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A Study on Intermolecular Interactions of Organic Binary Systems

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Abstruct: Intermolecular interaction of polar-nonpolar binary systems such as amine-benzene, alcohol-cyclohexane, and acetic acid-dioxane, and of polar-polar binary such as amine-water, alcohol-water, and acetic acid-water were studied by a viscosity method. These results exhibit the existence of the maximum viscosity in all polar-water binary systems, suggesting interesting intermolecular interactions. The maximal viscosity and their positions are 2.19, 2.44, and 2.94 centi poise (cP), and 80, 50, and 65 vol. %, for acetic acid-water, n-propyl amine-water, n-propyl alcohol-water binary systems, respectively, in which amine or alcohol molecule is bound by about three molecules of water and two molecules of acetic acid, a dimer, interact with two water molecules. The dimer of acetic acid makes the intermolecular frictions in dioxane increase but them in cyclohexane or benzene decrease. No evidence for a dimer of alcohol or amine are detected by this viscosity method.

Introduction

A similar tendency in boiling points involved in a series of hydrocarbons, acyl chlorides, and halides is interpreted to be arised from their weak Van der Waals forces.[1] Intermolecular interactions in polar molecules such as amines, alcohols, carboxylic acids, and water are known to be resulted from the hydrogen bonds and to produce much higher boiling points than those expected from corresponding hydrocarbons with similar molecular weights.[1,2]

Few reports have been, however, done on intermolecular interactions expected in organic binary systems of polar-polar or polar-nonpolar but the detection for the dimer of acetic acid in cyclohexane or carbon tetrachloride.[3] The facts that the ethyl alcohol-water binary system exhibits a minimum boiling point at 95 vol. % and produces a minimum volume at 50

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vol. % of ethyl alcohol, respectively, have been recognized by various physical measurements.[3] Also some lower alcohols are considered to be indefinitely dissolved in water because of similar molecular structure and hydrogen bonds.[4] Such intermolecular interaction phenomena, changes in their physical properties, have not been correlated with the new hydrogen bonds or new compounds expected in the alcohol-water binary systems.

It is reasonable to presume a formation of a new compound in various binary systems and an effect on an apparent molecular weight or density, resulting in changes for boiling point, volume, viscosity and so on. Changes in viscosity are essentially considered as a result of frictional changes between molecular layers associated by hydrogen bonds, and as a measure of the strength of intermolecular interactions.[4]

In this paper, present authors intend to report such an intermolecular interaction existed in polar-nonpolar or polar-polar binary systems, on the assumption that the viscosity method is the best one for a kinetic research in such binary systems, including water, alcohol, and acetic acid.

Experimental

All organic solvents were purchased from Tokyo Kasei kogyo Co., LTD., and stored under a dry box after redistillation. Viscosities in all samples were measured by the use of Ostwald type viscosity meter with 90.0 ± 0.1 sec. for water at 25°C. The viscosity meter was vertically held under all measurements by a special holder in a thermostat with a precision of 0.005°C. All samples prepared by volumetric method were placed in thermostat and kept at the temperature for 10 min. before measurements. Then the sample was transferred into the viscosity meter without warming up or cooling down. All data were averaged out 5 measurements for each sample. Densities of all samples were calculated from their weight. Viscosities for pure solvents measured at 25°C were 0.902, 0.719, 1.752, 2.359, 0.497, 1.093, 1.110, 0.676, 0.894, 1.087, and 0.563 for water, methyl alcohol, ehtyl alcohol, n-propyl alcohol, n-propyl amine, acetic acid, propionic acid, denzene, cyclohexane, dioxane, and carbon tetrachloride, respectively.

Results and Discussion

Polar-Nonpolar binary systems: As polar solvents with approximately similar molecular weight, n-propyl amine, n-propyl alcohol, and acetic acid were selected, whereas as nonpolar solvents, dioxane, cyclohexane, and benzene with similar structure of six-member ring. Relationships of the viscosity-composition between the polar molecules listed up above, and benzene or dioxane binary systems are plotted in Figures 1 and 2. As can be seen from these figures, the viscosities of both benzene and dioxane illustrate the similar upward curvature

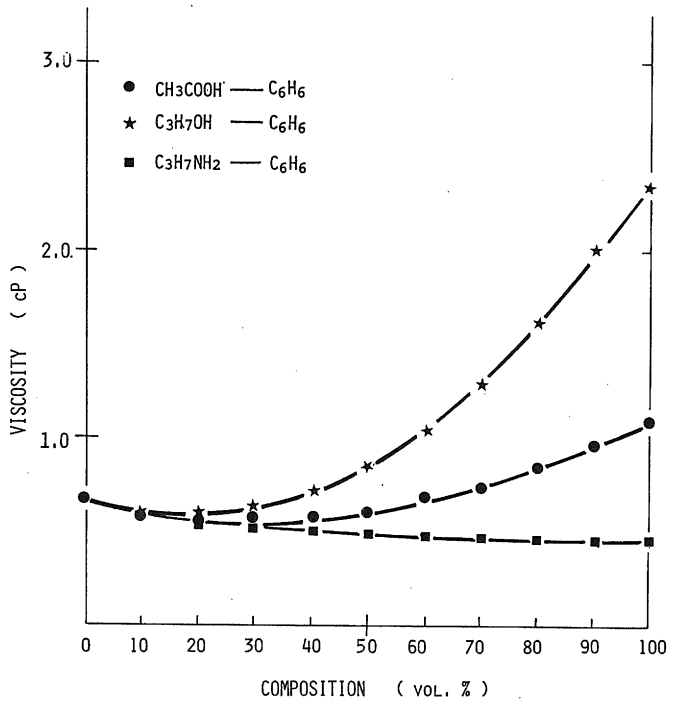

Fig. 1. Relationship of the viscosity-composition for three polar-benzene binary systems.

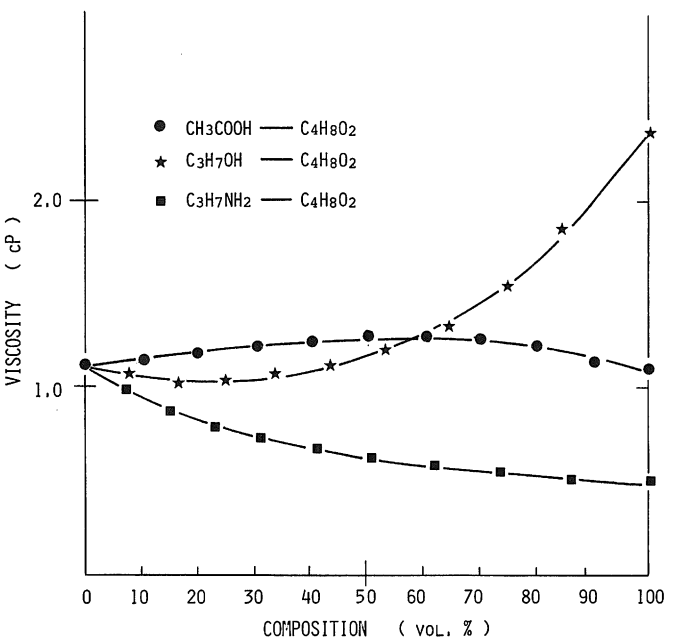

Fig. 2. Relationship of the viscosity-composition for three polar-dioxane binary systems.

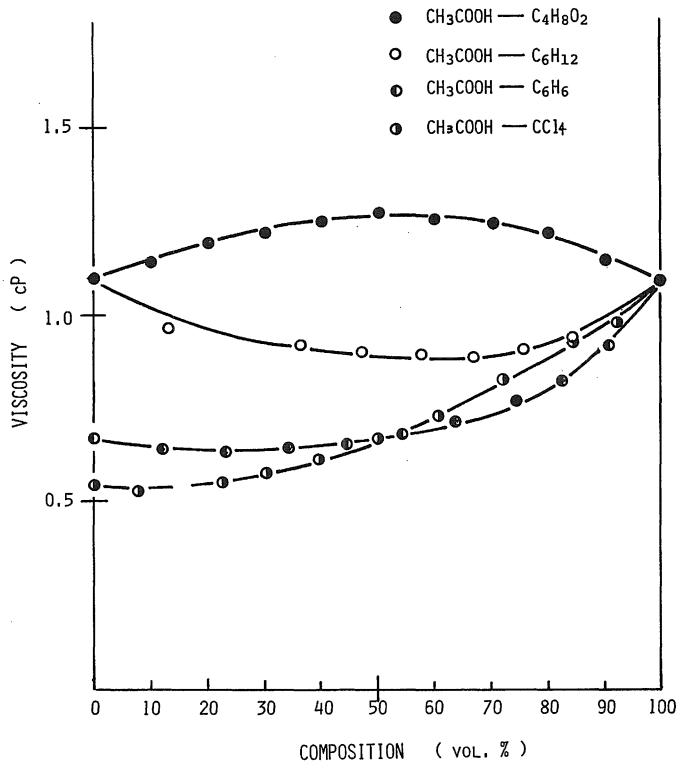

Fig. 3. Relationship of the viscosity-composition for four acetic acid-nonpolar binary systems.

with increasing volume of n-propyl alcohol and eventually approach that of n-propyl alcohol, 2.359 cP., while they display the downward linear relationship with increasing volume of n-propyl amine. Such linear relationship may be interpreted to exhibit no intermolecular interactions for these four binary systems.

On the other hand, relationships between acetic acid-benzene and acetic acid-dioxane may suggest an interesting intermolecular interaction involved in both systems, in which acetic acid exhibits the minimum viscosity in benzene solvent and the maximum viscosity in dioxane. The existence of the minimum or the maximum viscosity is interpreted as a result of different intermolecular interaction from a normal friction expected in these binary systems but may not offer a direct evidence in an existence for a dimer of acetic acid.[4)]

Other nonpolar solvents are used to confirm an abnormality of acetic acid in nonpolar binary systems and the results for the viscosity-composition relationships between the acetic acid-cyclohexane and acetic acid-carbon tetrachloride binary systems are shown in Fig. 3, together with the two curvatures obtained in Figs. 1 and 2 for comparison. In carbon tetrachloride solvent, the viscosity of acetic acid decreases with decreasing volume of acetic acid and eventually approaches that of carbon tetrachloride, 0.563 cP. The acetic acid-cyclohexane binary system exhibits the similar viscosity-composition curvature with the

acetic acid-benzene binary and shows more clearly the existence of the minimum viscosity.

This viscosity method is considered to offer a clear result for the existence of the dimer of acetic acid in both cyclohexane and dioxane, although the difference between the minimum viscosity in acetic acid-cyclohexane and the maximum value in acetic acid-dioxane is involved. Such the difference in the acetic acid-nonpolar binary systems may depend upon their properties of nonpolar solvents, especially dioxane includes two oxygen atoms with stronger electronegativity or ability for a hydrgen bond. This structural character should result in the existence of the maximum viscosity found in the acetic acid-dioxane binary system, apart from other acetic acid-nonpolar binary systems.

The dimer formation of acetic acid in dioxane may produce such new intermolecular interactions between dimer-dimer, dimer-monomer, and dimer-dioxane, increasing intermolecular friction, whereas the dimer of acetic acid in cyclohexane may give rise to a weak intermolecular interaction, decreasing its friction. An enhancement of such effect on their viscosities, resulted from the dimer formation of acetic acid in dioxane, is expected to be enhanced by a use of polar molecules as water or alcohol with stronger hydrogen bonds.

Polar-Polar binary systems: Some lower alcohols are well known to be indefinitely dissolved in water because of similar molecular structure and to form a new hydrogen bond as intermolecular combination. To research the intermolecular interactions of the lower alcohols and water binary systems, methyl alcohol, ethyl alcohol, and n-propyl alcohol were selected. The maximal viscosities for these three binary systems are 1.633, 2.441, and 2.939 cP, and their positions deviate from 40 to 65 vol. % for methyl alcohol, ethyl alcohol, and n -propyl alcohol, respectively. This result is in accord with the decrease in solubility of lower alcohols in water.[5] Furthermore, the fact that a mixing of ethyl alcohol with equivalent volume of water leads to the decrease in volume because of a formation of a stronger hydrogen bond agrees with the results that the position of the maximal viscosity is exhibited at around 60 vol. % of alcohol. The maximal viscosity decreases with the increase in temperature and leads to a reduction of intermolecular interactions. The position of the maximal viscosity deviates to lower composition with lowering temperature for ethyl alcohol and n-propyl alcohol, while it remains constant at 50 vol. % for methyl alcohol.

The viscosity in these binary systems are confirmed to be affected by the intermolecular interactions, the formation of the new hydrogen bond between alcohol and water. On the basis of this fact, subsequent experiments were carried out to acetic acid-water, n-propyl amine-water, and n-propyl alcohol-water binary systems. As can be found in these data plotted in fig. 4, the maximal viscosities involved in these three binary systems are 2.443, 2.939, and 2.190 cP and their positions lie at around 50, 65, and 80 vol. % for n-propyl amine -water, n-propyl alcohol-water, and acetic acid-water binary, respectively. Such a tendency is also observed in the case of the alcohol-water binary systems, in which the molecular size

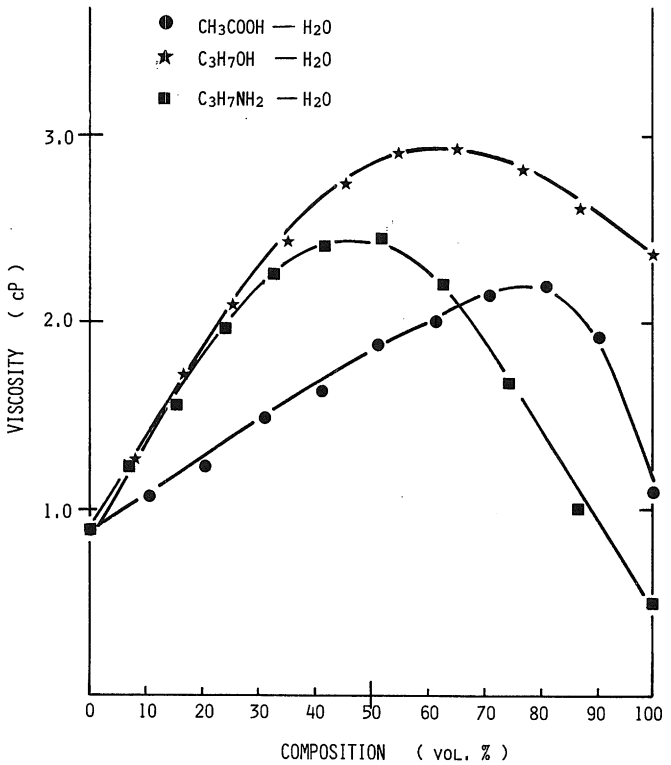

Fig. 4. Relationship of the viscosity-composition for three polar-water binary systems.

of alcohol affects the position and the value of the maximal viscosity.

Acetic acid behaves like two molecules with regard to molecular weight, suggesting a dimeric formation of acetic acid. Accordingly, these apparent viscosities should be evaluated by considering the additivity of viscosities due to intermolecular interactions and solvents themselves. The additivity in viscosity between solvents is found to be linear, if they were nonassociated solvents,[4] and then the viscosity due to solvents should be substracted from the curvature observed in Fig. 4.

The true position of the maximal viscosity is necessary to take into account their molecular weight and weight concentration, and estimates as about 42, 45, and 60 wt. % for n-propyl amine-water, n-propyl alcohol-water, and acetic acid-water binary systems, respectively. The existent ratio of between polar molecule and water in these organic binary systems were calculated as follows;

$$C_2H_7NH_2 : H_2O = \frac{42}{59} : \frac{58}{18} \fallingdotseq 1 : 5 \qquad CH_3COOH : H_2O = \frac{60}{60} : \frac{40}{18} \fallingdotseq 1 : 2$$

$$C_3H_7OH : H_2O = \frac{45}{60} : \frac{55}{18} \fallingdotseq 1 : 4 \qquad C_2H_5OH : H_2O = \frac{44}{46} : \frac{56}{18} \fallingdotseq 1 : 3$$

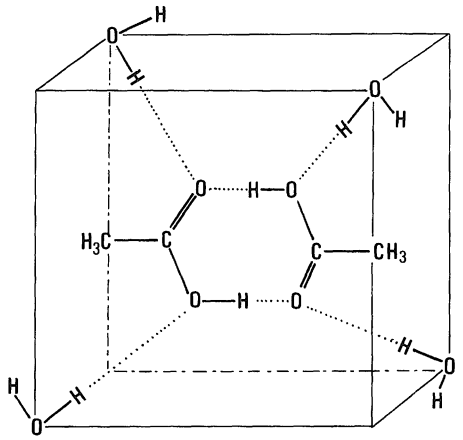

Fig. 5. Model structure for intermolecular interaction detween acetic acid and water.

This calculation provides the first evidence for the existence of a dimer of acetic acid, in which the dimer is surrounded by four molecules of water. The new association state is illustrated in Fig. 5. As can be seen in Figure, the dimer occupied at a center of an apparent cubic lattice are surrounded by four water molecules. For ethyl alcohol, one molecule may occupy at one corner and the center of the similar cube, and its hydroxy group is surrounded by three molecules of water which occupy at special three corner. Furthermore, n-propyl alcohol or n-propyl amine may be interacted with four or five water molecules, suggesting the low solubility in water.

In this paper, present authors succeeded in the explanation of the interesting intermolecular interaction found in organic binary systems by the discovery of the new association state, in which they were formed by the hydrogen bond. Some association state may produce an increase or decrease in viscosity of binary systems. To further confirm such intermolecular interactions in organic binary systems, other binary systems as alcohol-acetic acid, alcohol -amine, or amine-acetic acid should be studied.

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