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ASYMMETRIC ADSORPTION OF ALANINE AND ALANINE HYDROCHLORIDE BY QUARTZ FROM ETHANOL SOLUTION AT - 80°C

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It was found that the L-isomers of alanine and alanine hydrochloride were adsorbed preferentially by l-quartz, while the D-isomers were adsorbed by d-quartz from ethanol solution at - 80°C. The asymmetricity of adsorption fell in the range 1.3 - 2.2.

It has been a great concern of many workers whether quartz surface adsorbs racemic adsorbates asymmetrically, because this phenomenon perhaps relates to the genesis of the first optically active molecules in nature.[1] Various results showing the asymmetric adsorption were reported, however, their reliabilities were recently questioned.[2] In 1974, Bonner et al. reported that they first succeeded to obtain the unambiguous evidence for the occurence of this phenomenon, by using the radioactive alanine hydrochloride in rigorously dehydrated dimethylformamide (DMF) solution.[3,4] In the present work, we studied the adsorptions of alanine and alanine hydrochloride by quartz from ethanol solution at - 80°C, and confirmed that the asymmetric adsorption does occur. To stimulate the studies in this field, it should be worthwhile to describe our experimental procedures and results briefly.

The same amounts of d- and l-quartz powders in the uniform size (145 - 285 mesh, BET surface area = 0.080 m^2/g) were placed in two pyrex adsorption cells separately and degassed simultaneously at 150°C and at 10^{-4} Torr for 1 hr. Then 20 ml of ethanol solution containing the D- or L-isomers (the initial amount, N_i, was 5 - 12 x 10^{-7} mol/20 ml) was introduced into each of the adsorption cells. After being equilibrated at - 80°C for 20 hrs, the supernatant solution was centrifuged and an aliquot (5 ml) of it was transferred into a test tube, and dried on a water bath. Then 5 ml of water was added to the test tube and the concentration of alanine was determined colorimetrically by using the rigorously deoxygenated ninhydrin - hydrindantin reagent.[5] The value of extinction coefficient, ε, of the colored species was (2.22± 0.04) x 10^5 $M^{-1}cm^{-1}$ at 570 nm.

The results were summarized in Table I. Table I clearly shows that the L-isomers are adsorbed preferentially by l-quartz, while the D-isomers by d-quartz. This trend is the same as that obtained by Bonner et al. in the DMF solution.[3,4] The degree of the asymmetric adsorption was

expressed by the asymmetric adsorption factor, As = R_l/R_d for the L-isomers and As = R_d/R_l for the D-isomers. Here R_d and R_l denote the ratio for the amounts of the isomers in adsorbed and liquid phases, (N_{ads}/N_{liq}), over d- and l-quartzs, respectively. The results were summarized in Column 7 in Table I. The mean values of As for alanine (A group) are 2.1 in dehydrated solution (water content of 100 ppm) and 1.2 in wet solution (water content of 2000 ppm). The mean value of As for alanine hydrochloride (B group) in wet solution is 1.6. These values are slightly larger than the value in the rigorously dehydrated DMF solution (water content of 26 ppm), 1.1 - 1.5, obtained by Bonner et al. at room temperature.[3,4] The rigorous dehydration of the solvent was not necessary to observe the asymmetric adsorption as far as the present study concerns. The present work has shown that the ninhydrin-colorimetry can be used to determine the degree of the asymmetric adsorption and suggests that this method may be more effective when combined with the tracer method. Suppose the case where the mixture of D- and L-alanine isomers, one of which is labeled by ^{14}C, is adsorbed. Since adsorbed amounts of the labeled and total alanines can be determined by the tracer method and the colorimetry, respectively, the value of As can be determined on one kind of quartz. This combined method may be more accurate way to determine the value of As than the methods used by Bonner et al. and by the present authors. In the latter methods, both d- and l-quartzs in the same uniform size are needed.

Table I. The data for the asymmetric adsorption

Group	Adsor-bent[a]	Adsor-bate	N_i[b] x 10^{-7}mol/20 ml	N_{liq} x 10^{-7}mol/20 ml	N_{ads} x 10^{-7}mol/sample	As
A	d	D-ala.	10.3	7.2	**3.1**	1.2
	l	in wet EtOH		7.6	2.7	
	d	L-ala.	7.56	5.3	2.3	1.2
	l	in wet EtOH		5.0	2.6	
	d	D-ala. in	5.52	4.0	1.5	2.2
	l	dehyd. EtOH		4.7	0.8	
	d	L-ala. in	12.4	10.6	1.8	2.0
	l	dehyd. EtOH		9.2	3.2	
B[c]	d	L-ala.HCl	4.80	2.8 ± 0.3	2.0 ± 0.3	1.8 ± 0.4
	l	in wet EtOH		2.1 ± 0.2	2.7 ± 0.2	
	d	D-ala.HCl	4.70	2.1 ± 0.1	2.6 ± 0.1	1.5 ± 0.2
	l	in wet EtOH		2.6 ± 0.1	2.1 ± 0.1	

a) 10 g for A group and 20 g for B group were used.
b) The accuracy of the concentration determination was within ± 2 %.
c) Three measurements were averaged.

References

1) G. Karagunis and G. Coumoulos, Nature, 142,162 (1938).
2) A. Amariglio, H. Amarigrio, and X. Duval, Helv.Chim. Acta, 51,2110 (1968).
3) W. A. Bonner, P. R. Kavasmaneck, and F. S. Martin, a) Science, 186, 143 (1974), b) Origins of Life, 6, 367 (1975).
4) W. A. Bonner and P. R. Kavasmaneck, J. Org. Chem., 41, 2225 (1976).
5) S. Moor, J. Biol. Chem., 243, 6281 (1968).

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