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EXCESS HEAT CAPACITIES AT T=298.15 K AND EXCESS ENTHALPIES AT T=293.15 AND 298.15 K OF AQUEOUS SOLUTION OF 2-METHOXYETHANOL

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Abstract

Excess isobaric heat capacities of mixture (2-methoxyethanol+water) were measured at T=298.15 K and excess enthalpies at T=293.15 and 298.15 K. Excess enthalpies were extremely exothermic, up to -1290 J mol^{-1} at T=293.15 K and –1240 J mol^{-1} at T=298.15 K. Excess isobaric heat capacities were positive and very large, approximately 9 J K^{-1} mol^{-1} at the maximum. In contrast to the data reported by Page and coworkers, the excess heat capacity data were positive in the entire composition range and there was no change in their signs. Consistently, no crossing was found between the curves of excess enthalpies at T=298.15 and 293.15 K.

Keywords: aqueous solution of 2-methoxyethanol, excess enthalpy, excess isobaric heat capacity

Introduction

Excess isobaric heat capacities C_p^E obtained for aqueous 2-methoxyethanol (1-hydroxy-2-methoxy-ethane) solution at T=298.15 K and the excess enthalpies H^E at T=298.15 and 293.15 K were reported in this paper as a part of a series of thermodynamic studies on aqueous solutions of alkoxyethanols [1–3]. Page and his coworkers have reported C_p^E of aqueous 2-methoxyethanol solution and the other thermodynamic properties except for excess enthalpy H^E [4]. Their values of C_p^E change sign at the mole fraction, x, at 0.6 and for x>0.6, they were negative. Our previous data of for aqueous solutions of homologues, 2-ethoxyethanol and 2-isopropoxyethanol [1, 2], and the present data are positive. This means that the values of H^E at a higher temperature are always higher than those at a lower temperature, and both curves of H^E should not cross each other. This is indeed what

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Table 1 Excess heat capacities C_p^E of the mixture [x2-methoxyethanol + (1–x)water] at T=298.15 K

x	C_p^E/J K^{-1} mol^{-1}	x	C_p^E/J K^{-1} mol^{-1}	x	C_p^E/J K^{-1} mol^{-1}	x	C_p^E/J K^{-1} mol^{-1}
0.01000	1.30	0.08003	6.91	0.30007	7.69	0.65008	5.13
0.02001	2.43	0.09003	7.36	0.35008	7.35	0.70007	4.62
0.03001	3.42	0.10003	7.74	0.40008	6.97	0.75006	4.09
0.04001	4.34	0.11003	7.98	0.45009	6.65	0.80006	3.46
0.05002	5.10	0.15004	8.76	0.50009	6.31	0.85005	2.71
0.06002	5.77	0.25007	8.08	0.55009	5.93	0.90003	1.86
0.07002	6.57	0.27507	7.85	0.60008	5.55		

we found for the present 2-methoxyethanol solutions at 298.15 and 293.15 K and for aqueous 2-ethoxyethanol at 298.15 and 303.15 K [1].

Experimental

2-methoxyethanol (Aldrich, 99.8% anhydrous, water content <0.005%) was used without further purification. The molar purity was better than 0.9997 by g.l.c. (Shimadzu, GC-8A, column, TSG-1, which is sensitive for water in polar liquids). The density of 2-methoxyethanol was 0.960101 g cm^{-3} at 298.15 K and 0.964565 g cm^{-3} at 293.15 K which was measured by a vibrating-tube densimeter (Anton Paar, DMA602). The temperature was controlled within 1 mK. The details of measurements are given elsewhere [5]. Water was purified by passage through a Milli Q Labo (Millipore) osmosis membrane after the treatment with an ion-exchange resin. The conductance was $5.5\cdot10^{-6}$ S m^{-1}.

Excess isobaric heat capacities, C_p^E, were measured by a flow microcalorimeter constructed in our laboratory of Osaka City University for heat capacity measurements. The calorimeter was immersed in a water bath, the temperature of which was controlled within 0.3 mK. The precision was better than 0.03 J mol^{-1} K^{-1} . The details of measurement are reported elsewhere [6].

Excess enthalpies, H^E, were measured by a flow microcalorimeter (LKB 10700) immersed in a water bath controlled within 1 mK. The precision was better than 0.3%. Details are given elsewhere [7]. However, the calorimeter was operated with a reduced flow rate of 0.003 cm^3 s^{-1} from the normal rate of 0.005 cm^3 s^{-1}. This was to avoid a difficulty associated with micro bubble formation due to an otherwise intense local heating by the exothermic process of mixing.

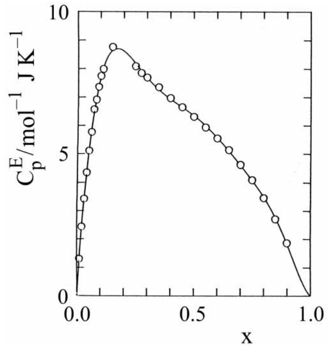

Fig. 1 Excess heat capacity of aqueous 2-methoxyethanol solution at 298.15 K

Table 2 Excess enthalpies H^E of the mixture [x2-methoxyethanol + (1–x)water] at T = 293.15 and 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}
			T=293.15 K				
0.02500	–354	0.15000	–1218	0.39997	–1145	0.79999	–384
0.05000	–641	0.20000	–1284	0.49997	–1071	0.89999	–174
0.07501	–860	0.25000	–1282	0.49998	–988		
0.10001	–1023	0.30000	–1254	0.59998	–802		
0.12500	–1138	0.34998	–1207	0.69999	–596		
			T=298.15 K				
0.02500	–343	0.15000	–1157	0.34999	–1176	0.69998	–592
0.05000	–617	0.17500	–1188	0.39998	–1101	0.79999	–364
0.07500	–828	0.19999	–1226	0.44999	–1038	0.89999	–175
0.10000	–966	0.24999	–1266	0.49997	–952		
0.12500	–1085	0.30000	–1204	0.59999	–797		

Table 3 Parameters of Eq. (1) of excess heat capacity and excess enthalpies of the mixture [x2-methoxyethanol + (1–x) water]

	A_1	A_2	A_3	A_4	A_5	A_6	A_7	s
				T=293.15 K				
H^E/J mol^{-1}	–3952	–3298	–2502	–3979	–2672			6
				T=298.15 K				
C_p^E/J K^{-1}mol^{-1}	25.38	12.90	13.16	30.94	74.70	20.31	–43.20	0.06
H^E/J mol^{-1}	–3851	–3125	–2347	–3789	–2432			11

Results and discussion

The value of isobaric heat capacity of water, C_p=75.30 JK^{-1} mol^{-1} , reported by Ginnings and Furukawa [8], was used as the reference. The C_p value of pure 2-methoxyethanol previously determined, 174.25 J K^{-1} mol^{-1} [9], was used to calculate C_p^E.

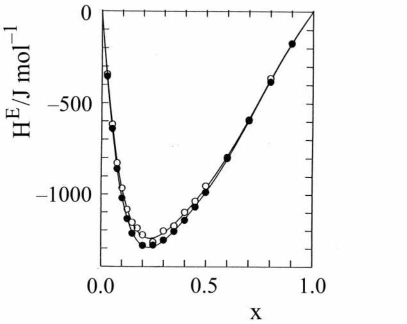

Fig. 2 Excess enthalpies of aqueous 2-methoxythanol solution, ● – at 293.15 K and ○ – at 298.15 K

The values of excess isobaric heat capacities C_p^E are given in Table 1 and plotted in Fig. 1. The values of excess enthalpies H^E obtained at T=293.15 and 298.15 K are given in Table 2 and plotted in Fig. 2. The curves in both figures are represented by the following Redlich–Kister equation [10],

$$C_p^E/(\mathrm{J\ K^{-1}\ mol^{-1}})\ \mathrm{or}\ H^E/(\mathrm{J\ mol^{-1}})=x(1-x)\sum A_i(1-2x)^{i-1}, \qquad (1)$$

where x is mole fraction of 2-methoxyethanol. Coefficients A_i are obtained by the least square method and given in Table 3.

The values of C_p^E are positive in the whole range of mole fraction, contrary to the findings by Page *et al.* [4], in which C_p^E values were negative in the region, x>0.6. The general x-dependence of C_p^E shown in Fig. 1 is similar to those of the homologue solutions, aqueous 2-ethoxyethanol and 2-isopropoxyethanol solutions [1–3]. The maximum value of C_p^E for aqueous 2-methoxyethanol, about 8.7 J mol^{-1} K^{-1} is hardly different from those of the other homologue solutions (about 9.3 J mol^{-1} K^{-1}), although the width of the hump becomes smaller as the alkyl group becomes larger; $0.05<x<0.4$ for methoxy-, $0.05<x<0.2$ for ethoxy- and $0.05<x<0.15$ for *iso*-propoxy-ethanol. This general similarity in the x-dependence and the maximum value itself (except for the width of the hump) suggests that the mixing state or scheme is similar to each other. Namely, as is discussed in detail for aqueous 2-alkoxyethanol [1–3], the model that two kinds of microphase clusters, one rich in H_2O and the other rich in alcohol, exist in equilibrium in solution seems appropriate for the present aqueous 2-methoxyethanol also.

The values of H^E are extremely exothermic for both temperatures, about –1290 J mol^{-1} for 293.15 K, and –1240 J mol^{-1} for 298.15 K at maximum, suggesting the hydrogen bond formed between unlike molecules is very stable. The curves are asymmetric and show a steep descent in the small x region, which could be due to en-

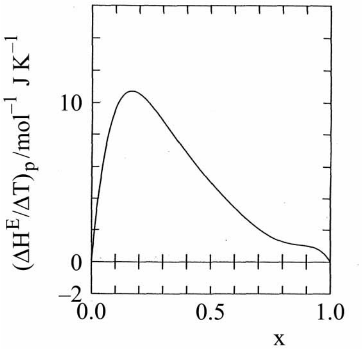

Fig. 3 Temperature dependence of excess enthalpy of aqueous 2-methoxyethanol solution: $\Delta H^E/\Delta T_p$/(J K^{-1} mol^{-1})=[H^E(298.15 K)–H^E(293.15 K)]/5 estimated from the Eq. (1) and the parameters in Table 3

hancement of the hydrogen bonds in the vicinity of 2-methoxyethanol molecules, that is, hydrophobic hydration.

The maximum value of H^E of the present system, –1240 J mol^{-1}, is the largest found for aqueous alkoxyethanol, followed by –1000 J mol^{-1} for 2-ethoxyethanol–H_2O and –810 J mol^{-1} for 2-isopropoxyethanol system [1, 2]. The bulkiness of the alkyl chain limits the hydrogen bonding, and the above order seems reasonable.

The dependence of H^E on temperature, $(\Delta H^E/\Delta T)_p$, is calculated by the Eq. (1) with the parameters in Table 3 and plotted in Fig. 3. The resulting values are positive in the whole concentration range, which is consistent with the directly measured C_p^E data shown in Fig. 1. We thus conclude that our C_p^E data presented here are more reliable.

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