August, 1975] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(8), 2367—2371 (1975) 2367

The Partial Molal Volumes of Normal Chain Alcohols in Water–Ethanol Mixtures at 25 °C

Masahiro Manabe and Masaharu Koda

Department of Technical Chemistry, Niihama Technical College, Niihama, Ehime 792

(Received April 4, 1975)

The partial molal volumes ($\bar{V}^0$) of *n*-alcohols (R_mOH, $m=1-7$) at an infinitely dilute concentration in water-ethanol mixtures of various compositions have been determined by means of dilatometry. The $\bar{V}^0$ value does not depend on the concentration of the solute alcohol within the region studied in any composition of the solvent mixtures. The excess volume, the difference between $\bar{V}^0$ and the molal volume (V^0), is negative and is at a minimum in water-rich mixtures (<16 wt% ethanol) for all of the alcohols studied. On the other hand, in the moderate composition range the excess volumes for R_4OH and higher alcohols are positive and reach a maximum distinct from the disappearance of the maximum for R_3OH and lower alcohols. The volumetric contribution of a methylene group ($\bar{V}^{me}$) to $\bar{V}^0$ was separately evaluated. From the results, a linear relation was found between $\bar{V}^0$ and the alkyl chain length of the alcohols in the mixtures of 0—8 and 55—100 wt% ethanol, while in the mixtures the relationship was rather quadratic. Such volumetric behavior was discussed on the basis of the structural properties of the water–ethanol mixtures.

It is well known that a substance with alkyl groups such as surfactants or tetraalkylammonium halides shows anomalous behavior in the water-rich region of water-organic solvents (cosolvent) mixtures. For example, the critical micelle concentration (CMC)[1–3] and the Krafft point[4] of surfactants decrease with an increase in the content of such cosolvents as lower alcohols. Some of the phenomena can be interpreted on the basis of the structure-making effect of water, (hydrophobic interaction) upon the addition of the cosolvent. In more cosolvent-rich aqueous mixtures, however, the CMC increases, *via* a minimum, with the cosolvent content[5] and the micelle formation can not be detected at any specific composition of the mixture,[6,7] Ralston and Hoerr[8] investigated the solubility of dodecylammonium chloride in water–ethanol mixtures at various temperatures and found a maximum of solubility in a moderate composition range of the mixed solvent (*ca.* 40—80 wt% ethanol). Such a maximum solubility was attributed to the micelle formation.[9] Lee and Hyne[10] reported, after a study of the partial molal volume of tetraalkylammonium chlorides in water–ethanol mixtures, that the partial molal volumes of the cation showed a minimum at the 0.1 mol fraction of ethanol as well as a maximum at the 0.3 mol fraction, while that of the anion showed a minimum at the 0.3 mol fraction. These results were interpreted in terms of the structure of the solvent. A knowledge of the volumetric properties of model compounds, such as *n*-alcohols in water-cosolvent mixtures, will help us to understand the behavior of amphipathic compounds in the mixtures, mainly in relation to the structural effect of the mixtures. No systematic study of a homologous series over a complete concentration range of water-cosolvent mixrures has ever been reported.

In this study, we have determined the partial molal volume of *n*-alcohols, a typical homologous series, in water–ethanol mixtures by means of dilatometry, which is capable of determining the partial molal volume of a higher alcohol at a much lower concentration than it possible with the density method. We have attempted to see how the partial molal volume of *n*-alcohols and the contribution of a methylene group to it vary with the composition of the mixed solvent.

Experimental

A series of *n*-alcohols with 1—7 carbon atoms (R_mOH) was used in the present work. The lower alcohols ($m=1—4$) were distilled after refluxion over C_aO, while the higher alcohols were distilled under atomspheric or reduced pressures. They were confirmed to be pure by gas-liquid chromatography. The water used as the solvent was obtained by the distillation of water deionized with ion-exchange resin.

The dilatometer used for the measurement of the partial molal volumes of solute alcohols in water–ethanol mixtures is shown in Fig. 1. It consists of a glass bulb with a capacity of 120—200 ml, equipped with a magnetic roter coated with Teflon, a vertical uniform capillary (1.8 mm internal diameter), and an injection aperture which is sealed with a silicone rubber fixed with a metal fitting. The capillary was calibrated exactly with mercury. The dilatometer was filled with a mixed solvent of a given composition through a polyethylene tube fine and long enough to reach the bulb under pressure reduced by means of an aspirator to remove any dissolved air.[11] In each run, about 30 mg of R_mOH (weighing 1/100 mg) was injected through the injection aperture into the dilatometer by means of a microsyringe

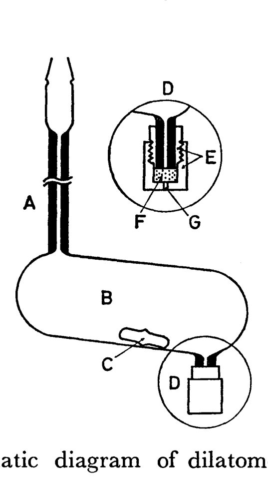


Fig. 1. Schematic diagram of dilatometer and its injection.
A: uniform capillary, 20 cm long and 1.8 mm internal diameter. B: grass bulb, capacity of 120—200 ml. C: magnetic roter. D: injection. E: metal fitting. F: silicone rubber. G: injection aperture.

TABLE 1. PARTIAL MOLAL VOLUMES OF *n*-ALCOHOLS IN WATER-ETHANOL MIXTURES AT 25 °C

Ethanol content (wt%)	Chain length						
	1	2	3	4	5	6	7
0	38.00	54.92	70.40	86.12	101.8_1	117.5_6	133.4_3
4	37.56	54.09	69.49	85.01	100.4_8	115.9_7	131.3_9
8	37.30	53.32	68.65	83.99	99.40	114.7_9	130.1_6
12	37.12	52.85	68.18	83.69	99.29	115.1_3	131.1_9
16	36.96	52.62	67.89	83.87	100.1_1	116.5_2	133.1_8
20	37.30	53.12	68.82	85.51	102.4_6	119.9_0	137.5_5
25	37.68	53.70	70.04	87.30	105.1_4	123.9_4	142.8_8
30	37.75	54.27	71.35	89.30	108.1_8	128.1_0	148.4_4
35	38.13	55.06	72.66	91.01	110.3_0	130.1_0	150.1_7
40	38.53	55.77	73.48	92.14	111.7_5	131.3_8	151.2_3
45	38.63	56.08	74.17	92.99	111.9_8	131.0_9	150.3_0
55	39.01	56.64	74.94	93.46	111.9_2	130.3_1	148.6_2
70	39.44	57.34	75.18	93.00	110.8_5	128.4_9	146.1_5
90	40.15	58.20	75.18	92.12	109.2_0	126.1_5	143.2_0
100	40.20	58.34	75.13	91.75	108.4_0	124.9_1	141.5_3
0[a)]	38.05	54.97	70.20	85.77	101.92		
$\bar{V}^{\circ}$ [b)]	40.74	58.69	75.38	92.07	108.76	125.46	142.15

a) Data from Ref. 14 (20 °C) b) The molal volumes of pure alcohols calculated from Eq. (1) except for R_1OH and the value of R_1OH was taken from Ref. 17.

five times successively. After each of the injections, the solution was stirred with a magnetic stirrer until the dissolution was complete.

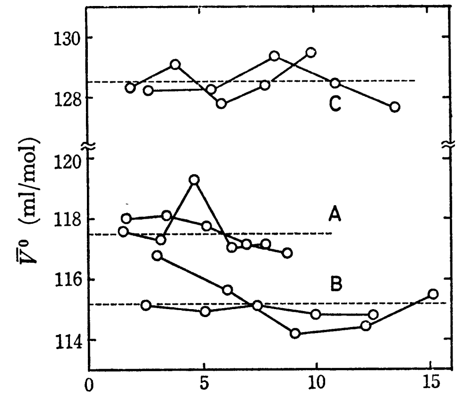
The height of the meniscus of the solution in the capillary was read to 0.01 mm with a cathetometer. The partial molal volume of the solute alcohol could be calculated from the difference in the height of the meniscus and the quantity of alcohol added. The final concentration of the solute alcohol in any mixed solvent was far lower than its solubility in water.[12)] The measurement was carried out at least two runs for each system. The standard deviations of these partial molal volumes were about 0.5% of their mean values.

All of the measurements were made at 25 °C in a water thermostat, the temperature of which was carefully controlled at ±0.001 °C.

Results and Discussion

Concentration Dependence of the Partial Molal Volume. No appreciable change in the partial molal volume of solute alcohol with its concentration was found within the limits of experimental error during one run in any water–ethanol mixture. Some illustrative examples for R_6OH are shown in Fig. 2. Franks and Smith[13)] suggested that in the absence of solute-solute interactions, the apparent molal volume had no concentration dependence in the region of infinite dilution. The present measurements were carried out at very low concentrations, lower than 1 g/l. The mean value of the partial molal volumes of alcohols determined in water is in good agreement with the published values[14)] obtained by extrapolating the density data to an infinite dilution. Therefore, the mean value can be regarded as the partial molal volume ($\bar{V}^0$) of the solute alcohol in an infinitely diluted solution; it is shown in Table 1.

Ethanol-Content Dependence of the Partial Molal Volume. It is well known that many physicochemical properties show anomalous behavior in a predominantly aqueous composition range of water-lower alcohols binary systems.[15)] Such behavior has generally been interpreted in terms of a structure-making effect, which continues up to a certain concentration of alcohol. The concentration dependence of the intensities of the X-ray diffraction band for water-cosolvent mixtures directly reveals the structural property; the high-intensity peak in a dilute aqueous solution of ethanol confirms the concept of a structure-making effect, and for the water–dioxane system the intensities falling below those calculated on the basis of additivity suggest a water-structure-breaking effect of dioxane.[16)] The first derivatives of the viscosity-concentration curve, $d\eta/dC$, for the water–ethanol system increase to a maximum as the ethanol concentration increases; this fact suggests a structure-making effect. In the water–dioxane system, $d\eta/dC$ decreases with an increase



Concentration of R_6OH (mmol/l)

Fig. 2. Concentration dependence of $\bar{V}^0$ for R_6OH in water-ethanol mixtures. Experimental value (○), mean value (----). Ethanol content in wt%; A: 0, B: 12, C: 70.

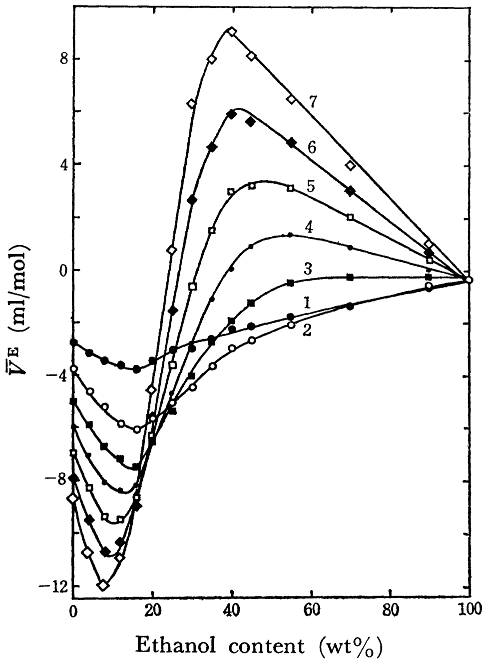


Fig. 3. The $\bar{V}^E$ values as a function of ethanol content in water-ethanol mixtures. The numbers indecate chain length of *n*-alcohols.

in the dioxane concentration, exhibition a structure-breaking effect, as has been pointed out by Franks.[5] The feature of the concentration dependence of the intensity of the X-ray diffraction band is in accordance with the dependence of the $d\eta/dC$ in both systems on the structural effect.

A comparison of the $\bar{V}^0$ values with each other and with V^0, a molal volume in the pure state for alcohols, makes it possible to calculate the excess molal volume ($\bar{V}^E$) from this definition, $\bar{V}^E = \bar{V}^0 - V^0$, where V^0 is given by

$$V^0 = 16.69m + 25.30 \quad (m=2-7) \tag{1}$$

except for R_1OH. The two constants in this equation were determined by using the densities of pure alcohols reported in the literature.[17-19] The plots of $\bar{V}^E$ *vs.* the compositions of the water–ethanol mixtures are given in Fig. 3. The $\bar{V}^0$ values of R_2OH in the water–ethanol binary system are in good agreement with those obtained from the densities of the mixture.[20] The concentration dependence of $\bar{V}^E$ for R_2OH shows two distinct features. One is a negative dependence observed at lower ethanol concentrations (<16 wt% ethanol), and the other is a positive dependence observed at higher concentrations. The concentration at which the partial molal volume of R_2OH reaches its minimum is roughly compatible with that at which the intensity peak of the X-ray diffraction and the maximum of $d\eta/dC$ appear. Therefore, it may be concluded that the negative concentration dependence of $\bar{V}^E$ on R_2OH reflects a structure-making tendency, and the positive dependence of $\bar{V}^E$, a structure-breaking one. On the other hand, for the water–doxane system no such negative dependence of $\bar{V}^E$ on dioxane appears; only a positive one appears and the excess volume reaches positive values.[21] This may be attributed to the structure-breaking effect of dioxane.

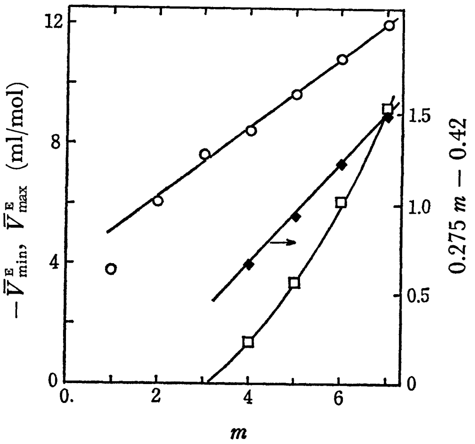


Fig. 4. Chain length dependence of $\bar{V}^E_{min}$ and $\bar{V}^E_{max}$.
○: $\bar{V}^E_{min}$, □: $\bar{V}^E_{max}$, ◆: $(\bar{V}^E_{max}+1.36)/m$,
——: $0.275\,m-0.42$, in Eq. (5).

Hardly no anomalous volumetric behavior for three-component systems has yet been reported.[10] In the present study, the system includes a very small quantity of the third component (*n*-alcohol), so that the interaction between solute molecules is negligible, judging from the independence of $\bar{V}^0$ of the solute concentration, as is shown in Fig. 2. Therefore, it may be considered that the added alcohol behaves volumetrically as a probe for the structuredness of a mixed solvent itself. As is shown in Fig. 3, the $\bar{V}^E$ values for all of the *n*-alcohols studied here are negative in the water-rich mixtures and decrease with an increase in the ethanol content (<16 wt% ethanol). This can be explained as follows: the solute alcohol is accommodated well in cavities which are formed with water molecules upon the addition of a small amount of ethanol in water, and the process of accommodation requires less space for the solute alcohol, leading to a decrease in the partial molal volume.

At a certain composition of ethanol, that at which the $\bar{V}^E$ value attains its minimum, the structuredness of the water–ethanol mixtures also reaches a maximum (8—16 wt% ethanol). The minimum value of $\bar{V}^E$, denoted by $\bar{V}^E_{min}$, exhibits a linear relation with the chain length of alcohols except for R_1OH, as is shown in Fig. 4. This relation may be expressed as:

$$\bar{V}^E_{min} = -1.17m - 3.86 \quad (m=2-7) \tag{2}$$

This relation may be converted into the following one for $\bar{V}^0_{min}$ by considering both Eq. (1) and the difinition of $\bar{V}^E$.

$$\bar{V}^0_{min} = 15.52m + 21.44 \quad (m=2-7) \tag{3}$$

where $\bar{V}^0_{min}$ is the minimum partial molal volume of a solute alcohol. This linear relation suggests that, at the specific composition of the mixed solvent where $\bar{V}^E$ reaches its minimum, the dissolved state of each methylene group is the same as that for the solute alcohol and the group occupies the cavities formed with water molecules in the same way. In other words, at the specific solvent composition the methylene groups may be dissolved into the corresponding state.

In the mixtures with moderate compositions of ethanol (8—55 wt%), the $\bar{V}^E$ value of the solute alcohol increases with an increase in the ethanol content, while the value for R_4OH and higher alcohols becomes positive and reaches a maximum, denoted by $\bar{V}^{E}_{\max}$, though the value for R_3OH and lower alcohols increases monotonously *i.e.*, $\bar{V}^{E}_{\max}$ disappears, as is shown in Fig. 3. The increases in $\bar{V}^{E}$ for all of the alcohols with an increase in the ethanol content may contribute to the structure-breaking tendency of the solvent mixtures as the ethanol content increases. Such a volumetric behavior that $\bar{V}^{E}$ becomes positive and reaches a maximum value has not previously been known for any binary systems of water–lower alcohol mixtures. It may be due to the fact that higher alcohols are not sufficiently miscible with water. If a long-chain compound could be dissolved in water up to relatively high concentrations, such a volumetric behavior might appear even in the binary system, just as is seen in the water–dioxane binary system.[21] The appearance of $\bar{V}^{E}_{\max}$ in the present ternary system means that the water–ethanol mixture at the composition corresponding to $\bar{V}^{E}_{\max}$ has, essentially, a closer-packed structure around the solute alcohol molecule than any other mixture and pure ethanol. That is, the dissolution of the solute requires a maximum expansion of the solvent to accommodate the solute, with a consequent minimum free volume and $\bar{V}^{E}_{\max}$ becomes higher as the size of the solute molecule increases. The plots of $\bar{V}^{E}_{\max}$ against the chain length of alcohol are also shown in Fig. 4. The curve is concave upward, distinct from the linear relation between $\bar{V}^{E}_{\min}$ and m, it may be expressed as in the following relation by the method of least squares in the second order:

$$\bar{V}^{E}_{\max} = 0.275m^2 - 0.42m - 1.36 \quad (m=4-7) \qquad (4)$$

This equation can then be rewritten as follows:

$$(\bar{V}^{E}_{\max} + 1.36)/m = 0.275m - 0.42 \quad (m=4-7) \qquad (5)$$

The value of the left-hand side falls on the straight line obtained from the right-hand-side values, as is shown in Fig. 4. When $\bar{V}^{E}_{\max}=0$, $m=3.1$ from the equation; this value of m indicates the shortest chain length for $\bar{V}^{E}_{\max}$ to appear, that is, for R_3OH and lower alcohols, the maximum of $\bar{V}^{E}$ does not appear. This finding does not conflict with the results shown in Fig. 3. That $\bar{V}^{E}_{\max}$ is equal to zero means that the environment of the solute alcohol in the mixed solvent having a close-packed structure is volumetrically the same as that in pure ethanol, as is apparent from the definition of $\bar{V}^{E}$.

At a higher content of ethanol, the $\bar{V}^{E}$ values for all of the alcohols converge toward zero in pure ethanol with an increase in the ethanol content, as is shown in Fig. 3. This suggests that the properties of the water–ethanol mixtures come close to that of pure ethanol as the ethanol content increases. The fact that the $\bar{V}^{E}$ values for all of the alcohols in pure ethanol are equal to zero means that the mixing of any alcohol and ethanol is volumetrically ideal.

The compositions of the solvent at which $\bar{V}^{E}$ reaches its minimum and its maximum shift toward a lower ethanol content with an increase in the chain length of alcohols higher than R_3OH. In addition, the longer the alkyl chain length the larger $\bar{V}^{E}$ becomes.

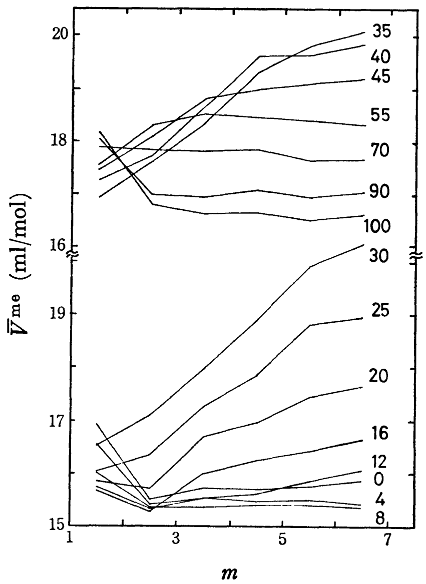


Fig. 5. Chain length dependence of $\bar{V}^{me}$ for *n*-alcohol. The numbers indecate the ethanol content in wt% in water–ethanol mixtures.

Such behavior can be discussed on the basis of the difinite volumetric contribution of the methylene group to the $\bar{V}^{0}$ of the solute alcohols.

Contribution of the Methylene Group to the Partial Molal Volume. The difference in $\bar{V}^{0}$ between two successive homologous alcohols is taken as the volumetric contribution of a methylene group ($\bar{V}^{me}$) to $\bar{V}^{0}$. Here, we will denote the contribution of the methylene group of a definite couple as $\bar{V}^{me}$ $(m, m+1)$, if necessary. The $\bar{V}^{me}$ value is plotted against the chain length, m, in Fig. 5; the features of the figure may be summarized as follows:

(I) $\bar{V}^{me}$ is independent of m in the mixtures at compositions lower than that at which $\bar{V}^{E}$ reaches its minimum (0—8 wt%).

(II) The increment in $\bar{V}^{me}$ is nearly linear with an increase in the chain length in the mixtures of 12—35 wt%.

(III) In the much more ethanol-rich region (40—100 wt%), $\bar{V}^{me}$ tends to be nearly constant with the methylene groups apart from the hydroxyl group in the alcohol molecule. The contribution of the methylene group obtained for both R_1OH and R_2OH, $\bar{V}^{me}$ (1, 2), is anomalous in the water or ethanol-rich mixtures compared with the moderate-content region. It is well known that various properties of *n*-alcohols usually have a linear dependence on the chain length. This is the case for $\bar{V}^{me}$ in water-rich and ethanol-rich mixtures, as is shown in Fig. 5. However, it is obvious from (II) that, in the mixtures with moderate compositions (12—35 wt%), $\bar{V}^{0}$ is the quadratic or the higher-order function of the chain length of the solute alcohol. In other words, even the methylene groups apart from the hydroxyl group in the alcohol molecule may be affected by the latter group. Therefore, the volumetric behavior of the alcohols in these mixtures is complex.

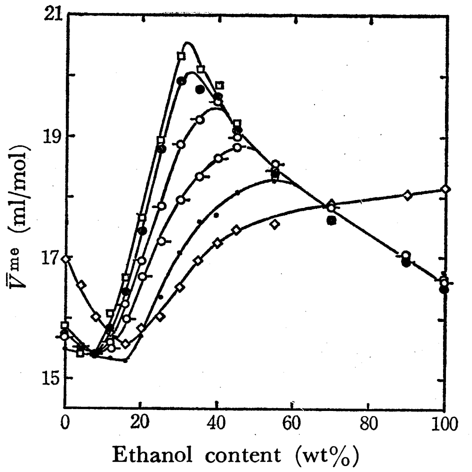


Fig. 6. The $\bar{V}^{me}$ values as a function of ethanol content in water-ethanol mixtures.
◇: (1,2), •: (2,3), ○-: (3,4), -○: (4,5), ●: (5,6), □: (6,7)
The numbers in parentheses indicate chain length of *n*-alcohols.

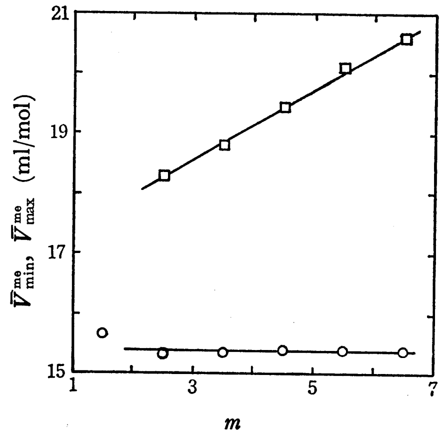


Fig. 7. Chain length depencence of $\bar{V}^{me}_{min}$ and $\bar{V}^{me}_{max}$.
○: $\bar{V}^{me}_{min}$, □: $\bar{V}^{me}_{max}$.

Figure 6 shows the relation between $\bar{V}^{me}$ and the ethanol content in the water–ethanol mixtures. The gross features of the curves are similar to those of the curves in Fig. 3; that is, the curve of $\bar{V}^{E}$ (1, 2) exhibits a minimum but no maximum and other curves in either case. It may be noted that the curve for $\bar{V}^{me}$ (2, 3) exhibits a maximum, although the curves for $\bar{V}^{E}$ of R_2OH and R_3OH exhibit no maximum in Fig. 3. The s-type curves except for that corresponding to lower alcohols gather to become a single line in the water and the ethanol-rich region, as may be seen from (I) and (II).

We denote the minimum and maximum of $\bar{V}^{me}$ in Fig. 6 as $\bar{V}^{me}_{min}$ and $\bar{V}^{me}_{max}$ respectively; then, $\bar{V}^{me}_{min}$ (1, 2) means $\bar{V}^{me}_{min}$ for the definite couple of R_1OH and R_2OH. The chain-length dependence of these values is shown in Fig. 7. It may be found from this figure that $\bar{V}^{me}_{min}$ is constant, 15.35 ml/mol, except for $\bar{V}^{me}_{min}$ (1, 2); this value is a little smaller than $d\bar{V}^{0}_{min}/dm$, 15.52 ml/mol, in Eq. (3). The ethanol content at which $\bar{V}^{me}_{min}$ appears is the same (8 wt%) for methylene groups further apart from the hydroxyl group. These features are different from the monotonous decrease in the ethanol content, during which $\bar{V}^{E}_{min}$ appears with an increase in the chain length, as is shown in Fig. 2. The chain-length dependence of $\bar{V}^{me}_{max}$ gives a linear relation;

$$\bar{V}^{me}_{max} = 0.58m + 16.83 \quad (m=2-7) \tag{6}$$

which is also shown in Fig. 7. The feature that the ethanol content of the mixture at which $\bar{V}^{me}_{max}$ appears decreases with the methylene group more apart from the hydroxyl group of the alcohol molecule is similar to that for $\bar{V}^{E}_{max}$ in Fig. 3. The appearance of $\bar{V}^{me}_{min}$ and $\bar{V}^{me}_{max}$ in the mixture must result from the structural effect of the mixture.

The authors wish to thank Professor Ryohei Matuura of Kyushu University and Assistant Professor Keishiro Shirahama of Saga University for their helpful discussions and advice.

References

1) K. Shinoda, T. Nakagaki, B. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press Inc., New York, N.Y. (1963), p. 69.
2) B. D. Flockhart, *J. Colloid Interface Sci.*, **12**, 557 (1957).
3) N. Nishikido, Y. Moroi, H. Uehara, and R. Matuura, This Bulletin, **47**, 2634 (1974).
4) K. Shirahama, M. Hayashi, and R. Matuura, *ibid.*, **42**, 1206 (1969).
5) F. Franks, "Physico-Chemical Processes in Mixed Aqueous Solvents," Heinemann Educational Books Ltd., London (1969), p. 50.
6) P. Becher, *J. Colloid Interface Sci.*, **20**, 728 (1965).
7) K. Deguchi, T. Mizuno, and K. Meguro, *ibid.*, **48**, 474 (1974).
8) A. W. Ralston and C. W. Hoerr, *J. Amer. Chem. Soc.*, **68**, 851 (1946).
9) K. Shirahama and R. Matuura, This Bulletin, **38**, 373 (1965).
10) L. Lee and J. B. Hyne, *Can. J. Chem.*, **46**, 2333 (1968).
11) G. Wada and S. Umeda, This Bulletin, **35**, 646 (1962).
12) K. Kinoshita, H. Ishikawa, and K. Shinoda, *ibid.*, **31**, 1081 (1958).
13) F. Franks and H. T. Smith, *Trans. Faraday Soc.*, **64**, 2962 (1968).
14) M. E. Friedman and H. A. Scheraga, *J. Phys. Chem.*, **69**, 3795 (1965).
15) F. Franks and D. I. G. Ives, *Quart. Rev.*, **20**, 1 (1966).
16) K. A. Covington and P. Jones, "Hydrogen-Bond Solvent Systems," Taylor & Francis Ltd. London (1968), p. 39.
17) "International Critical Table," McGrow-Hill Book Co. Inc., New York, N. Y. (1928), Vol. III.
18) "Bussei Josuu," Maruzen Publising Co., Tokyo (1971), Vol. 9 and (1972), Vol. 10.
19) J. A. Riddick and E. E. Toops, "Organic Solvents," Interscience Publishers, Ltd., London (1955).
20) Ref. 17) Vol. III, p. 116.
21) G. N. Malcolm and J. S. Rowlinson, *Trans. Fraaday Soc.*, **53**, 921 (1957).