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# The Adsorption Equilibria of DL-Mandelic Acid on Starch in an Aqueous Phase

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The selective adsorption of D- or L-mandelic acid on starch from an aqueous solution of racemate has been quantitatively investigated. L-Mandelic acid has been judged from the distinct negative value of the optical rotation in the solution to be adsorbed preferentially over the D-isomer. The separation factor for the adsorption of the two enantiomers was $1.06 \pm 0.02$ at 0°C. From the saturation value estimated by the Langmuir equation for adsorption, the ratio of the glucose residue to the DL-mandelic acid adsorbed has been calculated as 5, indicating that not all the glucose residues in the starch constitute adsorption sites for mandelic acid.

The asymmetric adsorption of racemate on optically active adsorbents has so far been studied by the batch adsorption or the chromatographic technique.[1] Despite the effort devoted to this subject, however, little progress has been made in the quantitative estimation of the stereospecific adsorption of optical antipodes. The lack of the observation of large rotation angles and the absence of a distinct difference in adsorption between enantiomers in the systems investigated have hampered any further clarification of this subject, although several reliable and somewhat systematic attempts using the batch method have been reported for such systems as wool - DL-mandelic acid,[2] and silica-gel - DL-*s*-butanol.[3]

It has been investigated by several authors,[4] and well established in this laboratory,[1] that starch, when used as an optically active column packing, takes up the L-(+)-isomer selectively

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[1] See, for example, M. Ohara, I. Fujita and T. Kwan, This Bulletin, **35**, 2049 (1962); M. Ohara, K. Ohta and T. Kwan, ibid., **37**, 76 (1964).

[2] W. Bradley and G. C. Easty, *J. Chem. Soc.*, **1951**, 499; ibid., **1953**, 1519; W. Bradley and R. A. Brindley, ibid., **1956**, 1622; W. Bradley, R. A. Brindley and G. C. Easty, *Discussions Faraday Soc.*, **No. 16**, 152 (1954).

[3] E. I. Klabunovskii, A. E. Agoronomov, L. M. Volkova and A. A. Balandin, *Izv., A. N. S. S. S. R. Otd. Chim. Nauk.*, **1963**, 228.

[4] H. Krebs, J. Diewald and J. A. Wagner, *Chem. Ber.*, **89**, 1875 (1956); W. Lautsch and D. Heinicke, *Kolloid Z.*, **154**, 1 (1957); D. Braun, "Anomalien bei Ionenaustauschvorgängen," Ionenaustauscher in Einzeldarstellungen, Bd. 2, Vol. I, Akademie-Verlag, Berlin (1962), p. 393.

through the passage of DL-mandelic acid from an aqueous solution. The selective adsorption of this kind has now been further investigated by utilizing a batch technique. In this paper, we will report on the first quantitative investigation on the adsorption equilibria of DL-mandelic acid on starch, in which the separation factor of the isomers is evaluated as 1.06±0.02 at the temperature of 0°C.

## Experimental

**Materials.**—Commercial DL-mandelic acid of a high grade was used (m. p. 118°C). The elementary analysis showed:

Found: C, 63.28; H, 5.32; O, 31.40. Calcd. for $C_8H_8O_3$: C, 63.15; H, 5.30; O, 31.55%.

Potato starch of a reagent grade was used without special pretreatment. It contained 18±0.1% moisture.

**General Procedure.**—Samples of starch, weighing 18 g., 13.5 g., 9 g. and 4.5 g., were immersed in a 50 ml. Erlenmeyer flask equipped with a stopper. The closed flask was then kept at 0°C for 48 hr. with occasional agitation until equilibrium was attained. After the starch had been allowed to settle, the supernatant liquid equilibrated was withdrawn; the optical rotation of the solution $\alpha_D^{15}$ was then determined in a 10 cm. tube in a Yanagimoto Model OR-20-type photomagnetic polarimeter within a ±0.002 accuracy. The concentration of the acid was determined by means of the optical absorption at 257 m$\mu$.

## Results

First, the adsorption of DL-mandelic acid on starch was studied by means of the optical rotatory dispersion. The results were compared with those of the two control experiments. Hence the systems studied were:

1) 10 w/v% DL-mandelic acid aqueous solution (30 ml.) - untreated starch (18 g.)
2) water (30 ml.) - starch (18 g.)
3) 14.3 w/v% glycolic acid aqueous solution* (30 ml.) - starch (18 g.).

The optical rotatory dispersion was determined in a 5 cm. tube on a Nippon Bunko Model ORD/UV-5-type recording spectrophotometer. In Fig. 1 the observed curves are compared with that of authentic D-(−)-mandelic acid.

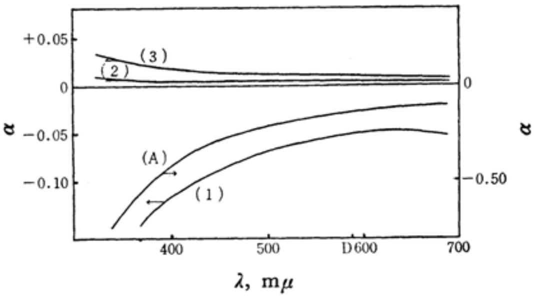

Fig. 1. The optical rotatory dispersion curves of DL-mandelic acid solution (1), water (2) and glycolic acid solution (3) in contact with starch as compared with that of D-(−)-mandelic acid (A).

Cell length: 5 cm.
Temp. : 12—14.5°C
D : Sodium D line

The curve 3 bends slightly to the (+) side, while the curve 2 indicates no definite rotation, suggesting that glycolic acid slightly decomposes or extracts the optically active starch component. On the other hand, the curve 1 bends on a large scale to the (−) side, as does that of the authentic sample. The difference between 1 and 3 gives a (−) sign of rotation; this may be ascribed to the net rotation value of mandelic acid in a solution. It is apparent, therefore, that L-(+)-mandelic acid is preferentially adsorbed from the racemate solution. This finding is consistent with those revealed by the column chromatography.[1)]

Let us proceed to the principal subject. It was previously confirmed that the adsorption of DL-mandelic acid on starch reaches an equilibrium within 8 hr. at 0°C. However, the equilibrium data were recorded after the solution had been left standing over 2 days. By carying the amount of DL-mandelic acid, on the one hand, and the amount of starch on the other, the adsorption isotherm was determined as usual at the temperature of 0°C. Table I lists some of the adsorption data,

TABLE I. ADSORPTION EQUILIBRIUM DATA OF DL-MANDELIC ACID ON STARCH ($T$=0°C)

| Sample No. | $C_i$ | $C_e$ | Amount adsorbed | Optical rotation of solution | | $\Delta W/W$ | $f$ |
|---|---|---|---|---|---|---|---|
| | mg./ml. | mg./ml. | mg. | $\alpha_D^{15}$ | $[\alpha]_D^{15}$ | % | |
| B1 | 25.05 | 21.8 | 137 | −0.017 | −0.78 | 2.2 | 1.05 |
| B2 | 50.0 | 43.8 | 265 | −0.036 | −0.82 | 2.4 | 1.06 |
| B3 | 74.5 | 66.5 | 360 | −0.045 | −0.68 | 2.2 | 1.05 |
| B4 | 100.3 | 91.8 | 420 | −0.060 | −0.66 | 2.6 | 1.06 |
| D1 | 25.05 | 19.7 | 232 | −0.035 | −1.8 | 2.5 | 1.07 |
| D2 | 50.0 | 39.4 | 461 | −0.061 | −1.6 | 2.2 | 1.07 |
| D3 | 74.5 | 61.4 | 614 | −0.082 | −1.3 | 2.2 | 1.06 |
| D4 | 100.3 | 84.2 | 785 | −0.103 | −1.2 | 2.2 | 1.06 |

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* Glycolic acid was chosen as the control sample, since (1) it is of almost the same acidity as mandelic acid; (2) it has a chemical structure similar to that of mandelic acid, and (3) it is an optically-inactive organic acid.

obtained along with parameters estimated therefrom.

In Table I, the signs B and D stand for the amount of starch used, 9 g. and 18 g. respectively, while $C_i$ and $C_e$ are the initial and equilibrium concentrations of the acid respectively. To determine the amount of mandelic acid adsorbed, $W$, the usual method would be to measure the change in the concentration of the solution after equilibrium. However, this method was thought to be inadequate for the present investigation, as the untreated starch, which contains 18% moisture, sorbs addition water, Consequently, $W$ was estimated from the following revised equation:

$$W=30C_i-(30-Gw)C_e$$

where $G$ is the amount of the untreated starch and $w$, the volume of the additionally sorbed water (ml.) per gram of the untreated starch. It was estimated at about 0.2 ml. from the difference between the amount of moisture in the untreated starch and that of water bound to potato starch suspended in an aqueous solution. The amount of bound water, about 33%, was based upon the data in the literature.[5] $\Delta W$ is the difference between enantiomers in the amount of mandelic acid adsorbed, and $f$ is the separation factor, which will be defined later.

The net angle of rotation of mandelic acid in the solution is indicated in the 5 th column of Table I. These values were corrected for the rotation due to the optically active starch component produced by the interaction of the acid with starch. In Table II typical data are given on the interaction of an acid with starch.

TABLE II. $\alpha_D^{15}$ OF THE GLYCOLIC ACID SOLUTION IN CONTACT WITH STARCH ($T=0°$C)

| Concn. of glycolic acid mg./ml. | Weight of starch g. | Reaction time hr. | $\alpha_D^{15}$ of the solution after reaction |
|---|---|---|---|
| 143 | 4.5 | 48 | +0.001 |
| 143 | 9.0 | 48 | +0.003 |
| 143 | 13.5 | 48 | +0.006 |
| 143 | 18.0 | 48 | +0.009 |

It was recognized that the $\alpha_D^{15}$ of the solution was little dependent on the concentration of the glycolic acid, but very dependent on the amount of starch used.

Using the data of Table I, the adsorption isotherm of DL-mandelic acid on starch is plotted in Fig. 2. The equilibrium concentration of the acid was in the range from 3.1 to 95 mg./ml.

The limited solubility of the acid did not permit the observation of the adsorption over the higher equilibrium concentrations. However, the Langmuir equation, $W=W_m bC_e/(1+bC_e)$, seemed to apply to the observed data. The Langmuir equation may be tested by arranging it in the form:

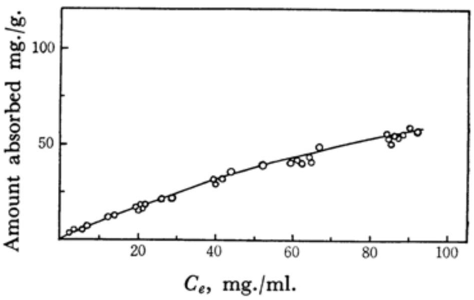

Fig. 2. Adsorption isotherm of DL-mandelic acid on starch at 0°C.

$$C_e/W=C_e/W_m+1/bW_m$$

In Fig. 3 plots of $C_e$ vs. $C_e/W$ are shown. They yield approximately a straight line. From the slope $1/W_m$, a reciprocal of the saturated amount of adsorption can be calculated. It was found to be $W_m=188$ mg.

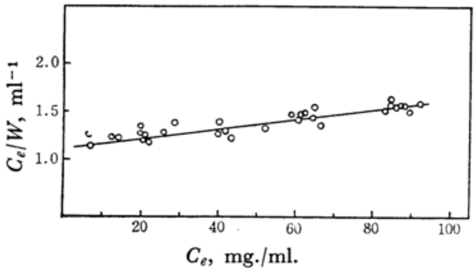

Fig. 3. Adsorption isotherm of DL-mandelic acid plotted according to the Langmuir equation.

The amounts of D- or L-isomers adsorbed on the surface of the starch were computed from the data of the specific rotation in the solution. The concentration of each isomer in the solution may be calculated by assuming that the additivity rule holds between $[\alpha]_D$ and the composition of each isomer, and that the $[\alpha]_{DP}$ of the acid is independent of the concentration. Here, $[\alpha]_{DP}$ is the specific rotation of optically pure mandelic acid. The difference between enantiomers in the amount adsorbed may be expressed as:

$$\Delta W=W_d-W_l=(30-Gw)C_e \mid [\alpha]_D/[\alpha]_{DP} \mid$$

where $W_d$ and $W_l$ are, respectively, the amount of the L- or D-isomer adsorbed. Consequently, $\Delta W/W$ may be obtained as:

$$\Delta W/W=(30-Gw) \mid [\alpha]_D/[\alpha]_{DP} \mid C_e/W$$

The substitution of 0.2 and ±157 for $w$ and $[\alpha]_{DP}$ respectively in the above equation yields a $\Delta W/W$ value for each $G$, values which range between 2.1% and 2.6%. These values are shown in the 7 th column of Table I.

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[5] F. Schierbaum and K. Täufel, *Die Stärke*, **15**, 161 (1963).

Finally, the separation factor, *f*, as defined by the ratio of the adsorption equilibrium constants of the isomers, is expressed as:

$$f=\frac{W_d/C_{ed}}{W_l/C_{el}}=\frac{1+\mid[\alpha]_D/[\alpha]_{DP}\mid}{1-\mid[\alpha]_D/[\alpha]_{DP}\mid}\times\frac{1+\Delta W/W}{1-\Delta W/W}$$

where $C_{ed}$ and $C_{el}$ are the concentrations of L- and D-isomers respectively in the liquid phase at equilibrium.

On the basis of this equation, *f* may be estimated to be 1.06±0.02. The values of *f* are presented in the last column of Table I.

## Discussion

It is interesting to note that the adsorption of mandelic acid on starch obeys the Langmuir equation. This would mean that the surface of starch is rather homogeneous for the adsorption of mandelic acid, and that no interaction between the adsorbed molecules is present. The saturation value for the adsorption was found, according to the Langmuir equation, to be 188 mg./g. starch. This value corresponds to $7.4\times10^{20}$ molecules. Since one gram of starch consists of about $3.7\times10^{21}$ glucose residues, the following stoichiometric relation may hold at saturation:

Glucose residue: Mandelic acid ≈ 5 : 1

Let us discuss the problem in connection with bound water. In a series of investigations bearing the title of "The Hydration of Starch," Schierbaum and Täufel have definitely shown that bound water in the starch may be distinguished from free water. The literature[5] estimates the amount of bound water to be 32.5—33.8% for potato starch. This value corresponds to:

Glucose residue : Water molecule ≈ 1 : 4

The logical sites for the adsorption of mandelic acid or water seem to be the hydroxyl groups of the starch. If so, three available sites are found in each glucose residue. It may be suggested, therefore, that not all glucose residue are effective in the adsorption of mandelic acid, and that bound water occupies almost all the active sites.

The surface area of starch effective in the adsorption of mandelic acid may be evaluated from the saturation value.

Assuming that the molecular shape of mandelic acid is a sphere, the molecular area, $\sigma_m$, of acid is estimated to be:

$$\sigma_m=34\ \text{sq. Å}$$

Consequently, the surface area is given by $S=250\ \text{m}^2/\text{g}$.

The surface area of potato starch was determined by Hellman and Melvin[6] by the BET method, using nitrogen as the adsorbate at −195°C. Accordingly, the area was $0.11\ \text{m}^2/\text{g}$. The same author found that the surface area of the same starch was about $300\ \text{m}^2/\text{g}$. when the adsorption of water vapor was applied to the BET plot at 25°C.

The amount of water adsorbed at the monolayer, according to these authors, corresponded to:

Glucose residue : Water molecule ≈ 1 : 1

Therefore, the amount of bound water is about four times as great as that of the monolayer.

The discrepancy between the BET area obtained by the nitrogen adsorption at −195°C and that due to the water adsorption at room temperature is well known in the surface area of organic high polymers, such as cellulosic fibers and proteins[7] and coal[8]. In Table III the surface areas of some organic polymers as determined by the nitrogen adsorption method and by the water (methanol) adsorption method are compared, using those of titanium dioxide (anatase) as a reference sample.

TABLE III. THE SURFACE AREA OF SOME ORGANIC HIGH POLYMERS AS DETERMINED BY DIFFERENT METHODS

| Material | Area Determined by nitrogen at −195°C m²/g. | Area Determined by water at 25°C m²/g. | Lit. |
|---|---|---|---|
| Potato starch | 0.11 | 296 | 6 |
| Wool | 0.96 | 206 | 7 |
| Cotton | 0.76 | 108 | 7 |
| Nylon | 0.31 | 45.0 | 7 |
| Coal | 0.1—10 | 20—200** | 8 |
| Titanium dioxide | 7.90 | 7.0 | 7 |

Obviously, the nitrogen adsorption method at −195°C would be inadequate for the measurement of the surface area of organic polymers. On the other hand, the surface area of starch, estimated from the saturation of the mandelic acid adsorption, is not very different from that of water adsorption as determined by Hellman and Melvin. The adsorption of mandelic acid on starch is probably to be considered as a kind of inclusion of the adsorbate molecule on the internal surface of starch.

The difference in the adsorption of D- and L-mandelic acid, established in this paper, must be investigated further with regard to the structural correlation of the adsorbate molecule with starch.

The authors wish to express their gratitude to Professor Syun-ichi Yamada and Dr. Kazuo Achiwa of The University of Tokyo for letting them use both the ORD spectrophotometer and the polarimeter.

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[6] N. N. Hellman and E. H. Melvin, *J. Am. Chem. Soc.*, **72**, 5186 (1950).

[7] J. W. Rowen and R. L. Blaine, *Ind. Eng. Chem.*, **39**, 1659 (1947).

[8] D. W. Van Krevelen and J. Schuyer, "Coal Science," Elsevier Publishing Company, Amsterdam (1957), p. 129.

** Determined by methanol.