Heats of Mixing of Optical Isomers in Solution: Calorimetric Evidence of Stereospecific Effect

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FUNDAMENTAL studies on the thermodynamic properties of solutions involving optically active substances are important in relation to optical resolution and reaction mechanisms in biological systems.

In terms of a quasi-lattice model, a statistical mechanical theory for solutions containing D- and L-optical isomers has been developed by one of the present authors.[1,2] We report here some calorimetric evidence of such stereospecific interactions obtained by direct microcalorimetry. A new rotating twin-calorimeter of the conduction type was used, whose temperature-sensitive mechanism consisted of two thermomodules used as a thermoelectric pile.[3] The mixing vessels (without vapour space) were made of glass. In each, 2 c.c. of the aqueous solutions (same concentration) of the D- and L-isomers were separated by pure mercury before mixing. The Table shows the measured heats of mixing, Q. The last column shows the heats of mixing of the aqueous solutions of optical isomers when the total amount of solutes is one mole, namely $\Delta H^{M} = Q/(n_D + n_L)$ where n_D and n_L are the number of moles of D- and L-isomer in solution, respectively.

In aqueous tartaric acid solution, the experimental results show that energetically, the D–L contacts are slightly less stable than the D–D or L–L contacts, but are the reverse in aqueous threonine solution. Since the solubility of (±)-glutamic acid is small, the heat of mixing could not be detected for aqueous solutions of D- and L-glutamic acids.

From the Gibbs function of mixing of D- and L-isomers derived theoretically by Amaya,[1] the heat of mixing is expressed as a function of T^{-1}. Heats of mixing obtained so far are too small to test the relation, but can be used to obtain the order of magnitude of the interchange energies in aqueous solutions.

The purities of the materials used were determined by optical rotation.

Heats of mixing of D- *and* L-*isomers in aqueous solution of tartaric acid, glutamic acid, and threonine at* 25·6°

Solution	Concentration (wt % solute)	Sample size (g.)	Q (mJ)	ΔH^{M} (J/mole of solute)
D-tart	15·619	2·1882	$9{\cdot}3 \pm 0{\cdot}2$	$1{\cdot}9_9 \pm 0{\cdot}04$
L-tart	15·616	2·2780		
D-tart	15·619	2·2325	$10{\cdot}1 \pm 0{\cdot}2$	$2{\cdot}1_7 \pm 0{\cdot}04$
L-tart	15·616	2·2362		
D-tart	15·619	2·3535	$7{\cdot}9 \pm 0{\cdot}2$	$1{\cdot}6_8 \pm 0{\cdot}04$
L-tart	15·610	2·1544		
	Average			$1{\cdot}9_5 \pm 0{\cdot}2_7$
D-glu	0·7175	1·9234	—	—
L-glu	0·7178	1·9629		
D-thr	8·3438	2·1364	$-16{\cdot}0 \pm 0{\cdot}2$	$-5{\cdot}4_6$
L-thr	8·3420	2·0473		

(*Received, March* 11*th*, 1968; *Com.* 286.)

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