. The difference between the concentration of the original solution and the final solution was considered as the quantity sorbed by the plastic. In all cases duplicate tubes were run as well as a control tube (no plastic). Equilibrium sorption studies were conducted at 40, 50, 60, and 70°.

Table I presents the sorption data for the four acids at each of the temperatures studied, as amount of acid sorbed in moles per kilogram. These data permitted further calculations which allowed the construction of Freundlich sorption isotherms for each temperature studied. Figure 1 illustrates a Freundlich plot for butyric acid and formic acid at 50°; as may be noted, the butyric acid follows a straight line, while the formic acid has a definite curvature. The acetic and propionic acids produced linear relationships in a manner like that of butyric acid.

To evaluate the saturation value for each of the acids at each temperature, the data were fitted to a form of the Langmuir relationship

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

where q is the amount of solute sorbed at equilibrium in moles per kilogram, K is a constant, S is the saturation value (moles per kilogram) when sites in the nylon are filled, and C is the equilibrium concentration of the acid (moles per liter) in the solution. Representative plots of $1/q$ versus $1/C$ for butyric acid at each of the temperatures are shown in Fig. 2. Intercepts for each of these lines give $1/S$, from which S may be calculated. Calculations for each of the

TABLE II.—CONSTANTS DERIVED FROM EQUILIBRIUM SORPTION STUDIES

Acid	Temp.,[a] ° C.	S,[b] moles/Kg.	$\Delta\mu°$,[c] cal./mole	$\Delta H°$,[d] cal./mole
Formic	40	0.559	183.9	40.60
	50	0.805	180.4	
	60	0.826	181.1	
	70	0.655	179.6	
Acetic	40	0.0712	566.1	− 41.40
	50	0.103	389.8	
	60	0.373	417.9	
	70	0.654	442.1	
Propionic	40	0.335	− 64.10	−238.8
	50	0.565	5.870	
	60	0.396	3.360	
	70	0.308	21.52	
Butyric	40	0.225	−445.6	−701.0
	50	0.292	−450.3	
	60	0.498	−448.6	
	70	0.708	−418.5	

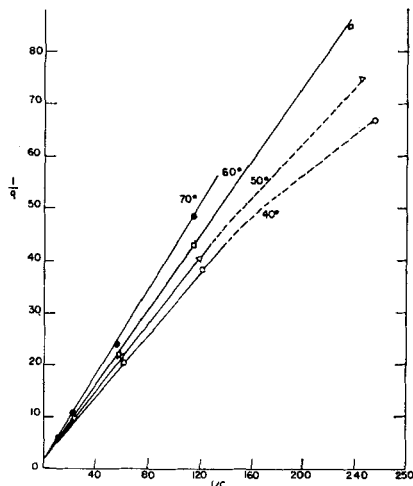[a] ±0.02° C. [b] S = Saturation value. [c] $\Delta\mu°$ = Standard affinity. [d] $\Delta H°$ = Standard heat of sorption.

Fig. 2.—Langmuir sorption isotherms of butyric acid for evaluating saturation values at different temperatures (nylon 66).
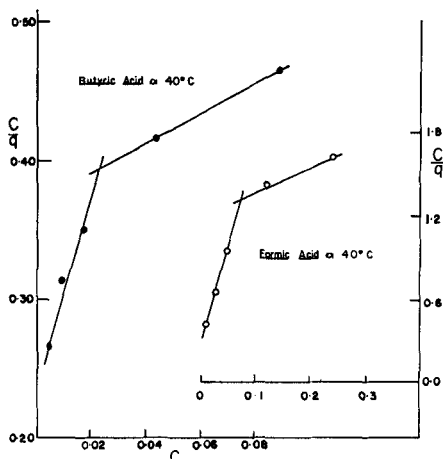
the decision was made to plot the same data as C/q *versus* C (another form of the Langmuir expression). Figure 3 illustrates this type of plot for both butyric acid and formic acid. By this method there is a definite break in the curve, a suggestion that a more complex mechanism of sorption is probably in operation. The other two acids also demonstrated an inflection point, as in Fig. 3.

Affinity and Heat of Sorption.—The standard affinity was calculated for each of the acids at each of the temperatures using

$$-\Delta\mu^\circ = RT \ln C_s/C_L \qquad \text{(Eq. 2)}$$

where $-\Delta\mu^\circ$ is the difference in standard chemical potential between the solute in the liquid (C_L) and the solute in the solid (C_s). The ratio, C_s/C_L, was obtained by plotting C_s *versus* C_L and finding the slope by least squares. A representative plot of this type is shown in Fig. 4 for formic acid at four different temperatures. As will be observed, the points did not intersect at zero in this case. The other three acids, however, did have straight-line relationships which did approach zero on the figures. Affinity values for each of the acids at each temperature

Fig. 3.—Langmuir sorption isotherms of butyric acid and formic acid (nylon 66).
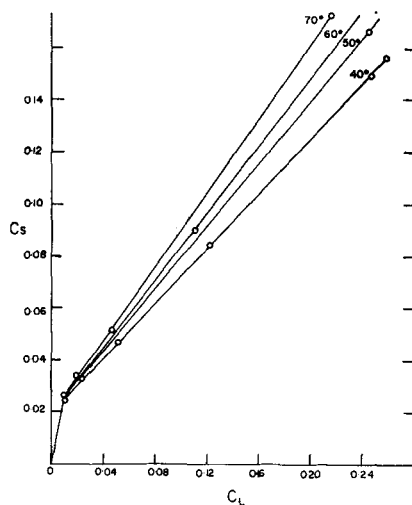
Fig. 4.—Sorption isotherms of formic acid at different temperatures.

acids at each temperature were performed by least squares and the saturation values obtained. These values are included in Table II.

Figure 2 reveals (and this trend was noted with all the acids) that the points representative of the more dilute concentrations fell off the curve. This trend has been noted previously with other compounds and suggests that, depending upon the concentration ranges explored, different values will result. In this study, only the points falling on a straight line in the most concentrated solutions were used for the least-square calculations. Figure 2 demonstrates that with butyric acid there is a decrease in the uptake of the acid by the nylon (line approaching the $1/q$ axis) with an increase in temperature. Both acetic and propionic acids followed the same general pattern, but in formic acid the relation was the opposite. (More acid was sorbed with an increase in temperature.)

Since there appeared to be an inflection in the curves for the $1/q$ *versus* $1/C$ plots (as in Fig. 2),
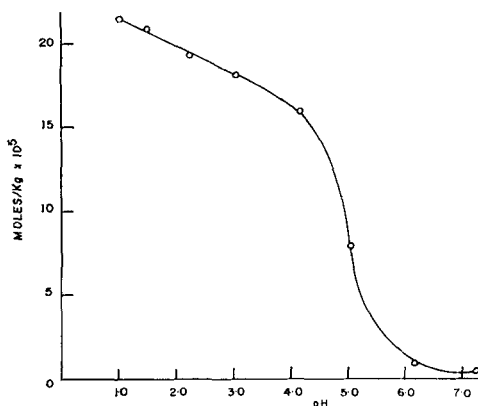

Fig. 5.—Effect of pH on the equilibrium sorption of butyric acid by nylon 66 at 50°.

TABLE III. —FRACTIONAL UPTAKE OF A GROUP OF WEAK ORGANIC ACIDS BY NYLON 66 AS A FUNCTION OF THE SQUARE ROOT OF TIME

Acid	40° C.		50° C.		60° C.		70° C.	
	$\sqrt{t}$	$M_t/M_\infty{}^a$	$\sqrt{t}$	M_t/M_∞	$\sqrt{t}$	M_t/M_∞	$\sqrt{t}$	M_t/M_∞
Formic	0.500	0.083	0.288	0.110	0.288	0.132	0.288	0.457
	0.707	0.145	0.408	0.135	0.408	0.214	0.408	0.527
	0.866	0.208	0.500	0.217	0.500	0.296	0.500	0.701
	1.00	0.283	0.577	0.205	0.577	0.419	0.577	0.747
	1.41	0.512	0.707	0.327	0.645	0.487	0.707	0.953
	1.73	1.00	0.866	0.479	0.707	0.542	0.866	1.00
	2.00	1.00	1.00	0.647	0.866	0.578	1.00	1.00
	3.00	1.00	1.41	0.995	1.00	0.988	1.41	1.00
	5.00	1.00	2.00	1.00	1.41	1.00		
Acetic	1.00	0.074	0.500	0.008	0.408	0.106	0.288	0.067
	1.414	0.297	0.707	0.017	0.577	0.191	0.408	0.202
	2.00	0.783	0.866	0.246	0.707	0.289	0.577	0.318
	2.50	0.952	1.00	0.309	0.866	0.491	0.707	0.376
	3.00	0.948	1.22	0.563	1.00	0.586	0.866	0.695
	4.00	1.00	1.41	0.761	3.24	1.00	1.00	1.00
Propionic	1.00	0.182	0.500	0.159	0.500	0.157	0.288	0.189
	1.22	0.262	0.707	0.185	0.707	0.339	0.409	0.270
	1.41	0.408	0.866	0.239	1.00	0.631	0.500	0.330
	1.58	0.446	1.00	0.384	1.41	0.870	0.645	0.466
	1.73	0.563	1.41	0.699	1.73	0.975	0.866	0.679
	2.12	0.784	1.73	0.873	2.00	1.00	1.00	0.839
	2.73	0.967	2.00	0.916			2.64	1.00
	4.74	0.995	3.00	1.00				
	6.81	1.00	4.00	1.00				
Butyric	1.00	0.173	0.707	0.189	0.500	0.188	0.288	0.183
	1.22	0.232	0.866	0.246	0.707	0.334	0.408	0.246
	1.41	0.302	1.00	0.351	1.00	0.578	0.500	0.321
	1.73	0.472	1.11	0.394	1.41	0.837	0.645	0.414
	2.00	0.543	1.22	0.475	2.39	0.969	0.816	0.577
	2.44	0.844	1.41	0.579	3.24	0.976	1.00	0.742
	4.89	0.960	4.47	1.00	8.48	1.00	2.06	0.979
	5.56	1.00	5.09	1.00			2.69	1.00

^{a} M_t = Uptake at time t; M_∞ = at equilibrium.

are included in Table II. It is interesting that the affinity values for formic, acetic, and propionic acid came out as positive values, while the butyric values were negative.

Heats of sorption (ΔH°) for each of the acids were evaluated by plotting $\Delta\mu^\circ/T$ *versus* $1/T$, from which ΔH° (slope) was obtained. These values are included in Table II. The extremely low values (in calories rather than kilocalories, as with other compounds studied previously) indicate the weak interaction forces holding these solutes to the polymers.

Effect of pH.—An equilibrium sorption experiment was conducted on butyric acid at different pH values. The data obtained were then plotted as the amount of acid sorbed *versus* pH, as shown in Fig. 5. As may be noted, little or no significant uptake or sorption appears to occur at pH values of 6 and above. Sorption increases, however, as the pH is reduced. A sudden increase in uptake takes place around a pH of 5.0, with gradual further increase as the pH reaches 1.0. This pattern has been observed with a number of acids and suggests that the acids arei nteracting with the nylon primarily in their unionized state (1-3).

Diffusion and Activation Energy of Diffusion.— Diffusion experiments were conducted on each of the acids at four different temperatures (40, 50, 60, and 70°). The procedure used was essentially that reported by Rodell *et al.* except that in this case only one original concentration (1.0%) was used (3).

Over a period of time, samples of solution were withdrawn and analyzed for acid content. The data were then calculated as fractional uptake (M_t/M_∞) per unit weight of nylon at various time periods until equilibrium was established. Table III includes these figures, from which were constructed plots of (M_t/M_∞) *versus* square root of time. Plots for butyric acid are depicted in Fig. 6. Slopes of these lines permitted the evaluation of apparent diffusion coefficients for each of the acids at each temperature using Berthier's method, described in a previous paper (1). Table IV shows these D values, with the final total uptake (M_∞) as a per cent.

The diffusion coefficients for each of the acids at each of the temperatures permitted the evaluation of the activation energy (ΔE).[1] These values are also included in Table III.

Diffusion studies were also conducted on the same nylon by inserting an appropriate sheet of plastic between two chambers—one filled with the solution and the other with distilled water. The quantity of acid entering the water chamber through the plastic was followed over a period of time at isothermal conditions. The data were then plotted as amount of acid (entering water chamber) *versus* time, from which it was possible to deduce the time lag before a steady-state permeation had developed. By using Barrer's time-lag equation

$$D = L^2/6t \qquad \text{(Eq. 3)}$$

[1] Log D = log D_o − $\Delta E/2.303\ RT$.

where D is the diffusion coefficient in cm.²/second, L is the thickness of the film or sheet of plastic in centimeters, and t is the time lag value in seconds. The calculated D values from this diffusion method were in every case lower than the D values from the sorption method by a factor of $^1/_5$ to $^1/_{10}$. Part of this difference can be attributed to experimental error, while part may be due to studying diffusion essentially under nonsteady-state conditions (sorption) on one hand and under steady-state conditions (time-lag method) on the other.

DISCUSSION

As the equilibrium sorption experiments revealed, the data for all the acids, except formic acid, followed the Freundlich relationship in the concentration range studied. When the data were plotted by the Langmuir equation for evaluating the saturation values for each of the acids at the various temperatures, the plots of $1/q$ versus $1/C$ followed the general pattern seen in Fig. 2 for butyric acid. All of the lines representing the four temperatures converged to nearly the same point on the $1/q$ axis (or giving $1/S$). Actual calculations of the intercepts by least squares, however, did produce different values for S, as may be noted in Table II. Here for all of the acids at all of the temperatures studied the S value fell into a range of approximately 0.1 mole/Kg. to 0.8 mole/Kg. Generally also, there was a trend for the S value to increase with an increase in temperature. As has been mentioned earlier, some reservations should be made in re-
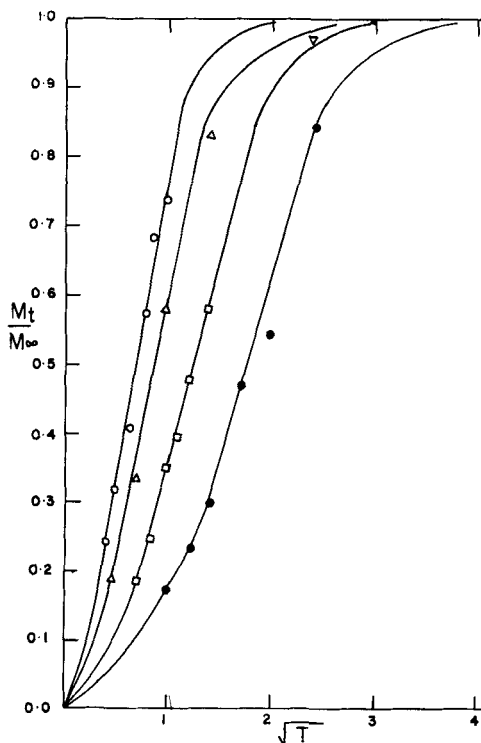
TABLE IV.—APPARENT DIFFUSION COEFFICIENTS AND ACTIVIATION ENERGIES FOR A GROUP OF ALIPHATIC ACIDS (NYLON 66)

Acid	Temp.,[a] ° C.	Final % Uptake	$D \times 10^8$,[b] cm.²/Sec.	ΔE,[c] kcal./mole
Formic	40	4.61	1.32	2.79
	50	4.68	5.12	
	60	4.26	6.32	
	70	4.93	6.93	
Acetic	40	5.25	1.81	7.63
	50	4.55	4.52	
	60	4.20	4.62	
	70	4.95	5.78	
Propionic	40	9.92	1.44	7.26
	50	10.5	2.19	
	60	9.92	2.73	
	70	9.64	4.15	
Butyric	40	19.2	0.996	6.86
	50	19.2	1.31	
	60	18.6	2.12	
	70	18.2	2.95	

[a] ±0.02° C. [b] D = Apparent diffusion coefficient. [c] ΔE = Activation energy of diffusion.

viewing the validity of these S values, since it is apparent that, depending upon the concentration range studied, different sorption isotherms may result, which in turn would give different values of S. Figure 3 demonstrates clearly that when the data are plotted as C/q versus C, a definite break in the curve results. The exact interpretation of these results is difficult to explain, except that the mechanism of sorption of these acids is more complex than a simple sorption isotherm. One of the reasons for the break in the curve may be attributed to the effect the solute molecules might have on ordering and disordering the polymer chains in the amorphous zone of the nylon, thereby opening up new sites previously not accessible to the solute. Kawasaki *et al.*, in their study of the effect of sorbed water by nylon, treated the data according to the Brunauer-Emmett-Teller (B.E.T.) equation for multimolecular physical sorption on a free surface (5). They concluded that, at least with water, water molecules will first interact with free amide groups in the polymer; and at higher concentrations, free water molecules will interact with amide sites previously bonded with the adjacent polymer chains. On further increase in concentration, the water molecules will form a multilayer at the bonding sites. In the studies reported here it was not possible to resolve the results according to the B.E.T. equation.

The various standard affinity values (Table II) for each of the acids at each temperature studied showed the low order of attracting ability of the nylon for these low molecular acids. In fact, for all of the acids except butyric, the $\Delta\mu°$ values were positive, an indication of the preference of these acids for the water phase over the solid phase. When one compares these affinity values for those of a group of acidic compounds having a phenyl group, the importance of the hydrophobic moiety in a molecule is noted dramatically. For example, affinity values for the group of weak organic acids having phenyl groups fell into the range of -2 to -3 Kcal./mole, while those of the low molecular aliphatic acids were less than -0.5 Kcal./mole for butyric acid to positive values for the other acids (1, 2).

Fig. 6.—Fractional uptake (M_t/M_∞) vs. square root of time for butyric acid at different temperatures (nylon 66). Key: ●, 40°C.; □, 50°C.; △, 60°C.; ○. 70°C.
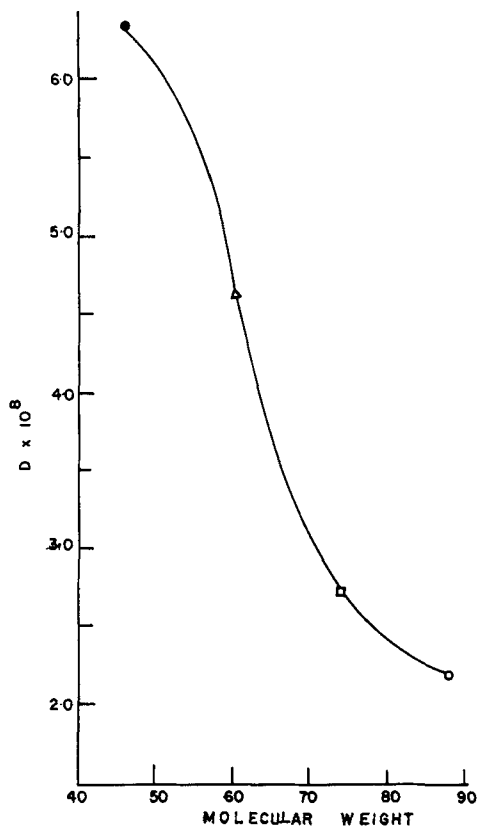
Fig. 7.—Diffusion coefficients *vs.* molecular weight of a group of aliphatic acids. Key: ●, formic acid, 46.02; △, acetic acid, 60.05; □, propionic acid, 74.08; ○, butyric acid, 88.10.

Heats of sorption (Table II) again illustrate that the bonding energies between the acids and the nylon were of low order. From Table I it will be noted that ΔH° for butyric acid was -701 cal./mole, for propionic acid -238 cal./mole, for acetic acid -41 cal./mole, and for formic acid the ΔH° became positive or 40 cal./mole. The extremely low ΔH° values for formic and acetic acid may suggest that the energies for interaction are slightly greater than those for the water molecules (with the nylon) which are being displaced by both acids. As the molecular weight of the acids increases, a definite increase can be seen in the strength of the interaction. These values, however, are lower than the -2 to -4 Kcal./mole (heats of sorption) for the group of weak organic acids having the phenyl groups. It is interesting that sorbic acid, a 6-carbon acid, had affinity values comparable to those phenyl acids mentioned above and a heat of sorption approaching a value of -10.0 Kcal./mole. This high value has been attributed to a double hydrogen bond formation between the sorbic acid and the nylon (4).

The pH study on butyric acid (Fig. 5) demonstrates that these low molecular weight acids interact primarily as the unionized acid, following the same general sorption pattern noted for other acids (1, 2). The pH sorption isotherm (Fig. 5) also indicates that these acids for the most part interact with the amide groups in the polymer chains. Some sorption, however, is probably taking place at the end amino groups, most likely through an ion–ion interaction.

The diffusion experiments produced results which indicate that, as the molecular weight of the acids increases, a fall in the apparent diffusion coefficient occurs. This relationship has been illustrated in Fig. 7, a plot of the diffusion coefficient (D) *versus* molecular weight (at 60°). When D values for sorbic acid and then other acids previously studied with nylon are included, the trend of decreasing D with molecular weight is still noted. For example, for these aliphatic acids the D value was of the order of 10^{-8} cm.²/second, while for a group of acids having phenyl groups D was in the range of 10^{-9} to 10^{-10} cm.²/second.

Activation energies of diffusion for these aliphatic acids were quite low (*i.e.*, 2.79 Kcal./mole for formic and around 7.0 Kcal./mole for the other acids), a demonstration that resistance to movement or diffusion of these molecules in the plastic was less than those for larger molecules. In previous studies on weak organic acids, the ΔE values were all above 12 Kcal./mole, reaching values close to 21.0 Kcal./mole (1, 2).

SUMMARY

1. Sorption and diffusion studies were conducted on a group of low molecular weight aliphatic acids (formic, acetic, propionic, and butyric) in nylon 66.

2. From the various experiments, the saturation value of each agent in nylon was found as well as the following constants: (*a*) standard affinities and (*b*) heats of sorption, (*c*) apparent diffusion coefficients, and (*d*) activation energies of diffusion.

3. Results indicated that the affinity of these agents are extremely low toward the nylon, but that it (affinity) increases with an increase in molecular weight. Heats of sorption in calories per mole were of an extremely low order and confirm that the interaction forces between the acids and the nylon are low.

4. Sorption studies as a function of pH revealed that, in general, the acids interacted with the nylon in the unionized state and that the site of interaction was most likely at the amide linkages in the polymer chains.

5. Diffusion studies confirmed the general theory that small molecules have less difficulty traveling through a maze of polymer chains than larger molecules.

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