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EXCESS MOLAR HEAT CAPACITIES OF ((*R*)-(+)-α-PINENE+(*S*)-(–)-α-PINENE) AT TEMPERATURES BETWEEN 293.15–308.15 K

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To our knowledge, there is no published information on heat capacities of mixing two couples of *S*- and *R*-enantiomers. In order to reveal the origin of chiral discrimination, excess molar heat capacities of ((*R*)-(+)-α-pinene + (*S*)-(–)-α-pinene) were determined by using a differential scanning calorimeter at temperatures between 293.15–308.15 K. Excess molar heat capacities are decreased with increased of temperature. π–π interactions change with the composition dependence, on account of changes of the symmetry. From the above-mentioned reasons, it was considered that complex curves were obtained.

Keywords: *chiral compound, excess molar heat capacities, (R)-(+)-α-pinene, (S)-(–)-α-pinene*

Introduction

Molecular recognition and discrimination may be caused by the interactions among contacting surfaces of colliding molecules in solutions and mixtures. In particular, stereospecific interactions due to neighbouring surfaces may play the leading role in, for examples, enzyme-substance reactions, antigen-antibody reactions, some kinds of mechanisms of the senses of smell and taste, etc. Takagi *et al*. [1–2] discovered in 1966 that the small enthalpies of mixing of two enantiomers the some compounds are measurable by microcalorimetry. Thereafter, the influences of stereospecific interactions and densities in the liquid state have been evaluated by others [3–9].

In our previous papers [10–12], enthalpies of mixing of 16 systems of (*R*)- and (*S*)-enantiomers were reported. All measured systems showed a very small enthalpy changes. Heat capacities [13–14] and excess heat capacities [15–16] of binary solutions have been reported by many researchers. However, to our knowledge, there is no published information on heat capacities of mixing two couples of *S*- and *R*-enantiomers. In this paper, the composition dependence of the excess isobaric molar heat capacity C_P^E at the temperatures (293.15, 298.15, 303.15 and 308.15 K) were also determined for the system of (*R*)-(+)-α-pinene + (*S*)-(–)-α-pinene.

Experimental

(*R*)-(+)-α-pinene and (*S*)-(–)-α-pinene (Azmax. GR) were fractionally distilled over freshly activated molecular sieves 4A which had been evacuated at 453 K for 12 h under 10^{-2} to 10^{-3} Pa. Their chemical purities obtained from gas-vapour phase chromatography by using each 2 m column of 10% SE-30 on chromosorb and 20% PEG-1000 on celite 545 with FID on Yanagimoto G180FP are more than 99.9%. Water contents obtained by a coulometric Karl-Fischer's method on a Mitsubishi Moisture Meter, model CA-02 (Mitsubishi Chemical Ind.) are listed in Table 1. Densities of the samples measured by a vibrating-tube densimeter (Anton Paar D60) at (298.15±0.001) K are also listed in Table 2. The details of densitimetric procedures were same as those described previously [17]. Enantiopurity of each was determined on a polarimeter (Horiba SEPA-200). Specific rotations of (*R*)-(+)-α-pinene and (*S*)-(–)-α-pinene are listed in Table 1.

Calorimetric measurements were carried out using a CSC 5100 differential scanning calorimeter (Calorimetry Science Corp. USA). Data were collected from 278

Table 1 Purities at 298.15 K of the enantiomers used

Samples	$[a]D^{25}$	Water content/mol%
(*R*)-(+)-α-pinene	+50.2	0.030
(*S*)-(–)-α-pinene	–50.0	0.027

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Table 2 Densities ρ of (x(*R*)-(+)-α-pinene+(1–x) (*S*)-(–)-α-pinene)

x	ρ/g cm^{-3}	ρ/g cm^{-3}	ρ/g cm^{-3}	ρ/g cm^{-3}
	293.15 K	298.15 K	303.15 K	308.15 K
0.0	0.857631	0.853619	0.849595	0.845584
0.07107	0.857632	0.853622	0.849461	0.845532
0.13301	0.857697	0.853676	0.849618	0.845584
0.17718	0.857786	0.853799	0.849751	0.844865
0.31119	0.857779	0.853810	0.849777	0.845780
0.46736	0.857885	0.853888	0.849854	0.845842
0.51988	0.857857	0.853835	0.849785	0.845758
0.66502	0.858030	0.854037	0.850016	0.846011
0.73940	0.857991	0.853799	0.849928	0.845900
0.81221	0.858121	0.854116	0.850084	0.846071
0.91785	0.858058	0.854025	0.849957	0.845917
1.0	0.858175	0.854181	0.850160	0.846158

to 313 K at a heating rate of 0.0167 K s^{-1}. Molar heat capacities were calculated from the results for C_p/V using the densities of the mixtures, and of the pure components. The heat capacities were calibrated by using acetone and *n*-hexane.

Results and discussion

The isobaric molar heat capacities obtained for the pure enantiomers in Table 3.

Table 3 Heat capacities of (*R*)-(+)-α-pinene and (*S*)-(–)-α-pinene

T/K	C_P/J K^{-1} mol^{-1}	C_P/J K^{-1} mol^{-1}
	(*R*)-(+)-α-pinene	(*S*)-(–)-α-pinene
293.15	246.80	246.80
298.15	248.91	248.90
303.15	251.08	251.06
308.15	253.15	253.07

Table 4 Excess molar heat capacity C_P^E at constant pressure of (x(*R*)-(+)-α-pinene+(1–x) (*S*)-(–)-α-pinene)

x	C_P^E/J K^{-1} mol^{-1}	C_P^E/J K^{-1} mol^{-1}	C_P^E/J K^{-1} mol^{-1}	C_P^E/J K^{-1} mol^{-1}
	293.15K	298.15 K	303.15 K	308.15 K
0.09835	0.096	–0.036	–0.139	–0.207
0.19956	0.030	–0.076	–0.154	–0.210
0.31557	0.049	–0.059	–0.143	–0.204
0.38881	0.005	–0.084	–0.149	–0.206
0.50327	–0.075	–0.165	–0.230	–0.265
0.61146	–0.032	–0.096	–0.147	–0.180
0.70246	–0.028	–0.089	–0.138	–0.169
0.80463	–0.060	–0.109	–0.150	–0.176
0.90032	–0.051	–0.098	–0.137	–0.160

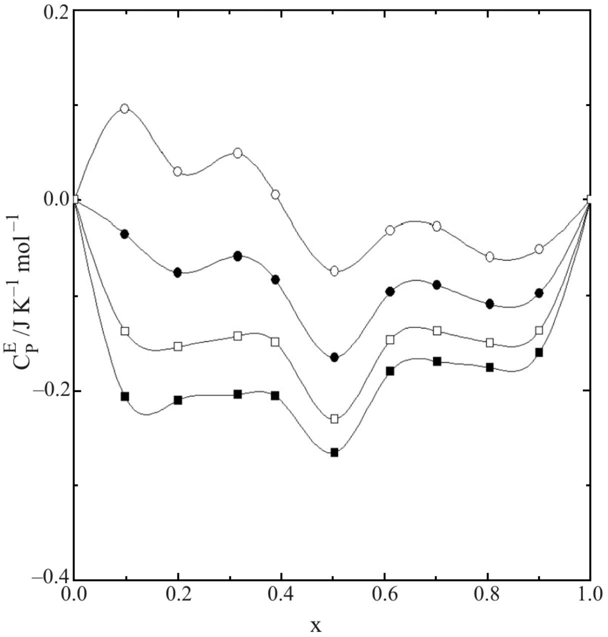

Fig. 1 Excess isobaric heat capacities C_P^E of ((*R*)-(+)-α-pinene+(*S*)-(–)-α-pinene), ○ – T=293.15 K, ● – T=298.15 K, □ – T=303.15 K, ■ – T=308.15 K

The excess isobaric molar heat capacity for the binary system (x(*R*)-(+)-α-pinene+(1–x)(*S*)-(–)-α-pinene} 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 (*R*)-(+)-α-pinene, for (*S*)-(–)-α-pinene, respectively, C_p is the molar heat capacity of a mixture of (x((*R*)-(+)-α-pinene)+(1–x) (*S*)-(–)-α-pinene), and x is the mole fraction of (*R*)-(+)-α-pinene. Composition dependence of excess molar heat capacity, at chosen temperature, is shown in Table 4 and Fig. 1. These curves were obtained by spline interpolation. Excess molar heat capacities are negative except region for $0<x<0.4$ at 293.15 K. Excess molar heat capacities are decreased with increase of temperature. There are two maximum at $x\approx 0.35$ and 0.65 and three minima at $x\approx 0.15$ and 0.5 and 0.85, at 303.15 and 308.15 K. There are two maximum at $x\approx 0.35$ and 0.65 and three minima at $x\approx 0.2$ and 0.5 and 0.85, at 298.15 K. There are three maximum at $x\approx 0.1$ and 0.3 and 0.65 and three minima at $x\approx 0.2$ and 0.5 and 0.85, at 293.15 K. The intermolecular interaction of bond dipoles of (x((*R*)-(+)-α-pinene)+(1-x) ((*S*)-(–)-α-pinene)) is small [11]. π–π interaction between (*R*)-(+)-α-pinene and (*S*)-(–)-α-pinene, between (*R*)-(+)-α-pinene and (*R*)-(+)-α-pinene, between (*S*)-(–)-α-pinene and (*S*)-(–)-α-pinene, these interactions change with the composition dependence, on account of changes of the symmetry. From the above-mentioned reasons, it was considered that complex curves were obtained.

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