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Thermochimica Acta 459 (2007) 80–86

thermochimica acta

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Thermodynamic properties of binary mixtures of 2,2,2-trifluoroethanol with water or alkanols at $T = 298.15$ K

Takashi Minamihonoki[a,*], Hideo Ogawa[a], Hiroyasu Nomura[a], Sachio Murakami[b]

[a] *Graduate School of Science and Engineering, Tokyo Denki University, Hatoyama,*
Hiki-gun, Saitama 350-0394, Japan
[b] *Frontier Research and Development Center, Tokyo Denki University, Hatoyama,*
Hiki-Gun, Saitama 350-0394, Japan

Received 30 November 2006; received in revised form 17 April 2007; accepted 18 April 2007
Available online 24 April 2007

Abstract

Excess molar enthalpies (H_m^E) and excess molar volume (V_m^E) at $T = 298.15$ K for binary mixtures of {2,2,2-trifluoroethanol (TFE) + water or alcohols (methanol, ethanol, 1-propanol)} were obtained by calorimetry and densimetry. Excess molar enthalpies for the (TFE + water) system showed endothermic mixing, except for the low TFE concentration range ($x_1 < 0.1$) in which they showed exothermic one. On the other hand, excess molar volumes for this system were negative over the whole range of concentration. Excess molar enthalpies for all the (TFE + alcohol) systems were exothermic over the whole range of concentration and decrease in absolute value with increase of the carbon number of the alkyl group in the alcohol molecules (n_C). Excess molar volumes were positive over the whole range of concentration and increase with n_C. Moreover, we estimated excess partial molar enthalpy ($H_{m,i}^{E,\infty}$) and volume ($V_{m,i}^{E,\infty}$) at infinite dilution from the experimental results. These results were discussed qualitatively from the viewpoint of the intermolecular interactions in the pure component liquids and the mixtures.

Keywords: 2,2,2-Trifluoroetanol; Water; Methanol; Ethanol; 1-Propanol; Excess molar enthalpy; Excess molar volume

1. Introduction

Organic solvents containing fluorine atom have been used in the field of the cleaning technology of electronic industry, because of a little risk in the destruction of the natural environment. For example, hydrofluoroether (HFE) has been proposed as the alternative solvent to the chlorofluorocarbon, which destroys the ozone layer.

We have studied thermodynamic properties of binary mixtures containing HFE recently [1–5]. However, HFE is the water-insoluble material and then the development of the water-miscible and non-flammable organic solvent containing fluorine atom has been strongly desired in the field of the cleaning technology. 2,2,2-trifluoroethanol (TFE) is non-flammable, water-miscible organic material containing fluorine atom. Then, we will report H_m^E and V_m^E for binary mixtures of TFE and water or alcohols, in order to obtain further information for the thermodynamic properties of the TFE mixtures.

2. Experimental

2.1. Materials

TFE (CF_3CH_2OH) in special grade reagent from Kanto Chemical Co., Inc. was used as the first component liquid. Water purified by ultra pure water system (Toray Industries Inc., TORAYPURE LV-10T), methanol (MeOH), ethanol (EtOH) in dehydration grade reagent and 1-propanol (1-PrOH) in special grade reagent from Kanto Chemical Co., Inc. were used as the second component liquids.

TFE and 1-PrOH were dried over fleshly activated molecular sieves 4A and distilled in a 1 m in height column with helipak. Since MeOH and EtOH contain small amount of moisture, only distillation was done. The purities of these sample materials were evaluated by g.l.c. (GC-17A) from Shimadzu Corporation and a

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[*] Corresponding author at: 236-2 Ohji-cho, Tenri, Nara 632-0086, Japan. Tel.: +81 743 64 3902.
E-mail address: taka-mi@m4.kcn.ne.jp (T. Minamihonoki).

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doi:10.1016/j.tca.2007.04.012

Table 1
Density (ρ) at $T = 298.15$ K, water content and purity of the components

Component	ρ (g cm^{-3})[a]	ρ (g cm^{-3})[b]	Mass fraction $H_2O \times 10^{-6}$	Mass fraction purity
CF_3CH_2OH	1.38341	1.38266	11	0.99996
H_2O	0.99705	0.99705	Specific resistance = 18.1 MΩ cm	
CH_3OH	0.78630	0.78637	51	0.99999
CH_3CH_2OH	0.78483	0.78493	18	0.99999
$CH_3(CH_2)_2OH$	0.79930	0.79960	177	0.99990

[a] This work.
[b] Literature values [13].

Karl–Fischer moisture meter from Kyoto Electronics Manufacturing Co., Ltd. These results are given in Table 1 with density (ρ).

2.2. Apparatus and procedure

Excess enthalpy of mixing is measured by using a flow microcalorimeter produced newly by Minamihonoki. The design of the calorimeter constructed in this study is essentially same as that reported by Ogawa and Kojima [6]. This apparatus consists of a calorimeter unit immersed in a water bath controlled within $\pm 1 \times 10^{-3}$ K in temperature and a pair of home-made cylindrical pumps, one of which consists of a double-walled glass cylinder with a precision bore, a precision ball screw-rod and driving mechanism composed of a bearing box, a gear box and a pulse motor. Reproducibility in the flow rate of the both pumps was estimated to be more than 99.8%. The sample liquids are fed into the calorimeter cell at a constant total flow rate by the pumps and then, the concentration of the mixture was kept constant within 1×10^{-5} in the mole fraction.

We measured excess enthalpy of mixing (H_m^E) for the {benzene(1) + *cyclo*-hexane(2)} mixture at $T = 298.15$ K as a performance test of our calorimeter, and the result obtained was compared with those reported by Fujihara et al. [7] and Murakami and Benson [8]. The former measured by using an LKB10700-1 flow microcalorimeter, and the latter measured by using an isothermal displacement calorimeter. The results agreed excellently with each other and the differences of our values from their data were about 0.7%, as shown in Fig. 1.

Densities of the sample liquids were measured with a vibrating-tube densimeter (Anton Paar, DMA-5000) controlled within $\pm 1 \times 10^{-3}$ K in temperature. The two constants characteristic of the densimeter were determined by using several standard liquids, whose densities were measured by an Ostwald type of pyknometer with volume of 50 cm^3. Then, the accuracy of densimetry was restricted to $\pm 1 \times 10^{-5}$ g cm^{-3} by the pycnometry used in the calibration of the densimeter, and the reproducibility of the densimetry was believed to be within $\pm 3 \times 10^{-6}$ g cm^{-3}. Details of measurements are given elsewhere [9].

3. Result and discussion

The values of H_m^E for the mixtures of {TFE(1) + water(2) or alcohol(2)} at 298.15 K are listed in Table 2 and plotted in Fig. 2. The values of V_m^E are listed in Table 3 and plotted in Fig. 3.

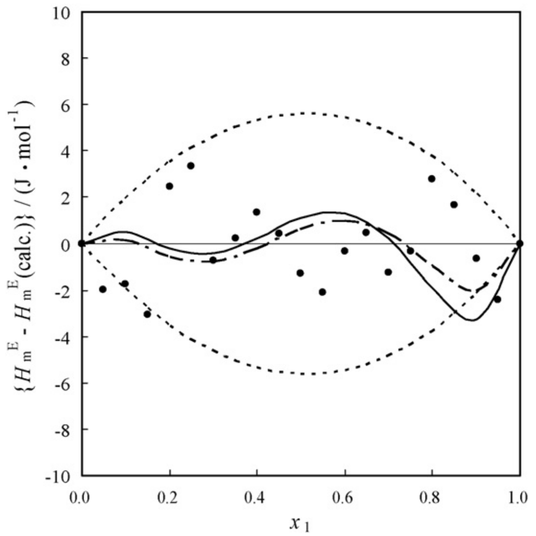

Fig. 1. Comparison of excess enthalpies, H_m^E for the (benzene + *cyclo*-hexane) system at 298.15 K where the mole fraction of benzene, x_1 and H_m^E (calc), is the values calculated from the Eq. (1) with coefficients from Table 4. (●) deviation of our experimental points from the Eq. (1); (—) Fujihara et al. [7]; (-·-) 2 Murakami and Benson [8]; (- - -) 0.7% deviations.

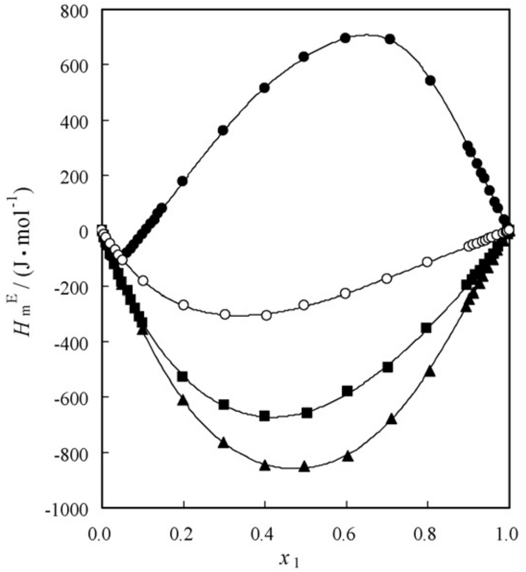

Fig. 2. Excess molar enthalpies (H_m^E) of the {2,2,2-trifluoroethanol(1) + water or alcohol(2)} systems at $T = 298.15$ K: (●) {$CF_3CH_2OH(1) + H_2O(2)$}; (▲) {$CF_3CH_2OH(1) + CH_3OH(2)$}; (■) {$CF_3CH_2OH(1) + CH_3CH_2OH(2)$}; (○), {$CF_3CH_2OH(1) + CH_3(CH_2)_2OH(2)$}.

Table 2
Excess molar enthalpies (H_m^E) of the mixtures containing 2,2,2-trifluoroethanol(1) at $T = 298.15$ K

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
$CF_3CH_2OH(1) + H_2O(2)$					
0.00546	−28.8	0.10998	3.3	0.80788	542.3
0.01088	−54.3	0.11926	22.1	0.89800	305.3
0.02028	−91.5	0.12987	40.6	0.90543	284.2
0.03060	−105.5	0.13852	59.9	0.92020	239.8
0.04018	−103.0	0.14862	80.2	0.93005	208.9
0.04984	−94.0	0.19832	177.4	0.93870	187.1
0.05985	−81.8	0.29878	362.0	0.95285	144.1
0.07002	−66.6	0.39883	514.5	0.96457	104.2
0.07952	−51.0	0.49554	626.4	0.97321	79.2
0.08986	−33.1	0.59888	695.0	0.98797	40.3
0.09937	−14.0	0.70779	690.0	0.99521	14.0
$CF_3CH_2OH(1) + CH_3OH(2)$					
0.00548	−21.7	0.39879	−846.6	0.93370	−162.4
0.01037	−39.7	0.49711	−851.6	0.94632	−133.3
0.02045	−80.1	0.60273	−811.6	0.96016	−102.9
0.02995	−118.3	0.70985	−676.2	0.97070	−70.9
0.04012	−157.4	0.80439	−506.0	0.98377	−36.6
0.04831	−192.2	0.89288	−270.9	0.99535	−11.7
0.09938	−356.5	0.90165	−245.4	0.99867	−2.7
0.19965	−611.1	0.91130	−225.3		
0.29705	−764.4	0.92507	−189.3		
$CF_3CH_2OH(1) + CH_3CH_2OH(2)$					
0.00586	−19.7	0.09891	−333.4	0.91596	−159.6
0.01060	−39.6	0.19903	−525.7	0.92785	−144.2
0.02013	−80.8	0.29919	−628.9	0.93892	−122.6
0.03032	−118.6	0.39946	−670.9	0.95158	−100.5
0.03992	−154.4	0.50385	−656.9	0.96177	−83.3
0.04851	−187.3	0.60290	−580.3	0.97287	−58.3
0.06244	−216.5	0.70144	−493.5	0.98258	−37.7
0.07146	−248.6	0.79638	−352.9	0.99202	−14.9
0.08127	−278.7	0.89450	−195.8	0.99876	−3.8
0.09052	−309.0	0.90719	−178.1		
$CF_3CH_2OH(1) + CH_3(CH_2)_2OH(2)$					
0.00540	−12.5	0.40412	−305.3	0.94094	−34.8
0.00920	−24.2	0.49620	−269.8	0.94863	−29.4
0.02045	−46.3	0.59738	−225.7	0.95771	−24.2
0.03258	−68.3	0.69983	−174.6	0.96937	−17.1
0.04077	−90.0	0.79867	−114.9	0.98393	−10.8
0.05100	−108.8	0.90033	−57.4	0.99160	−4.5
0.10129	−183.6	0.91077	−51.5	0.99615	−1.7
0.20133	−268.7	0.92106	−46.1		
0.30226	−301.7	0.93326	−40.9		

Each set of results was fitted by the following Myers–Scott equation [10]:

$$H_m^E \text{ or } V_m^E = x_1(1-x_1)\{1-G(1-2x_1)\}^{-1}\sum A_i(1-2x_1)^{i-1}, \quad (1)$$

where x_1 is mole fraction of TFE. The coefficients, A_i, were determined by the method of un-weighed least-squares with an iterated G, which is a skew parameter proposed by Myers and Scott. The parameters A_i and G are given in the Table 4 with standard deviations.

As shown in Fig. 2, H_m^E values are a little negative (exothermic mixing) in the low TFE concentration range and positive (endothermic mixing) at of $x_1 \geqq 0.1$ for the (TFE + water) system (Table 4). On the other hand, H_m^E values are negative (exothermic) over the whole range of concentration in the (TFE + alcohol) systems. The minimum values of H_m^E for the alcohol systems was in order: 1-PrOH > EtOH > MeOH in magnitude.

The V_m^E values observed are shown in Fig. 3 over the whole range of concentration. They are negative (contraction in volume) for the (TFE + H_2O) system and on the other hand, positive (expansion in volume) in all the alcohol systems studied. Sassi and Atik have reported previously V_m^E for the (TFE + water) or a series of alcohol systems without 1-PrOH system [14]. Our result agree with theirs within experimental accuracy (±0.02 cm^3 mol^{-1}), except for the lower concentration region in the (TFE + water) system in which our values are more negative than theirs. The maximum values of V_m^E for the alcohol systems are in the order: 1-PrOH > EtOH > MeOH in magnitude.

Table 3
Densities (ρ) and excess molar volumes (V_m^E) of the mixtures containing 2,2,2-trifluoroethanol(1) at $T = 298.15$ K

x_1	ρ (g cm^{-3})	V_m^E (cm^{-3} mol^{-1})	x_1	ρ (g cm^{-3})	V_m^E (cm^{-3} mol^{-1})
$CF_3CH_2OH(1) + H_2O(2)$					
0	0.99705		0.59954	1.34154	−0.505
0.00478	1.00599	−0.030	0.73034	1.35916	−0.356
0.01029	1.01628	−0.069	0.83898	1.37038	−0.216
0.01855	1.03119	−0.129	0.90619	1.37617	−0.122
0.02226	1.03771	−0.156	0.96962	1.38116	−0.038
0.10017	1.13998	−0.492	0.98003	1.38189	−0.022
0.19849	1.21551	−0.620	0.98995	1.38259	−0.008
0.29997	1.26559	−0.664	0.99495	1.38297	−0.003
0.39835	1.29893	−0.653	1	1.38341	
0.49650	1.32287	−0.598			
$CF_3CH_2OH(1) + CH_3OH(2)$					
0	0.78630		0.57971	1.19876	0.565
0.00435	0.79062	0.014	0.69055	1.25374	0.463
0.00909	0.79528	0.030	0.83314	1.31738	0.279
0.01643	0.80243	0.054	0.91962	1.35257	0.145
0.01555	0.80157	0.052	0.97009	1.37213	0.057
0.06693	0.84962	0.207	0.97993	1.37589	0.037
0.18622	0.94942	0.458	0.99130	1.38001	0.024
0.31905	1.04513	0.596	0.99494	1.38147	0.012
0.38499	1.08780	0.619	1	1.38341	
0.48078	1.14491	0.615			
$CF_3CH_2OH(1) + CH_3CH_2OH(2)$					
0	0.78483		0.60121	1.16007	0.798
0.00449	0.78800	0.011	0.70247	1.21772	0.703
0.00898	0.79110	0.025	0.78508	1.26415	0.573
0.02012	0.79887	0.054	0.91088	1.33411	0.280
0.02992	0.80561	0.083	0.92000	1.33916	0.254
0.04022	0.81270	0.111	0.92990	1.34465	0.225
0.05208	0.82082	0.141	0.94966	1.35558	0.166
0.10019	0.85317	0.272	0.95972	1.36114	0.134
0.20027	0.91854	0.496	0.96971	1.36665	0.103
0.30008	0.98136	0.662	0.97985	1.37226	0.069
0.39988	1.04213	0.772	0.98969	1.37767	0.038
0.50027	1.10160	0.820	1	1.38341	
$CF_3CH_2OH(1) + CH_3(CH_2)_2OH(2)$					
0	0.79930		0.60569	1.13149	1.048
0.00607	0.80248	0.022	0.70744	1.19238	0.945
0.01063	0.80492	0.033	0.80290	1.25185	0.745
0.02216	0.81094	0.076	0.90234	1.31656	0.428
0.03141	0.81581	0.107	0.96715	1.36054	0.157
0.10320	0.85369	0.335	0.97854	1.36842	0.104
0.20221	0.90648	0.601	0.98982	1.37624	0.052
0.31176	0.96559	0.844	0.99475	1.37983	0.021
0.40797	1.01850	0.990	1	1.38341	
0.50848	1.07513	1.063			

3.1. Thermodynamics quantities for the whole range of concentration

In order to discuss the thermodynamic properties of these systems, we may divide into two types of systems.

One is the (TFE + H_2O) system. As described above, H_m^E values of this system are positive with the concentration of $x_1 \geqq 0.1$, and V_m^E values are negative at the whole range of concentration. As shown in Fig. 2, the positive H_m^E values at $x_1 \geqq 0.1$ mean that the hydrogen bond interactions are considered to be dominant in the pure component liquids, and on the other hand, the three dimensional hydrogen bond structure of the water in the pure state by the mixing of TFE may be broken in solution, and although the hydrogen bond intermolecular interaction between the dissimilar molecules is newly formed with TFE, it is weaker than the similar intermolecular hydrogen bond interactions in the pure components, and then solution becomes thermally unstable. On the other hand, the H_m^E value in the lower TFE concentration range is small negative. It may be supported by the following researches due to other investigators. The microstructure of solution in the (TFE + H_2O) system has been reported in detail by Takamuku et al. [11]. According to the radical distribution function which was obtained from the X-ray diffraction study, three TFE molecules are assembled in average

Table 4
Coefficients, G, A_i and standard deviations, s of Eq. (1)

Property	G	A_1	A_2	A_3	A_4	A_5	s
$CF_3CH_2OH(1) + H_2O(2)$							
H_m^E ($J\,mol^{-1}$)	0.747	2511	−3959	1953	850	−2743	7.0
V_m^E ($cm^3\,mol^{-1}$)	0	−2.382	−1.300	−0.599	−1.785	−1.546	0.0072
$CF_3CH_2OH(1) + CH_3OH(2)$							
H_m^E ($J\,mol^{-1}$)	0	−3463	−316	49	−656		6.5
H_m^E ($cm^3\,mol^{-1}$)	0	2.429	0.781	0.254			0.0025
$CF_3CH_2OH(1) + CH_3CH_2OH(2)$							
H_m^E ($J\,mol^{-1}$)	0	−2602	−836	−468	−205		5.0
V_m^E ($cm^3\,mol^{-1}$)	0	3.277	−0.276	−0.095			0.0036
$CF_3CH_2OH(1) + CH_3(CH_2)_2OH(2)$							
H_m^E ($J\,mol^{-1}$)	0	−1079	−824	−371			3.3
V_m^E ($cm^3\,mol^{-1}$)	0	4.231	−0.793				0.0026

by hydrogen bonding in the pure state. In the observation of ^{1}H, ^{19}F NMR chemical shift, the solution structure change such that the TFE molecules are inserted into the three dimensional water structure appears at $x_1 < 0.2$. It is reported from the small angle neutron diffraction and the Raman spectroscopic measurements that the solution at $x_1 = 0.15$ has the most heterogeneous structure with the largest cluster size. Therefore, in the process of the concentration change from the high x_1 to the lower one, there causes the large solution structure change such as the insertion of TFE molecules into the three dimensional water structure (inclusion compound composed from hydrates is formed), resulting in the change from endothermic process to the exothermic one by mixing.

The V_m^E values in this system are negative in the whole range of concentration in spite of the endothermic system except for the lower concentration region, as shown in Fig. 3. In general speaking, volume change by mixing is positive in endothermic system. However, aqueous solution does not belong to this classification and has abnormal property in volume. It is attributed to the three dimensional hydrogen bond structure of water, which is bulky in space. The bulky structure of water is broken by mixing with TFE and the volume may be reduced in solution. On the other hand, destruction of the three dimensional hydrogen bond structure is endothermic reaction and then, solution becomes unstable in energy. In $x_1 < 0.1$, the solution volume may be reduced by the formation of the inclusion compound, in addition of the construction due to the destruction of the three dimensional hydrogen bond structure. Therefore, V_m^E values show negative in the whole range of concentration.

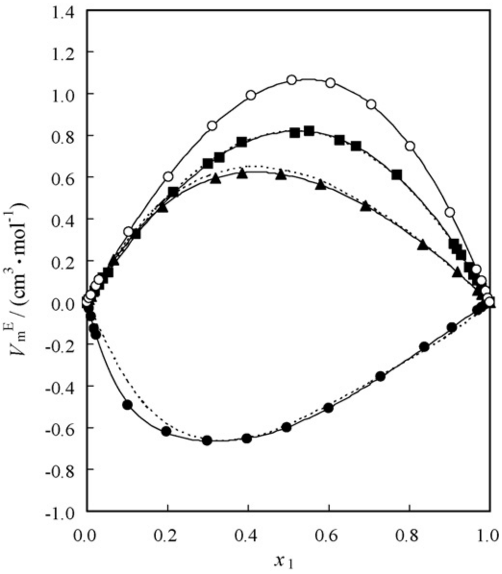

Fig. 3. Excess molar volumes (V_m^E) of the {2,2,2-trifluoroethanol(1) + water or alcohol(2)} systems at $T = 298.15$ K: (●) {$CF_3CH_2OH(1) + H_2O(2)$}; (▲) {$CF_3CH_2OH(1) + CH_3OH(2)$}; (■) {$CF_3CH_2OH(1) + CH_3CH_2OH(2)$}; (○) {$CF_3CH_2OH(1) + CH_3(CH_2)_2OH(2)$}; (- - -), literature values except for the 1-propanol system [14].

The other is the (TFE + alcohol) systems. In these systems, H_m^E values are negative, V_m^E values indicate positive. The negative H_m^E values in these systems depend on the formation of the stronger dissimilar intermolecular interaction in the solution than the like intermolecular interaction in the pure state of both component liquids. However, the volumes of these systems expand by mixing. As described previously, according to the radical distribution function which was obtained from the X-ray diffraction study, three TFE molecules are assembled in average by hydrogen bonding in the pure components [11] and it is known that alcohol is also self-associated as TFE. In this reason, both the component molecules form clusters partially in the pure state, respectively. The partially-formed clusters in the pure state are destroyed by mixing and the dissimilar intermolecular hydrogen bond between TEE and alcohols molecules is newly formed. However, the solution structure is more bulky than the structure formed by the clusters in the pure state, resulting in volume expansion. This peculiar behavior has been observed in other TFE solutions. For example, the (ethyl acetate + TFE) system is reported by Hu et al. [12].

3.2. Thermodynamics quantity at infinite dilution of i component

In order to discuss the contribution of excess molar thermodynamic properties to the component molecules and dependence of apparent molar solvation enthalpies, $\Delta_{solv}H_i$, on n_C, excess

Table 5

Partial molar excess enthalpies at infinite dilution ($H^{\mathrm{E},\infty}_{\mathrm{m},i}$), molar enthalpies of vaporization ($\Delta_{\mathrm{vap}}H_i$) and apparent molar enthalpies of salvation ($\Delta_{\mathrm{solv}}H_i$) of the i component liquids at $T = 298.15$ K

Component i		$H^{\mathrm{E},\infty}_{\mathrm{m},1}$ (kJ mol^{-1})	$\Delta_{\mathrm{vap}}H_1$ (kJ mol^{-1})	$\Delta_{\mathrm{solv}}H_1$ (kJ mol^{-1})	$H^{\mathrm{E},\infty}_{\mathrm{m},2}$ (kJ mol^{-1})	$\Delta_{\mathrm{vap}}H_1$ (kJ mol^{-1})	$\Delta_{\mathrm{solv}}H_2$ (kJ mol^{-1})
1	2						
CF_3CH_2OH	H_2O	−7.0	10.5[a]	−17.5	3.0	44.0[a]	−41.0
CF_3CH_2OH	CH_3OH	−4.1	10.5[a]	−14.6	−2.5	37.4[a]	−40.0
CF_3CH_2OH	CH_3CH_2OH	−5.2	10.5[a]	−15.7	−2.3	42.3[a]	−44.6
CF_3CH_2OH	$CH_3(CH_2)_2OH$	−2.4	10.5[a]	−13.0	−0.6	47.2[a]	−47.8

[a] Reference [13].

Table 6

Partial molar excess volumes at infinite dilution ($V^{\mathrm{E},\infty}_{\mathrm{m},i}$), partial molar volumes at infinite dilution ($V^{\infty}_{\mathrm{m},i}$) and molar volumes at pure state ($V^{\infty}_{\mathrm{m},i}$) of the i component liquids at $T = 298.15$ K

Component i		$V^{\mathrm{E},\infty}_{\mathrm{m},1}$ (cm^3 mol^{-1})	$V^{\infty}_{\mathrm{m},1}$ (cm^3 mol^{-1})	$V^{*}_{\mathrm{m},1}$ (cm^3 mol^{-1})	$V^{\mathrm{E},\infty}_{\mathrm{m},2}$ (cm^3 mol^{-1})	$V^{\infty}_{\mathrm{m},2}$ (cm^3 mol^{-1})	$V^{*}_{\mathrm{m},2}$ (cm^3 mol^{-1})
1	2						
CF_3CH_2OH	H_2O	−8.0	64.3	72.3	−1.4	16.6	18.1
$CF3CH_2OH$	CH_3OH	3.4	75.5	72.3	1.6	42.5	40.8
CF_3CH_2OH	CH_3CH_2OH	2.7	75.0	72.3	3.4	62.1	58.7
CF_3CH_2OH	$CH_3(CH_2)_2OH$	3.5	75.8	72.3	5.1	80.3	75.2

partial molar enthalpies ($H^{\mathrm{E}}_{\mathrm{m},i}$) and volumes ($V^{\mathrm{E}}_{\mathrm{m},i}$) and $\Delta_{\mathrm{solv}}H_i$ were calculated by the following Eq. (2):

$$X^{\mathrm{E}}_{\mathrm{m},i} = X^{\mathrm{E}}_{\mathrm{m}} - x_{\mathrm{j}}\left(\frac{\partial X^{\mathrm{E}}_{\mathrm{m}}}{\partial x_{\mathrm{j}}}\right)_{x_i} \qquad (2)$$

where $X^{\mathrm{E}}_{\mathrm{m},i}$ is $H^{\mathrm{E}}_{\mathrm{m},i}$ and $V^{\mathrm{E}}_{\mathrm{m},i}$. Excess partial molar enthalpies ($H^{\mathrm{E},\infty}_{\mathrm{m},i}$) and volumes ($V^{\mathrm{E},\infty}_{\mathrm{m},i}$) at an infinite dilution of the component i were calculated from the values of $H^{\mathrm{E}}_{\mathrm{m}}$ and $V^{\mathrm{E}}_{\mathrm{m}}$ in the dilute concentration regions of $x_{\mathrm{i}} < 0.15$, by using Eq. (3):

$$X^{\mathrm{E},\infty}_{\mathrm{m},i} = \lim_{(x_i \to 0)} X^{\mathrm{E}}_{\mathrm{m},i} \qquad (3)$$

$\Delta_{\mathrm{solv}}H_i$ were estimated from $H^{\mathrm{E},\infty}_{\mathrm{m},i}$ calculated by Eq. (4) and the literature values of the vaporization enthalpy of the component liquids, $\Delta_{\mathrm{vap}}H_i$:

$$\Delta_{\mathrm{solv}}H_i = H^{\mathrm{E},\infty}_{\mathrm{m},i} - \Delta_{\mathrm{vap}}H_i. \qquad (4)$$

The literature values of $\Delta_{\mathrm{vap}}H_i$ are given in the Table 5 [13]. Partial molar volumes at an infinite dilution of the component i, $V^{\infty}_{\mathrm{m},i}$ were estimated from $V^{\mathrm{E},\infty}_{\mathrm{m},i}$ and the molar volume of the pure component i, $V^{*}_{\mathrm{m},i}$, by using Eq. (5):

$$V^{\infty}_{\mathrm{m},i} = V^{*}_{\mathrm{m},i} + V^{\mathrm{E},\infty}_{\mathrm{m},i}. \qquad (5)$$

These values obtained are given in Tables 5 and 6, and are plotted against n_{C} in Figs. 4 and 5.

As shown in Table 5 and Fig. 4, the values of $H^{\mathrm{E},\infty}_{\mathrm{m},1}$ and $H^{\mathrm{E},\infty}_{\mathrm{m},2}$ are −7.0 to −2.4 kJ mol^{-1} and −2.5 to 3 kJ mol^{-1}, respectively. $\Delta_{\mathrm{vap}}H_2$ for water corresponds to destabilization energy due to the destruction of hydrogen bonding between the pure water molecules and on the other hand, $\Delta_{\mathrm{solv}}H_2$ corresponds to stabilization energy due to hydrogen bonding formed newly between TFE and water. $\Delta_{\mathrm{vap}}H_2$ is greater than $\Delta_{\mathrm{solv}}H_2$ in this system, and then, it is clear that H_2O molecule contribute to the essential destabilization of the solution.

Further, the dependence of $H^{\mathrm{E},\infty}_{\mathrm{m},1}$ on n_{C} is 1.2 kJ mol^{-1} $n_{\mathrm{C}}{}^{-1}$ at infinite dilution of THE and 1.0 kJ mol^{-1} $n_{\mathrm{C}}{}^{-1}$ at infinite dilution of alcohol in the (TFE + alcohol) systems, respectively. It is clear from these slopes of the lines, in this figure, that the thermally stabilization decreases with increase of n_{C} in the (TFE + alcohol) systems. The dependence of $\Delta_{\mathrm{solv}}H_i$ for TFE on n_{C} increases (1.2 kJ mol^{-1} $n_{\mathrm{C}}{}^{-1}$), and on the other hand, that

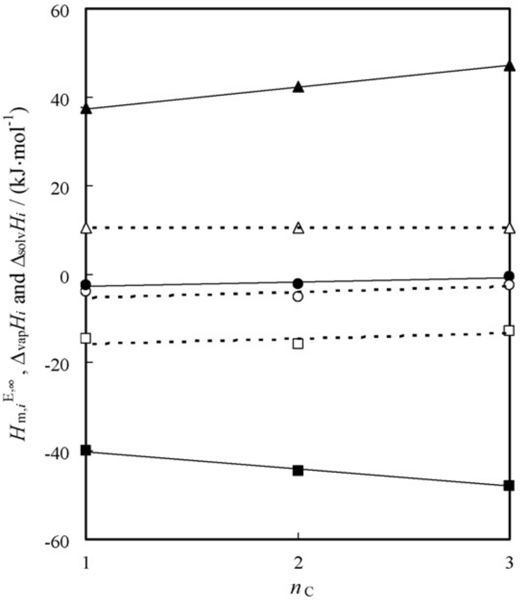

Fig. 4. Dependence of the enthalpies on the number of carbon atoms in the alcohol molecules (n_{C}): (●) and (○), partial molar excess enthalpies at infinite dilution of the alcohols and TFE ($H^{\mathrm{E},\infty}_{\mathrm{m},2}$ and $H^{\mathrm{E},\infty}_{\mathrm{m},1}$); (▲) and (△), molar vaporization enthalpies of the alcohols and TFE ($\Delta_{\mathrm{vap}}H_2$ and $\Delta_{\mathrm{vap}}H_1$); (■) and (□), apparent molar solvation enthalpies of the alcohols and TFE ($\Delta_{\mathrm{solv}}H_2$ and $\Delta_{\mathrm{solv}}H_1$).

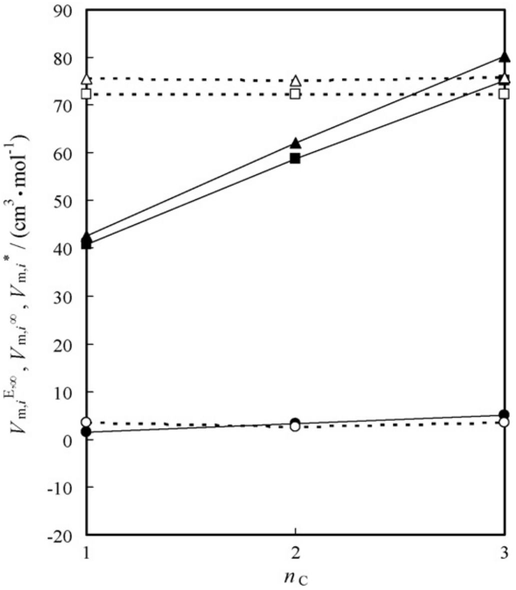

Fig. 5. Dependence of the volumes on the number of carbon atoms in the alcohol molecules (n_C): (●) and (○) partial molar excess volumes at infinite dilution of the alcohols and TFE ($V_{m,2}^{E,\infty}$ and $V_{m,1}^{E,\infty}$); (▲) and (△) partial molar volumes at infinite dilution of the alcohols and TFE ($V_{m,2}^{\infty}$ and $V_{m,1}^{\infty}$); (■) and (□) molar volumes of the pure alcohols and pure TFE ($V_{m,2}^{*}$ and $V_{m,1}^{*}$).

for the alcohol decreases (-3.9 kJ mol^{-1} $n_C{}^{-1}$). It means that the stabilization energy for TFE decreases, and on the other hand, that of alcohol increases with increase of n_C.

As shown in Table 6 and Fig. 5, $V_{m,1}^{E,\infty}$ is negative in the water system, and on the other hand, those of the alcohol systems are positive, respectively. This means that in the water system, the destruction of the three dimensional water structure contributes essentially to the contraction in volume at the infinite dilute region of both molecules, and in the alcohol systems, the values of $V_{m,1}^{E,\infty}$ and $V_{m,1}^{*}$ change almost in parallel and then, the values of $V_{m,1}^{E,\infty}$ are almost same at infinite dilution of HFE and are slightly positive change with increase of n_C at infinite dilution of alcohol.

4. Conclusion

Thermodynamic behavior due to the difference of the second component liquids has been studied for the four kinds of TFE solutions. The bulky water structure in the pure water is destroyed by mixing with TFE, resulting in the thermally destabilization besides the lower concentration range of TFE and the contraction in volume for the whole concentration range. On the other hand, in the (TFE + alcohol) systems, the like intermolecular hydrogen bond is partially destroyed and the stronger dissimilar intermolecular hydrogen bond is newly formed by mixing, and as the result, the solution is thermally stabilized and the thermal stabilization in the solution decreases with increase of n_C. However, the relation of the H_m^E and V_m^E in solution is inconsistent. It may be considered that both the component molecules associate by the strong like and dissimilar intermolecular hydrogen bonding in both the solution and the pure component liquids and the large structure change will be generated by mixing. The degree of the structure change will depend on the systems. The abnormal thermodynamic behavior will be resolved by discussion of the microstructure of the solution.

References

[1] T. Minamihounoki, T. Takigawa, K. Tamura, S. Murakami, J. Chem. Thermodynamics 33 (2001) 189–203.
[2] T. Takigawa, T. Minamihounoki, K. Tamura, J. Chem. Thermodynamics 34 (2002) 841–847.
[3] H. Ogawa, S. Karashima, T. Takigawa, S. Murakami, J. Chem. Thermodynamics 35 (2003) 763–774.
[4] T. Minamihonoki, H. Ogawa, S. Murakami, H. Nomura, J. Chem. Thermodynamics 37 (2005) 1186–1195.
[5] T. Minamihonoki, H. Ogawa, S. Murakami, H. Nomura, J. Chem. Thermodynamics 38 (2006) 1254–1259.
[6] H. Ogawa, M. Kojima, J. Therm. Anal. 38 (1992) 1873–1881.
[7] I. Fujihara, M. Kobayashi, S. Murakami, J. Chem. Thermodynamics 15 (1983) 1–6.
[8] S. Murakami, G.C. Benson, J. Chem. Thermodynamics 1 (1969) 559–572.
[9] S. Miyanaga, K. Tamura, S. Murakami, J. Chem. Thermodynamics 24 (1992) 1077–1086.
[10] D.B. Myers, R.L. Scott, Ind. Eng. Chem. 55 (7) (1963) 43–46.
[11] T. Takamuku, T. Kumai, R. Yoshida, T. Yamaguchi, T. Otomo, K. Kosugi, N. Nishi, The 27th Symposium on Solution Chemistry, vol. 108, Hatoyama, November 19, 2004, p. 14.
[12] J. Hu, K. Tamura, S. Murakami, Fluid Phase Equilib. 134 (1997) 239–253.
[13] J.A. Riddick, W.B. Bunger, T.K. Sakano, Techniques of Chemistry Organic Solvents, vol. 2, fourth ed., Wiley-Interscience, New York, 1986.
[14] M. Sassi, Z. Atik, J. Chem. Thermodynamics 35 (2003) 1161–1169.