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# ON THE RELATION BETWEEN ENTHALPIC VIRIAL COEFFICIENT AND THE SIZE OF ALKYL GROUP IN DILUTE AQUEOUS SOLUTION OF ALCOHOLS

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## SUMMARY

Molar excess enthalpies for aqueous solutions of 2-methoxyethanol(ME), 2-ethoxyethanol(EE), 2-i-propoxyethanol(i-PE), and 2-i-butoxyethanol(i-BE) have been measured at 298.15 K over the whole composition range(except for ME) with an LKB flow microcalorimeter. All the solutions exhibit negative enthalpies of mixing, the absolute value of which decreases with the increase in the size of alkyl group. The enthalpic pair interaction parameter has been evaluated from the experimental data. It has fairly large positive value which increases with the size of alkyl group. The results are discussed in terms of hydrophobic hydration and interaction.

## INTRODUCTION

Alkoxyethanols($ROCH_2CH_2OH$) are called as cellosolve and widely used as useful industrial solvent. Thermodynamic behavior of aqueous solutions of these compounds is similar to that of alkylalcohols in that their properties such as the excess volume, the excess heat capacity, etc. change regularly with their carbon number(refs. 1~2). In the case of alkylalcohols, only the first three member and its isomer can mix with water completely at room temperature, and higher members exhibit only a limited solubility to water, except for t-butylalcohol. However, the solubility to water can be greatly enhanced by introducing an ether oxygen into alkyl chain, and even butoxyethanols(carbon number is 6) can mix with water completely at room temperature. Thus, alkoxyalcohols are one of the most appropriate materials for studying the combined effects of hydrophobic and hydrophilic groups to water.

We have recently measured the heats of mixing $H^E$ for aqueous solutions of 2-butoxyethanol(BE) and 2-T-butoxyethanol(t-BE) and evaluated the excess partial molar enthalpy $H_x^{E,\infty}$ and the enthalpic second virial coefficient $h_{xx}$(ref. 3). It is found that $H_x^{E,\infty}$ for BE is larger(less exothermic) than that for t-BE, while $h_{xx}$ for BE is larger than that for t-BE. This suggests that the hydrophobic hydration and hydrophobic interaction effects, as estimated from $H_x^{E,\infty}$ and $h_{xx}$, respectively, are not parallel with each other. In order to obtain further information on the hydrophobic effects in homologous series of alkoxyalcohols and to compare it with the case of alkylalcohols, we have made similar measurements with other alkoxyethanols. In this paper, we report $H^E$, $H_x^{E,\infty}$ and

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$h_{xx}$ values for aqueous solutions of 2-methoxyethanol(ME), 2-ethoxyethanol(EE), 2-i-propoxyethanol(i-PE) and 2-i-butoxyethanol(i-BE) at 298.15 K.

## EXPERIMENTAL

Alkoxyethanols purchased from Tokyo Kasei Co. were purified by repeated distillations with a column of 30 theoretical plates. The sample of water was deionized and fractionally distilled. These samples were degassed twice by freezing and thawing under vacuum immediately before use. The heats of mixing, or the heats of dilution in the case of concentrated or highly dilute alcohol solution, were measured with an LKB flow microcalorimeter(type 2107-121) at 298.15 K. The data obtained were used to calculate $H^E$, $H_x^{E,\infty}$ and $h_{xx}$. Further details of the calorimetry have been given previously(ref. 3).

## RESULTS AND DISCUSSION

### Excess molar enthalpy of mixing

The excess molar enthalpies $H^E$ for aqueous solutions of the four alkoxyethanols obtained at 298.15 K are given in Table 1 and plotted as a function of the mole fraction $x_1$ of alkoxyethanols in Fig. 1. Literature values(refs. 3-5) of $H^E$ for aqueous solutions of ME, BE and t-BE are also included in the figure.

### Virial expansion of excess enthalpy

According to the McMillan-Mayer theory, $H^E(m_x)$ can be expressed by the power series expansion of molality $m_x$. If $m_x$ is sufficiently low, the expansion can be truncated at the second order term and the following simple equation is obtained(ref. 6),

$$H^E(m_x) = (H_x^{\ominus} - H_x^{o})m_x + h_{xx}m_x^2 \qquad (1)$$

where $H_x^{\ominus}$ is the partial molar enthalpy of solute at infinite dilution and $H_x^{o}$ is the molar enthalpy of pure solute.

Then, if accurate measurements can be done in extremely dilute solutions, both $(H_x^{\ominus} - H_x^{o})$, the excess partial molar enthalpy at infinite dilution, and $h_{xx}$ are evaluated from the intercept and slope of $H^E(m_x)/m_x$ vs. $m_x$ plot, as shown in Fig. 2.

Table 2 summarizes the results for $H_x^{E,\infty}$ and $h_{xx}$ thus obtained. We first note that our $H_x^{E,\infty}$ values for ME, EE, i-PE and BE are in good agreement with literature values(ref. 1). It is also seen from the table that the $H_x^{E,\infty} - H_v$, ($H_v$ is heat of vaporization) a measure of hydrophobic hydration at infinite dilution, should increase with the size of alkyl group, and that the $h_{xx}$ value is positive for all the alkoxyethanols, indicating the presence of hydrophobic interaction effect. The absolute value of $h_{xx}$ increases with increasing the

TABLE 1

Molar excess enthalpies for aqueous solutions of 2-methoxyethanol, 2-ethoxyethanol, 2-i-propoxyethanol and 2-i-butoxyethanol at 298.15 K.

| $x_1$ | $H^E$ (J mol$^{-1}$) | $x_1$ | $H^E$ (J mol$^{-1}$) | $x_1$ | $H^E$ (J mol$^{-1}$) |
|---|---|---|---|---|---|
| | | 2-Methoxyethanol(1) + Water(2) | | | |
| 0.0004 | -5.44 | 0.0050 | -74.83 | 0.0404 | -528.7 |
| 0.0007 | -10.37 | 0.0051 | -76.17 | 0.0443 | -567.5 |
| 0.0010 | -14.87 | 0.0057 | -85.69 | 0.0594 | -717.5 |
| 0.0012 | -18.94 | 0.0066 | -99.15 | 0.0595 | -720.1 |
| 0.0015 | -22.74 | 0.0092 | -136.2 | 0.0651 | -763.4 |
| 0.0021 | -32.39 | 0.0129 | -188.0 | 0.0656 | -770.7 |
| 0.0025 | -38.23 | 0.0178 | -254.8 | 0.0718 | -819.1 |
| 0.0030 | -45.22 | 0.0257 | -354.6 | 0.0777 | -856.5 |
| 0.0032 | -47.90 | 0.0267 | -368.7 | 0.0849 | -910.7 |
| 0.0034 | -51.89 | 0.0282 | -389.4 | 0.1075 | -1037.7 |
| 0.0037 | -56.37 | 0.0292 | -400.2 | 0.1171 | -1089.8 |
| 0.0038 | -57.15 | 0.0321 | -435.3 | | |
| | | 2-Ethoxyethanol(1) + Water(2) | | | |
| 0.0004 | -6.35 | 0.0263 | -416.8 | 0.2062 | -1110.1 |
| 0.0007 | -12.13 | 0.0321 | -491.6 | 0.2178 | -1106.7 |
| 0.0010 | -17.39 | 0.0348 | -524.1 | 0.2452 | -1084.0 |
| 0.0012 | -22.26 | 0.0468 | -658.0 | 0.2707 | -1077.6 |
| 0.0015 | -26.81 | 0.0513 | -701.9 | 0.3082 | -1040.1 |
| 0.0022 | -38.42 | 0.0567 | -752.8 | 0.3255 | -1022.1 |
| 0.0030 | -54.02 | 0.0615 | -786.5 | 0.3576 | -985.1 |
| 0.0038 | -67.73 | 0.0672 | -827.6 | 0.4005 | -931.4 |
| 0.0042 | -75.40 | 0.0933 | -970.1 | 0.4261 | -896.1 |
| 0.0052 | -90.92 | 0.1101 | -1028.8 | 0.4551 | -849.7 |
| 0.0056 | -98.15 | 0.1190 | -1045.5 | 0.4676 | -840.0 |
| 0.0064 | -112.9 | 0.1221 | -1062.6 | 0.5269 | -760.2 |
| 0.0075 | -130.8 | 0.1292 | -1078.3 | 0.5672 | -694.8 |
| 0.0087 | -150.4 | 0.1339 | -1081.3 | 0.6042 | -638.5 |
| 0.0094 | -163.7 | 0.1397 | -1086.3 | 0.6448 | -576.3 |
| 0.0105 | -180.6 | 0.1565 | -1097.5 | 0.7385 | -427.8 |
| 0.0160 | -267.8 | 0.1749 | -1108.5 | 0.8540 | -239.3 |
| 0.0231 | -372.5 | 0.1882 | -1111.8 | 0.9473 | -85.96 |
| | | 2-i-Propoxyethanol(1) + Water(2) | | | |
| 0.0003 | -6.74 | 0.0100 | -188.8 | 0.0820 | -855.4 |
| 0.0007 | -12.84 | 0.0153 | -276.2 | 0.0833 | -855.3 |
| 0.0009 | -18.46 | 0.0220 | -379.9 | 0.1049 | -915.6 |
| 0.0012 | -23.59 | 0.0229 | -399.8 | 0.1352 | -947.1 |
| 0.0014 | -28.28 | 0.0233 | -403.7 | 0.1663 | -963.0 |
| 0.0017 | -33.94 | 0.0259 | -440.7 | 0.2122 | -958.6 |
| 0.0021 | -40.38 | 0.0304 | -493.4 | 0.2588 | -930.2 |
| 0.0029 | -56.47 | 0.0308 | -499.6 | 0.3328 | -877.3 |
| 0.0036 | -70.63 | 0.0336 | -536.5 | 0.4280 | -791.0 |
| 0.0048 | -94.09 | 0.0409 | -622.6 | 0.4994 | -712.6 |
| 0.0051 | -98.68 | 0.0448 | -652.5 | 0.5258 | -672.6 |
| 0.0053 | -103.0 | 0.0455 | -657.5 | 0.5994 | -588.1 |
| 0.0061 | -118.6 | 0.0503 | -692.8 | 0.6403 | -529.5 |

TABLE 1 Continued

| $x_1$ | $H^E$(J mol$^{-1}$) | $x_1$ | $H^E$(J mol$^{-1}$) | $x_1$ | $H^E$(J mol$^{-1}$) |
|---|---|---|---|---|---|
| 0.0072 | -137.2 | 0.0538 | -719.7 | 0.7051 | -443.3 |
| 0.0083 | -157.5 | 0.0589 | -749.4 | 0.8321 | -261.1 |
| 0.0090 | -170.9 | 0.0650 | -791.8 | 0.9383 | -97.25 |
| 2-i-Butoxyethanol(1) + Water(2) | | | | | |
| 0.0003 | -5.12 | 0.0085 | -127.2 | 0.1704 | -368.7 |
| 0.0006 | -9.57 | 0.0087 | -131.1 | 0.1820 | -373.3 |
| 0.0008 | -13.80 | 0.0090 | -133.6 | 0.1954 | -375.7 |
| 0.0011 | -17.60 | 0.0092 | -137.1 | 0.2108 | -376.4 |
| 0.0013 | -21.15 | 0.0095 | -140.2 | 0.2288 | -374.0 |
| 0.0017 | -27.41 | 0.0097 | -144.0 | 0.2503 | -372.8 |
| 0.0022 | -35.18 | 0.0101 | -147.5 | 0.2764 | -369.0 |
| 0.0028 | -45.08 | 0.0103 | -151.6 | 0.3080 | -359.4 |
| 0.0033 | -52.52 | 0.0107 | -155.3 | 0.3484 | -330.4 |
| 0.0035 | -55.36 | 0.0110 | -159.9 | 0.4006 | -291.4 |
| 0.0037 | -59.67 | 0.0114 | -164.0 | 0.4688 | -240.8 |
| 0.0039 | -62.03 | 0.0118 | -169.0 | 0.5684 | -164.2 |
| 0.0040 | -63.57 | 0.0123 | -173.6 | 0.6187 | -123.7 |
| 0.0044 | -69.76 | 0.0127 | -178.9 | 0.6516 | -99.31 |
| 0.0045 | -71.29 | 0.0132 | -183.6 | 0.6698 | -97.29 |
| 0.0049 | -76.60 | 0.0138 | -190.3 | 0.6943 | -85.19 |
| 0.0050 | -78.58 | 0.0144 | -194.2 | 0.7088 | -81.88 |
| 0.0053 | -83.40 | 0.0165 | -216.5 | 0.7174 | -77.14 |
| 0.0057 | -89.05 | 0.0510 | -286.7 | 0.7276 | -73.91 |
| 0.0059 | -91.22 | 0.0744 | -310.6 | 0.7600 | -65.37 |
| 0.0064 | -99.60 | 0.0965 | -328.7 | 0.7882 | -57.48 |
| 0.0067 | -102.4 | 0.1178 | -341.6 | 0.8190 | -49.75 |
| 0.0071 | -109.0 | 0.1292 | -350.4 | 0.8521 | -40.97 |
| 0.0073 | -111.8 | 0.1358 | -355.3 | 0.8937 | -29.84 |
| 0.0077 | -117.3 | 0.1430 | -357.1 | 0.9295 | -20.44 |
| 0.0079 | -119.6 | 0.1511 | -360.8 | 0.9605 | -11.79 |
| 0.0082 | -124.6 | 0.1602 | -365.3 | 0.9790 | -6.21 |

size of alkyl group.

It is interesting to compare the present results for $h_{xx}$ of alkoxyethanols with those of previous studies for BE, t-BE and alkylalcohols(refs. 3, 7-8). Fig. 3 shows that the $h_{xx}$ for alkoxyethanols are generally larger than those for alkylalcohols. However, it is difficult to compare these $h_{xx}$ values because of the presence of the contribution due to polar groups which is not clearly understood at the present stage. Kato(ref. 9) has shown that the hydrophobic interaction of EE is smaller than that of ethanol. However, inspection of Fig. 3 suggests that $h_{xx}$ generally increases with the number of carbon atoms in the molecule for all the alcohols. Moreover, the difference in $h_{xx}$ between BE and t-BE is almost equal to that between n-butylalcohol and t-butylalcohol. Therefore, $h_{xx}$ values may be used as a quantitative measure of the hydrophobic interaction.

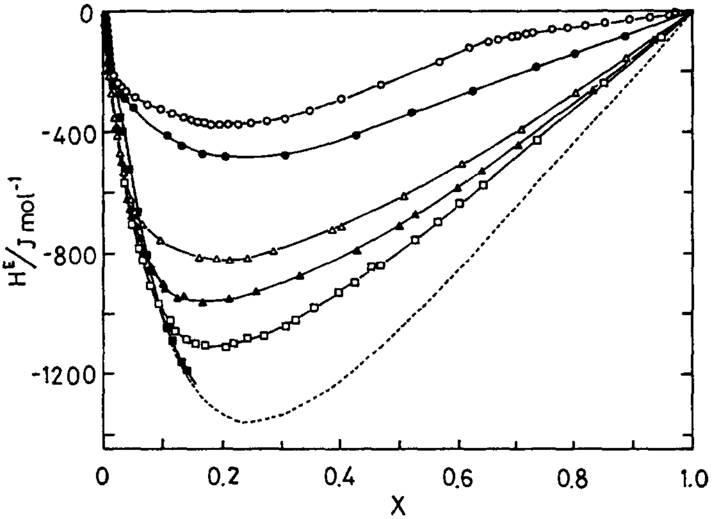

Fig. 1. Molar excess enthalpies at 298.15 K for (1-X) $H_2O$ + :
○ , $X(CH_3)_2CHCH_2OCH_2CH_2OH$; ● , X $CH_3CH_2CH_2CH_2OCH_2CH_2OH$;
△ , X $(CH_3)_3COCH_2CH_2OH$; ▲ , X $(CH_3)_2CHOCH_2CH_2OH$;
□ , X $CH_3CH_2OCH_2CH_2OH$; ■ and ----- (ref. 4 ), X $CH_3OCH_2CH_2OH$.

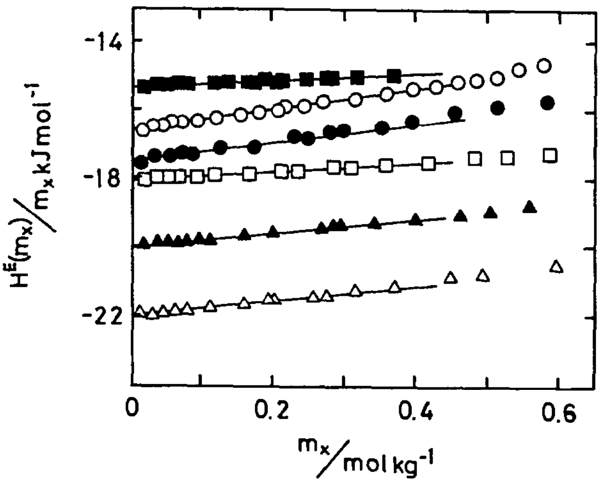

Fig. 2. Plots of pair interaction parameters according equation ( 1 ). $H^E(m_x)/m_x$ vs. $m_x$. Symbols as for figure 1.

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TABLE 2

Pair interaction parameters $h_{xx}$ and partial molar excess enthalpies at infinit dilution $H_x^{E,\infty}$ for alkoxyethanols in water at 298.15 K.

| Solute X | $H_x^{E,\infty}$(kJ $mol^{-1}$) | | $h_{xx}$(kJ $mol^{-2}$ kg) |
|---|---|---|---|
| | This work | Reference 1 | |
| ME | -15.36 | -15.27 | 1.04 |
| EE | -18.05 | -18.15 | 1.30 |
| i-PE | -20.01 | -20.41 | 1.90 |
| BE | -17.63 | -17.05 | 3.19 |
| i-BE | -16.62 | | 3.19 |
| t-BE | -22.08 | | 2.48 |

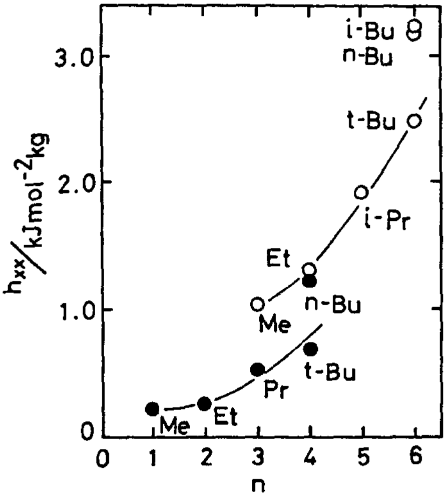

Fig. 3. Pair interaction parameters $h_{xx}$ plotted against the number n of carbon atoms; ○ , $ROCH_2CH_2OH$; ● , ROH (refs. 7,8)

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