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DEUTERIUM ISOTOPE EFFECT ON EXCESS ENTHALPIES OF METHANOL OR ETHANOL AND THEIR DEUTERIUM DERIVATIVES AT 298.15 K

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Abstract

Excess enthalpies of six binary mixtures of CH_3OD+CH_3OH, CH_3OD+CD_3OD, CD_3OD+CH_3OH, C_2D_5OD+C_2H_5OH, C_2D_5OD+C_2H_5OD, C_2H_5OD+C_2H_5OH have been determined over the whole range of mole fractions at 298.15 K in order to know the isotopic effect on hydrogen-bonding accurately, although there are many reports on the differences in the strength of hydrogen-bonding between OH and OD.

All excess enthalpies measured are very small and endothermic. The mixtures of CH_3OD+CH_3OH, and C_2D_5OD+C_2H_5OH showed the largest excess enthalpies among each methanol and ethanol mixtures. The difference of intermolecular interaction between OH and OD in methanol and ethanol was almost same value of (1.82±0.04) J mol^{-1}.

Excess enthalpies of 1,4-dimethylbenzene+1,3-dimethylbenzene and 1,4-dimethylbenzene+1,2-methylbenzene were measured by three different principle calorimeters at 298.15 K in order to know the precision of calorimetry for a small enthalpy change.

Keywords: deuterium isotope effect, ethanol, ethanol-d_1, ethanol-d_6, excess enthalpy, methanol, methanol-d_1, methanol-d_4

Introduction

In order to understand the origin of isotope effect on intermolecular interactions and excess thermodynamic functions of binary mixtures of simple molecules under ambient conditions, precise experimental results are necessary. Lal and Swinton showed that the mixtures composed of a compound and its superdeuterated equivalent were far from being an ideal solution [1]. Excess enthalpies of C_6H_6+C_6D_6, C_6H_{12}+C_6D_{12}, $CHCl_3$+$CDCl_3$ and CH_2Cl_2+CD_2Cl_2 were reported in previous papers [2, 3]. All the excess enthalpies were small. The former three mixtures, *i.e.* C_6H_6+C_6D_6, C_6H_{12}+C_6D_{12}, and $CHCl_3$+$CDCl_3$ were endothermic but CH_2Cl_2+CD_2Cl_2 were exothermic.

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In order to get further information on the deuterium isotopic effect on intermolecular interactions, the excess enthalpies of three binary mixtures of methanol (CH_3OH) and its deuterium derivatives (CD_3OH and CH_3OD) and three binary mixtures of ethanol (C_2H_5OH) and its deuterium derivatives (C_2D_5OH and C_2D_5OD) have been determined at 298.15 K.

Experimental

Methanol and ethanol (Kishida Chemical, for spectrum) and 1,2-, 1,3- and 1,4-dimethylbenzene (Kishida Chemical, Special grade) 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.

Deuterated methanol-d_1 (Aldrich Chemical), methanol-d_4 (Merck, uvasol), ethanol-d_1 (Acros), and ethanol-d_6 (Aldrich Chemical) in ampoule were stored over the freshly activated 4A molecular sieves. The results of purity analyses with the gas-liquid chromatograms obtained by using 2 m columns of 10 per cent SE-30 on WAW chromosorb and 20 per cent PEG-1000 on celite 545 with FID on Yanagimoto model G180FP and with the coulometric Karl–Fischer's method on a Mitsubishi Moisture Meter model CA-02 (Mitsubishi Chemical Ind.) are summarized in Table 1. Densities of the samples measured by a vibrating-tube densitometer (Anton Paar D60) at (298.15±0.001) K are listed in the fourth column of Table 1. The details of densimetric procedures were the same as those described elsewhere [4].

Table 1 Purities and densities of samples

	Glc/ %	Water content/ mole%	Deuterium content/ atomic%	ρ(298.15 K)/ g cm^{-3}	V/ cm^3 mol^{-1}
CH_3OH	99.99	0.001		0.78637	40.750
CH_3OD	99.99	0.001	99.5[a]	0.80980	40.793
CD_3OD	99.98	0.002	99.8[b]	0.88811	40.547
C_2H_5OH	99.99	0.001		0.78493	58.692
C_2H_5OD	99.97	0.002	99.5[c]	0.80159	58.710
C_2D_5OD	99.99	0.001	99.0[a]	0.89044	58.422
1,2-dimethylbenzene	99.99	0.001		0.87595	
1,3-dimethylbenzene	99.99	0.002		0.86010	
1,4-dimethylbenzene	99.99	0.001		0.85661	

[a]Stated by Aldrich Chemical
[b]Stated by Merck
[c]Stated by Acros

A twin-microcalorimeter of heat-conduction type, Thermal Activity Monitor (Thermometric AB, Järfälla, Sweden) with mixing vessel of 0.8 cm^3 which was modified by the present authors and others [5, 6], was used for the measurements of excess enthalpies at 298.15 K over the whole range of mole fractions. The details of calorimetric procedures of batch calorimeter [7–9] of Larkin–McGlashan type [10], flow calorimeter [11] and titration calorimeter system [5, 6] were described.

In order to know the precision of the calorimeter for small enthalpy change, excess enthalpies of 1,4-dimethylbenzene+1,3-dimethylbenzene and 1,4-dimethylbenzene+1,3-dimethylbenzene at 298.15 K were measured by three different principle calorimeters.

Results and discussion

The excess enthalpies of 1,4-dimethylbenzene+1,3-dimethylbenzene and 1,4-dimethylbenzene+1,2-dimethylbenzene are given in Table 2 and shown in Figs 1 and 2.

Table 2 Enthalpies of mixing of (1–x)1,4-dimethylbenzene+x1,3-dimethylbenzene and (1–x) 1,4-dimethylbenzene+x1,3-dimethylbenzene at 298.15 K by three different types of calorimeters.

x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}
(1–x)1,4-dimethylbenzene+x1,3-dimethylbenzene by flow calorimeter							
0.05000	–1.586	0.4500	–7.299	0.6500	–6.621	0.8500	–3.721
0.15000	–3.853	0.5500	–7.134	0.7500	–5.673	0.9500	–1.424
0.25000	–5.652						
(1–x)1,4-dimethylbenzene+x1,2-dimethylbenzene by titration calorimeter							
0.03701	0.8352	0.1612	3.313	0.5458	6.553	0.8574	3.082
0.05451	1.240	0.1745	3.579	0.5837	6.433	0.8698	2.826
0.07138	1.597	0.1874	3.805	0.6158	6.168	0.8826	2.559
0.08766	1.936	0.2860	5.047	0.6489	5.914	0.8958	2.265
0.10340	2.224	0.3754	5.858	0.7349	5.156	0.9093	1.966
0.11860	2.509	0.4094	6.132	0.8223	3.760	0.9525	0.8964
0.13330	2.806	0.4420	6.380	0.8337	3.570	0.9678	0.4815
0.14750	3.065	0.4803	6.452	0.8454	3.341		
(1–x)1,4-dimethylbenzene+x1,2-dimethylbenzene by batch calorimeter							
0.13450	2.812	0.3283	5.665	0.5921	6.192	0.8122	3.881
0.20420	4.166	0.3916	6.103	0.6611	5.807	0.8562	3.109
0.25170	4.703	0.4545	6.401	0.7134	5.301		
0.29490	5.266	0.5064	6.515	0.7891	4.202		
(1–x)1,4-dimethylbenzene+x1,2-dimethylbenzene by flow calorimeter							
0.05000	0.956	0.3500	5.408	0.6500	5.750	0.9500	1.295
0.15000	2.835	0.4500	5.996	0.7500	4.693		
0.25000	4.299	0.5500	6.104	0.8500	3.262		

The values were fitted to Eq. (1) by a method of least squares.

$$H^{\mathrm{E}}/\mathrm{J\ mol^{-1}}=(1-x)x\sum_{\mathrm{i=1}}^{\mathrm{k}}A_{\mathrm{i}}(1-2x)^{\mathrm{i-1}} \tag{1}$$

The coefficients A_{i} in Eq. (1) and standard deviations of the fits s_{f}:

$$s_{\mathrm{f}}=\left[\sum_{\mathrm{i=1}}^{\mathrm{k}}\left\{H^{\mathrm{E}}(\mathrm{expt})-H^{\mathrm{E}}(\mathrm{calc})\right\}_{\mathrm{i}}^{2}/(n-k)\right]^{1/2} \tag{2}$$

are given in Table 3. The calculated values using Eq. (1) with the coefficients of Table 3 are plotted in Figs 1 and 2. Excess enthalpies of previously reported results [6] and isothermal displacement calorimeter results [12] were also shown in Figs 1 and 2. The reproducibility test of Larkin–McGlashan type calorimeter was

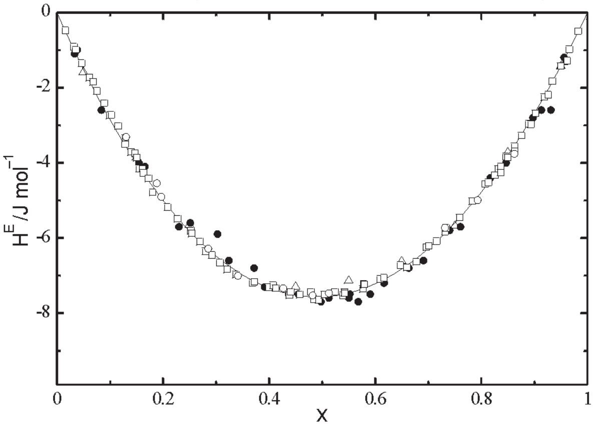

Fig. 1 Enthalpies of mixing of (1–x)1,4-dimethylbenzene+x1,3-dimethylbenzene at 298.15 K. o – titration calorimeter [6], □ – batch calorimeter [6], Δ – flow calorimeter, ● – isothermal displacement calorimeter

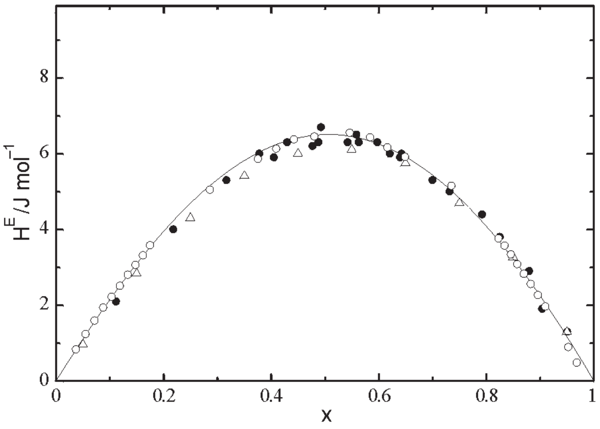

Fig. 2 Enthalpies of mixing of (1–x)1,4-dimethylbenzene+x1,2-dimethylbenzene at 298.15 K. o – this calorimeter, Δ – flow calorimeter, ● – isothermal displacement calorimeter

already reported with the results of international standard system of *n*-hexane+*c*-hexane at 298.15 K [9]. Excess enthalpies determined by Larkin–McGlashan type calorimeter for (C_6H_6+CCl_4) also agree with those reported by Stokes, Marsh and Tomlins [14] within ±0.3 per cent deviation [7]. Exothermic excess enthalpies of the batch type calorimeter for (C_6H_5Cl+$C_6H_5CH_3$) were in agreement with those obtained by Tanaka and Benson [13] within ±0.3 per cent deviation [7]. Figures 1 and 2 showed that the results by four different principle calorimeters agreed well. In detail, the results by flow type calorimeter showed slightly systematically lower values than those of other type calorimeters. Those of isothermal displacement type calorimeter were scattered, however, the deviations were within the range of their precision.

Table 3 Best fit coefficients of Eq. (1) for the mixtures of dimethylbenzene isotopes

System	A_1	A_2	A_3	s_f/J mol^{-1}
1,4-dimethylbenzene+1,3-dimethylbenzene	–30.28	–1.18	0.75	0.14
1,4-dimethylbenzene+1,2-dimethylbenzene	26.01	–0.70	–2.59	0.11

The experimental results for the excess enthalpies of isotope mixtures are listed in Table 4. Although the excess enthalpies of all the systems are nearly athermal, significant non-zero heats are obtained. The experimental excess enthalpies and the calculated values using Eq. (1) with the coefficients of Table 5 are plotted in Figs 3 and 4. The results for the isotope mixtures of methanols and ethanols are slightly endothermic over the whole mole fraction range. The excess enthalpies of CD_3OD+CH_3OH showed the largest enthalpy on mixing in this work and previous work [3] for the mixtures containing deuterium. Here H and D represent ^{1}H and ^{2}H atom, respectively. The results showed that the difference in intermolecular interactions of H–D contact from the arithmetical mean of the intermolecular interactions of H–H and D–D contacts became unstable according to the sequence in methanol mixtures: (CH_3OD+CD_3OD)<(CH_3OD+CH_3OH)<(CD_3OD+CH_3OH) and in ethanol mixtures: (C_2D_5OD+C_2H_5OD)<(C_2H_5OD+C_2H_5OH)<(C_2D_5OD+C_2H_5OH).

The mixtures of CD_3OD+CH_3OH, CH_3OD+CH_3OH, CH_3OD+CD_3OD, C_2D_5OD+C_2H_5OD, C_2H_5OD+C_2H_5OH involve the interactions of the deuterium isotope effect on hydrogen bonding and non hydrogen bonding hydrogen. The deuterium isotope effect on the strength of hydrogen bonding may differ from the molecular interactions in simple compounds without hydrogen bond like the mixtures of C_6H_6+C_6D_6, C_6H_{12}+C_6D_{12}, and CH_2Cl_2+CD_2Cl_2. The excess enthalpies of (RH–OH+RD–OH) and (RH–OD+RD–OD) involving no deuterium exchange of hydroxide are less positive than those of (RH–OH+RH–OD) and (RD–OH+RD–OD) involving deuterium exchange of hydroxide: (RH, CH_3 or C_2H_5; RD, CD_3 or C_2D_5). The intermolecular interactions of deuterium should have a different effect on hydrogen-bonding H–D owing to the contact of OD–OH, and non-hydrogen-bonding H–D owing to contacts among CH_3–OD, CD_3–OH, C_2H_5–OD, and C_2D_5–OH. In the previous papers [2, 3], excess enthalpies of mixing of isotopic mixtures showed that the deuterium isotope effect on the strength of hydrogen bonding might differ from the molecular interactions in simple compounds without hydrogen bond. The London dispersion forces decrease with the increase of the number of C–D bonds, in place of C–H bonds from the results of non-hydrogen-bonding mixtures of C_6H_6+C_6D_6, C_6H_{12}+C_6D_{12}, and CH_2Cl_2+CD_2Cl_2 [2] and the hydrogen bonded mixture, $CHCl_3$+$CDCl_3$, did not follow this correlation as shown in a previous paper [3]. It might be understood from the fact that the decrease in polarizability occurs by the deuterium exchange of hydrogen-carbon bond [1, 15].

Table 4 Excess enthalpies of isotopes mixtures of methanols and ethanols at 298.15 K

x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}
$(1-x)CH_3OH+xCD_3OD$							
0.01931	0.3615	0.1627	3.695	0.5406	8.453	0.8554	4.718
0.02077	0.4041	0.1702	3.879	0.5553	8.436	0.8627	4.622
0.03789	0.8339	0.1780	4.057	0.5760	8.428	0.8747	4.309
0.03296	0.7345	0.1911	4.217	0.5947	8.362	0.8751	4.350
0.05578	1.3168	0.1970	4.351	0.5966	8.397	0.8870	3.972
0.06149	1.4348	0.2038	4.402	0.6094	8.301	0.8997	3.533
0.07301	1.7070	0.2228	4.815	0.6306	8.220	0.9128	3.140
0.07427	1.7302	0.2799	5.908	0.6409	8.140	0.9263	2.718
0.09444	2.2133	0.3379	6.797	0.6493	8.068	0.9411	2.263
0.09589	2.2061	0.3683	7.263	0.6625	7.988	0.9429	2.230
0.1112	2.6229	0.4299	7.910	0.6635	7.951	0.9544	1.758
0.1129	2.5573	0.4152	7.708	0.6911	7.718	0.9552	1.776
0.1308	2.9760	0.4422	7.987	0.7142	7.400	0.9691	1.222
0.1293	2.9714	0.4570	8.049	0.7452	6.999	0.9697	1.284
0.1451	3.3009	0.4904	8.270	0.7832	6.426	0.9843	0.6473
0.1451	3.3471	0.5071	8.362	0.8269	5.523	0.9846	0.6427
0.1559	3.5996	0.4964	8.293	0.8416	5.161		
0.1584	3.5381	0.5426	8.425	0.8510	4.988		
$(1-x)CD_3OH+xCH_3OH$							
0.02618	0.1387	0.3889	1.767	0.5512	1.830	0.8339	1.006
0.05102	0.2742	0.4092	1.821	0.5647	1.837	0.8340	1.008
0.07463	0.4093	0.4124	1.801	0.5674	1.807	0.8542	0.9083
0.09709	0.5330	0.4257	1.838	0.5891	1.809	0.8543	0.9081
0.1185	0.6391	0.4431	1.811	0.6178	1.745	0.8677	0.9072
0.1373	0.8021	0.4469	1.823	0.6212	1.739	0.8755	0.7912
0.1389	0.7428	0.4625	1.819	0.6324	1.733	0.8756	0.7910

Table 4 Continued

x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}
0.1493	0.8434	0.4673	1.880	0.6675	1.611	0.8978	0.6634
0.1564	0.8538	0.4810	1.852	0.6862	1.624	0.8979	0.6636
0.1584	0.8530	0.4837	1.827	0.7080	1.536	0.9213	0.5332
0.2229	1.268	0.4884	1.857	0.7663	1.317	0.9215	0.5330
0.2414	1.405	0.4923	1.838	0.7785	1.178	0.9461	0.3573
0.2598	1.463	0.5129	1.878	0.7786	1.228	0.9463	0.3571
0.2704	1.434	0.5223	1.825	0.7960	1.124	0.9723	0.1786
0.3231	1.608	0.5265	1.854	0.7961	1.174	0.9725	0.1784
0.3449	1.701	0.5269	1.801	0.8146	1.062		
0.3574	1.747	0.5343	1.832	0.8147	1.112		
0.3645	1.708	0.5480	1.822	0.8290	0.9937		
$(1–x)CD_3OH+xCH_3OD$							
0.02184	0.07788	0.1674	0.3958	0.5372	0.7884	0.8544	0.4772
0.04275	0.1187	0.1826	0.4471	0.5920	0.7814	0.8726	0.4395
0.06279	0.1677	0.1972	0.4623	0.6592	0.7386	0.8915	0.3881
0.08200	0.2102	0.2293	0.5156	0.7437	0.6582	0.9113	0.3276
0.1004	0.2670	0.3085	0.6113	0.7888	0.6016	0.9319	0.2577
0.1182	0.3054	0.3730	0.6655	0.8042	0.5748	0.9536	0.1832
0.1295	0.3211	0.4265	0.7218	0.8203	0.5419	0.9762	0.0847
0.1352	0.3473	0.4716	0.7674	0.8370	0.5110		
0.1516	0.3696	0.4917	0.7840	0.8530	0.4942		
$(1–x)C_2D_5OD+xC_2H_5OD$							
0.02154	0.07431	0.1497	0.3092	0.4681	0.6716	0.8356	0.3543
0.02310	0.07741	0.1499	0.3326	0.4914	0.7054	0.8408	0.3607
0.04217	0.1287	0.1591	0.3344	0.5136	0.6957	0.8529	0.3621
0.04517	0.1332	0.1755	0.3695	0.5357	0.7020	0.8531	0.3295
0.06394	0.1638	0.2509	0.4817	0.5689	0.6995	0.8714	0.3030
0.07329	0.1942	0.2607	0.4894	0.5912	0.6850	0.8905	0.2756
0.08092	0.2156	0.3344	0.5882	0.6217	0.6864	0.8905	0.2801
0.09198	0.2302	0.3460	0.5720	0.6377	0.6672	0.9104	0.2365
0.09914	0.2490	0.3976	0.6184	0.6626	0.6455	0.9313	0.1867
0.1058	0.2593	0.4011	0.6392	0.6703	0.6126	0.9531	0.1497
0.1167	0.2746	0.4137	0.6378	0.7253	0.5565	0.9760	0.0928
0.1243	0.2955	0.4202	0.6610	0.7305	0.5502		

Table 4 Continued

x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}	x	H^E/ J mol^{-1}
0.1335	0.2933	0.4299	0.6456	0.7482	0.5558		
0.1420	0.3168	0.4530	0.6897	0.8028	0.4435		
0.1434	0.3170	0.4557	0.6640	0.8187	0.3686		
$(1–x)C_2D_5OD+xC_2H_5OH$							
0.04306	0.5494	0.2361	2.975	0.4763	4.242	0.8609	1.963
0.04615	0.6295	0.2391	2.795	0.4830	4.246	0.8684	1.838
0.06324	0.8120	0.3126	3.389	0.5135	4.165	0.8813	1.718
0.06767	0.9283	0.3202	3.521	0.5320	4.337	0.8879	1.582
0.08257	1.056	0.3667	3.739	0.5406	4.118	0.9027	1.403
0.08823	1.205	0.3778	3.737	0.5465	4.220	0.9083	1.312
0.1011	1.281	0.3982	3.892	0.6065	4.038	0.9252	1.063
0.1079	1.459	0.4055	3.887	0.6158	3.962	0.9296	0.9983
0.1190	1.529	0.4098	3.977	0.6970	3.441	0.9489	0.7126
0.1268	1.739	0.4348	3.901	0.8227	2.354	0.9519	0.6965
0.1361	1.779	0.4412	4.1190	0.8320	2.268		
0.1448	2.021	0.4412	4.169	0.8415	2.176		
0.1526	2.005	0.4742	4.256	0.8498	2.062		
$(1–x)C_2H_5OD+xC_2H_5OH$							
0.02590	0.09300	0.1181	0.5795	0.3443	1.531	0.8299	0.7233
0.02608	0.09467	0.1181	0.5795	0.4093	1.740	0.8291	0.8245
0.02608	0.09467	0.1231	0.5500	0.4184	1.738	0.8471	0.6685
0.0273	0.08433	0.1376	0.6328	0.4442	1.727	0.8473	0.6274
0.0505	0.1761	0.1384	0.6694	0.4528	1.806	0.8660	0.6068
0.05083	0.2390	0.1384	0.6694	0.4861	1.853	0.8688	0.6649
0.05083	0.2390	0.1441	0.6336	0.4894	1.791	0.8695	0.5535
0.05314	0.1816	0.1525	0.6327	0.5246	1.829	0.8858	0.5369
0.07388	0.2550	0.1570	0.7637	0.5435	1.769	0.8928	0.4706
0.07435	0.3425	0.1578	0.7675	0.5697	1.756	0.9065	0.4433
0.07435	0.3425	0.1578	0.7675	0.6179	1.586	0.9174	0.3929
0.07765	0.3421	0.1642	0.7477	0.6234	1.584	0.9282	0.3352
0.09615	0.3705	0.1754	0.9120	0.6882	1.353	0.9434	0.2881
0.09674	0.4688	0.1764	0.8477	0.708	1.306	0.9510	0.2369
0.09674	0.4688	0.1764	0.8477	0.7693	1.033	0.9709	0.1629
0.1009	0.4626	0.1834	0.8712	0.8063	0.7694	0.9749	0.1309
0.1174	0.5085	0.2632	1.174	0.8263	0.6931		

Table 5 Best fit coefficients of Eq. (1)

System	A_1	A_2	A_3	s_f/J mol^{-1}
$(1-x)CD_3OD+xCH_3OH$	33.191	–8.541	1.090	0.046
$(1-x)CH_3OD+xCH_3OH$	7.449	–0.204	–0.935	0.037
$(1-x)CD_3OD+xCH_3OD$	3.073	–0.651	0.574	0.029
$(1-x)C_2D_5OD+xC_2H_5OH$	16.720	–0.720	–2.150	0.042
$(1-x)C_2H_5OD+xC_2H_5OH$	7.140	0.222	–3.580	0.043
$(1-x)C_2D_5OD+xC_2H_5OD$	2.760	–0.195	0.059	0.025

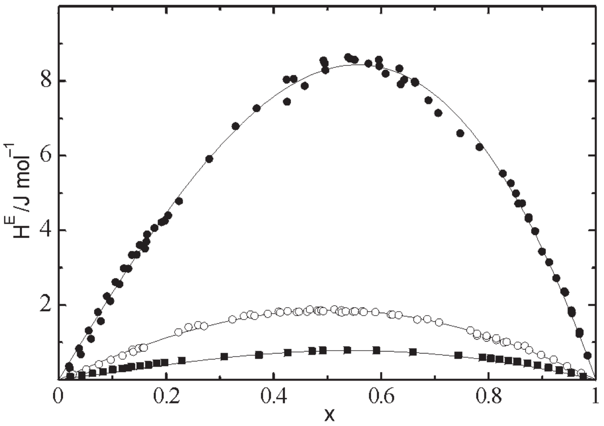

Fig. 3 Excess enthalpies of isotopes mixtures of methanols at 298.15 K. o – $(1-x)CH_3OD+xCH_3OH$, ■ – $(1-x)CH_3OD+xCD_3OD$, ● – $(1-x)CD_3OD+xCH_3OH$

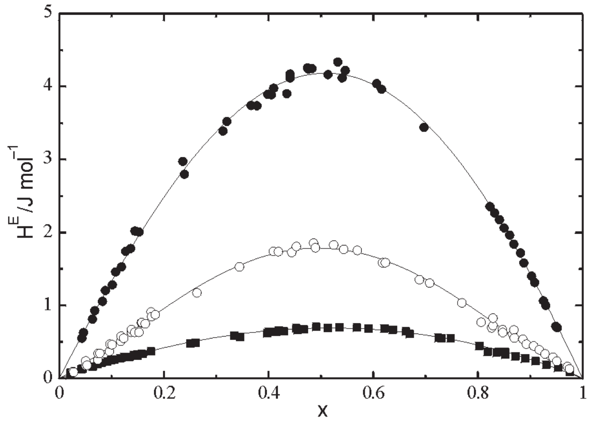

Fig. 4 Excess enthalpies of isotopes mixtures of ethanols at 298.15 K. o – $(1-x)C_2H_5OD+xC_2H_5OH$, ■ – $(1-x)C_2D_5OD+xC_2H_5OD$, ● – $(1-x)C_2D_5OD+xC_2H_5OH$

Excess enthalpy containing deuterium compounds calculated from the Eq. (1) with the coefficients of Table 5 at x=0.5 are listed in Table 6. Difference of excess enthalpy between OH and OD in methanol and ethanol system was almost the same value of (1.82±0.04) J mol^{-1} at equimolar mixture. The different points for those mixtures is the functional group of light and heavy alcohol that might exchange together for each system. However, there is no effect on the excess enthalpy when the functional group of the OH of those compounds is replaced by that of their OD, respectively. Excess enthalpies of CH_3OD+CD_3OD and C_2H_5OD+C_2D_5OD at x=0.5 for the pairs of light and heavy functional groups of methyl and ethyl was 0.768, 0.690 J mol^{-1}, respectively. Enthalpic difference between CH_3–CD_3 and C_2H_5–C_2D_5 in methanol and ethanol was almost the same value of (0.73±0.05) J mol^{-1}. Compared with excess enthalpies of the same pair of deuterium isotope mixtures of methanols and ethanols, the excess enthalpies were almost same except the mixtures of CH_3OH+CD_3OD and C_2H_5OH+C_2D_5OD. The difference between the same pair of deuterium isotope mixtures of methanols and that of ethanols are 0.08 J mol^{-1} as showed in the third column in Table 6. The deuterium isotope effect of the strength of hydrogen-bonding interaction on alkyl chain groups was 54 times larger. Excess enthalpies of CD_3OD+CH_3OH, C_2D_5OD+C_2H_5OH were quite larger than other mixtures. Deuterium substitution in OH and alkyl residue might lead to a significant effect on hydrogen bonding formation.

Table 6 Enthalpy difference between methanol systems and ethanol systems at equimolar mixture

System	H^E(x=0.5)/ J mol^{-1}	H^E(methanol)–H^E(ethanol)/ J mol^{-1}
CD_3OD+CH_3OD	0.768	
C_2D_5OD+C_2H_5OD	0.690	0.078
CH_3OD+CH_3OH	1.862	
C_2H_5OD+C_2H_5OH	1.786	0.076
CD_3OD+CH_3OH	8.325	
C_2D_5OD+C_2H_5OH	4.180	4.145

Enthalpy of vaporization [16] of methanol [$\Delta_{vap}H(CH_3OH)$=37.43 kJ mol^{-1}] is smaller than that of ethanol [$\Delta_{vap}H(C_2H_5OH)$=42.31 kJ mol^{-1}]. However, cohesive energy density of methanol [$\delta(CH_3OH)$=30.31 (J cm^{-3})$^{1/2}$] is larger than that of ethanol [$\delta(C_2H_5OH)$=26.85 (J cm^{-3})$^{1/2}$]. Volume differences between methanol and its deuterium isotopes were smaller than those between ethanol and its deuterium isotopes as shown in Table 1. The isotope effect on site-site interactions between methanol with its isotopes might be larger than those between ethanol with its isotopes. Volume changes on mixing of methanol and ethanol with each isotope might have a significant effect on excess enthalpies. Furthermore, accurate values of cohesive energies and heat capacities of deuterated compounds are not available, above results might present a valuable information for further studies on deuterium isotope effects.

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