解　説

Netsu Sokutei **30** (3) 137-145

解　説

Excess Molar Enthalpy Measurements of Multicomponent Alcohol-Ether Mixtures and their Representation in Terms of an Association Model

Mohammad Mainul Hossain Bhuiyan, and Kazuhiro Tamura

(Received May 19, 2003; Accepted June 4, 2003)

Our recent studies on the measurement of excess molar enthalpies of alcohol-ether multicomponent solutions are reviewed in terms of a UNIQUAC associated-solution model. In this model, we have taken into account the self-association like alcohols, multicross-association of unlike alcohols and solvation between alcohols and ethers. The UNIQUAC associated-solution model, which includes association constants, solvation constants and optimally fitted binary parameters obtained solely from the pertinent binary correlation, can predict the ternary excess molar enthalpies with an excellent accuracy.

1. Introduction

When two or more pure liquids mix at a constant temperature and pressure, the enthalpy change will be produced owing to molecular interactions. Excess enthalpy contains a substantial and significant amount of information about the nonidealities of liquid mixtures. Methods for measurement, correlation, calculation and prediction of the solution nonidealities occupy much of the attention of the world's thermodynamicists. Among many considerable factors producing the large nonideality of liquid mixtures, we focused our attention on strong interactions between molecules, known as association phenomena. Besides the associated substances such as alcohols are widely utilized in industry and the nonideality of such systems is generally large and sometimes shows peculiar behavior. Especially a knowledge of the main factors involved in the strong nonideality of multicomponent liquid solutions is fundamental to a better understanding of excess enthalpies from the view point of chemical engineering, because many kinds of strongly nonideal solutions are treated in chemical processes. Mixing or separation of substances is very common in chemical production and processing; in all such cases, excess enthalpies of the multicomponent liquid mixtures are involved.

Studies on thermodynamic properties of alcohol solution are of great interest of our laboratory and enthalpies of mixing for a large number of binary[1-5] and ternary[6-11] solutions those contain alcohol had been measured in the last 25 years or so.

The alcohols and ethers solutions comprise a substantial portion of liquid mixtures of practical importance. Tertiary alkyl ethers are nontoxic, nonpolluting, and high octane number blending agents for gasoline; therefore, they have importance in the petrochemical industry from technological, ecological and economical point of view. Recently, mixtures containing tertiary alkyl ethers have extensively been reviewed by Marsh *et al.*[12] Methyl *tert*-butyl ether (MTBE) is one of the oxygenated additives used in gasoline to reduce the polluting components in exhaust gases. On the other hand, the study of thermodynamic behavior for the mixtures of alkanols and cyclic ethers is a subject of considerable interest because they represent a class of technically important compounds frequently used as solvents in the chemical industry. Cyclic polyethers have attracted interest as model substances for bio-systems and in relation to their use in synthetic method in organic chemistry.[13-15] In addition, cycloethers such as 1,4-dioxane, 1,3-dioxolane, 1,3,5-trioxane *etc.* might also serve as fuel additives in near future. The

interaction between the hydroxyl group of alkanol and the oxygen atom of cycloether is not negligible.[16,17] The recent investigations[18-22] suggested a relatively strong association between alkanol and ether. Letcher *et al.*[18] also shown that the interaction between alkanol and cycloether is generally greater than that of alkanol and branched ether. Thus our recent research deals with the excess molar enthalpy for the mixtures formed by aliphatic lower alcohols (C_1-C_3) and aliphatic branched mono-ether, cyclic mono- or di-ether both experimentally and theoretically. In this article we shed light on the excess molar enthalpy measured for aliphatic alcohols (C_1-C_3) and MTBE or tetrhydropyran or 1,4-dioxane mixtures with an associated-solution model.

2. Excess Molar Enthalpy Measurements

The apparatus for measuring enthalpies of mixing have been designed to satisfy the measurement condition and to meet the objects of measurements. The introduction to the measurement apparatus can be found in the Shin Jikken Kagaku Koza 2, Kiso Gijutsu 1, Netsu Atsuryoku,[23] and Classical Thermodynamics Vol.2.[24] According to these, we can classify the apparatus depending on the mixing procedure as batch, successive dilution, and flow calorimeter; those have been used for the measurements of enthalpies of mixing. In the recent years there has been an increasing interest in the determination of enthalpies of mixing of non-electrolytes by flow procedures. The mixing efficiency is of critical importance in flow calorimetry. Several designs of mixing cell were tested and found to be inadequate at experiments where a complete mixing was required. In our laboratory, a flow microcalorimeter[25] was modified in order to improve the completeness of mixing in the mixing tube. This flow microcalorimeter is same as that described by Ogawa and Murakami[26] except for a few modification. This calorimeter is suitable for studying both the endothermic and exothermic mixtures, the measurements require short time and only small amount of components with the wide range of composition. We used this type of modified flow microcalorimeter during the course of our recent measurements of excess molar enthalpies of ternary mixtures (15 ternary mixtures are measured) formed by two alcohols (C_1-C_3) and MTBE or tetrahydropyran or 1,4-dioxane at 298.15 K. Details of the equipment and its operational procedure are found in the literature.[22,25]

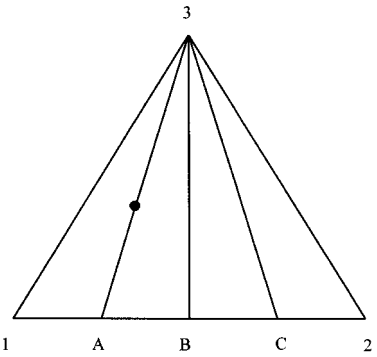

Fig.1 Experimental procedure for ternary mixture.

The ternary excess molar enthalpy measurement was carried out as pseudobinary mixture composed of a binary mixture of known compositions and a pure component. **Fig.1** shows the procedure of the experiment. 1, 2, and 3 in **Fig.1** represent 1st, 2nd and 3rd component respectively of each ternary mixture. Points A, B, and C denote the molar ratios of 0.25, 0.50 and 0.75 of 1st component of three alcohol binary mixtures respectively. All of the alcohol binary mixtures were prepared by mixing component 1 and 2. These three compositions were chosen to cover complete composition ranges of the ternary mixtures. As for mixture A, the measurement was done along the line from point A to point 3 as shown in **Fig.1**. A ternary mixture at point D on the section A to 3, is described as a liquid mixture of x_3 mole of the component 3 and $(1-x_3)$ mole of the binary alcohol mixtures initially prepared by component 1 and 2. The excess enthalpy for a mole of a ternary mixture corresponding to point D as shown in **Fig.1** can be expressed as follows:

$$H^{E}_{m,123} = \Delta H^{E}_{m} + (1-x_3)_D H^{E}_{m,A} \quad (1)$$

where, $H^{E}_{m,123}$ is the excess enthalpy per mole of ternary mixture D, and ΔH^{E}_{m} is the excess enthalpy measured for the pseudobinary mixture, which is obtained by mixing the binary mixture A with component 3. $H^{E}_{m,A}$ is the excess enthalpy for the binary mixture A. The same holds true with the mixtures B and C as in mixture A.

Since in the experiments, the ternary mixtures under present scheme are considered as pseudobinary mixtures, the binary alcohol mixture obtained before hand [methanol (1)+ ethanol (2)], [methanol (1)+ 1-propanol (2)],

[methanol (1)+2-propanol (2)], [ethanol (1)+1-propanol (2)], [ethanol (1)+2-propanol (2)], and [1-propanol (1)+2-propanol (2)] was separately mixed with the remaining component 3 (MTBE, or tetrahydropyran, or 1,4-dioxane).

As the excess molar enthalpies of the binary mixtures obtained before hand was taken as zero, it is necessary to add the binary experimental excess molar enthalpy value with the excess molar enthalpies of pseudobinary mixture to get the ternary experimental excess enthalpy. The values of $H^{E}_{m,A}$ in equation (1) for the binary alcohols excess molar enthalpies at three specified composition (the approximate composition of these mixtures were 25, 50 and 75 mol% of component 1) were interpolated by means of spline-fit method.

3. Data Analysis Using an Associated-Solution Model

The solution theory, which treats the associated complexes as new, distinguishable and independent molecular species, has been called the associated solution theory. Associated solution theories have been applied to explain closely the thermodynamic excess properties,[27-41] the spectroscopic properties,[42-45] or the other physical properties[46] of alcohol-nonpolar solvent solutions. The extensive data on enthalpies of mixing for alcohols-hydrocarbon system[47-51] has enabled the solution thermodynamicists to make more detailed test of the theory of associated solutions than has been possible previously. For the mixtures of alcohols and saturated hydrocarbons, there prevails a relatively simple situation wherein one component is self-associated and interacts with other only by physical forces. The excess molar enthalpy data of alcohols solutions plays an important role in examining the associated-solution model. The excess molar enthalpy measurements for ternary alcohol-hydrocarbon mixtures made in our laboratory so far are the mixtures of one alcohol and two hydrocarbons and chemical model[52] was used to analyze the experimental data. Previous model was ill suited to represent the real behavior of mixtures containing two alcohols. The UNIQUAC associated-solution model has been modified[53] and is well able to describe the alcohol-alcohol binary and alcohols-hydrocarbon ternary mixtures. Nagata *et al.*[54] again modified the UNIQUAC associated-solution model for the accurate reproduction of ternary excess molar enthalpies formed by two alcohols and one active nonassociating component taken into account the formation of ternary complexes between alcohol copolymers and an active nonassociating component in addition to the formation of alcohol copolymers. This model satisfactorily explained the ternary mixtures composed of two alcohols and benzene.[1] However, the analysis according to the UNIQUAC associated-solution model[54] is not yet appeared in the literature to the solutions that contains aliphatic lower alcohols and branched mono ether, cyclic mono- or di-ether. We applied this associated-solution model to the 15 ternary solutions formed by two lower alcohols (methanol, ethanol, 1-propanol, and 2-propanol) and MTBE, or tetrahydropyran, or 1,4-dioxane, and 17 constituent binary mixtures. The applicability of this model has been clarified to the enthalpies of mixing and succeeded in confirming its usefulness concerning solutions that contains alcohols and branched or cyclic ether.

3.1 Theory of the UNIQUAC Associated-Solution Model

3.1.1 Working Equation

The UNIQUAC associated-solution theory gives the expression of excess molar enthalpy as the sum of a chemical and a physical contribution term.

$$H^{E}=H^{E}_{chem}+H^{E}_{phys} \tag{2}$$

The H^{E}_{phys} term comes from the residual part of original UNIQUAC equation,[55] which is primarily responsible for the enthalpy of mixing. Accordingly, H^{E}_{phys} is obtained from differentiation by reverse temperature in accordance with Gibbs-Helmholtz relation. The energy parameter a_{ij} in the UNIQUAC model could be expressed by a linear function of temperature as follows:

$$a_{ij}/R=C_{ij}+D_{ij}\{(T/\mathrm{K})-273.15\} \tag{3}$$

On the other hand, the chemical contribution term, H^{E}_{chem} is defined as

$$H^{E}_{chem}=H_f-x_A H^{0}_{fA}-x_B H^{0}_{fB} \tag{4}$$

where H_f is the total enthalpy of complex formation, H^{0}_{fA} is the value of H_f at pure state of alcohol A and H^{0}_{fB} is that of pure state of alcohol B. The UNIQUAC associated-solution model employed in our present investigation was modified by introducing the association, solvation of the component molecules to the chemical contribution term, H^{E}_{chem}. So the theory concerns the chemical contribution term and is discussed briefly as follows.

3.1.2 Binary Alcohol-Alcohol Mixtures:

According to the associated-solution model assumptions, the associating component alcohols A and B undergo self-association to form linear polymer by hydrogen-bonding through the hydroxyl group of the alcohols and can be considered the following stepwise reactions:

$$A_i + A_1 = A_{i+1} \tag{5}$$

$$B_i + B_1 = B_{i+1} \tag{6}$$

Molecules of the generic polymers A_i and B_i are considered of r_{Ai}, r_{Bi} segments, and each molecule are assumed to have an external surface area proportional to q_{Ai}, q_{Bi}. It is assumed that the structural parameters r_{Ai}, r_{Bi} and q_{Ai}, q_{Bi} can be expressed in terms of those for the monomer, r_A and r_B, and q_A and q_B, as $r_{Ai} = i r_A$ and $r_{Bi} = i r_B$ and $q_{Ai} = i q_A$, $q_{Bi} = i q_B$. The association constants of two alcohols A and B are defined by

$$K_A = \frac{C_{A_{i+1}}}{C_{A_i}\, C_{A_1}} \cdot \frac{1}{r_A} = \frac{\Phi_{A_{i+1}}}{\Phi_{A_i}\, \Phi_{A_1}} \cdot \frac{i}{(i+1)} \tag{7}$$

$$K_B = \frac{C_{B_{i+1}}}{C_{B_i}\, C_{B_1}} \cdot \frac{1}{r_B} = \frac{\Phi_{B_{i+1}}}{\Phi_{B_i}\, \Phi_{B_1}} \cdot \frac{i}{(i+1)} \tag{8}$$

where C_{A_i} and C_{B_i} stand for the concentration of associated polymers A_i and B_i, and Φ_{A_i} and Φ_{B_i} the segment fraction of the polymers A_i and B_i. In the mixtures of different kinds of alcohols, alcohol molecules undergo cross-association through H-bonding because of the presence of their available hydroxyl group. Hence, in addition to the above stepwise self-association reactions, the UNIQUAC associated-solution theory assumes the following successive solvation reactions:

$$A_i + B_j = A_i B_j \qquad B_i + A_j = B_i A_j \tag{9}$$

$$A_i B_j + A_k = A_i B_j A_k \qquad B_i A_j + B_k = B_i A_j B_k \tag{10}$$

$$A_i B_j A_k + B_l = A_i B_j A_k B_l \qquad B_i A_j B_k + A_l = B_i A_j B_k A_l \tag{11}$$

The suffixes i, j, k, and l in the above reactions go from one to infinity. We use only a single value of the solvation constant K_{AB} for many consecutive reactions. For example, K_{AB} for $A_i B_j + A_k = A_i B_j A_k$ is defined by

$$K_{AB} = \frac{C_{A_i B_j A_k}}{C_{A_i B_j}\, C_{A_k}} \cdot \frac{1}{r_A r_B} = \frac{\Phi_{A_i B_j A_k}}{\Phi_{A_i B_j}\, \Phi_{A_k}} \cdot \frac{r_{A_i B_j}\, r_{A_k}}{r_{A_i B_j A_k}\, r_A r_B} \tag{12}$$

The final expression of H^{E}_{chem} according to the UNIQUAC associated-solution model for alcohol-alcohol binary mixtures is shown elsewhere.[53] The segment fraction of alcohol monomer, Φ_{A1} and Φ_{B1}, in the mixture and that in pure alcohol states are simultaneously solved from mass balance equations expressed in terms of the association constant and the segment fraction of alcohol monomer.

3.1.3 Binary Alcohol- Active Nonassociating Component Mixtures:

It is assumed that alcohol A forms binary complex with an active nonassociating component B according to the following solvation reaction

$$A_i + B_1 = A_i B \tag{13}$$

The solvation constant K_{AB} of the above reaction is defined by

$$K_{AB} = \frac{C_{A_i B}}{C_{A_i}\, C_{B_1}} \cdot \frac{1}{r_A r_B} = \frac{\Phi_{A_i B}}{\Phi_{A_i}\, \Phi_{B_1}} \cdot \frac{r_{A_i}}{r_{A_i B}\, r_A} \tag{14}$$

The H^{E}_{chem} can be derived from the chemical equilibria and the final expression of H^{E}_{chem} according to the UNIQUAC associated-solution model for alcohol-active nonassociating mixtures is shown elsewhere.[54]

3.1.4 Ternary Mixtures Involving Two Alcohols and one Active Nonassociating Component:

This model further postulates that in addition to the binary complexes, ternary complexes are formed between alcohol copolymers and an active nonassociating component. Two alcohols denoted by A and B and active nonassociating component C undergo solvation according to the following complex formation

$$(A_i B_j)_k + C = (A_i B_j)_k C \tag{15}$$

$$(B_i A_j)_k + C = (B_i A_j)_k C \tag{16}$$

$$A_i (B_j A_k)_l + C = A_i (B_j A_k)_l C \tag{17}$$

$$B_i (A_j B_k)_l + C = B_i (A_j B_k)_l C \tag{18}$$

For example, the solvation constant of the reaction $A_i (B_j A_k)_l + C = A_i (B_j A_k)_l C$ is defined by

$$K_{AC} = \frac{C_{A_i B_j A_k}}{C_{A_i B_j}\, C_{A_k} C_{C_1}} \cdot \frac{1}{r_A r_C} = \frac{\Phi_{A_i B_j A_k C}}{\Phi_{A_i B_j A_k} \Phi_{C_1}} \cdot \frac{r_{A_i B_j A_k C}}{r_{A_i B_j A_k}\, r_A} \tag{19}$$

According to the above solvation reactions, the final expression of H^{E}_{chem} in the framework of the UNIQUAC associated-solution model is given in the reference.[54]

Table 1 Values of self-association constants of alcohols at 323.15 K and enthalpies of hydrogen-bond formation.

Component	K_A	$-h_A$ / kJ mol^{-1}
Methanol	173.9	23.2
Ethanol	110.4	23.2
1-Propanol	87.4	23.2
2-Propanol	49.1	23.2

Table 2 Values of solvation constants and enthalpies of complex formation between unlike molecules.

System (A＋B)	K_{AB}	$-h_{AB}$ / kJ mol^{-1}	T /K
Methanol＋ethanol	99.0	23.2	323.15
Methanol＋1-propanol	72.0	23.2	323.15
Methanol＋2-propanol	70.0	23.2	323.15
Methanol＋MTBE	22.0	19.5	298.15
Methanol＋tetrahydropyran	27.0	18.5	298.15
Methanol＋1,4-dioxane	51.5	16.3	298.15
Ethanol＋1-propanol	49.0	23.2	323.15
Ethanol＋2-propanol	47.6	23.2	323.15
Ethanol＋MTBE	18.0	19.5	298.15
Ethanol＋tetrahydropyran	20.0	18.5	298.15
Ethanol＋1,4-dioxane	47.9	16.3	298.15
1-Propanol＋2-propanol	36.1	23.2	323.15
1-Propanol＋MTBE	6.0	19.5	298.15
1-Propanol＋tetrahydropyran	10.0	18.5	298.15
1-Propanol＋1,4-dioxane	45.0	16.3	298.15
2-Propanol＋MTBE	5.0	19.5	298.15
2-Propanol＋1,4-dioxane	21.0	16.3	298.15

4. Calculated Results

4.1 Binary Mixtures

The ternary constituent binary mixtures that were calculated in the present research scheme are methanol＋ethanol, ＋1-propanol, ＋2-propanol, ＋MTBE, ＋tetrahydropyran, ＋1,4-dioxane, ethanol＋1-propanol, ＋2-propanol, ＋MTBE, ＋tetrahydropyran, ＋1,4-dioxane, 1-propanol＋2-propanol, ＋MTBE, ＋tetrahydropyran, ＋1,4-dioxane, 2-propanol＋MTBE, ＋1,4-dioxane.

The equilibrium association constants of alcohols at 323.15 K are taken from Brandani.[56] The enthalpies of hydrogen bond formation in pure alcohols are taken as −23.2 kJ mol^{-1}, which is equivalent to the enthalpy of dilution of ethanol in *n*-hexane at 298.15 K.[57] This value is assumed to be temperature-independent and provides the temperature dependence of the association constant by means of the following van't Hoff equation

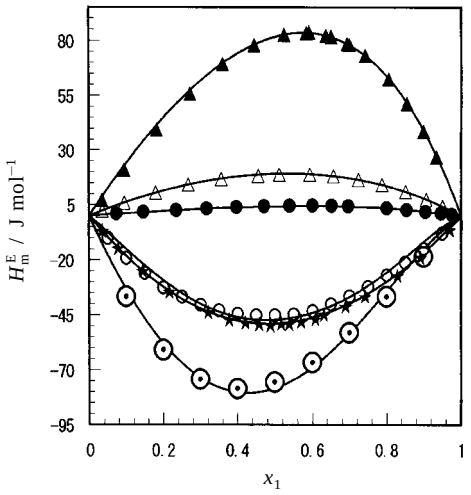

Fig.2 Comparison of experimental and correlated results of ternary constituent binary alcohol-alcohol mixtures at 298.15 K. ●, methanol (1)＋ethanol (2); ▲, methanol (1)＋1-propanol (2); ▼, methanol (1)＋2-propanol (2); △, ethanol (1)＋1-propanol (2); ○, ethanol (1)＋2-propanol (2); ★, 1-propanol (1)＋ 2-propanol (2); －, Correlated by the UNIQUAC association model.

$$\frac{\partial \ln K}{\partial (1/T)} = -\frac{h}{R} \tag{20}$$

The self-association constant of alcohols and enthalpies of hydrogen bond formation are inserted in **Table 1**. The monomer structural size and surface parameters r and q were calculated by the method of Vera *et al.*[58] The cross-association constants and enthalpies of hydrogen bond formation of alcohols are inserted in **Table 2**. The solvation constant and enthalpies of complex formation between alcohols and ether are fixed in this work. The values of the solvation constants summarized in **Table 2** are treated as adjustable parameters to give the better fit to the experimental data. The enthalpies of complex formation between unlike alcohols and ether are estimated from the difference between the enthalpies of dilution of ethanol in n-hexane and those of ethanol in ether. The calculated results are compared with the experimental excess enthalpy data of alcohol-alcohol, alcohol-ether mixtures at 298.15 K and shown in **Figs.2-5**.

4.2 Ternary Mixtures

The ternary mixtures predicted as a part of our recent research are methanol＋ethanol＋MTBE, ＋

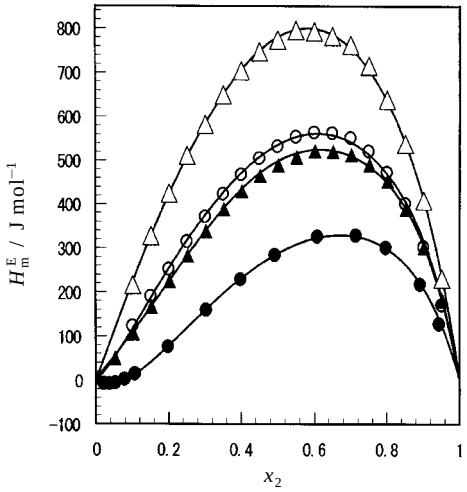

Fig.3 Comparison of experimental and correlated results of ternary constituent binary alcohol-MTBE mixtures at 298.15 K. ●, methanol (1)+MTBE (2); ▲, ethanol (1)+MTBE (2); ○, 1-propanol (1)+MTBE (2); △, 2-propanol (1)+MTBE (2); −, Correlated by the UNIQUAC association model.

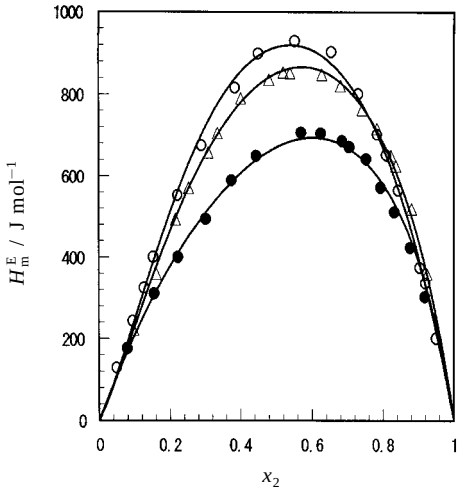

Fig.4 Comparison between experimental and correlated results for ternary constituent alcohol-tetrahydropyran binary mixtures at 298.15 K. ●, methanol (1)+tetrahydropyran (2); △, ethanol (1)+tetrahydropyran (2); ○, 1-propanol (1)+tetrahydropyran (2); −, Correlated by the UNIQUAC association model.

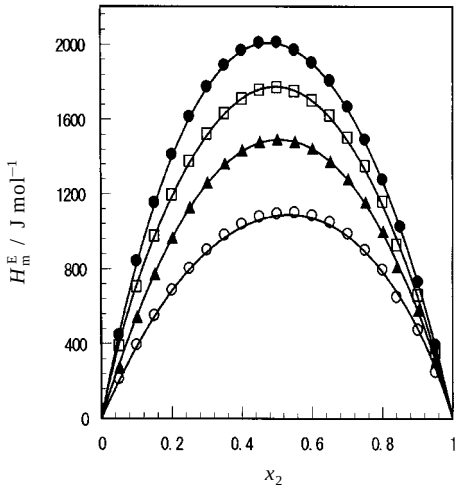

Fig.5 Comparison between experimental and correlated results of ternary constituent alcohol-1,4-dioxane binary mixtures at 298.15 K. ○, methanol (1)+1,4-dioxane (2); ▲, ethanol (1)+1,4-dioxane (2); □, 1-propanol (1)+1,4-dioxane (2); ●, 2-propanol (1)+1,4-dioxane (2); −, Correlated by the UNIQUAC association model.

Table 3 Predicted results of ternary mixtures at 298.15 K.

Mixtures	AAD/J mol^{-1}
Methanol＋ethanol＋MTBE	6.3
Methanol＋ethanol＋tetrahydropyran	18.8
Methanol＋ethanol＋1,4-dioxane	15.5
Methanol＋1-propanol＋MTBE	14.3
Methanol＋1-propanol＋tetrahydropyran	16.8
Methanol＋1-propanol＋1,4-dioxane	17.7
Methanol＋2-propanol＋MTBE	11.2
Methanol＋2-propanol＋1,4-dioxane	16.3
Ethanol＋1-propanol＋MTBE	14.7
Ethanol＋1-propanol＋tetrahydropyran	19.8
Ethanol＋1-propanol＋1,4-dioxane	11.4
Ethanol＋2-propanol＋MTBE	12.8
Ethanol＋2-propanol＋1,4-dioxane	15.7
1-Propanol＋2-propanol＋MTBE	9.8
1-Propanol＋2-propanol＋1,4-dioxane	10.8

Number of experimental data points of each ternary mixture is 57.
$AAD = | H^E_{Expt.} - H^E_{Predict.} | /n$
where n is the number of experimental data points.

tetrahydropyran, ＋1,4-dioxane, methanol＋1-propanol ＋MTBE, ＋tetrahydropyran, ＋1,4-dioxane, methanol＋2-propanol＋MTBE, ＋1,4-dioxane, ethanol＋1-propanol ＋MTBE, ＋tetrahydropyran, ＋1,4-dioxane, ethanol＋2-propanol＋MTBE, ＋1,4-dioxane, 1-propanol＋2-propanol ＋MTBE, ＋1,4-dioxane.

The results predicted with the UNIQUAC associated-solution model having association constants (as listed in **Table 1**), solvation constants (as listed in **Table 2**)

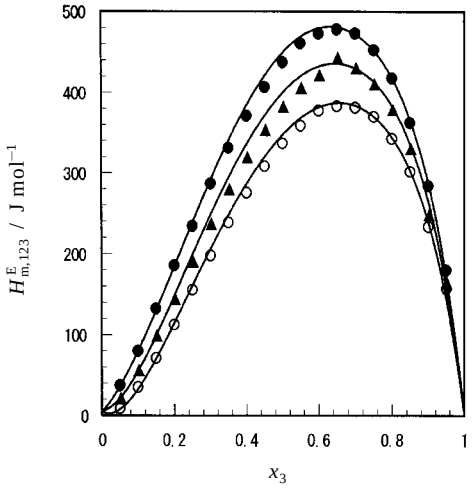

Fig.6 Excess molar enthalpies $H^E_{m,123}$/J mol^{-1} for the ternary mixtures of {methanol (x_1)+ethanol (x_2)+ MTBE (x_3)} at 298.15 K. (●) $x'_1=0.25$, (▲) $x'_1=0.50$, (○) $x'_1=0.75$; −, Predicted by the UNIQUAC association model.

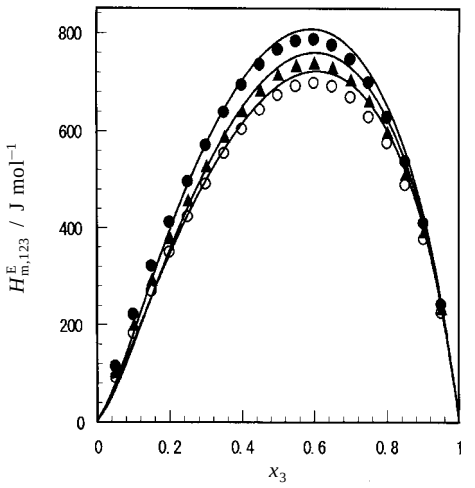

Fig.7 Excess molar enthalpies $H^E_{m,123}$/J mol^{-1} for the ternary mixtures of {methanol (x_1)+ethanol (x_2)+ tetrahydropyran (x_3)} at 298.15 K. (●) $x'_1=0.25$, (▲) $x'_1=0.50$, (○) $x'_1=0.75$; −, Predicted by the UNIQUAC association model.

and optimally fitted binary parameters are presented in **Table 3** for the above 15 ternary mixtures. Comparison between experimental and predicted results is shown in **Figs.6-8** for the (methanol + ethanol + MTBE), (methanol + ethanol + tetrahydropyran), and (methanol + ethanol + 1,4-dioxane) systems respectively. The graphical representation of ternary predicted values for all the other systems shows fair agreement with experimental values.

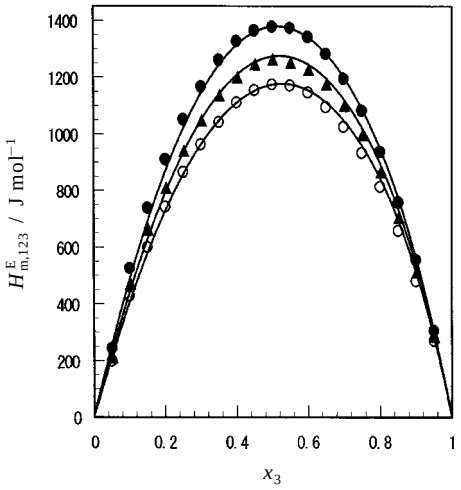

Fig.8 Excess molar enthalpies $H^E_{m,123}$/J mol^{-1} for the ternary mixtures of {methanol (x_1)+ethanol (x_2)+ 1,4-dioxane (x_3)} at 298.15 K. (●) $x'_1=0.25$, (▲) $x'_1=0.50$, (○) $x'_1=0.75$; −, Predicted by the UNIQUAC association model.

5. Conclusions

The experimental excess molar enthalpies of alcohols (C_1-C_3)+MTBE or tetrahydropyran or 1,4-dioxane mixtures are analyzed with a UNIQUAC associated solution model. This model satisfactorily explained the binary and ternary mixtures with the association constants, solvation constants and binary information alone.

References

1) I. Nagata and K. Tamura, *Fluid. Phase Equlib.* **41**, 27 (1988).
2) I. Nagata and K. Tamura, *J. Chem. Thermodyn.* **21**, 955 (1989).
3) I. Nagata and K. Tamura, *Fluid Phase Equilib.* **15**, 67 (1983).
4) I. Nagata and K. Tamura, *J. Chem. Thermodyn.* **16**, 975 (1984).
5) I. Nagata and K. Tamura, *Fluid Phase Equilib.* **24**, 289 (1985).
6) I. Nagata and K. Tamura, *J. Chem. Thermodyn.* **17**, 747 (1985).
7) K. Tamura and I. Nagata, *J. Chem. Eng. Data* **31**, 410 (1986).

8) I. Nagata and K. Tamura, *Thermochim. Acta* **104**, 179 (1986).
9) I. Nagata, K. Tamura, H. Kataoka, and A. Ksiażczak, *J. Chem. Eng. Data* **41**, 593 (1996).
10) I. Nagata, K. Tamura, and K. Miyai, *Fluid Phase Equilib.* **149**, 147 (1998).
11) K. Tamura, M. Saito, and T. Yamada, *J. Chem. Eng. Data* **44**, 626 (1999).
12) K. N. Marsh, P. Niamskul, J. Gmehling, and R. Bölts, *Fluid Phase Equilib.* **156**, 207 (1999).
13) D. J. Cram and J. M. Cram, *Science* **183**, 803 (1974).
14) R. F. Jameson, in: H. A. Skinner (Ed.), *Thermochemistry and Thermodynamics, MTP International Review of Science*, Butterworths: London (1972).
15) H. V. Kehiaian, in: H. A. Skinner (Ed.), *Thermochemistry and Thermodynamics, MTP International Review of Science*, Butterworths: London (1972).
16) E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. V. R. Schleyer, *J. Am. Chem. Soc.* **92**, 2365 (1970).
17) C. N. R. Rao, P. C. Dwivedi, H. Ratajczak, and W. J. Orville-Thomas, *J. Chem. Soc. Faraday Trans. 2.* **71**, 955 (1975).
18) T. M. Letcher and U. P. Govender, *J. Chem. Eng. Data* **40**, 1097 (1995).
19) T. M. Letcher and P. U. Govender, *J. Chem. Eng. Data* **40**, 997 (1995).
20) K. Tamura, M. M. H. Bhuiyan, and T. Yamada, *Thermochim. Acta* **376**, 9 (2001).
21) M. M. H. Bhuiyan, K. Tamura, and T. Yamada, *J. Chem. Eng. Data* **46**, 1499 (2001).
22) K. Tamura, M. M. H. Bhuiyan, and T. Yamada, *Int. J. Thermophys.* **22**, 1739 (2001).
23) Nihon Kagaku Kai: Shin Jikken Kagaku Kouza 2 Kiso Gijyutsu 1 Netsu. Atsuryoku, Maruzen (1977).
24) M. L. McGlashan, chief-in-editor: *Chemical Thermodynamics Vol 2, The Chemical Society*, Burlington, London (1978).
25) I. Nagata, K. Tamura, S. Ozaki, and K. Myohen, *Thermochim Acta* **209**, 31 (1992)
26) H. Ogawa and S. Murakami, *Netsu Sokutei* **12**, 163 (1985).
27) W. E. Jr. Arcee, "*Thermodynamic Properties of Nonelectrolyte Solutions*", Academic Press, Inc., London (1984).
28) K. Marsh and F. Kohler, *J. Molecular Liq.* **30**, 13 (1985).
29) J. M. Prausnitz, R. N. Lichtenthaler, and E. G. de Azevedo, "*Molecular Thermodynamics of Fluid Phase Equilibria*", 2nd edn., Prentice-Hall Inc., Englewwood Cliffs. NJ. (1980).
30) A. Anderko, *Fluid Phase Equilib.* **61**, 145 (1990).
31) R. W. Haskel, H. B. Holinger, and H. C. Van Ness, *Ibid.* **72**, 4534, (1968).
32) S. C. P. Hwa and W. T. Ziegler, *J. Phys. Chem.* **70**, 2572 (1960).
33) C. B. Kretschmer and R. Weibe, *J. Chem. Phys.* **22**, 1697 (1954).
34) H. Renon and J. M. Prausnitz, *Chem. Eng. Sci.* **22**, 299, Errata, 1891, (1967).
35) L. Sarolea-Malhot, *Trans. Faraday Soc.* **49**, 8 (1953).
36) I. A. Wiehe, *Chem Eng. Sci.* **23**, 1283 (1968).
37) I. A. Wiehe and E. B. Bagley, *Ind. Eng. Chem. Fundamentals* **6**, 209 (1967).
38) T. Nitta and T. Katayama, *J. Chem. Eng. Japan* **6**, 1 (1973).
39) T. Nitta and T. Katayama, *J. Chem. Eng. Japan* **6**, 224, (1973).
40) H. Renon and J. M. Prausnitz, *Chem. Eng. Sci.* **22**, 299 (1967).
41) I. Nagata, *Z. Phys. Chem.* (*Leipzig*) **254**, 273 (1973).
42) W. C. Coburn and E. Grunwald, *J. Am. Chem. Soc.* **80**, 1318 (1958).
43) A. N. Fletcher and C. A. Heller, *J. Phys. Chem.* **71**, 3742 (1967).
44) H. Kempter and R. Mecke, *Z. Physik. Chem.* (*Leipzig*) **46**, 229 (1940).
45) M. Saunders and J. B. Hyne, *J. Chem. Phys.* **29**, 1319 (1958).
46) F. E. Tuker, S. B. Farnham, and S. D. Christian, *J. Phys. Chem.* **73**, 3820 (1969).
47) C. G. Savani, D. R. Winterhater, and H. C. Van Ness, *J. Chem. Eng. Data* **10**, 171 (1965).
48) C. G. Savani, D. R. Winterhater, and H. C. Van Ness, *J. Chem. Eng. Data* **10**, 168 (1965).
49) H. C. Van Ness, *Personal Communication* (1966).
50) J. Gmehling and T. Holderbaum, *Heats of Mixing Data Collection, Chemistry Data Series Vol. III, Part 3, Frankfurt am Main*, April (1991).
51) J. J. Christensen, R. L. Rowley, and R. M. Izzat, *Handbook of Heats of Mixing*, Wiley Interscience, April (1988).
52) I. Nagata and Y. Kawamura, *Z. Physik. Chem. Neue Folge* **107**, 141 (1977).
53) I. Nagata and K. Gotoh, *Thermochim. Acta* **102**, 207 (1986).
54) I. Nagata, K. Tamura, and K. Gotoh, *Thermochim. Acta* **104**, 179 (1986).

55) D. S. Abrams and J. M. Prausnitz, *Am. Inst. Chem. Eng. J.* **21**, 116 (1795).
56) V. A. Brandani, *Fluid Phase Equilib.* **12**, 87 (1983).
57) R. H. Stokes and C. Burfitt, *J. Chem. Thermodyn.* **5**, 6236 (1973).
58) J. H. Vera, S. G. Sayegh, and G. A. Ratcliff, *Fluid Phase Equilib.* **1**, 113 (1977).

要　旨

アルコールおよびエーテルを含む多成分溶液の過剰エンタルピーの測定法および多成分系過剰エンタルピーを工学的に表す方法について述べられている。解析モデルとしてアルコールの水酸基による分子間会合およびアルコールとエーテル間の異種分子間会合を考慮したUNIQUAC会合溶液モデルを紹介する。注目した多成分系として，2種類のアルコールとエーテルから成る3成分系溶液では，それぞれのアルコールの自己会合ならびに異種アルコール間での多重溶媒和した会合種，およびアルコールとエーテル間の異種分子間会合がモデル化されている。この3成分溶液の過剰エンタルピーは3成分系を構成している三つの構成2成分系パラメータのみを用いて，良好に推算できることが示されている。

Mohammad Mainul Hossain Bhuiyan
Dept. of Applied Chemistry and Chemical Technology, Faculty of Applied Science and Technology, Islamic Univ., Kushtia 7003, Bangladesh, e-mail: bhuiyan2003@hotmail.com
研究テーマ：Thermodynamics of Multicomponent Liquid Mixtures
趣味：Sight Seeing, Listen to Music

Kazuhiro Tamura
Dept. of Chemistry and Chemical Engineering, Kanazawa Univ., TEL. 076-234-4804, FAX. 076-234-4829, e-mail: tamura@t.kanazawa-u.ac.jp
研究テーマ：Molecular Thermodynamics of Fluid Phase Equilibria
趣味：Music

【 会員のページ 】

科学雑誌の使命
－実験データは「おまけ」か？－

最近科学雑誌を読んだり，投稿したりするときに，大変気になっていることがあります。それは，掲載される論文から実験や観察の詳細な結果が消えていることです。これはよく読まれている雑誌ほどその傾向が強いと思われます。雑誌の言い分は，年々論文数が増えるので論文ごとのページ数を圧縮せざるをえないと言うことでしょうか。たとえば，アメリカ化学会ACSのJACSでは，実験の詳細は冊子体には掲載されずに，論文付随の「おまけ」SupplementとしてACSのホームページから引き出すようになっています。実際にどの程度丁寧に査読されているのかは不明ですが，査読する者の立場に立てば，どうしても「おまけ」の扱いは軽くなってしまいます。最近，物理や考古学で論文の捏造が問題になっていますが，実験や観察の詳細が直ぐに分からない状況を科学雑誌自身が作り出しています。

冊子体となった科学雑誌は将来の利用のために図書館に収められます。実際に，私たちが図書館に収められている古い雑誌の論文を読むことを思い起こしてみると，実験とその結果の詳細，あるいは理論の丁寧な導出を知るためにそれらを読んでいることに気づきます。実験の最終結果や要約は，重要なものであれば，いずれどこかに必ず引用されるので，わざわざ原論文で確認する必要もないからです。実験の詳細が分からない雑誌は，その当時何が流行していたかを示すだけの単なる文化遺産と言うことになります。これでは駅の売店で売られている通俗雑誌と同じです。科学雑誌の基本的使命は，実験や観測の詳細を知り，それによって導き出された値や結論を将来に亘って評価できるようにすることであると思います。現在の科学雑誌は，その最も大切な部分を安易に削っているのではないでしょうか。果たして，100年後の研究者たちは我々の時代の科学雑誌を図書館に残しておく価値があると評価してくれるでしょうか。

（大阪大学　長野八久）