Asymmetric Adsorption of Alanine by Quartz Powder from Ethanol Solution

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The asymmetric adsorption of the racemic alanine by the optically active quartz from ethanol solution at 8 °C was studied by the ^{14}C-tracer method and the newly developed ^{14}C-tracer·ninhydrin-colorimetry combination method. The preferential adsorption of L-alanine by levorotatory quartz (*l*-quartz) and D-alanine by dextrorotatory quartz (*d*-quartz) was confirmed. The asymmetric adsorptivity (A_s) falls in the range of 1.1—1.3, which is comparable with the value determined at −80 °C in the previous paper. The effects of water content in the ethanol solution and of the adsorption temperature upon the adsorption affinity of alanine to quartz were also measured. The cause for the asymmetric adsorption is discussed from the crystallographic point of view.

It has been a great concern of many workers whether quartz surface adsorbs racemic adsorbates asymmetrically, because this phenomenon may relate to the genesis of the first optically active molecules in nature.[1] Various results showing the asymmetric adsorption had been reported. However, their reliability was recently questioned.[2] In 1974, Bonner *et al.* reported that they had succeeded in obtaining the unambiguous evidence for the occurrence of this phenomenon by using the radioactive alanine hydrochloride in rigorously dehydrated *N,N*-dimethylformamide (DMF) solution.[3,4] In the previous work, we also confirmed the occurrence of the asymmetric adsorption of alanine and alanine hydrochloride from an ordinary or a rigorously dehydrated ethanol solution at −80 °C by using the ninhydrin-colorimetry technique.[5]

In the present study, we checked the effects of water content in solution and of adsorption temperature upon the adsorption affinity of alanine. The value of asymmetric adsorptivity, A_s, for alanine by quartz powder at 8 °C was determined by the ^{14}C-tracer method and the newly developed ^{14}C-tracer·ninhydrin-colorimetry combination (TN) method. The TN method has the advantage that it can determine the value of A_s by one adsorption experiment, as will be demonstrated later. The cause of the asymmetric adsorption by quartz is also discussed from the crystallographic point of view.

Experimental

Materials. Dextrorotatory (*d*-) and levorotatory (*l*-) quartzs ($[\alpha]_D=22°$) were purchased from Toyo Communication Equipment Co. Ltd. They were ground by an agate-motor into powders of two uniform sizes. Sample A has 105—53 μm of average particle size and 0.08 $m^2 g^{-1}$ of the BET surface area. The values for sample B are <53 μm and 0.38 $m^2 g^{-1}$ respectively. D- and L-(U-^{14}C)-alanine (20—40 and 150 mC_i $mmol^{-1}$ respectively) were supplied from Radiochemical Center Amersham. Reagent grade racemic alanine was dissolved in a 99.8% ethanol to obtain DL-alanine solutions of various concentrations. D- or L-(U-^{14}C)-alanine was then added to them to prepare the *DL- and D*L-alanine stock solutions, whose radioactivity ranged from 4000 to 6000 cpm (asterisk denotes ^{14}C). The rigorously deoxygenated ninhydrin-hydrindantin reagent was prepared as follows.[6] 20 cm^3 of lithium acetate buffer solution (pH=5.2±0.5) was added to 60 cm^3 of dimethyl sulfoxide. After 15 min agitation, 1.6 g of ninhydrin and 0.12 g of hydrindantin were dissolved successively in the solution (all these treatments were carried out under a highly deoxygenated nitrogen stream).

Procedure for ^{14}C-Tracer Method. 5 g of the *d*- or *l*-quartz powder was degassed in a Pyrex sample tube for 1 h at 150 °C under a vacuum of 10^{-3} Pa. After cooling in a dry box, the powder was transferred into a polyethylene bottle containing 5 cm^3 of *DL- or D*L-alanine solution. After a vigorous agitation, the sample was equilibrated for 2 h. Then its supernatant solution was centrifuged for 10 min and three aliquots (0.5 cm^3) of it were transferred into a glass bottle containing 2.0 cm^3 of PCS scintillant. The decrease in the radioactivity due to the adsorption was determined by an Aloka LSC-651 Scintillation Counter. The deviation in nine countings (three countings for each aliquot) was within 2%.

Procedure for ^{14}C-Tracer·Ninhydrin-Colorimetry Combination (TN) Method. 8 g of the *l*-quartz B was treated as above and placed in 20 cm^3 of *DL- and D*L-alanine solution. After the measurement of the decrease in the radioactivity, 5 cm^3 of the solution was transferred into a test tube and dried on a water bath. Then 5 cm^3 of the deoxygenated water and 3 cm^3 of the deoxygenated ninhydrin-hydrindantin reagent were successively added into the test tube. After being sealed, the test tube was heated at 100 °C for 15 min. The magnitude of the absorption at 570 nm ($\varepsilon=(2.22\pm0.04)\times10^5$ M^{-1} cm^{-1}) for the colored solution was measured to determine the decrease in the total alanine concentration due to the adsorption.

Results and Discussion

The amount of D-alanine adsorbed by the *d*-quartz B from 0.94×10^{-5} M *DL-alanine solution was measured by the ^{14}C-tracer method at 8 °C as a function of water content. The plot in Fig. 1 shows that the amount of D-alanine adsorbed decreases almost linearly with the increase in water content up to 10% and becomes negligible at 20%. However, this test showed that a rigorous dehydration of ethanol (for example to less than 100 ppm as in the previous work[5]) is not indispensable for the present purpose.

The adsorption isotherm for D-alanine by the *d*-quartz B was measured at 8 °C and −80 °C using various concentrations of *DL-alanine solutions. Figure 2 shows that D-alanine is more strongly adsorbed at −80 °C than at 8 °C, although the difference is not as prominent as expected from the large difference in the adsorption temperature. The small temperature dependence of the adsorption affinity of D-alanine to *d*-quartz means that the magnitude of the

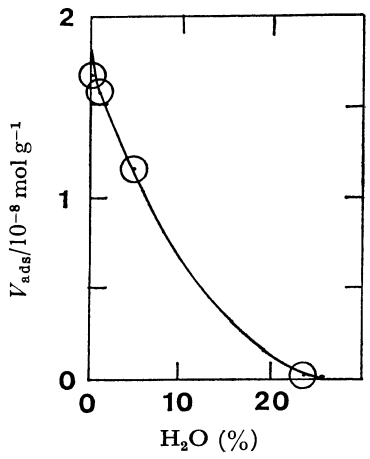

Fig. 1. Effect of water content in ethanol upon the amount of *D-alanine adsorbed (V_{ads}).
2 g of the *d*-quartz B was contacted with 10 cm^3 of (0.94×10^{-5} M) *DL-alanine solution for 2 h.

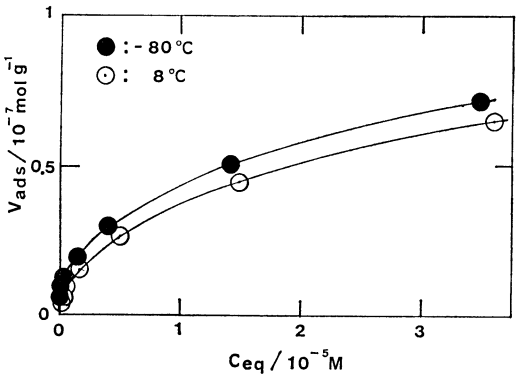

Fig. 2. Adsorption isotherm of *D-alanine on *d*-quartz B at 8 and −80 °C.
2 g of the *d*-quartz B was contacted with 10 cm^3 of ($(0.094-9.4)\times10^{-5}$ M) *DL-alanine solution for 2 h. The values for V_{ads} and C_{eq} are for the *D-alanine only.

isosteric heat of adsorption, q_{st}, for D-alanine is almost comparable with that for ethanol. However, since the concentration of D-alanine is almost 10^{-6} times as small as that of ethanol, it is certain that the adsorption affinity to *d*-quartz of D-alanine is much larger than that of ethanol. The entropy of adsorption for D-alanine, therefore, must be much larger than that for ethanol. The reason can be well explained if one borrows the term "chelate effect" which is frequently used in coordination chemistry.[7] As will be discussed later, a D-alanine molecule forms three hydrogen bonds with three surface hydroxyl groups when it is adsorbed by the *d*-quartz (two by the carboxyl group and one by the amino group). However, since these two groups are attached to the same molecule, the loss of the translational freedom by the adsorption is three per one molecule. On the other hand, nine translational freedoms are lost when the corresponding three ethanol molecules are adsorbed. This smaller number of losses of the translational degrees of freedom may be the principal cause for the larger entropy of adsorption, and thus the larger adsorption affinity, of D-alanine than those of ethanol. (That the number of losses in the rotational freedom for a D-alanine molecule is smaller than that for three corresponding ethanol molecules (three *vs.* nine) may partially contribute to the larger entropy of adsorption of D-alanine. The vibrational term, however, is essentially unrelated to the entropy of adsorption.) However, since the strengths of the hydrogen bonds of O–H---O and O–H---N are almost equal,[8] the magnitude of q_{st} for D-alanine (precisely speaking, the q_{st} per hydrogen bond in D-alanine) becomes nearly equal to that for ethanol.

By applying the Langmuir equation to the isotherm in Fig. 2, the monolayer capacity for DL-alanine is obtained as 1.8×10^{-7} mol g^{-1}. This, when combined with the value of the BET surface area (0.38 m^2 g^{-1}), yields a value of 3.5 nm^2 molecule^{-1} for the adsorption cross section for DL-alanine.

The asymmetric adsorptivity (A_s) is defined as follows:

$$A_s = \left(\frac{V_{ads}}{C_{eq}}\right)_{L(\text{or D})} \Big/ \left(\frac{V_{ads}}{C_{eq}}\right)_{D(\text{or L})}. \quad (1)$$

Here V_{ads} and C_{eq} denote the amount of alanine adsorbed and the equilibrium concentration respectively. The value of A_s for alanine by quartz was determined at 8 °C with the ^{14}C-tracer method. The result is summarized in Table 1. Table 1 shows that the *d*-quartz preferentially adsorbs D-alanine and the *l*-quartz adsorbs L-alanine, as found in the preceding experiments.[3-5] The value of A_s for alanine falls in the range of 1.1—1.3 at the higher alanine concentrations. This is almost the same as the value (1.2) determined at −80 °C by the ninhydrin-colorimetry in the previous paper,[5] but slightly lower than the value for alanine hydrochloride (1.4—1.7) from the rigorously dehydrated DMF solution determined by Bonner *et al.*[4] The present value is also apparently lower than the value (≈2) determined by the present authors at −80 °C using the rigorously dehydrated ethanol solution.[5] The value determined at the lowest concentration is apparently small, although we do not know the reason.

To determine the A_s value by the tracer method or the ninhydrin-colorimetry alone, two separate adsorption experiments are necessary. For example, the A_s value obtained from the data of Bonner *et al.* is determined by the combination of the values of the amounts for the labeled enantiomer adsorbed by the *d*- and *l*-quartzs separately.[4] In the present study, the A_s value was obtained from the difference between the amounts of the two enantiomers adsorbed by the *d*- or *l*-quartz. However, since there is no guarantee that the surface properties of the two quartzs or the water content in the two alanine solutions are identical, it was feared that the A_s value might contain a large error. To eliminate this fear, we have developed the TN method by which the A_s value can be determined from one adsorption experiment. According to this method, the values of V_{ads} and C_{eq} of the labeled enantiomer are determined by the tracer method, while the values for the total alanine are obtained by the ninhydrin-colorimetry. The difference between the two measurements yields the values for the nonlabeled enantiomer. The results obtained by the TN method

Table 1. The data for the asymmetric adsorption of alanine at 8 °C determined by the ^{14}C-tracer method

Quartz[a]	*DL			D*L			A_s
		$\left(\frac{10^8 V_{ads}}{\text{mol g}^{-1}}\right)_D$	$\left(\frac{10^5 C_{eq}}{\text{M}}\right)_D$		$\left(\frac{10^8 V_{ads}}{\text{mol g}^{-1}}\right)_L$	$\left(\frac{10^5 C_{eq}}{\text{M}}\right)_L$	
d	b)	3.22	20.28	c)	2.89	20.61	1.13
l	d)	5.10	18.40	e)	6.02	17.48	1.24
d	f)	2.43	6.97	g)	2.29	7.11	1.08
l	h)	3.65	5.75	i)	4.01	5.39	1.17
d	j)	1.88	2.82	k)	1.57	3.13	1.33
l	l)	2.56	2.14	m)	2.66	2.04	1.09
l	n)	0.813	0.127	o)	0.817	0.123	1.04

a) 5 g of the powder A was placed in 5 cm^3 of DL-alanine solution. Radioactivity (count per 5 min) of the alanine solution measured before and after the adsorption was; b) 37185 and 32091. c) 27388 and 24019. d) 37185 and 29119. e) 27388 and 20382. f) 33321 and 24721. g) 28653 and 21656. h) 33321 and 20385. i) 28653 and 16415. j) 33378 and 20053. k) 28662 and 19063. l) 33378 and 15209. m) 28662 and 12398. n) 33556 and 4535. o) 28523 and 3743.

Table 2. The data for the asymmetric adsorption of alanine at 8 °C determined by the TN method

Quartz[a]	Alanine[b]	$(10^9 V_{ads}/\text{mol g}^{-1})/(10^5 C_{eq}/\text{M})$			A_s
		D+L	D	L	
l	*DL	33.2/3.37	15.2/1.74	(18.0/1.63)[c,d]	1.26
l	D*L	29.6/3.52	(13.2/1.82)[c,e]	16.4/1.70	1.33

a) 8 g of the *l*-quartz B. b) 20 cm^3. The initial concentration of DL-alanine solution is 4.70×10^{-5} M. c) Calculated value. The radioactivity (counts per 5 min) of the alanine solution measured before and after the adsorption was; d) 37149 and 27403 e) 27403 and 19748.

are summarized in Table 2. The value of A_s ($\approx$1.3) accords well with the value determined by the tracer method.

Now it becomes unambiguous that the *d*-quartz preferentially adsorbs D-alanine and the *l*-quartz adsorbs L-alanine. Our next step is to solve the question "on what plane does the asymmetric adsorption occur?" According to an electron-microscopic observation, the powdered sample seems to contain various planes randomly. Therefore the A_s value obtained on the powdered sample is not helpful to solve this question. We are obliged to discuss this matter solely from the crystallographic point of view.

The projections of silicon and oxygen atoms on the (0001) and (10$\bar{1}$0) planes of quartz are schematically represented in Figs. 3 and 4. As can be seen in Fig. 3, silicon and oxygen atoms locate in nearly the same level on the (10$\bar{1}$0) plane. However, it is shown in Fig. 4 that the configuration of silicon atoms on the (10$\bar{1}$0) plane of *l*- and *d*-quartz is identical, while that of oxygen atoms is mirror-symmetrical to each other. The (10$\bar{1}$0) plane is a chiral plane where the asymmetric adsorption of alanine may occur.

Many workers have shown that the surface of the

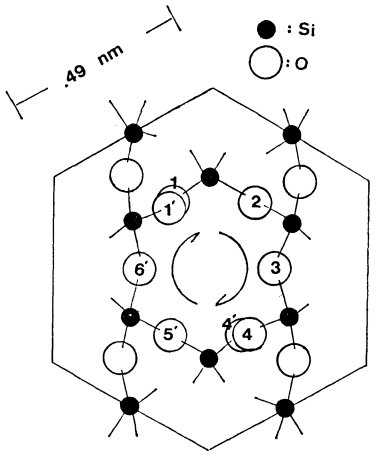

Fig. 3. A schematic representation of the (0001) plane of quartz.
Pairs of 1 and 4′, 2 and 5′, 3 and 6′, and 4 and 1′ oxygen atoms exist in the same plane.
If the helix of oxygen atoms (1-2-3-4) is clockwise, the quartz is *l*-quatz.

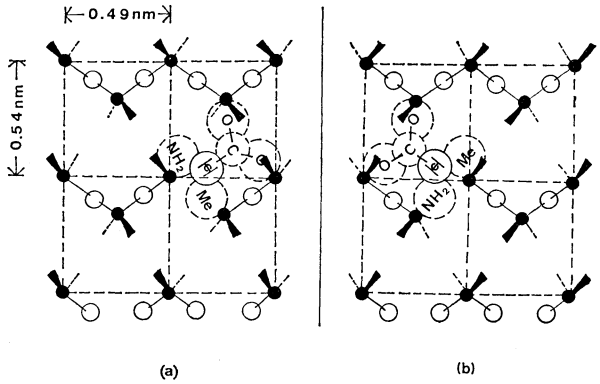

Fig. 4. Schematic representations of the (10$\bar{1}$0) plane of *l*-and *d*-quartzs, and of the configuration of the adsorbed L-alanine molecule.
(a): *l*-Quartz, (b): *d*-quartz, ●: silicon atom, ○: frame oxygen atom, ◄: surface hydroxyl group.

powdered quartz is covered by hydroxyl groups which can not be removed even by heating up to 150 °C.[9] If this is the case, the $(10\bar{1}0)$ planes of the present *l*- and *d*-quartz samples have the hydroxyl groups which are disposed mirror-symmetrically to each other, as shown in Fig. 4. The carboxyl, amino, and even methyl groups of the alanine molecule, when the molecule is adsorbed on the $(10\bar{1}0)$ plane, interact (*i.e.*, form the hydrogen bond) with the surface hydroxyl group. However, it may be the carboxyl group which interacts with the hydroxyl group most strongly and, therefore, principally determines the adsorbed structure of the alanine molecule. The pairs of the hydroxyl groups which can interact satisfactorily with the carboxyl group are limited. If an L-alanine molecule is put on the $(10\bar{1}0)$ plane of the *l*-quartz, as shown in Fig. 4, we notice that not only the carboxyl group but also the amino group can interact with the surface hydroxyl group very well, although the methyl group can not. However, if an L-alanine molecule is put on the *d*-quartz surface so that the carboxyl group preferably interacts with a pair of the hydroxyl groups, the amino group can not interact with the hydroxyl group well. Instead, the methyl group interacts with the hydroxyl group preferably. It is well known that the hydrogen bond between an amino group and a hydroxyl group is stronger than that between a methyl group and a hydroxyl group (16—29 kJ mol^{-1} against 11 kJ mol^{-1}).[8] It may not be unreasonable to conclude that the larger interaction between NH_2 and OH groups than that between CH_3 and OH groups is the principal cause (or at least one of the principal causes) for the preferential adsorption of L-alanine by the *l*-quartz than by the *d*-quartz. The same may be true for the preferential adsorption of D-alanine by the *d*-quartz rather than by the *l*-quartz.

The explanation above seems to work well. However, two questions are raised to the adsorption model. (1) If the asymmetric adsorption results from the different heat of formation for NH_2–OH hydrogen bond and for CH_3–OH hydrogen bond, the A_s value must be temperature dependent. Is the fact that the A_s value at 8 °C is apparently comparable with the value at −80 °C obtained in the previous study inconsistent with the above model?[5] (2) Does the present model work well even in aqueous solution where the alanine molecule dissociate to the dipolar ion $CH_3(H)C(COO^-)NH_3^+$? We can not answer the first question definitely, partly because the techniques and conditions adopted in the two experiments are quite different and, therefore, the certainty of the data can not bear the quantitative discussion. We should establish the experimental technique and condition to solve this question. As to the second question, we assert that the model works well even in the aqueous solution. However, if the strength of the NH_3^+–OH bond is weaker than the CH_3–OH bond, the asymmetric adsorptivity becomes opposite (*i.e.*, the *d*-quartz adsorbs preferentially the L-alanine and the *l*-quartz adsorbs the D-alanine). However, since the adsorption affinity of alanine falls drastically in the aqueous solution and the amount adsorbed of it by quartz is extremely low, as shown in Fig. 1, the experimental determination of the A_s value must be very difficult. The lateral electrostatic interaction between the adsorbed dipolar alanine ions can be neglected if the concentration of the adsorbed species is quite low.

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