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Isotope effects on thermodynamic properties: mixtures of $x(D_2O$ or $H_2O) + (1 - x)CH_3CN$ at 298.15 K ☆

Masanori Nakamura, Katsutoshi Tamura *, Sachio Murakami

Department of Chemistry, Faculty of Science, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

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Abstract

Excess molar enthalpies, excess isobaric molar heat capacities, densities and speeds of sound of the mixtures $x(H_2O$ or $D_2O) + (1 - x)CH_3CN$ were measured at 298.15 K. Considerable isotope effects were observed in H^E_m, V^E_m, $C^E_{p,m}$, $C^E_{V,m}$, κ^E_S, and κ^E_T. $D_2O + CH_3CN$ mixture was more positive for the positive excess properties and more negative for the negative ones than those for the $H_2O + CH_3CN$ mixture. This can be ascribed to the stronger hydrogen bonds of D_2O water than H_2O water. Excess properties of both mixtures are very similar to each other. H^E_m values are positive except for the region $x > 0.97$, where they show a small negative value. $C^E_{p,m}$ values are very large and positive, and the trend to more positive values makes an anomalous hump in the region $x > 0.8$, which corresponds to the negative part of H^E_m. $C^E_{V,m}$ values are smaller than those of $C^E_{p,m}$ and resemble them. V^E_m, κ^E_S and κ^E_T values are negative for the whole concentration range.

Keywords: Acetonitrile; Binary system; Deuterium oxide; Isotope effect; Thermodynamics

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*Corresponding author.

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1. Introduction

Mixtures of water and acetonitrile (CH_3CN) are partially miscible below the upper critical solution temperatures of 271.80 [1] or 272.25 K for normal water H_2O and 278.25 K for heavy water D_2O at a mole fraction of water of about 0.62 [2]. Both mixtures will show a concentration inhomogeneity similar to a phase separation at 298.15 K. The excess properties of $xH_2O + (1-x)CH_3CN$ have been reported [3-7] but those of $xD_2O + (1-x)CH_3CN$ have rarely been published. We have tried to measure the excess properties of the mixtures of H_2O or $D_2O + CH_3CN$ in order to examine the isotope effects of the hydrogen atoms of water. The hydrogen bonding of D_2O is said to be stronger than that of H_2O. Acetonitrile is a weak acceptor for hydrogen bonds and its nitrogen scarcely forms hydrogen bonds. Therefore, the differences in excess properties between H_2O and D_2O mixtures must reflect the strengths of the hydrogen bonds of H_2O and D_2O.

2. Experimental

CH_3CN was purified by transferring in vacuo on molecular sieves 4A. The mole purity was more than 99.99% and the water mole content was less than 0.007%, estimated by GLC and Carl-Fischer methods. H_2O was purified by membrane osmosis (Milli-Q Labo) after ion exchange and distillation. Its conductivity was 10^{-18} S. D_2O (CEA, 99.8% D) was not purified further. The H_m^E and $C_{p,m}^E$ measurements have been described elsewhere [8,9]. The accuracy of the H_m^E values is $\pm 0.3\%$ and that of $C_{p,m}^E$ is $\pm 1\%$. The density and speed of sound measurements have also been described elsewhere [10,11]. The reproducibility of the density measurements is $\pm 3 \times 10^{-6}$ g cm^{-3} and the accuracy is $\pm 10^{-5}$ g cm^{-3} restricted by pycnometry. The reproducibility of the speed of sound is ± 0.03 m s^{-1} and the accuracy is ± 0.3 m s^{-1}.

Table 1
Physical properties of the materials at 298.15 K

Property	H_2O	D_2O	CH_3CN
$\rho/(\mathrm{g\ cm^{-3}})$	0.99703	1.10436	0.77654
$C_{p,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})$	75.23	84.67	89.28
$u/(\mathrm{m\ s^{-1}})$	1496.7	1399.2	1278.7
$\kappa_S/\mathrm{TPa^{-1}}$	447.7	462.5	787.5
$\kappa_T/\mathrm{TPa^{-1}}$	452.5	464.4	1117.9
$C_{V,m}/(\mathrm{J\ K^{-1}\ mol^{-1}})$	74.44	84.42	62.89
$\alpha/\mathrm{kK^{-1}}$	0.25705 [13]	0.1722 [12]	1.368 [13]

Table 2
Excess enthalpies of the mixtures 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})
$xD_2O+(1-x)CH_3CN$				$xH_2O+(1-x)CH_3CN$			
0.10000	680.4	0.60000	877.2	0.20000	926.9	0.60000	840.6
0.15000	847.4	0.65000	795.6	0.24999	1001.2	0.64999	758.9
0.20000	970.9	0.70000	701.7	0.30000	1044.3	0.69999	669.7
0.25000	1049.7	0.75000	597.7	0.34999	1058.5	0.74999	568.8
0.30000	1092.9	0.80000	481.1	0.39999	1045.6	0.80000	454.7
0.35000	1105.3	0.85000	347.3	0.44999	1015.2	0.85000	326.1
0.40000	1092.9	0.90000	196.1	0.49999	969.4	0.90000	180.6
0.45000	1060.2	0.95000	35.6	0.54999	909.7	0.95000	30.7
0.50000	1011.7	0.96500	3.3			0.97500	−8.5
0.55000	952.0	0.97500	−9.7				
		0.98500	−13.3				

Table 3
Excess molar heat capacities of the mixtures at 298.15 K

x	$C^E_{p,m}$/ (J K^{-1} mol^{-1})	x	$C^E_{p,m}$/ (J K^{-1} mol^{-1})	x	$C^E_{p,m}$/ (J K^{-1} mol^{-1})	x	$C^E_{p,m}$/ (J K^{-1} mol^{-1})
$xD_2O+(1-x)CH_3CN$				$xH_2O+(1-x)CH_3CN$			
0.04997	1.04	0.54977	8.97	0.04997	1.05	0.54986	8.54
0.09995	2.66	0.59986	8.70	0.09995	2.57	0.59987	8.28
0.14992	4.24	0.64986	8.24	0.14993	4.09	0.64988	7.83
0.19990	5.57	0.69988	7.60	0.19991	5.43	0.69988	7.23
0.24989	6.71	0.74989	6.82	0.24990	6.49	0.74990	6.61
0.29987	7.57	0.79990	6.10	0.29988	7.36	0.79991	5.91
0.34986	8.24	0.84992	5.36	0.34988	7.93	0.84993	5.25
0.39986	8.71	0.89994	4.91	0.39987	8.40	0.89995	4.71
0.44985	9.00	0.94997	3.84	0.44987	8.62	0.94997	3.51
0.49985	9.04	0.97499	2.46	0.49987	8.68	0.97499	2.15

3. Results and discussion

The properties of the pure substances are listed in Table 1. The H^E_m and $C^E_{p,m}$ values obtained are given in Tables 2 and 3 for both mixtures. The density ρ and speed of sound u values of the mixtures are given in Table 4, where the V^E_m, κ^E_S, κ^E_T and $C^E_{V,m}$ values calculated from them are also given. It must be noted that $\alpha^E = 0$ was assumed in the calculation of the κ_T and $C_{V,m}$ values of the mixtures. Excess values are represented by the following equation

$$F^E/(\text{unit}) = x(1-x)[1-G(1-2x)]^{-1}\sum A_i(1-2x)^{i-1} \qquad (1)$$

Table 4
Densities, speed of sound, excess volumes, excess isentropic and isothermal compressibilities, excess isochoric heat capacities of the mixtures at 298.15 K

x	ρ/ (g cm^{-3})	u/ (m s^{-1})	V_m^E/ cm^3 mol^{-1}	κ_S^E/ (TPa^{-1})	κ_T^E/ (TPa^{-1})	$C_{V,m}^E$/ (J K^{-1} mol^{-1})
xD$_2$O + (1 − x)CH$_3$CN						
0.00000	0.776527	1278.77				
0.02280	0.779372	1280.67	−0.0161	−9.13	−10.7	0.16
0.09942	0.790090	1285.95	−0.1001	−37.98	−46.9	1.60
0.19988	0.806528	1292.50	−0.2349	−73.15	−89.4	3.79
0.30075	0.825756	1300.17	−0.3637	−105.87	−124.5	5.30
0.40065	0.847853	1309.11	−0.4675	−134.34	−152.0	6.13
0.59982	0.904409	1338.15	−0.5866	−177.17	−188.3	6.31
0.69510	0.939929	1366.73	−0.5970	−191.60	−198.7	5.53
0.80140	0.989075	1416.42	−0.5623	−195.63	−199.1	4.47
0.89989	1.044451	1463.08	−0.4215	−161.23	−162.4	4.15
1.00000	1.104364	1399.19				
0.00000	0.776542	1278.78				
0.04889	0.782846	1282.65	−0.0408	−19.27	−23.2	0.54
0.14929	0.798096	1289.49	−0.1757	−56.28	−69.5	2.73
0.25031	0.815810	1296.21	−0.3021	−89.94	−107.9	4.65
0.35119	0.836536	1304.43	−0.4209	−120.77	−139.3	5.79
0.45051	0.860285	1314.19	−0.5099	−146.59	−163.1	6.37
0.55375	0.889504	1328.76	−0.5704	−168.64	−181.6	6.47
0.64971	0.922149	1351.35	−0.5959	−185.36	−194.4	5.96
0.74949	0.963388	1389.90	−0.5797	−196.14	−201.2	4.94
0.85088	1.015715	1442.42	−0.5096	−185.67	−187.8	4.23
0.95732	1.079116	1457.54	−0.2264	−96.97	−97.3	3.29
0.96576	1.084038	1450.87	−0.1850	−82.09	−82.3	2.93
1.00000	1.104367	1399.19				
xD$_2$O + (1 − x)CH$_3$CN						
0.00000	0.776559	1278.72				
0.02063	0.778314	1281.45	−0.0120	−7.58	−9.0	0.16
0.04930	0.780927	1285.11	−0.0346	−17.85	−21.8	0.57
0.15346	0.791991	1297.82	−0.1541	−53.26	−66.7	2.78
0.25018	0.804183	1310.75	−0.2774	−84.52	−103.0	4.50
0.35555	0.819551	1326.79	−0.3958	−115.78	−135.2	5.59
0.45667	0.836753	1344.89	−0.4855	−141.78	−159.5	6.03
0.55526	0.856366	1367.71	−0.5427	−162.99	−177.4	5.98
0.64011	0.876194	1395.23	−0.5680	−177.96	−188.9	5.51
0.75314	0.908150	1449.87	−0.5586	−189.63	−195.8	4.49
0.84988	0.941515	1511.80	−0.4844	−178.22	−181.2	3.91
0.95117	0.979942	1547.17	−0.2356	−100.51	−101.2	3.04
1.00000	0.997063	1496.68				
0.00000	0.776544	1278.72				
0.09674	0.785668	1290.89	−0.0843	−34.27	−42.8	1.53
0.20337	0.798033	1304.29	−0.2178	−69.60	−86.2	3.76
0.31264	0.813001	1320.02	−0.3509	−103.54	−123.0	5.24
0.40322	0.827287	1334.87	−0.4405	−128.53	−147.4	5.86
0.49813	0.844566	1353.69	−0.5123	−151.23	−167.7	6.07
0.60912	0.868552	1384.23	−0.5613	−173.01	−185.2	5.72

Table 4 continued

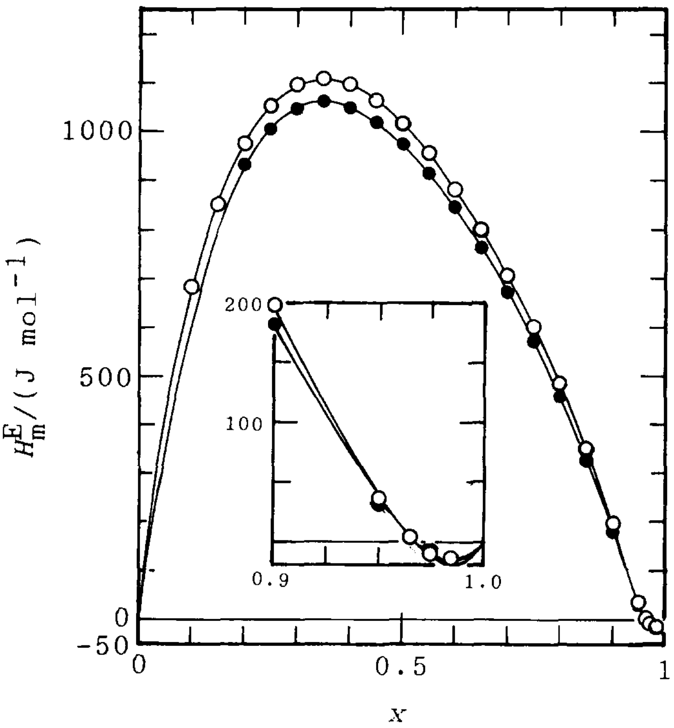
x	ρ/ ($g\ cm^{-3}$)	u/ ($m\ s^{-1}$)	V_m^E/ $cm^3\ mol^{-1}$	κ_S^E/ (TPa^{-1})	κ_T^E/ (TPa^{-1})	$C_{V,m}^E$/ ($J\ K^{-1}\ mol^{-1}$)
0.70869	0.894766	1425.60	−0.5716	−186.84	−194.8	4.90
0.80718	0.926057	1483.61	−0.5284	−187.32	−191.6	4.09
0.89057	0.956964	1535.36	−0.4174	−159.39	−161.4	3.81
0.98627	0.992355	1518.89	−0.0745	−35.12	−35.3	1.27
1.00000	0.997001	1496.69				

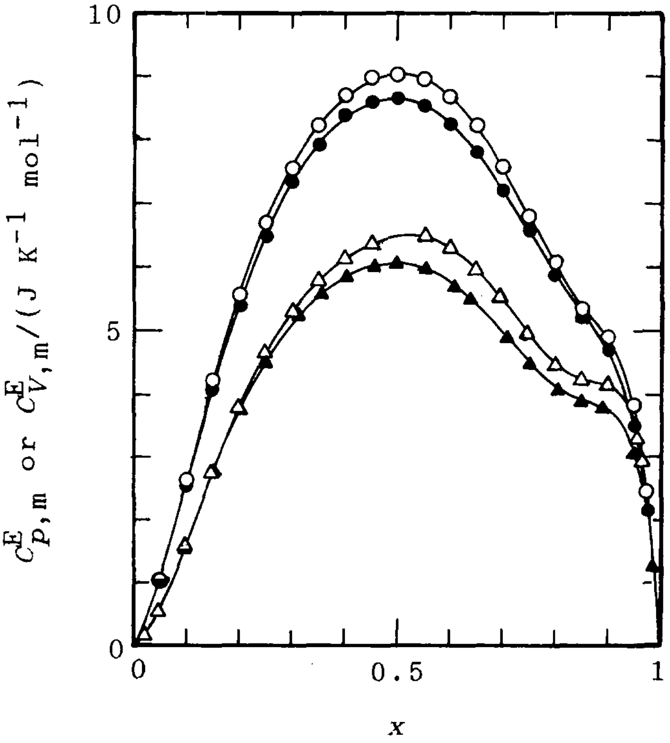
Table 5
The coefficients of Eq. (1) for excess properties

Property	A_1	A_2	A_3	A_4	A_5	A_6	G	s
$xD_2O+(1-x)CH_3CN$								
$H_m^E/(J\ mol^{-1})$	4020.7	5642.0	3783.4	2498.4			−0.86173	9.2
$C_{p,m}^E/(J\ K^{-1}\ mol^{-1})$	36.25	23.46	−0.26	12.93	−2.54	−47.53	−0.66932	0.04
$V_m^E/(cm^3\ mol^{-1})$	−2.1681	1.1769	−0.6206	1.2087	−0.7864	0.5540		0.0040
κ_S^E/TPa^{-1}	−630.71	−75.26	−85.06	167.06	33.43	−157.04	−0.79957	0.17
κ_T^E/TPa^{-1}	−690.4	−112.4	−193.6	176.0			−0.68662	0.3
$C_{V,m}^E/(J\ K^{-1}\ mol^{-1})$	25.98	15.01	−3.15	14.17	1.17	−49.63	−0.66778	0.006
$xH_2O+(1-x)CH_3CN$								
$H_m^E/(J\ mol^{-1})$	3869.4	5607.3	3402.8	1966.6			−0.90095	2.9
$C_{p,m}^E/(J\ K^{-1}\ mol^{-1})$	34.67	21.16	1.06	6.88	−1.58	−40.35	−0.59052	0.03
$V_m^E/(cm^3\ mol^{-1})$	−2.0538	1.1993	−0.5755	1.1870	−0.6116	0.3835		0.0016
κ_S^E/TPa^{-1}	−606.39	−24.56	−73.15	142.24	9.83	−108.49	−0.76073	0.11
κ_T^E/TPa^{-1}	−672.0	−83.1	−161.8	165.4			−0.67474	0.2
$C_{V,m}^E/(J\ K^{-1}\ mol^{-1})$	24.29	15.16	−1.40	7.79	1.50	−41.57	−0.60679	0.004

where F^E is the excess property, such as H_m^E, and x is the mole fraction of D_2O or H_2O; the parameters A_i and G are calculated by a least-squares method and are given in Table 5 together with the standard deviation s. Excess values are also plotted in Figs. 1–4, in which the curves are calculated from the parameters of Eq. (1).

The H_m^E of H_2O+CH_3CN have been reported by Morcom and Smith [3] and Stokes [7] and their values are approximately 20 and 10 J mol^{-1} larger than ours, respectively. The $C_{p,m}^E$ of H_2O+CH_3CN reported by De Visser et al. [4] is larger by 0.1 J K^{-1} mol^{-1} at maximum than ours. The V_m^E of H_2O+CH_3CN is in good agreement with those of van Meurs and Somsen [6] and Handa and Benson [5].


$H_m^E/(J\ mol^{-1})$
1000
500
0
-50
0
0.5
1
x
200
100
0.9
1.0


$C_{p,m}^E$ or $C_{V,m}^E/(J\ K^{-1}\ mol^{-1})$
10
5
0
0
0.5
1
x

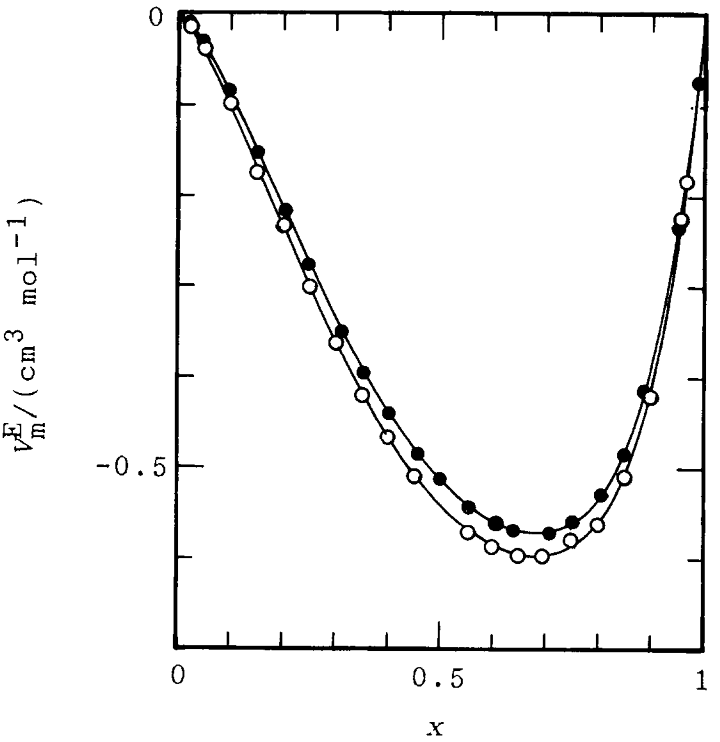


Fig. 3. Excess volumes of the mixtures at 298.15 K: ○, $D_2O + CH_3CN$; $H_2O + CH_3CN$.

3.1. Characteristics common to both systems

The H_m^E values are positive over almost the whole region and this suggests an unstable state in the solution. However, the H_m^E values are negative in the region $x > 0.98$. In the region of high x, dimeric acetonitrile molecules as non-polar particles make the water molecules reoriented in the higher hydrogen-bond network and squeeze into the cages formed by water; then the system is stabilized and shows negative H_m^E. For $C_{p,m}^E$, the positive trend ascribed to the above phenomena is certainly observed in the region $x \approx 0.95$. This trend is very strong and then forms a hump on the large positive $C_{p,m}^E$ values which is almost 9 J K^{-1} mol^{-1},

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Fig. 1 (opposite top). Excess enthalpies of the mixtures at 298.15 K: ○, $D_2O + CH_3CN$; ●, $H_2O + CH_3CN$.

Fig. 2 (opposite below). Excess isobaric and isochoric heat capacities of the mixtures at 298.15 K: ○, $C_{p,m}^E$ $(D_2O + CH_3CN)$; ●, $C_{p,m}^E(H_2O + CH_3CN)$; △, $C_{V,m}^E(D_2O + CH_3CN)$; ▲, $C_{V,m}^E(H_2O + CH_3CN)$.

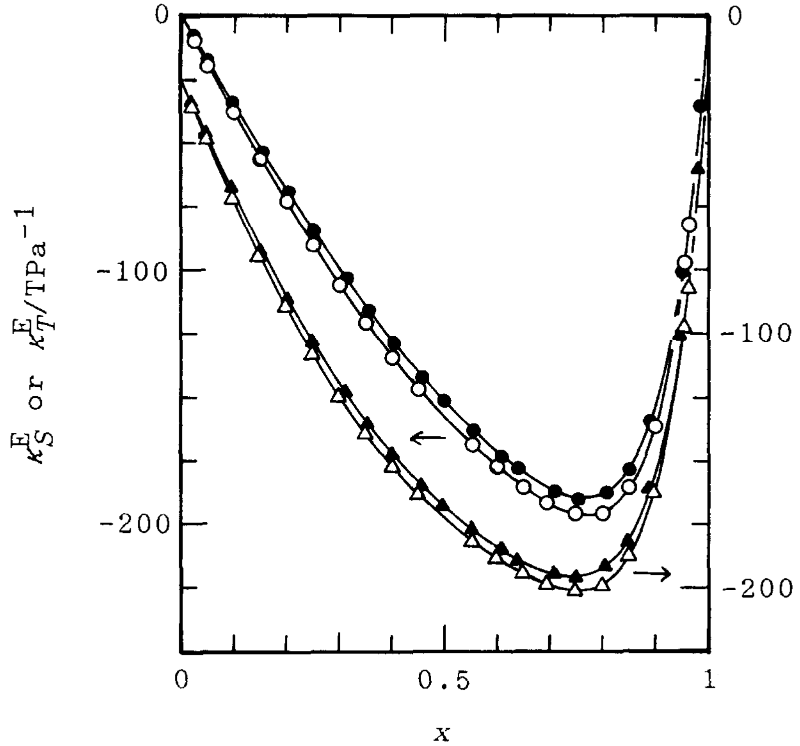

Fig. 4. Excess isentropic and isothermal compressibilities of the mixtures at 298.15 K: ○, $\kappa_S^E(D_2O + CH_3CN)$; ●, $\kappa_S^E(H_2O + CH_3CN)$; △, $\kappa_T^E(D_2O + CH_3CN)$; ▲, $\kappa_T^E(H_2O + CH_3CN)$.

corresponding to about 10% of the $C_{p,m}^E$ of an equimolar mixture. V_m^E is large and negative in spite of the large positive H_m^E. This means that acetonitrile molecules break the hydrogen bond network of water to show large positive H_m^E values and very negative V_m^E, and that in the high x region, local rearrangement of hydrogen bonds around the acetonitrile molecule does not give a positive effect on V_m^E. Negative excess compressibilities for these mixtures are consistent with the above explanation. The mixtures become less compressible because of the close packing of water molecules resulting on breaking the hydrogen bonds in medium-x value mixtures, and the hydrogen-bond network of water around acetonitrile molecules in large-x value mixtures.

From the $C_{p,m}^E$ values, the structures of mixtures of $x > 0.9$ are different from those of other mixtures. In the higher x region, water molecules reorient and form a hydrogen-bond network around the dimeric acetonitrile molecules, and with other values of x, the network of hydrogen bonds of the water molecules is broken and reduces the volume, which makes the mixture less compressible. The excess expansivity of $H_2O + CH_3CN$ has been reported by Handa and Benson [5]; it is positive over the whole concentration and very large, the largest value being nearly 10^{-4}

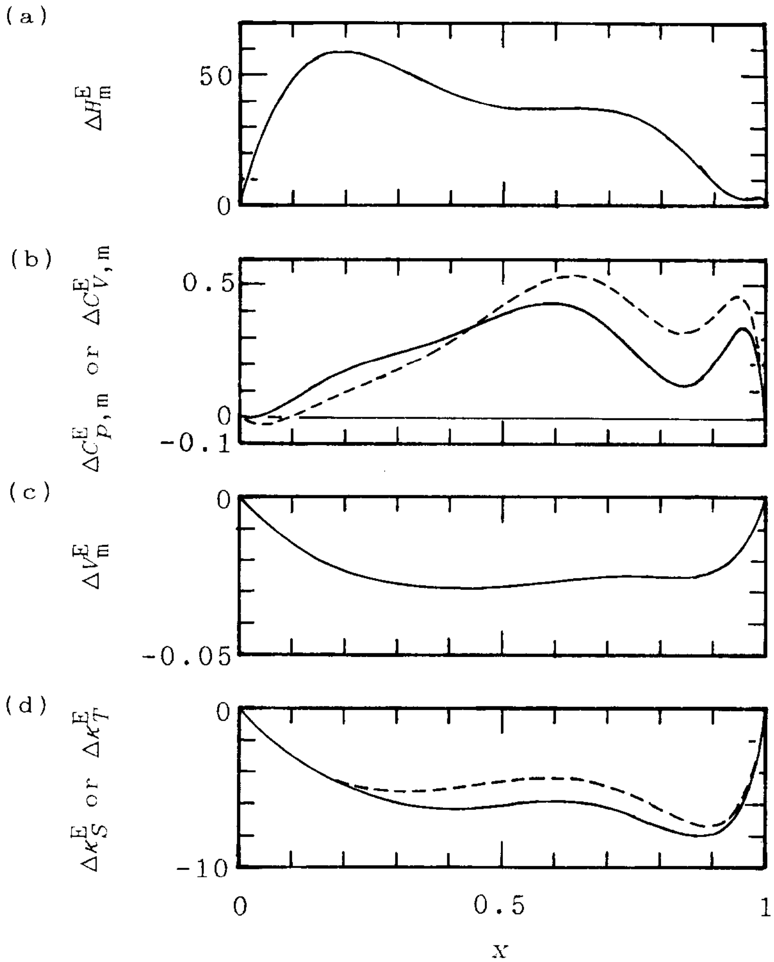

Fig. 5. Difference between the excess properties of the mixtures of $D_2O + CH_3CN$ and $H_2O + CH_3CN$. In b and d, the broken lines are $\Delta C^E_{V,m}$ and $\Delta \kappa^E_T$, respectively.

K^{-1} at 298.15 K, which compares with that of pure water. We have calculated κ^E_T and $C^E_{V,m}$, considering the value of α^E. The result is considerably different from the value for $\alpha^E = 0$. We will measure the excess volume at a few temperatures around 298.15 K and estimate the α^E value at 298.15 K for $D_2O + CH_3CN$, and report the result considering α^E in the future. The results of κ^E_T and $C^E_{V,m}$ in this paper are only tentative with respect to the isotope effect.

3.2. The isotope effects

The stronger hydrogen bond between D_2O molecules make the excess properties of D_2O mixture deviate, being more negative for negative properties and more positive for positive ones, compared to that of H_2O mixture. The deviation is about 4–5%, which is reasonable considering the difference in the strength of the hydrogen bonds between D_2O and H_2O in the pure state. The curve of deviation of the thermodynamic properties of $xD_2O + (1-x)CH_3CN$ from those of $xH_2O + (1-x)CH_3CN$ are plotted in Figs. 5a–d. The deviations are defined as

$$\Delta F^E = F^E(xD_2O + (1-x)CH_3CN) - F^E(xH_2O + (1-x)CH_3CN) \qquad (2)$$

The deviation curves of $C^E_{p,m}$ and H^E_m are anomalous in the region of high x which is due to the anomaly in the thermodynamic properties emphasized in the D_2O system.

The effect of α^E on κ^E_T and $C^E_{V,m}$ for the D_2O mixture will be as large as that of the H_2O mixture. The effect is probably larger than for the H_2O mixture because of the lower expansivity of pure D_2O than pure H_2O at this temperature.

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