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EXCESS MOLAR HEAT CAPACITIES OF (*L*-GLUTAMINE AQUEOUS SOLUTION+*D*-GLUTAMINE AQUEOUS SOLUTION) AT TEMPERATURES BETWEEN 293.15 AND 303.15 K

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Excess molar heat capacities of (*L*-glutamine aqueous solution+*D*-glutamine aqueous solution) were determined by using a differential scanning calorimeter at temperatures between 293.15 and 303.15 K. Excess molar heat capacities are all negative. Excess molar heat capacities decrease with increasing temperature.

Keywords: *chiral compound, D-glutamine, excess molar heat capacities, hydration, L-glutamine*

Introduction

In liquid phase a vast crowd of molecules gather closely, oscillating and rotating violently. Colliding with each other, they distinguish a kind of molecules from another ones. In particular, stereospecific interactions due to neighbouring surfaces may play the leading role in, e.g., enzyme-substrate reactions, antigen-antibody reactions, some kinds of mechanisms of senses of smell and taste, and so on. Therefore, elucidating the role of asymmetric intermolecular interactions owing to the stereospecific structures of molecules is really important for understanding the mechanisms of chemical and bio-chemical reactions. Thereafter, the influence of stereospecific interactions and densities in the liquid state have been evaluated by others [1–7]. In our previous papers [8–10], enthalpies of mixing of 11 systems of (*R*)- and (*S*)-enantiomers were reported. All measured systems showed a very small enthalpy changes. Excess thermodynamic functions of mixtures other than chiral compound have been reported by other researchers [11, 12]. However, to our knowledge, there is no published information on excess heat capacities of mixing two enantiomers of amino acid aqueous solutions. In this paper, the composition dependence of the excess isobaric molar heat capacity C_p^E at the temperatures 293.15, 298.15 and 303.15 K were also determined for the system of *L*-glutamine aqueous solution+*D*-glutamine aqueous solution.

Experimental

L-glutamine and *D*-glutamine (Nakarai tesque Co. Ltd.) were used without further purification. Enantiopurity of each was determined by a polarimeter (Horiba SEPA-200). Specific rotations of *L*-glutamine and *D*-glutamine are listed in Table 1. The concentration of the aqueous *L*-glutamine solution and the aqueous *D*-glutamine solution was 0.8763 and 0.8762 mass%, respectively. Details of the careful purification used for the water [13] was described earlier. All solutions were prepared by mass.

Table 1 Purities of the enantiomers used at 298.15 K

Sample	$[a]D^{25}$	Enantiopurity/%
L-glutamine	+6.6	>99.9
D-glutamine	–6.6	>99.9

Calorimetric measurements were carried out using a CSC 5100 differential scanning calorimeter (Calorimetry Science Corp. USA) in the temperature range of 278.15–313.15 K. Data were collected at a heating rate of 0.0167 K s^{-1}. Densities of the samples measured by a vibrating-tube densimeter (Anton Paar D60) at 293.15, 298.15 and 303.15±0.001 K are also listed in Table 2. The details of densimetric procedures were same as those described previously [14]. Molar heat capacities were calculated from the results for C_p/V using the densities of the mixtures. The heat capacities were calibrated by using sodium chloride solution. The uncertainty in the present measurements of C_p and C_p^E is estimated to be less than ±0.3 and ±1.0%, respectively.

Results and discussion

The excess isobaric molar heat capacity for the system {*xL*-glutamine aqueous solution+(1–*x*)*D*-glutamine

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Table 2 Densities ρ of $\{xL$-glutamine aq.$+(1–x)D$-glutamine aq.$\}$

x	ρ/g cm^{-3}		
	293.15 K	298.15 K	303.15 K
0	1.001684	1.000485	0.999109
0.17494	1.001631	1.000399	0.998986
0.24021	1.001580	1.000373	0.998941
0.30625	1.001594	1.000403	0.998965
0.44102	1.001512	1.000308	0.998878
0.56264	1.001549	1.000317	0.998919
0.60256	1.001448	1.000255	0.998838
0.72493	1.001466	1.000271	0.998825
0.73856	1.001441	1.000243	0.998823
0.88555	1.001395	1.000218	0.998805
1	1.001382	1.000189	0.998784

aqueous solution} was calculated by using the following equation:

$$C_p^E = C_p - xC_{p,A} - (1-x)C_{p,B} \qquad (1)$$

where $C_{p,A}$ and $C_{p,B}$ are the molar heat capacities for *L*-glutamine aqueous solution and *D*-glutamine aqueous solution, respectively, and C_p is the molar heat capacity of a mixture of $\{xL$-glutamine aqueous solution$+(1–x)D$-glutamine aqueous solution$\}$, and x is the mole fraction of *L*-glutamine aqueous solution. The experimental results for C_p^E are summarized in Table 3, they are smoothed by the function:

$$C_p^E/\text{J K}^{-1}\text{ mol}^{-1} = x(1-x)A_i(1-2x)^{i-1} \qquad (2)$$

where parameters A_i are given by a least-square method. The parameters are given in Table 4.

Composition dependence of excess molar heat capacity, at chosen temperature, is shown in Fig. 1. Excess molar heat capacities are all negative. Excess molar heat capacities decrease with increasing temperature. The direction of NH_2 as hydrogen bond donor of *D*-glutamine is different from that of *L*-glutamine. By mixing *D*-glutamine aqueous solution with *L*-glutamine aqueous solution, hydrogen bonding and hydration structure of each aqueous solution broke, and aqueous solution became random. The random contribution to C_p^E is negative [15]. The random contributions of (*L*-glutamine aqueous solution+*D*-glutamine aqueous solution) increase with increasing temperature.

Table 3 Excess molar heat capacity C_p^E at constant pressure of $\{xL$-glutamine aq.$+(1–x)D$-glutamine aq.$\}$

x	C_p^E/J K^{-1} mol^{-1}		
	293.15 K	298.15 K	303.15 K
0.09544	–0.692	–0.946	–1.519
0.19178	–1.223	–1.496	–2.483
0.30154	–1.656	–2.054	–3.312
0.41004	–1.928	–2.371	–3.727
0.49830	–1.998	–2.488	–3.932
0.60431	–1.946	–2.418	–3.718
0.69879	–1.767	–2.117	–3.324
0.79194	–1.422	–1.673	–2.483
0.89665	–0.721	–0.948	–1.452

Table 4 Parameters of Eq. (2) for the excess molar heat capacity C_p^E at constant pressure of $\{xL$-glutamine aq.$+(1–x)D$-glutamine aq.$\}$

x	A_1	A_2	A_3	A_4	s_f
293.15 K	–1.335	0.8920	–0.1615	–1.335	0.02
298.15 K	–9.894	0.8178	–0.4603	–1.673	0.03
303.15 K	–15.54	0.3343	–0.8456	–2.526	0.04

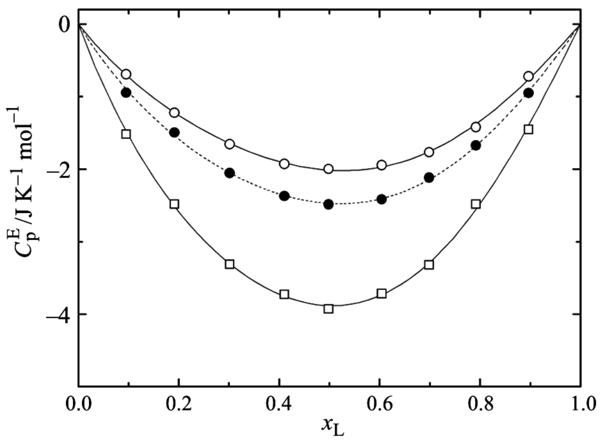

Fig. 1 Excess molar heat capacities of $\{xL$-glutamine aq.$+(1–x)D$-glutamine aq.$\}$, ○ – T=293.15 K; ● – T=298.15 K; □ – T=303.15 K

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