Journal of Thermal Analysis, Vol. 38 (1992) 1883-1890

ON A LARGE DIFFERENCE IN ENTHALPIC VIRIAL COEFFICIENT AMONG SOME ISOMERS OF ALKOXYALCOHOL

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Molar excess enthalpies for aqueous solutions of 3-methoxy-1-butanol (3–MB) and 1-methoxy-2-butanol (M–2B) have been measured at 298.15 K over the whole concentration range with a flow microcalorimeter. From the experimental data, we evaluated the enthalpic interaction parameter h_{xx} and obtained the following order:

$$h_{xx}(3\text{–MB}) \gg h_{xx}(\text{M–2B})$$

This large difference in h_{xx} provided us some new factors which might have the influence on hydrophobic interaction: 'fundamental frame', 'hydroxyl group', and 'ether oxygen atom'.

Keywords: flow microcalorimeter, hydrophobic interaction, molar excess enthalpies

Introduction

Hydrophobic interaction is much concerned with the stability of particular biopolymer conformations in aqueous solutions and also the stability of amphiphilic molecules as micelles. It has already been shown in aqueous solutions of alkylalcohol [1, 2, 3] and alkoxyalcohol [4] that hydrophobic interaction increases consistently with 'the total number of carbon atoms in the solute'. It is also known that 'the degree of alkyl group branching' reduces hydrophobic interaction. This is confirmed by the comparison [3] between 1-butanol (1-Bu) and t-butanol (t–Bu) and that [4] between 2-butoxyethanol (BE) and 2-t-butoxyethanol (t–BE).

In this paper, we report the molar excess enthalpies H^E for aqueous solutions of 3-methoxy-1-butanol (3–MB) and 1-methoxy-2-butanol (M–2B). From these measured data, we evaluated the excess partial molar enthalpies at the infinite

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dilution $H^{E,\infty}$, the solvation enthalpies $\Delta_{solv}H_m^{\infty}$, and the enthalpic pair interaction parameters h_{xx}. On the basis of these data, we discussed several factors contributing to the hydrophobic interaction.

Moreover, in order to confirm the relation between the hydroxyl group site and hydrophobic interaction, we discussed again the thermodynamic quantities for aqueous solutions of 1-propanol (1–Pr) and 2-propanol (2–Pr).

Experimental

We have measured the excess molar enthalpies for aqueous solutions of 3–MB, M–2B, 1–Pr, and 2–Pr at 25±0.01°C over the whole concentration range with an LKB 2107–121 flow microcalorimeter. These alcohols (guaranteed reagents from Tokyo Kasei Co. or Nacalai Tesque) were purified by distillation under reduced pressure with a column of 30 theoretical plates. Water was deionized and fractionally distilled. They were degassed by freezing in liquid nitrogen and melting under vacuum immediately before use. In the water rich region (mole fraction of alcohol $X_{solute}<0.03$), we measured the enthalpy changes in mixing with diluted solutions and indirectly computed the molar excess enthalpies; this is due to the flow rate limit of the microperpex pump (LKB2132) and reaction cell in the calorimeter. When the concentrations were required, we measured the densities of solutions with a bicapillary-type pycnometer (60 ml); as the density of water, we used the literature value, 0.997046 g/cm^{-3}.

Results and discussion

We summarized the H^E values for aqueous solutions of 3–MB and M–2B obtained at 298.15 K in Tables 1 and 2, respectively, and plotted them as a function of X_{Solute} in Fig. 1. We measured most of them in the water rich region and gave the data in the range $X_{Solute}<0.2$ in Fig. 2. In these figures, we also included that for 2-i-propoxyethanol (i–PE) obtained previously [4]. The H^E values for aqueous solutions of these alcohols are negative over the whole concentration range and the absolute values are substantially large.

According to the McMillan–Mayer theory, $H^E(m_x)$ can be expanded by the power series of molality m_x; hence, h_{xx} and $H^{E,\infty}$ can be easily estimated from the slope and the intercept of $H^E(m_x) / m_x$ *vs.* m_x plot in the low concentration range, where we need not consider third and higher order terms in the virial expansion equation [5]. The solvation enthalpy $\Delta_{solv}H_m^{\infty}$, i.e., a measure of hydrophobic hydration at infinite dilution, is evaluated from the following equation with $H^{E,\infty}$ and the enthalpy of vaporization for the solute ΔH_v:

$$\Delta_{solv}H_m^{\infty} = H^{E,\infty} - \Delta H_v \qquad (1)$$

Table 1 Molar excess enthalpies for 3-methoxy-1-butanol-water systems at 298.15 K

$X_{3\text{-MB}}$	H^{E} / J·mol^{-1}	$X_{3\text{-MB}}$	H^{E} / J·mol^{-1}
0.0004	–7.07	0.0344	–456.4
0.0005	–7.79	0.0359	–469.2
0.0008	–13.39	0.0374	–486.4
0.0011	–19.15	0.0394	–515.4
0.0014	–24.41	0.0416	–536.6
0.0017	–28.98	0.0446	–539.0
0.0021	–36.01	0.0580	–641.2
0.0027	–45.22	0.0682	–730.7
0.0028	–48.17	0.0771	–769.9
0.0034	–56.40	0.0888	–836.6
0.0042	–68.91	0.1047	–922.6
0.0048	–79.69	0.1232	–982.2
0.0054	–87.82	0.1351	–1030.0
0.0058	–94.51	0.1498	–1090.3
0.0065	–106.0	0.1898	–1178.5
0.0072	–115.8	0.2575	–1209.8
0.0084	–133.4	0.3447	–1245.0
0.0089	–141.4	0.3683	–1254.2
0.0095	–149.3	0.4380	–1197.0
0.0105	–164.6	0.4665	–1166.4
0.0122	–186.9	0.5383	–1096.9
0.0139	–210.4	0.5549	–1078.6
0.0170	–253.7	0.6058	–984.1
0.0217	–330.3	0.6362	–921.0
0.0286	–399.8	0.6975	–857.6
0.0298	–414.8	0.7777	–650.0
0.0324	–435.6	0.8218	–543.1
0.0339	–439.6		

We gave the values for h_{xx}, $H^{E,\infty}$, and $\Delta_{solv}H_m^{\infty}$ together with those for ΔH_v [6, 7] in Table 3. In Fig. 3, we plotted the h_{xx} values against the total number of carbon atoms in the solute molecule. This figure also includes the results [3] for 2-butanol (2–Bu), i-butanol (i–Bu), i-pentanol (i–Pe), and our previous studies [4].

Table 3 shows that 1–Pr has the nearly same $\Delta_{solv}H_m^{\infty}$ value as 2–Pr; this suggests that there is a little difference between the each hydration state surrounding the solute when the alcohol exists in the non-associated state in solution. On the other hand, there is a difference in the h_{xx} value: h_{xx}(1–Pr)>h_{xx}(2–Pr). It is con-

Table 2 Molar excess enthalpies for 1-methoxy-2-butanol-water systems at 298.15 K

$x_{\mathrm{M-2B}}$	H^{E} / J·mol^{-1}	$x_{\mathrm{M-2B}}$	H^{E} / J·mol^{-1}
0.0007	−13.84	0.0266	−438.7
0.0010	−19.85	0.0282	−458.8
0.0016	−30.34	0.0303	−474.3
0.0020	−37.94	0.0457	−635.9
0.0025	−48.28	0.0538	−676.9
0.0026	−50.65	0.0610	−733.1
0.0031	−60.65	0.0704	−775.0
0.0039	−74.91	0.0834	−822.6
0.0056	−108.1	0.1200	−902.6
0.0060	−115.5	0.1539	−926.9
0.0068	−129.7	0.2143	−927.6
0.0073	−138.4	0.2904	−870.2
0.0082	−155.5	0.3125	−847.6
0.0086	−162.1	0.3788	−792.1
0.0094	−185.7	0.4055	−756.1
0.0105	−196.0	0.4383	−715.5
0.0113	−202.1	0.4762	−680.4
0.0117	−211.9	0.4924	−658.7
0.0121	−221.6	0.5393	−599.7
0.0158	−282.9	0.5488	−592.4
0.0210	−358.8	0.5767	−551.7
0.0219	−371.3	0.6452	−459.4
0.0229	−396.3	0.6611	−436.2
0.0240	−407.3	0.7007	−383.8
0.0253	−417.0	0.7318	−340.2
0.0266	−431.3	0.7568	−318.7

sidered that the difference in the hydroxyl group site between the two molecules causes such a significant difference in h_{xx} value, that is, in the degree of hydrophobic interaction. The hydration shell around the hydroxyl group exists closer to that around the propyl one in 2–Pr than in 1–Pr. Hence, 2–Pr tends to associate propyl groups each other and to decrease the hydrophobic hydration shell, which causes the partial destruction of the hydration shell surrounding the hydroxyl group. In order to avoid this disadvantageous effect, the hydroxyl group in 2–Pr is considered to disturb the hydrophobic interaction; as a result, 2–Pr has a smaller h_{xx} value than 1–Pr.

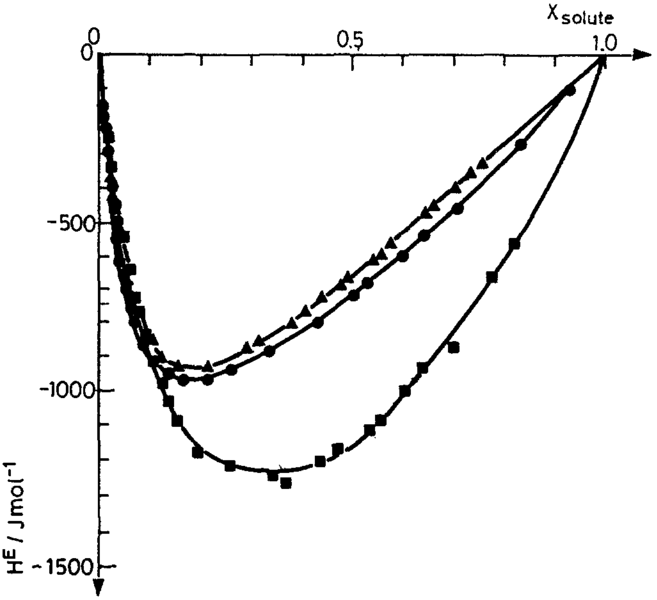

Fig. 1 Molar excess enthalpies for (1–X)H_2O + X alkoxyalcohol at 298.15 K: ■; 3–MB, ●; i–PE, ▲; M–2B

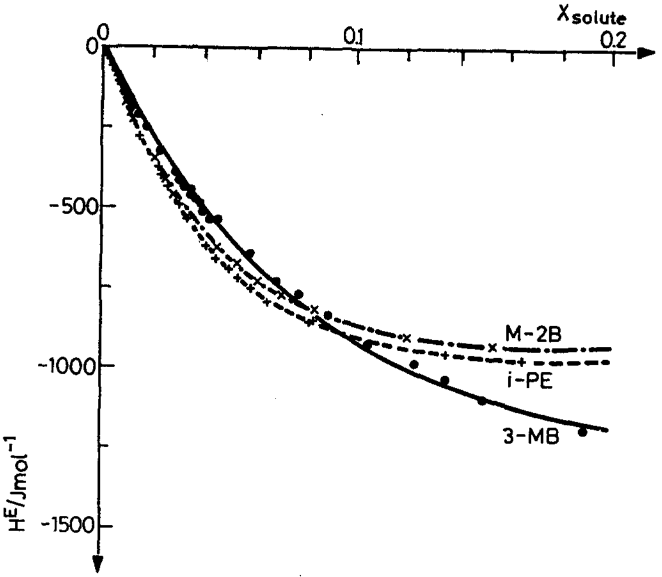

Fig. 2 Molar excess enthalpies for (1–X)H_2O + X alkoxyalcohol at 298.15 K: ●; 3–MB, +; i–PE, x; M–2B

Having the above consideration in mind, we compare M–2B with 3–MB. Table 3 and Fig. 3 show that M–2B has a far smaller h_{xx} value than 3–MB. In order to explain this relative magnitude in h_{xx}, we use the following two conjectures based on the difference between 'the fundamental frame' in these molecules, which mainly dominates the hydrophobic interaction.

Table 3 Enthalpy pair interaction parameters, partial molar excess enthalpies at infinite dilution, enthalpies of vaporization and solvation enthalpies for some alcohol–water systems at 298.15 K

	h_{xx} / kJ·mol^{-2} kg	$H^{E,\infty}$ / kJ·mol^{-1}	ΔH_v / kJ·mol^{-1}	$\Delta_{solv}H_m^{\infty}$/ kJ·mol^{-1}
1–PrOH	0.688	-9.74	47.32$^{a)}$	-57.06
2–PrOH	0.444	-12.52	45.23$^{a)}$	-57.75
3–MB	2.40	-17.09	53.8$^{c)}$ (b.p. 158°C)	-70.89
i–PE	1.90$^{d)}$	-20.01$^{d)}$	50.12$^{b)}$ (b.p.141°C)	-70.13
M–2B	1.69	-19.66	48.2$^{c)}$ (b.p. 135°C)	-67.86

$^{a)}$ Ref.6, $^{b)}$ Ref.7, $^{c)}$ the values obtained by interpolation based on Ref.7, $^{d)}$ Ref.4.

In the first place, we adopt 'butanol' as 'the fundamental frame'; the hydrophobic interaction in M–2B is mainly described with '2-butanol (2–Bu)', while that in 3–MB with '1-butanol (1–Bu)'. As mentioned above, secondary alcohol has the hydrophobic interaction distinctly less than primary alcohol, hence there is a difference in the h_{xx} value: h_{xx}(3–MB) > h_{xx}(M–2B). However, h_{xx} values [3] for 1–Bu and 2–Bu are 1.17 and 0.916, respectively. Such a small difference in h_{xx} between the two butanols is insufficient to explain the large difference between 3–MB and M–2B. In order to explain this order

$$h_{xx}(3\text{–MB}) \gg h_{xx}(\text{M–2B}) \qquad (2)$$

quantitatively, we have to notice ether oxygen atom (–O–) and compare the degrees to which the hydrophilic site can contact with the surrounding water. It is considered that the ether oxygen can contact with the surrounding water more easily in M–2B than in 3–MB, because the former is not so crowded around the ether oxygen with alkyl groups as the latter.

Supposing that ether oxygen atom breaks water structure [8, 9], we can expect that M–2B breaks the water structure surrounding the ether oxygen atom more appreciably than 3–MB.

This is consistent with the fact that M–2B has a smaller absolute value of $\Delta_{solv}H_m^{\infty}$ than 3–MB as seen in Table 3. As a result, the hydrophobic interaction is considered to be extraordinary reduced in M–2B.

In another explanation, we take into account 2-i-propoxyethanol(i–PE) [4] which has the same total number of carbon atoms (n = 5) as 3–MB and M–2B. We begin with the comparison between 3–MB and i–PE. Table 3 shows that 3–MB

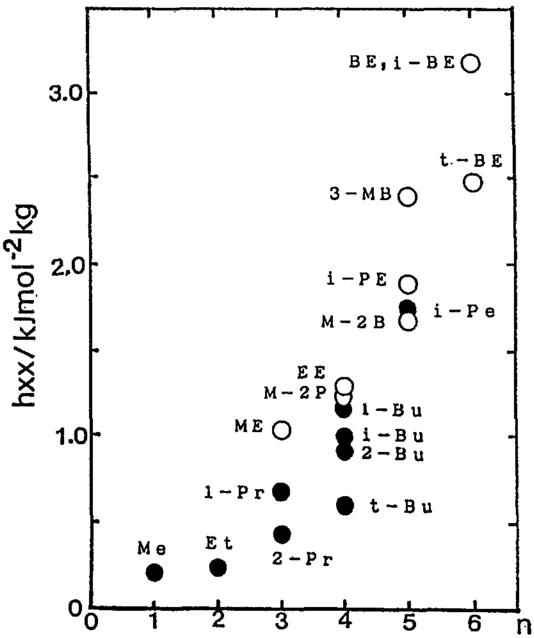

Fig. 3 Enthalpic pair interaction parameters at 298.15 K plotted against the number *n* of carbon atoms: O: alkoxyalcohol, • : alkylalcohol
ME ≡ methanol, EE ≡ ethanol, 1–Pr ≡ 1-propanol, 2–Pr ≡ 2-propanol, 1–Bu ≡ 1–butanol, i–Bu ≡ isobutyl alcohol, 2–Bu ≡ 2-butanol, t–Bu ≡ 2-methyl-2-propanol, i–Pe ≡ isopentyl alcohol, ME ≡ 2-methoxyethanol, EE ≡ 2-ethoxyethanol
M-2P≡ 1-methoxy-2-propanol, 3-MB ≡ 3-methoxy-1-butanol,
i-PE ≡ 2-i-propoxyethanol, M–2B ≡ 1-methoxy-2-butanol, BE ≡ 2-butoxyethanol,
i–BE ≡ 2-i-butoxyethanol, t–BE ≡ 2-t-butoxyethanol

has the nearly same $\Delta_{\mathrm{solv}}H_{\mathrm{m}}^{\infty}$ value as i–PE; therefore, there is little difference between the each hydrophobic hydration state surrounding the solute. However, we find a significant difference in h_{xx} value which reflects a relaxation magnitude of the hydrophobic hydration (Table 3 and Fig. 3). In order to solve this inconsistency, we adopt the following 'alkylalcohol' as 'the fundamental frame' which principally dominates hydrophobic interaction; we consider that 1-butanol(1–Bu)' and 'ethanol(Et)' mainly decide the h_{xx} values for 3–MB and i–PE, respectively. The large difference in h_{xx} between 'the fundamental frame' (Fig. 3) produces the following order:

$$h_{xx}(3\text{–MB}) \gg h_{xx}(\text{i–PE}) \tag{3}$$

Next, M–2B is compared with i–PE. In Table 3 and Fig. 3, we can see h_{xx} values for the two molecules in the following order:

$$h_{xx}(\text{i–PE}) > h_{xx}(\text{M–2B}) \tag{4}$$

In this case, we adopt 'methoxyethanol', which is common to the two alcohols, as 'the fundamental frame'. In M–2B, extra two carbon atoms are attached to the site near the hydroxyl group in this 'fundamental frame'; in i–PE, they are attached to the site far from the hydroxyl group. Since the carbon atom far from the hydroxyl group contributes to the hydrophobic interaction more notably than that near the hydroxyl group, as it is confirmed by the comparison between 1–Pr and 2–Pr, we have obtained the relation (4).

Thus, the discussion on the relations (3) and (4) successfully explains the relative magnitude (2).

Conclusion

We had previously adopted the concepts of 'the total number of carbon atoms' and 'the degree of alkyl group branching' as factors which have the influence on hydrophobic interaction. In addition, we propose 'the fundamental frame' as a main dominant factor for hydrophobic interaction, and we also take account of 'the distance between hydrophobic group and hydroxyl group', Moreover, we consider that it is very important for the explanation of the hydrophobic interaction quantitatively to notice 'how easily the ether oxygen atom can be in contact with surrounding water molecule'.

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Zusammenfassung — Mittels eines Fluß-Mikrokalorimeters wurden bei 298.15 K im gesamten Konzentrationsintervall die molaren Überschußenthalpien für wäßrige Lösungen aus 3-Methoxy-1-Butanol (3-MB) und 1-Methoxy-2-Butanol (M-2B) gemessen. Anhand der experimentellen Daten erstellten wir den Enthalpiepaar-Wechselwirkungsparameter h_{xx} und erhielten folgende Reihenfolge:

$$h_{xx}(\text{3-MB}) \gg h_{xx}(\text{M-2B})$$

Diese große Abweichung bei h_{xx} legte uns einige neue Faktoren nahe, die einen Einfluß auf die hydrophobe Wechselwirkung haben können: "Grundgerüst", "Hydroxylgruppen" als auch "Sauerstoffatome".