CHEMISTRY LETTERS, pp. 87-88, 1978. Published by the Chemical Society of Japan

HEATS OF SOLUTION OF CRYSTALLINE OPTICALLY ACTIVE AND RACEMIC AMINOACIDS IN WATER(*)

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The heats of solution of aminoacids crystals at 298.15 K have been measured. The difference between the heat of solution of optically active compounds and that of corresponding racemic compounds was appreciably large compared with the heat of mixing of concentrated aqueous solutions of D- and L-optical isomers, and the values were several kJ/mol at most.

In the theory of statistical thermodynamics for the solutions containing D- and L-optical isomers,$^{1)}$ it was derived by Amaya that the heat of mixing is dependent on 1/T. In fact Takagi et al. have measured the heat of mixing of D- and L-optical isomers in aqueous solution at 298.75 K but the values obtained so far were too small to test the relation.$^{2)}$ This is because the molecule rotates freely in the liquid state, and the difference of interaction energy is average out. However, in the solid state each molecule is confined in the cage formed by the sorrounding molecules and takes energetically most favorable configuration. As is expected from the theory much large difference compared with the case in aqueous solutions will be observed. The heat of solution of aminoacids crystals in water has been measured in a twin isoperibol calorimeter, a Model TIC-2D manufactured by Tokyo Riko Co., Ltd.

Before the measurements, the calorimeter was calibrated with the NBS standard reference material 724a, tris(hydroxymethyl)aminomethane and hydrochloric acid.$^{3)}$ The systematic error and precision obtained at present experiments were 1.4 % and 0.34 %, respectively. Alanine, L-Valine, Threonine and D-Glutamic acid were supplied by Takara Kosan Co., Ltd.and DL-Valine, DL-Glutamic acid and tartaric acid were supplied by Tokyo Kasei Co., Ltd,and they were used without further purification. All the samples were dried over silica-gels in a desiccator at room temperature at least for 3 days before use.

The measurements have been made at 298.15 K. Fifty to one hundred mili-grams of the sample was sealed in a glass ampoule, and the sample and the blank ampoule were set in the measuring and the reference Dewar vessels, respectively, filled with 0.1 dm^3 distilled water, and stood for 24 hours. The heat quantity was calculated by means of the ordinary method.$^{4)}$

The results obtained at 298.15 K are shown in Table I. The values in the second column of this table are the means of 3 determinations. As was expected, the difference between the heat of solution of DL-isomers in water and that of D- or L-

Table I

Compounds	Heat of solution kJ/mol at 298.15 K	Difference of heat of solution
DL-Alanine	9.35 ± 0.07	1.99
L-Alanine	7.36 ± 0.15	
DL-Glutamic acid	28.56 ± 0.12	4.03
D-Glutamic acid	24.53 ± 0.00	
DL-Threonine	9.61 ± 0.06	0.17
L-Threonine	9.78 ± 0.03	
DL-Valine	5.16 ± 0.00	2.29
L-Valine	2.87 ± 0.01	
DL-Tartaric acid	25.64 ± 0.07	9.52
L-Tartaric acid	16.12 ± 0.38	

isomers was appreciably large, and the values were several kJ/mol at most. The experimental data show that DL-isomers in the solid state are more stable than D- or L-isomers except for Threonine, by assuming that the energy of DL-isomers in aqueous solution is equal to that of D- or L-isomers. Experimental values of the heat of solution of DL-Alanine and L-Valine were slightly smaller than those of previous authors.[5,6]

We are grateful to Dr. S. Morimoto of Reseach Institute for Polymers and Textiles for a gift of the NBS tris(hydroxymethyl)aminomethane.

References and notes

(*) Presented at the 5th International Conference on Thermal Analysis, Kyoto, Japan August (1977)

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(Received October 13, 1977)