

# Enthalpies of mixing of ethanol solution of chiral limonenes at 298.15 K

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**Abstract** Enthalpies of mixing of ethanol solution of *R*- and *S*-enantiomers of limonene in large concentration have been measured at 298.15 K. The enthalpies of mixing were negligibly small for all concentrations. Enthalpies of mixing showed negative in less than 30 mol%, but positive in more than the high concentration of limonenes. The heterochiral solutions were more stable than each of the homochiral solutions in dilute solutions. The concentration dependence on enthalpies of mixing in dilute concentration of less than 10 mol% was much sharper in inclination than the dense solutions limonene.

**Keywords** *R*- and *S*- limonenes · Enthalpy of mixing · Concentration dependence on enthalpy of mixing · Ethanol solution

## Introduction

Enantiomers are unique molecules that have extensive effects throughout several aspects of Organic Chemistry, Biology, and Pharmacology. Hence physicochemical studies of model compounds in solutions are of fundamental importance in understanding the different aspects of chiral compounds. The enthalpies of mixing of enantiomers of 2,3-dihydroxyl-butanedioic acid, threonine and alanine were reported by Takagi et al. [1]. Other researchers have also studied the problem of chiral interaction [2–5]. Previous calorimetric work in our laboratory includes

measurement of the enthalpies of mixing for 34 binary liquid chiral systems [6–10]. All observed systems showed a very small enthalpy change over the whole range of mole fractions. Seven systems were slightly exothermic showing slight enthalpic stabilization, whereas the other 27 systems were endothermic, showing a small enthalpic destabilization on mixing at 298.15 K. The intermolecular interactions between hetero chiral compounds have been discussed. However, there is almost no literature on the mixing enthalpies in non-aqueous solution. Excess enthalpies of aqueous and ethanol solution of 2,3-dihydroxylbutanedioic acid [11] were observed for three different concentrations of aqueous and ethanol solutions of 2,3-dihydroxylbutanedioic acid. The enthalpies of mixing were exothermic for all the concentrations in both solvents. Enthalpic stabilization on mixing was increased with decreasing concentration of 2,3-dihydroxylbutanedioic acid for both solvents. Also, four chiral dicarboxylic acids and four camphor derivatives were determined to clarify the enthalpic chiral discrimination of enantiomers in the ethanol solution [12, 13]. All enthalpies of mixing the chiral dicarboxylic acids were exothermic for all the concentrations and decreased with increased concentration of dicarboxylic acid [11, 12]. Also, the enthalpies of mixing the chiral camphor and its derivative in ethanol were determined. The behaviors of camphor and its derivative were similar to those of dicarboxylic acids. All enantiomers of dicarboxylic acids and camphor derivatives in previous studies were solid sample. Those enantiomers have solubility in ethanol or water. In this study, in order to clarify the concentration dependence of enantiomer interaction in a wide concentration range, excess enthalpies of ethanol solution of chiral limonenes have been measured in ethanol solution for the whole range of mole fractions of limonene at 298.15 K.

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## Experimental

*R*- and *S*-limonene were supplied by ALDRICH Chemical. Ethanol (Kishida Kagaku, Special grade) and *R*- and *S*-limonenes {1-methyl-4-(prop-1-en-2-yl)cyclohex-1-ene, CAS No 5989-27-5, 5989-54-8} were distilled and dried by storage over molecular sieves 4A freshly activated. Their chemical purities obtained from gas chromatography by using a 2 m column of 10% SE-30 on chromosorb and a 2 m column of 20% PEG-1000 on celite 545 with FID on Yanagimoto G180FP were more than 99.99%. Water contents obtained by a coulometric Karl-Fischer's method on a Moisturemeter (Mitsubishi Chemical Ind., CA-02) were less than 0.001 mol%.

The excess enthalpies of mixing and dilution were measured by a microcalorimeter (Thermometric AB, Järfälla, Sweden) with a 0.8 mL mixing vessel at 298.15 K [14–16]. Details of the calorimetric procedure and precision test have been described previously [11, 14, 15]. The densities of the samples were measured by a vibrating-tube densimeter (Anton Paar DMA55) at  $(298.15 \pm 0.001)$  K. The densitometric procedures were the same as those described previously [17].

## Results and discussions

Experimental results of densities, average molar volumes of the ethanol + limonene are shown in Table 1.

The experimental results for enthalpies of  $(1-x)$  ethanol and  $x_{\text{limonene}}$  [(*R*)- and (*S*)-enantiomers] are summarized in Table 2 and Fig. 1. The results were fitted with Eq. 1 by the least squares method.

**Table 1** Densities and average molar volumes of  $(1-x)$ ethanol+ $x_{\text{limonene}}$  at 298.15 K

$x$	$\rho/\text{g cm}^{-3}$	$V/\text{cm}^3 \text{ mol}^{-1}$	$x$	$\rho/\text{g cm}^{-3}$	$V/\text{cm}^3 \text{ mol}^{-1}$
(1-x) ethanol + x <i>R</i> -limonene			(1-x) ethanol + x <i>S</i> -limonene		
0.0000	0.7790	59.14			
0.005000	0.7858	59.20	0.005000	0.7858	59.20
0.01000	0.7877	59.63	0.01005	0.7878	59.73
0.03000	0.7904	61.71	0.03002	0.7908	61.68
0.09990	0.7971	69.10	0.09977	0.7971	68.93
0.3003	0.8130	89.98	0.30020	0.8146	89.78
0.5000	0.8253	110.40	0.50000	0.8255	110.40
0.6994	0.8329	131.00	0.70000	0.8317	131.30
1.0000	0.8402	162.15			

$x$  = mole fraction of limonene derivatives

$M(\text{ethanol}) = 46.0690 \text{ g mol}^{-1}$ ,  $M(\text{limonene}) = 136.24 \text{ g mol}^{-1}$

**Table 2** Excess enthalpies of mixing of  $(1-x)$  ethanol and  $x$  limonenes at 298.15 K

$x$	$H^E/\text{J mol}^{-1}$	$x$	$H^E/\text{J mol}^{-1}$	$x$	$H^E/\text{J mol}^{-1}$
(1-x) ethanol and x <i>R</i> -limonene					
0.02669	71.58	0.3707	557.4	0.6177	645.4
0.05020	130.4	0.3996	575.9	0.6460	645.2
0.05199	135.9	0.4033	578.1	0.6617	640.6
0.07600	191.3	0.4215	588.9	0.6833	638.4
0.07668	191.3	0.4330	598.1	0.7124	625.0
0.09883	239.3	0.4334	594.5	0.7252	623.3
0.1017	243.1	0.4416	599.8	0.7716	591.5
0.1206	281.2	0.4495	606.5	0.7726	597.4
0.1254	288.1	0.4636	610.4	0.8266	548.7
0.1413	318.2	0.4673	614.8	0.8887	465.8
0.1479	327.5	0.4734	612.3	0.9187	398.6
0.1693	362.0	0.4865	622.7	0.9281	375.5
0.1955	387.2	0.4880	620.6	0.9377	348.7
0.2088	404.8	0.5074	629.8	0.9476	317.5
0.2242	423.2	0.5150	629.8	0.9576	281.6
0.2420	443.4	0.5301	636.7	0.9679	217.5
0.2628	465.7	0.5452	637.7	0.9783	151.0
0.2875	490.4	0.5550	642.4	0.9891	90.71
0.3046	506.2	0.5792	643.5		
0.3239	522.7	0.5823	646.0		
0.3457	539.7	0.6125	647.4		
(1-x) ethanol and x <i>S</i> -limonene					
0.02527	71.93	0.3418	529.6	0.8094	554.2
0.04930	132.8	0.3769	558.8	0.8412	519.6
0.07217	185.3	0.4201	583.4	0.8756	469.1
0.09396	231.1	0.4745	609.7	0.8921	435.7
0.1148	271.4	0.5450	634.5	0.9043	414.2
0.1346	307.2	0.6401	636.2	0.9130	397.8
0.1536	339.1	0.6598	633.6	0.9169	389.8
0.1718	362.9	0.6807	629.1	0.9297	360.7
0.1892	386.9	0.7031	622.5	0.9430	326.1
0.2059	409.5	0.7270	612.9	0.9566	278.0
0.2219	424.0	0.7525	599.8	0.9707	212.0
0.2373	447.7	0.7799	579.3	0.9851	126.8

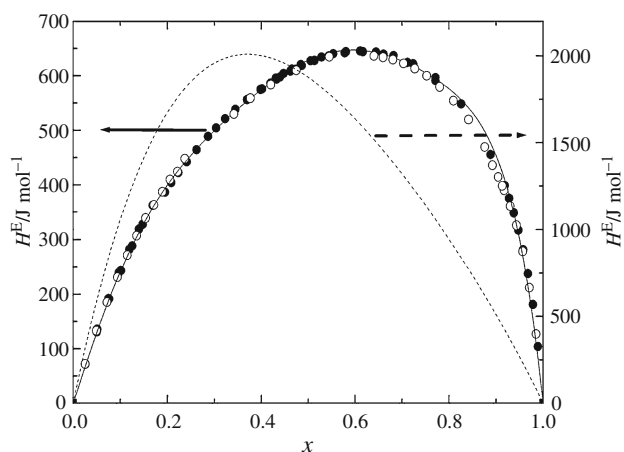
$x$  = mole fraction of limonene in ethanol solution:  $n_{\text{limonene}}/(n_{\text{limonene}} + n_{\text{ethanol}})$

$$H^E/\text{J mol}^{-1} = Q/(n_{\text{limonene}} + n_{\text{ethanol}})$$

$$H^E/\text{J} \cdot \text{mol}^{-1} = (1 - \zeta)x \sum_{i=1}^k (A_i(1 - 2\zeta)^{i-1}) \quad (1)$$

Here  $\zeta = x$  and  $x$  showed the mole fraction of limonenes for a binary solution of ethanol + limonenes. The coefficients  $A$  of Eq. 1 and the standard deviations of fits  $s_f$ :

$$s_f = \left[ \sum_{i=1}^n \{H^E(\text{obs.}) - H^E(\text{calc.})\}^2 / (n - 1) \right]^{1/2} \quad (2)$$



**Fig. 1** Excess enthalpies of mixing of  $(1-x)$ ethanol and  $x_{\text{limonene}}$  at 298.15 K: filled circle *R*-limonene; open circle *S*-limonene; Solid line, from Eq. 1 with coefficients in Table 3; broken line, calculated values from regular solution theory by Eq. 3

**Table 3** Best fit's coefficients of Redlich–Kister type equation

$A_1$	$A_2$	$A_3$	$A_4$	$A_5$	$A_6$	$s_f/\text{J mol}^{-1}$
2510.4	-816.6	588.3	918.5	2308.4	-2881.3	6.4

are shown in Table 3. Excess enthalpies of mixing of ethanol + limonenes were endothermic for whole mole fractions. The maximum concentration of excess enthalpies of mole fraction was not at equimolar concentration. And it was 0.816 and 0.799 for volume fraction and surface fraction, respectively. To estimate molecular properties, geometry optimization of molecular shapes of ethanol and limonene, and physicochemical properties were carried out by using ab initio quantum chemical methods based on the Gaussian programs [18] at the MP2/6-311G(d,p) level of theory. Here van der Waals volume and accessible surface area of ethanol and limonene were calculated (Chem. Plus version 1.05, HYPERCUBE, Inc.), as shown in Table 4.

Simple regular solution theory [19] calculated from Eq. 3 was also plotted as a broken line in Fig. 1, but it was three times larger than the observed value at equimolar concentration.

**Table 4** Physical properties of ethanol and limonene

	ASA/nm <sup>2</sup> ( $r = 0$ )	ASA/nm <sup>2</sup> ( $r = 232$ )	$\mu/10^{-30}$ Cm	$\mu_1^2\mu_2^2/(r_1+r_2)^6/10^{-62}$ C <sup>4</sup> m <sup>-2</sup>	$\Delta_v H/\text{kJ mol}^{-1}$
Ethanol	0.764	2.898	5.54	0.462	42.3
Limonene	1.95	4.868	2.25		46.6

ASA(accessible surface area) was estimated by Chemplus (Chem. Plus version 1.05, HYPERCUBE, Inc.) after optimization by Gaussian 03 MP2/6-311G(d,p) [18]. Here  $r$  is a solvent probe radius in pm. Dipolemoments were also estimated by Gaussian method. Enthalpies of vaporization were cited from James [20]

$$\Delta H^M = (x_1 V_1 + x_2 V_2) \left[ \left( \frac{\Delta_v H_1}{V_1} \right)^{\frac{1}{2}} - \left( \frac{\Delta_v H_2}{V_2} \right)^{\frac{1}{2}} \right]^2 \Phi_1 \Phi_2 \quad (3)$$

Here  $\Delta_v H$ ,  $V$ , and  $\Phi$  showed enthalpies of vaporization, molar volume, and volume fraction, respectively. The subscript 1 and 2 showed ethanol and limonene, respectively. The entropy of vaporization of ethanol and limonene was 121 and 110 J K<sup>-1</sup> mol<sup>-1</sup>, respectively, [20]. Both of them were larger than Trouton's Rule. And a large difference between the estimation values from the regular solution and the observed value might be from the large entropy of vaporization of ethanol and limonene.

The enthalpies of mixing of the ethanol solution of *R*-limonene + *S*-limonene at 0.500, 1.00, 3.00, 10.0, 30.0, 50.0, and 70.0 mol% for the whole range of pseudo-binary mole fractions were determined at 298.15 K, as shown in Table 5 and Fig. 2. Here  $f$  is defined as the pseudo-binary solution of each chiral compound as shown in Eq. 4.

$$f = n_S / (n_R + n_S) \quad (4)$$

Experimental results of excess enthalpies of heterochiral ethanol solution were fitted with Eq. 1 with  $\xi = f$ . Those best fits values are shown in Table 6 with standard deviation of the fits. Enthalpic stabilization of ethanol solutions of limonene decreased with increasing mole fraction as shown in Fig. 2. And the enthalpic unstabilization continuously increased until the mixtures of pure *R*- and *S*-limonenes.

The enthalpies of mixing of the ethanol solutions of chiral limonenes at an equimolar concentration of *R*- and *S*-limonenes in ethanol solution are plotted in Fig. 3. Enthalpic stabilization of ethanol solutions of limonene decreased with increasing mole fraction until  $x = 0.1$  with sharp inclination, but the rate of decrease fell with increasing concentration. Then those became positive over  $x = 0.37$ . And enthalpic unstabilization on mixing slightly increased with increasing concentration of limonenes over  $x = 0.37$ . Concentration behaviors of enthalpic stabilization of heterochiral limonene in ethanol solution showed a unique profile, but those were similar to the results of chiral dicarboxylic acids [11, 12] and camphor derivatives [13]. As an example, those of camphor and 2,3-di-hydroxybutanedioic acid are

**Table 5** Excess enthalpies of heterochiral limonene in ethanol solution at 298.15 K

$f$	$H^E/J \text{ mol}^{-1}$	$f$	$H^E/J \text{ mol}^{-1}$	$f$	$H^E/J \text{ mol}^{-1}$
Ethanol solutions of 0.4999 mol% <i>R</i> -limonene + 0.4999 mol% <i>S</i> -limonene					
0.1200	-17.02	0.4590	-47.63	0.6713	-38.32
0.1451	-19.61	0.5300	-47.6	0.7382	-32.97
0.2143	-28.25	0.5440	-47.07	0.7489	-29.93
0.2534	-31.28	0.5506	-47.27	0.7539	-30.57
0.2904	-36.41	0.5850	-43	0.8494	-20.46
0.3373	-39.86	0.5986	-43.36	0.8564	-19.69
0.3530	-40.29	0.6050	-42.94	0.8597	-19.6
0.4043	-44.57	0.6528	-38.97		
0.4055	-43.55	0.6654	-38.05		
Ethanol solutions of 1.000 mol% <i>R</i> -limonene + 1.0000 mol% <i>S</i> -limonene					
0.1159	-7.799	0.5615	-21.57	0.6979	-15.92
0.1294	-8.304	0.5655	-22.29	0.7191	-16.00
0.2077	-12.83	0.5743	-22.10	0.7320	-14.96
0.2292	-13.74	0.5773	-21.23	0.7649	-13.80
0.2822	-16.73	0.5809	-21.68	0.7713	-13.92
0.3084	-17.71	0.6193	-20.49	0.7761	-12.73
0.3439	-19.55	0.6277	-20.12	0.8366	-10.48
0.3729	-20.54	0.6306	-18.83	0.8453	-9.367
0.3959	-21.91	0.6341	-19.16	0.8668	-8.146
0.4264	-22.16	0.6455	-18.15	0.8709	-9.209
0.5060	-21.74	0.6845	-18.22	0.8739	-8.688
0.5221	-22.60	0.6921	-17.40		
Ethanol solutions of 3.004 mol% <i>R</i> -limonene + 3.004 mol% <i>S</i> -limonene					
0.1157	-2.885	0.4416	-6.871	0.6459	-6.642
0.1651	-3.636	0.4456	-7.164	0.6488	-6.175
0.1673	-4.080	0.4818	-7.288	0.7323	-5.738
0.2834	-5.526	0.4971	-6.886	0.7348	-5.581
0.2867	-6.031	0.5012	-7.030	0.7613	-5.265
0.3581	-6.226	0.5225	-6.926	0.8455	-3.617
0.3723	-6.716	0.5777	-6.762	0.8471	-4.012
0.3761	-6.851	0.5808	-6.465		
0.4266	-6.851	0.6145	-6.907		
Ethanol solutions of 10.00 mol% <i>R</i> -limonene + 10.00 mol% <i>S</i> -limonene					
0.1460	-0.80009	0.4414	-1.913	0.6158	-1.726
0.1482	-0.69073	0.4608	-1.983	0.6278	-1.617
0.1650	-0.93955	0.4652	-1.987	0.6301	-1.673
0.2548	-1.25251	0.4902	-1.941	0.7063	-1.581
0.2832	-1.39494	0.5030	-1.861	0.7167	-1.403
0.3390	-1.58548	0.5055	-1.971	0.8278	-1.094
0.3722	-1.72122	0.5459	-1.800	0.8350	-1.018
0.4061	-1.84741	0.5585	-1.702	0.8364	-0.8897
0.4103	-1.7768	0.5610	-1.822		
Ethanol solutions of 30.00 mol% <i>R</i> -limonene + 30.00 mol% <i>S</i> -limonene					
0.1607	-0.1193	0.4240	-0.2895	0.6229	-0.2855
0.1616	-0.1101	0.4301	-0.2136	0.6234	-0.2813
0.1684	-0.1854	0.4308	-0.2244	0.6312	-0.2253
0.2691	-0.2430	0.4337	-0.2150	0.7124	-0.2197

**Table 5** continued

$f$	$H^E/J \text{ mol}^{-1}$	$f$	$H^E/J \text{ mol}^{-1}$	$f$	$H^E/J \text{ mol}^{-1}$
0.2769	-0.2013	0.4792	-0.2795	0.7129	-0.2599
0.2783	-0.1896	0.4854	-0.2351	0.7196	-0.2137
0.3557	-0.2644	0.4862	-0.2446	0.8316	-0.1701
0.3614	-0.2193	0.4891	-0.2175	0.8324	-0.1362
0.3648	-0.2183	0.5621	-0.2402	0.8370	-0.1825
Ethanol solutions of 50.01 mol% <i>R</i> -limonene + 50.01 mol% <i>S</i> -limonene					
0.1613	0.1571	0.3918	0.3681	0.5748	0.3499
0.1768	0.2192	0.4033	0.2987	0.6282	0.3616
0.1851	0.2157	0.4348	0.3404	0.6342	0.3024
0.2526	0.2845	0.4803	0.3266	0.6979	0.2615
0.2778	0.2538	0.5034	0.3767	0.7223	0.2133
0.3005	0.3100	0.5099	0.3493	0.8221	0.1863
0.3124	0.2673	0.5178	0.3270	0.8388	0.1633
0.3658	0.2860	0.5653	0.3369		
Ethanol solutions of 70.00 mol% <i>R</i> -limonene + 70.00 mol% <i>S</i> -limonene					
0.1662	0.3418	0.5021	0.5678	0.7160	0.4539
0.1700	0.3398	0.5060	0.5965	0.7397	0.4426
0.2851	0.4866	0.5319	0.5838	0.7490	0.4389
0.2907	0.5193	0.5441	0.6284	0.8345	0.3097
0.3743	0.5614	0.5576	0.6086	0.8503	0.2843
0.3807	0.6002	0.5869	0.6087	0.8565	0.2745
0.4437	0.6103	0.6270	0.5738		
0.4504	0.6041	0.6545	0.5586		

$$f = n_S / (n_S + n_R)$$

$$H^E/J \text{ mol}^{-1} = q / (n_S + n_R)$$

also shown in Fig. 3. Concentration dependences were fitted to Eq. 5 by the method of least squares and coefficients are shown in Table 7 with standard deviation of fits. With sharp inclination

$$H^E = A + \frac{B}{x + C} \quad (5)$$

In the ethanol solution of limonenes, two states might be changed on mixing. One is the solvation of limonenes, the second is the formation of heterochiral contacts. The enthalpies of solvation were exothermic reaction.

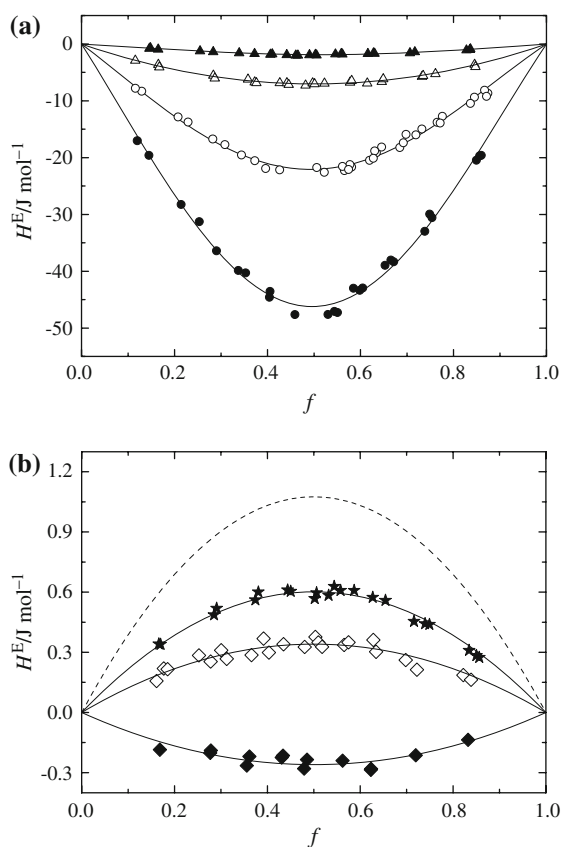
The surface fractions  $s = \text{ASA}(\text{limonenes}) / \{\text{ASA}(\text{limonenes}) + \text{ASA}(\text{ethanol})\}$  of the solutions observed were  $s = 0.073$  and  $s = 0.522$  for  $x = 0.1$  and  $x = 0.3$ , respectively. When the surface of molecules takes the grid surface from Table 4, the surface fractions correspond to the site fractions. So molecules of limonenes in ethanol solution may contact directly in the concentration range over  $x = 0.3$  because limonenes may strongly solvate with ethanol in the first solvated shell. The solvated ethanol in the first solvation shell of *R*- and *S*-limonenes solution might be strongly oriented to each enantiomer. In the case of dilute solution, there was also a possibility of relatively

strong solvation to the first solvation shell. But for the higher concentrations, the possibility might be decreased with increasing concentration of limonene. One of the major reasons for this is of the insufficient amount of solvent around the first shell. That might be the reason for less stable mixing at higher concentrations. As a result, exothermic enthalpy changes decreased with increasing concentration of limonenes.

The solvents in the first solvated shell were strongly oriented around the chiral solute. The orientation of solvents in second or higher order shells might not be as strong as the solvent in the first shell. When solutions of the enantiomers were mixed, the configuration of solvents in the second shell around the limonene might change largely. It might have significant dipole-dipole interaction effects on the excess enthalpies of the mixtures.

The effect of stabilization to excess enthalpy by dipole-dipole interaction of chiral compounds and solvents might be strongly affected. The dipole-dipole interaction energy of pair molecules [21] is shown as:

$$u_{12} = -\frac{2}{3(4\pi\epsilon_0)^2 kT} \left( \frac{\mu_1 \mu_2}{r^3} \right)^2 \quad (6)$$



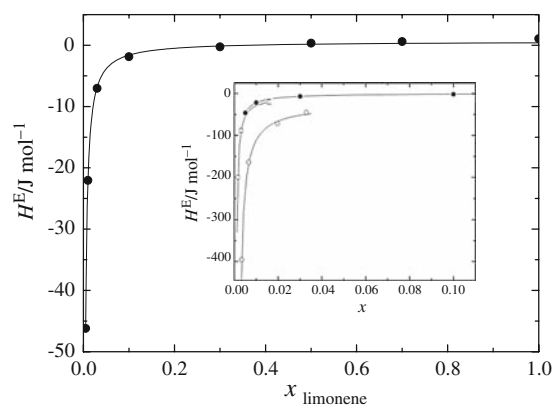
**Fig. 2** Excess enthalpies of mixing of  $(1-f)$  *R*-limonene and  $f$  *S*-limonene at 298.15 K. Limonene concentration in ethanol solution: **a** filled circle 0.5 mol%; open triangle 10 mol%; filled rhombus 30 mol%; **b** open rhombus 50 mol%; filled star 70 mol%; broken line 100 mol% [7]

**Table 6** Best fit's coefficients of Redlich–Kister type equation and excess enthalpies at equimolar concentration

mol%	$A_1$	$A_2$	$A_3$	$s_f$	$H_{f=0.5}^E/J \text{ mol}^{-1}$
0.4999	-184.8	-4.103	59.33	1.1	-46.20
1.000	-88.22	-3.526	29.90	0.66	-22.05
3.004	-28.12	0.435	-1.34	0.21	-7.030
10.00	-7.528	0.259	2.06	0.084	-1.882
30.00	-1.040	0.132		0.029	-0.260
50.01	1.352	0.082		0.027	0.338
70.00	2.418	0.139		0.018	0.605
100.0 <sup>a</sup>	4.30				1.08

<sup>a</sup> cited from [7]

where  $\mu$ ,  $r$ , and  $k$  are dipole moment, distance between molecules, and Boltzmann coefficient, respectively. The dipole moments estimated from Gaussian method are shown in Table 4 and dipole–dipole interactions calculated from Eq. 6 are shown in Table 4. Enthalpic stabilization at the same surface fraction of  $s = 0.013$  and dipole–dipole

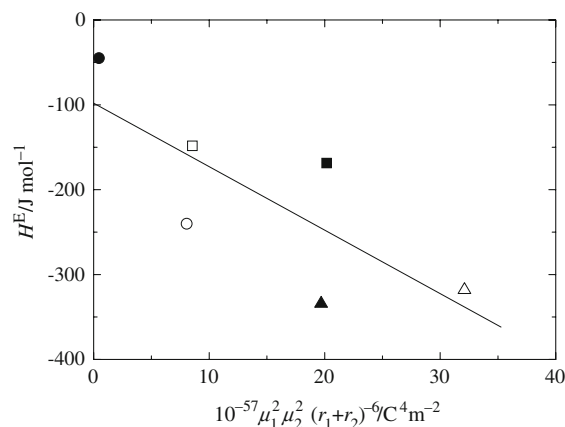


**Fig. 3** Excess enthalpies of mixing of the hetero chiral compounds in ethanol solution at equimolar concentration [ $f = 0.5$ , cf; Eq. 4]: filled circle limonene; open circle camphor [13]; open square 2,3-dihydroxybutanedioic acid [11].  $x$  shows the mole fraction of chiral compounds for pseudo-binary solutions of ethanol + chiral compounds

**Table 7** Best fits coefficients of Eq. 5 and standard deviation of the fits

$A/J \text{ mol}^{-1}$	$B/J \text{ mol}^{-1}$	$C$	$s_f/J \text{ mol}^{-1}$
0.6213	-0.2226	-0.0002418	0.30

$$H^E = A + \frac{B}{x+C}$$



**Fig. 4** Correlation between excess enthalpies and dipole–dipole interaction between chiral compounds and ethanol: open circle, Limonene; filled triangle Camphorsulfonyl chloride; open triangle Camphorsulfonic acid; open square Camphorsulfonamide; filled circle Camphor; filled square Camphorquinone

interaction for limonene and camphor derivatives (Camphor, 10-camphorsulfonic acid, camphor-quinone, 10-camphor sulfonamide, 10-camphor sulfonylchloride) showed good correlation as shown in Fig. 4. The results show that enthalpic stabilization on heterochiral solution significantly depends on solvation with chiral molecules.



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