Journal of Thermal Analysis and Calorimetry, Vol. 69 (2002) 841–848

ENTHALPIES OF DILUTION OF MONO-, DI- AND POLY-ALCOHOLS IN DILUTE AQUEOUS SOLUTIONS AT 298.15 K

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Abstract

The enthalpies of dilution of aqueous solutions of methanol, ethanol, l-propanol, 2-propanol, 1-butanol, l-pentanol, 1-hexanol, cyclohexanol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol and poly-alcohol(cyclohexaamylose) have been determined at high dilution as a function of the mole fraction of alcohol at 298.15 K, by a rocking twin-microcalorimeter of the heat-conduction type.

A smoothing equation of the enthalpies of dilution against the mole fractions of alcohols are given. The graphical comparison of experimental results with their smoothed values or literature ones, taking into account the dependence of the mole fractions, are also presented.

It has been found for the aqueous solutions of shorter *n*-alcohols than hexanol that at very high dilution, exothermic values of molar enthalpies of dilution from a definite mole fraction of alcohols to infinite dilution with the change of mole fraction is proportional to carbon number of *n*-alcohols. The molar enthalpies of infinite dilution of aqueous butanediol isomers and 1-hexanol were very large. Molar enthalpies of infinite dilution of aqueous poly-alcohol (cyclohexaamylose) were endothermic.

Keywords: alcohol, enthalpy of dilution, infinite dilution

Introduction

The enthalpies of solution of alcohols in water have been reported by many authors [1–4]. In the range of low concentration, however, no measurement is accurate enough to estimate the enthalpy of dilution.

In this paper we present the concentration dependence of enthalpies of dilution of dilute aqueous solutions of several alcohols at 298.15 K. The alcohols measured are methanol, ethanol, 1-propanol, 1-butanol, l-pentanol, 1-hexanol, 2-propanol, 1,3-butanediol(BD), 1,4-BD, 2,3-BD, cyclohexanol and cyclohexaamylose.

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1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Methanol and ethanol (Kishida Chemical Co., S.R. grade for chromatography), 1-propanol (Kishida Chemical Co., G.R. grade) and 1-butanol (Merck, Uvasol, G.R. grade), were rectified through a 1 m column packed with Helipac packing. 2-Propanol (S.R. grade for chromatography) and 1-pentanol (Kishida Chemical Co., G.R. grade) were refluxed over calcium oxide and then fractionally distilled through a 0.7 m column packed with Dixon packing. Cyclohexanol (Tokyo Kasei Co., G.R. grade) was dried with calcium oxide, and rectified twice under reduced pressure through a spinning-band column. *dl*-1,3-BD and 1,4-BD (Tokyo Kasei Co., G.R. grade) was dried with K_2CO_3 for two months and fractionally distilled under reduced pressure through a 1 m Helipack column. They were fractionally distilled further through a spinning-band column at high reflux ratios by passing dry N_2 gas under the reduced pressure of 0.4 kPa, after reflux over a total of 24 h. *meso*-2,3-BD (Tokyo Kasei Co.) were first treated by repeated fractional recrystallisation. Next it was distilled fractionally under reduced pressure of 1.3 kPa N_2 gas through a spinning-band column.The g.l.c. results by a (Hitachi Model 163) FID type gas chromatograph with a 3 m column (3 mm) of Thermon-l000 (10 %) and H_3PO_4 (1%) on Chromosorb W (8Q to 100 mesh) supplied by Wako Pure Chemical md., Ltd. showed that the purities of the alcohols except water were 99.98 for methanol, 99.95 for ethanol and 1-propanol, 99.99 for 2-propanol, 99.90 for 1-butanol, 99.84 for 1-pentanol, 99.70 for 1-hexanol, 99.70 and 99.55 for cyclohexanol by mass per cent. The water contents analyzed by Karl Fischer titration were 0.0281 for methanol, 0.14 for ethanol and l-propanol, 0.079 for 2-propanol, 0.01 for 1-butanol, 0.30 for 1-pentanol, 0.08 for 1-hexanol, and 0.024 for cyclohexanol by mass per cent. Details of the careful purification procedures for the cyclohexaamylose [5], water [6] and mercury [7] were described earlier. The mercury used was freshly distilled in vacuo before each measurement. All solutions were prepared by mass. The aqueous butanediol solutions were stirred for 10 min by a magnetic stirrer, and then vigorously agitated for ca. 15 min with a weak sonic washer (Taga Electric Co., Ltd., model UW-25, output frequency: 38 kHz, 45 W) at room temperature before charged into mixing vessels. These procedures ensures that the mixtures easily reach to equilibrium during the holding time of the measurement. Because Takagi *et al.* had found that the mixtures of water and 1,4-butanediol required up to 15 h to reach equilibria at room temperatures [8]. This information was presented at the informal meeting held at the 7th IUPAC Conference on Chemical Thermodynamics, London, 1982, and at the other symposia [9–11].

A rocking twin-microcalorimeter of the heat-conduction type was used for the measurements. The construction of the calorimeter and its operation have been described elsewhere [7]. In the present case, circulating water was controlled at 298.15 K within ±0.0005 K in a room thermostatted within ±0.1 to ±0.01 K. The distilled mercury was not shaken with the solvent (water). In each run about 0.75 g of aqueous alcoholic solution and about 3.0 g of water were loaded. Usually, about 24 h were required for thermal equilibration. Thermal *e.m.f.* was recorded with selected ranges from 1 to 30 μV full scale. The rocking was carried out ten times in each run.

Results and discussion

The experimental results of enthalpies of dilution $\Delta_{\mathrm{dil}}H_{\mathrm{m}}(m_{\mathrm{i}}\rightarrow m_{\mathrm{f}})$ of the alcohols with water at high dilution are tabulated in Table 1. Enthalpies of dilution of alcohols in water are exothermic, except for cyclohexaamylose+water system. To show the dependence of the observed enthalpy of dilution on the mole fraction of the alcohol, x, we assumed that the enthalpy of mixing of water (l) and alcohol (2) is expressed by the equation:

$$H_{\mathrm{m}}^{\mathrm{E}}=x(1-x)\sum_{\mathrm{i=0}}^{\mathrm{k-i}}A_{\mathrm{i}}(1-2x)^{\mathrm{i}} \qquad (1)$$

As the excess enthalpy per mole of alcohol is given by $H_{\mathrm{m}}^{\mathrm{E}}/x$, the enthalpy of dilution of an initial solution to a final solution per mole of alcohol is obtained through Eqs (2)–(3) and

$$\Delta_{\mathrm{dil}}H_{\mathrm{m}}=\frac{H_{\mathrm{m}}^{\mathrm{E}}(x_{\mathrm{f}})}{x_{\mathrm{f}}}-\frac{H_{\mathrm{m}}^{\mathrm{E}}(x_{\mathrm{i}})}{x_{\mathrm{i}}} \qquad (2)$$

$$=A_0(x_{\mathrm{i}}-x_{\mathrm{f}})+A_1[3(x_{\mathrm{i}}-x_{\mathrm{f}})-2(x_{\mathrm{i}}^2-x_{\mathrm{f}}^2)]+A_2[5(x_{\mathrm{i}}-x_{\mathrm{f}})-8(x_{\mathrm{i}}^2-x_{\mathrm{f}}^2)+4(x_{\mathrm{i}}^3-x_{\mathrm{f}}^3)]+\ldots \qquad (3)$$

where the first and the second terms in the right-hand side of Eq. (2) are the enthalpies of mixing of the aqueous solutions whose mole fractions are x_{f} and x_{i} respectively. The subscript letters *i* and *f* denote respectively initial and final which specify the quantities before and after the dilution.

The primary experimental results of the enthalpy of dilution $\Delta_{\mathrm{dil}}H$ shown in Table 1 are equal to $n_2\Delta_{\mathrm{dil}}H_{\mathrm{m}}$. For the present results use of only the first two coefficients ensures an adequate representation. Thus, Eq. (3) is changed to

$$\Delta_{\mathrm{dil}}H=a(x_{\mathrm{i}}-x_{\mathrm{f}})n_2+b(x_{\mathrm{i}}^2-x_{\mathrm{f}}^2)n_2+\ldots \qquad (4)$$

where

$$a=A_0+3A_1 \text{ and } b=-2A_1 \qquad (5)$$

The values of the coefficients a and b obtained by a least squares method are summarized in Table 2, together with the estimated deviations s_{f} for Eq. (4)

$$s_{\mathrm{f}}=\left[\frac{\sum\{\Delta_{\mathrm{dil}}H(\mathrm{obs.})-\Delta_{\mathrm{dil}}H(\mathrm{calc.})\}^2}{n-k}\right]^{1/2} \qquad (6)$$

For comparison of the experimental results with the calculated values and/or with literature values, taking account of the concentration dependence, the enthalpies of dilution per mole of alcohol to infinite dilution were estimated by putting $x_{\mathrm{f}}=0$ as shown in Fig. 1. In the Eq. (7), the subscripts are omitted for simplicity.

$$\Delta_{\mathrm{dil}}^{\infty}H_{\mathrm{m}}=ax+bx^2 \qquad (7)$$

Table 1 Enthalpies of dilution of alcohols in water at 298.15 K

m_i/ mol kg^{-1}	m_f/ mol kg^{-1}	$-\Delta_{dil}H$/ J mol^{-1}	m_i/ mol kg^{-1}	m_f/ mol kg^{-1}	$-\Delta_{dil}H$/ J mol^{-1}
	Methanol			1-Pentanol	
0.5343	0.1114	93.59	0.1512	0.03043	336.7
0.3938	0.0789	75.7	0.1111	0.02245	208.7
0.3136	0.0645	71.99	0.08756	0.01951	155.1
0.2476	0.0484	32.54	0.07348	0.01620	91.6
0.0863	0.0169	7.97	0.03746	0.00834	28.6
	Ethanol		0.02309	0.00344	75.8
0.7249	0.3554	152.9		1-Hexanol	
0.4927	0.2466	87.30	0.03971	0.008158	388.9
0.4564	0.2245	92.99	0.03424	0.00712	343.3
0.4101	0.2012	81.92	0.03248	0.006807	221.3
0.3760	0.1812	67.73	0.02404	0.00498	238.8
0.2162	0.1093	42.80	0.01975	0.004346	181.3
	1-Propanol		0.01975	0.004346	78.91
0.8310	0.1618	504.2		2-Propanol	
0.6441	0.1232	385.2	0.8499	0.1639	402.2
0.5508	0.1075	319.9	0.5851	0.1169	230.9
0.3888	0.0794	186.6	0.4528	0.09347	163.9
0.3563	0.0735	186.3	0.3753	0.07498	143.2
0.2828	0.0562	157.1	0.2939	0.05979	115.1
0.2390	0.0482	112.3	0.2371	0.04717	73.4
0.1618	0.0343	70.83	0.04717	0.00979	18.76
	1-Butanol			1,4-Butanediol	
0.2411	0.04313	197.2	0.1568	0.03000	155.3
0.1979	0.03664	168.8	0.1221	0.02367	126.7
0.1315	0.02591	78.44	0.1163	0.02178	151.7
0.1478	0.02608	116.6	0.1077	0.02004	117.2
0.06048	0.01131	64.36	0.1036	0.02019	117.2
	1,3-Butanediol		0.1019	0.01907	128.6
0.1547	0.02887	232.4	0.03613	0.00704	38.55
0.1335	0.02542	232.4			
0.1275	0.02423	224.1			
0.1083	0.02163	183.6			
0.09558	0.01931	149.4			

Table 1 Continued

m_i/ mol kg^{-1}	m_f/ mol kg^{-1}	$-\Delta_{dil}H$/ J mol^{-1}	m_i/ mol kg^{-1}	m_f/ mol kg^{-1}	$-\Delta_{dil}H$/ J mol^{-1}
	2,3-Butanediol			Cyclohexaamylose	
0.09252	0.04313	203.8	0.08143	0.05858	–121.8
0.08834	0.03664	228.7	0.0541	0.02625	–121.7
0.07571	0.02591	169.1	0.04451	0.02188	–105.8
0.06519	0.02608	139.9	0.04451	0.02069	–110.4
0.04966	0.01131	117.0	0.04451	0.02025	–102.6
	Cyclohexanol		0.03145	0.0154	–56.02
0.1099	0.02392	159.5			
0.1099	0.02081	168.8			
0.08884	0.01719	120.2			
0.07604	0.01585	137.2			
0.05568	0.01115	114.1			

Table 2 Parameters *a* and *b* and calculated standard deviations of the fit s_f for least-squares representation by equation of $\Delta_{dil}H_m$ for dilute aqueous solutions of alcohols at 298.15 K

Alcohols	*a*/kJ mol^{-1}	*b*/kJ mol^{-1}	s_f/mJ
Methanol	–15.69	275.7	3.0
Ethanol	–17.72	–293.3	2.4
1-Propanol	–33.33	–537.9	4.0
1-Butanol	–44.28	–2440	2.0
1-Pentanol	–57.43	–30090	1.0
1-Hexanol	–623.7	23220	1.6
2-Propanol	–15.24	–967.6	2.4
1,3-Butanediol	–114.6	1460	2.4
1,4-Butanediol	–107.0	11550	0.96
2,3-Butanediol	–151.3	–5070	1.0
Cyclohexanol	–105.6	–12.83	1.3
Cyclohexaamylose	193.6	40820	0.34

Once the explicit expression of the Eq. (7) is obtained, the enthalpy of dilution per mole of alcohol from x_i to x_f may be calculated through the equation:

$$\Delta_{dil}H_m = \Delta_{dil}^{\infty}H_m(x_i) - \Delta_{dil}^{\infty}H_m(x_f) \qquad (8)$$

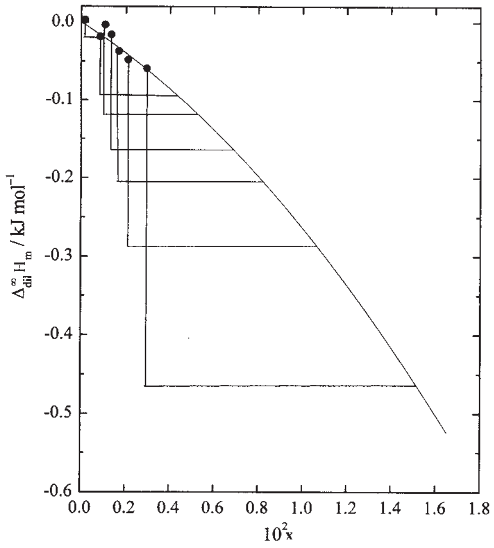

Fig. 1 Molar enthalpies of dilution of dilute aqueous 2-propanol solutions to infinite dilution at 298.15 K plotted *vs.* mole fraction x, where the curve represents smoothed values calculated

Figure 1 shows the comparison of the smoothed molar enthalpies of dilution with the experimental values for 2-propanol. Finally, we found for the n-alcohols measured that the initial slopes of the curves of $\Delta^{\infty}_{dil}H_m$ plotted *vs.* mole fractions of alcohols at infinite dilution in Fig. 2 are proportional, to the number of carbon atoms n of alcohols, the increment per one $-CH_3-$ or $-CH_2-$ is –11.0 kJ mol^{-1} as given in Eq. (9).

$$\left(\frac{d\Delta^{\infty}_{dil}H_m}{dx}\right)_{x=0}=-11.0n\text{ kJ mol}^{-1} \tag{9}$$

In the case of cyclohexanol, however, it is 2.3 times larger than an expected value of corresponding n-alcohol. It was also found that 1-hexanol stabilizes greatly in water, showing the value of –624 kJ mol^{-1} and butanediols stabilize larger in water than n-alcohol. The hydrophobic hydration is influenced by the hydrophilic group, which is in contact with the hydrophobic group. Since the size effect will show up if a solute molecule moreover becomes larger than 1-pentanol, it is considered that the additivity of methylene groups do not hold. To elucidate interactions in dilute aqueous solutions, thermodynamic interaction parameters were determined. The molar enthalpy of dilution $\Delta_{dil}H_m$ is identical to the change in the excess enthalpy following a dilution process the molality will change from an initial solution to a final solution.

$$\Delta_{dil}H_m(m_i\to m_f)=H^E_m(m_f)-H^E_m(m_i)=h_{xx}(m_f-m_i)+h_{xxx}(m_f^2-m_i^2)+\dots \tag{10}$$

Equation (11) were obtained from Eq. (10)

$$\frac{\Delta_{dil}H_m(m_i\to m_f)}{m_f-m_i}=h_{xx}+h_{xxx}(m_i+m_f) \tag{11}$$

Table 3 Enthalpy pair and triplet interactions coefficients for aqueous binary solutions of some alcohols at 298.15 K

Alcohol	h_{xx} / J mol^{-2} kg	H_{xxx} / J mol^{-3} kg^{2}	max m_i/ mol kg^{-1}	min m_f/ mol kg^{-1}	Ref.
Methanol	150	283	0.5343	0.01690	This work
	218	12	1.73	0.090	[1]
Ethanol	247	147	0.7249	0.07287	This work
	248	76	1.04	0.099	[1]
1-Propanol	542	237	0.8310	0.03429	This work
	540	213	0.91	0.077	[1]
1-Butanol	1421	517	0.2411	0.01131	This work
	1225		0.82	0.058	[1]
1-Pentanol	2267		0.1512	0.003442	This work
1-Hexanol	8451		0.03424	0.003111	This work
2-Propanol	429	115	0.8499	0.009793	This work
1,3-Butanediol	1353	14	0.1547	0.01828	This work
	750		0.8971	0.1263	[2]
1,4-Butanediol	2078	–8	0.1568	0.007044	This work
	787		1.202	0.2094	[2]
2,3-Butanediol	2766	51	0.09252	0.00998	This work
	837		2.470	0.0549	[3]
Cyclohexanol	3158	1192	0.1099	0.01115	This work
	1495		0.2793	0.02941	[4]
Cyclohexaamylose	–3256		0.08143	0.01540	This work
	–3920		0.1664	0.0270	[12]

The above results are summarized in comparison with other papers [1–4, 12] in Table 3. It turns out that the measured value in low concentration was obtained compared with other authors. The present results for methanol, ethanol, 1-propanol and 1-butanol agreed well with those reported by other authors. The pair coefficients of butanediol isomers were, however, larger than those of other authors. It is considered that the aging effect of butanediol + water system is also related to this disagreement. It seems that the hydrophobic interaction is in order of 2,3->1,4-> 1,3-butanediols. To make clear the difference of interaction of the water molecules and the BD isomers, the water accessible surface areas were calculated by computer modeling [13]. With a probe sphere, of radius 0.14 nm (water molecule), the water accessible surface areas were defined as the surface mapped out by the centre of the probe as if it were rolled around the van der Waals surface of the solute molecule. The calculated water accessible surface areas (nm^2) are as follows: 1,3-BD=2.58, 1,4-BD=2.56, 2,3-BD=2.50. The above result showed that hydrophobicity of 2,3-BD is large. Moreover, 2,3-BD cannot easily form the intramolecular hydrogen bond, different from

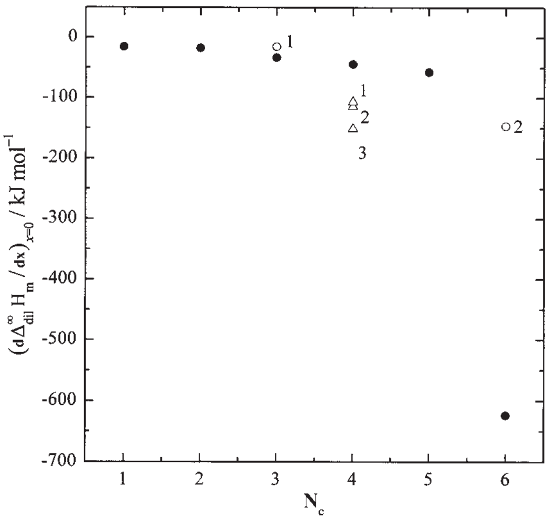

Fig. 2 Limiting slopes of the enthalpy of dilution of alcohols with respect to the mole fraction at infinite dilution: (●), *n*-alkane-1-ol; o1, 2-propanol; o2, cyclohexanol; Δ1, 1,4-butanediol ; Δ2, 1,3-butanediol; Δ3, 2,3-butanediol

1,3-BD and 1,4-BD. Therefore, it is thought that the degree of the intermolecular hydrogen bond and the hydrophobic interaction are large.

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