Studies on the Aqueous Solutions of Guanidinium Salt. XI. Volume Changes of Mixing of Aqueous Solutions of Guanidinium Bromide and Tetraalkylammonium Bromide at 25 °C

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(Received May 4, 1979)

The volume changes on mixing aqueous solutions of guanidinium bromide with those of tetrabutyl- and tetramethylammonium bromide were measured with a vibration densimeter at 25 °C. The excess volume change of mixing was positive and large for the system of tetrabutylammonium bromide–guanidinium bromide–water. On the basis of the interaction parameters of Friedman's formalism, this result was interpreted in terms of an interaction between guanidinium cation and tetrabutylammonium cation through the change of water structure.

In a previous paper,[1] we reported that the free energy of mixing for the ternary system, guanidinium bromide (GuBr)–tetrabutylammonium bromide (Bu_4NBr)–water was negative and large in magnitude. This result was interpreted in terms of either direct (complex formation) or indirect (through the change of water structure) interaction between the guanidinium cation (Gu^+) and the tetrabutylammonium cation (Bu_4N^+). In other words, $g_{B^+C^+}$, the interaction parameter of the mixed cation pair in Friedman's formalism,[2] was the predominant factor for the mutual salting-in of this system.

In contrast to this result, in the ternary system containing Bu_4NBr and alkali halides, such as KBr or CsBr,[3] the mutual salting-out was observed, in spite of the facts that both K^+ and Cs^+ were structure breaker ions similar to the guanidinium ion.

The volume changes of mixing for the ternary systems $KBr–Bu_4NBr–H_2O$[4] and NaBr–tetrapropylammonium bromide–H_2O[5] were also determined and large excess volume changes of mixing with positive signs were obtained. The increase of the solution volume by mixing was attributed mainly to the interaction of hydrophobic cations through the change of water structure.

Previously,[6] the authors reported that in organic solutes including ions, the size, shape, and functional groups were the important factors which determine the nature of the solute-water interaction. The structure breaking action of guanidinium ion would thus be different from K^+ and Cs^+, and similar to that of urea with regard to the hydrogen bonding with water molecules.

From these standpoints, it is interesting to investigate the volume change on mixing aqueous solutions of GuBr and Bu_4NBr. In this paper, we reported the volume changes of mixing of the ternary system GuBr–Bu_4NBr–H_2O and GuBr–tetramethylammonium bromide (Me_4NBr)–H_2O up to 2 molalities of total concentration. The data obtained were analyzed by Friedman's formalism and the results are discussed in terms of the interionic interactions and concomitant structural change of water.

Experimental

Materials. GuBr was prepared and purified by the method described elsewhere.[1] Bu_4NBr and Me_4NBr were purchased from Wako Junyaku Co., Ltd. and recrystallized two or more times from the appropriate solvents, as described elsewhere.[7] These compounds were dried *in vacuo* over phosphorous pentoxide before use. The salts were dissolved in redistilled and deionized water.

Method. Stock solutions of total molalities of 2 mol·kg^{-1} with different ionic mole fractions were prepared by weighing and mixing each salt solution. Each stock solution was diluted by weight to the desired molalities before use. About fifteen kinds of sample solutions with different molalities and the same ionic mole fraction were used for the measurement. Solution densities were determined by Seiko SDM 421 and 422 vibration densimeters, which were linked with a quartz oscillator and a digital counter. Pure water and aqueous sodium chloride solution were used as the standards for the calibration of the apparatus. Measurements were done at least twice for every solution and were accurate to $\pm 1\times 10^{-5}$ g/cm^3. The temperature of the cell chamber was maintained at 25±0.01 °C.

Results and Discussion

Apparent Molal Volumes. The apparent molal volume ϕ_V of the 1 : 1 electrolyte in the solution volume V has been defined in the molality scale:

$$\phi_V = \frac{V - 55.51\bar{V}_A{}^0}{m} \tag{1}$$

where $\bar{V}_A{}^0$ is the molal volume of pure water, and m is the solute molality. If we consider a solution in which two electrolytes, B and C having a common ion are dissolved, Eq. 1 can be modified into the following form by using the density and molality and rewriting ϕ_V as $\phi_V(x,m)$,

$$\phi_V(x, m) = \frac{1}{m}\left\{\frac{1000 + m_B M_B + m_C M_C}{d} - \frac{1000}{d_A}\right\}, \tag{2}$$

where d and d_A are the densities of the solution and pure water, respectively, and $m_B(m_C)$ and $M_B(M_C)$ are the molalities and molecular weight of B(C), respectively. In this paper, B denotes GuBr and C denotes tetraalkylammonium bromide. $\phi_V(x,m)$ is the mean apparent molal volume of the mixed electrolyte or the pseudo binary salt at total molality m and ionic mole fraction x, given as

$$m = m_B + m_C, \text{ and } x = m_C/m. \tag{3}$$

For the various x's, the relation between $\phi_V(x,m)$ and m is obtained from the density data, and is shown in Fig. 1 for the GuBr–Bu_4NBr–H_2O system and in Fig. 2

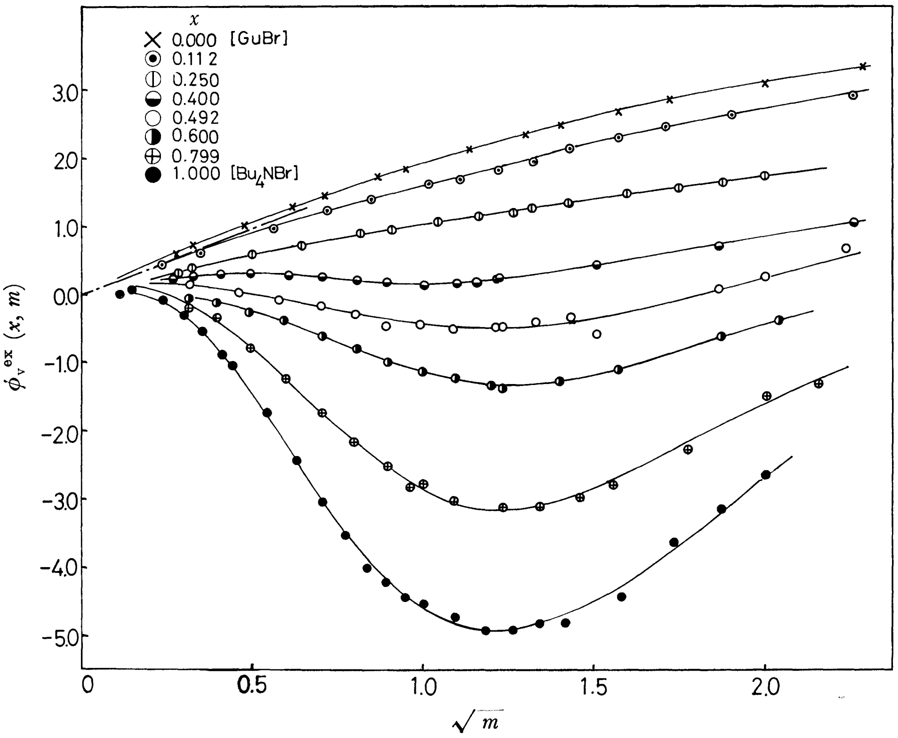

Fig. 1. The concentration dependence of the excess apparent molal volume of H_2O–GuBr–Bu_4NBr system at 25 °C. —— Debye-Hückel line.

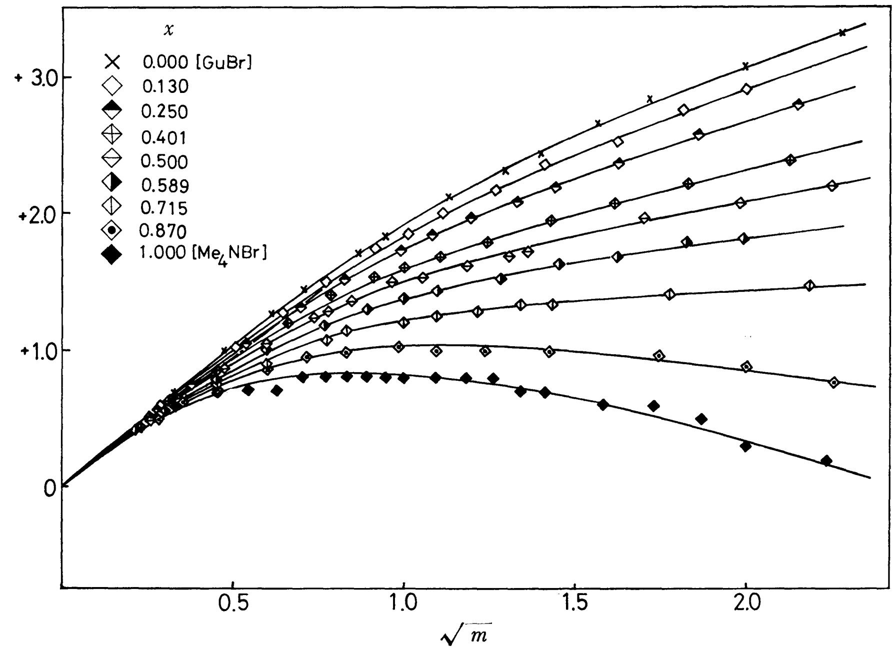

Fig. 2. The concentration dependence of the excess apparent molal volume of H_2O–GuBr–Me_4NBr system at 25 °C. —— Debye-Hückel line.

for the GuBr–Me_4NBr–H_2O system. In both figures the ordinate represents the excess apparent molal volume $\phi_v^{ex}(x,m)$, defined as the deviation from $\phi_v(x,0)$, the mean apparent molal volume at infinite dilution.

$$\phi_v^{ex}(x, m) = \phi_v(x, m) - \phi_v(x, 0). \tag{4}$$

The additivity rule has to hold for $\phi_v(x,0)$ as

$$\phi_v(x, 0) = x\phi_v(1, 0) + (1-x)\phi_v(0, 0), \tag{5}$$

where $\phi_v(0,0)$ and $\phi_v(1,0)$ are the apparent molal volume at infinite dilution for the electrolyte B and C, respectively. As seen in Figs. 1 and 2, the concentration dependence curves of $\phi_v^{ex}(x,m)$ are located between those of binary solutions in both the systems. These curves are expressed in the form of Eq. 6:

$$\phi_v^{ex}(x, m) = \sum_i q_i m^{i/2}, \quad (q_1 = 1.865) \tag{6}$$

and each q_i coefficient is obtained by a least squares fit with a computer program. These coefficients represent the various intetractions contributing to the solution volumes; they are not useful, however, for interpreting the volume change in terms of ionic interactions, except for calculating ϕ_V at the desired molality.

In the mixing of inorganic electrolytes, the Young's mixture rule[8] is an adequate description of the volume properties of a mixture:

$$\phi_V(x, m) = x\phi_V(1, m) + (1-x)\phi_V(0, m). \tag{7}$$

Equation 7 means that the mixing of two binary solutions at constant total molality produces a ternary solution whose volume is exactly the sum of the volumes of the binary solutions. Combining Eqs. 4, 5, and 7, we have

$$\phi_V{}^{ex}(x, m) = x\phi_V{}^{ex}(1, m) + (1-x)\phi_V{}^{ex}(0, m). \tag{8}$$

This equation may express that the volume changes resulting from the new ionic interaction in the ternary solution are equal to the arithmetic means of the volume changes resulting from the ionic interaction in each binary solution. Most inorganic electrolyte mixtures obey this rule, although slight deviations are obtained.[9] The x-dependence of $\phi_V{}^{ex}(x,m)$ is shown in Fig. 3 at m=0.5, 1.0, and 2.0 for the GuBr–Bu$_4$NBr–H$_2$O system, for which the mixture rule does not hold, and a positive deviation from Eq. 8 is observed. In this case, the addition of term Δ to Eq. 8 is required:

$$\phi_V{}^{ex}(x, m) = x\phi_V{}^{ex}(1, m) + (1-x)\phi_V{}^{ex}(0, m) + \Delta. \tag{9}$$

In the case of the common anion mixing, this deviation may be attributed to the difference in the cation-cation interactions; these are discussed in next section.

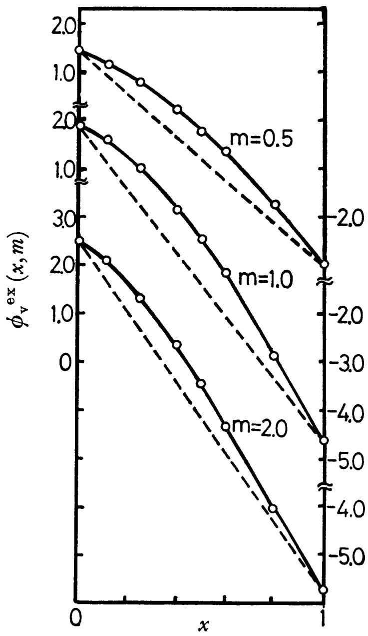

Fig. 3. The relationship between $\phi_V{}^{ex}$ and x for H$_2$O–GuBr–Bu$_4$NBr system at various m. Dotted line is obtained from Young's rule. Solid line is obtained from experiment.

Excess Volume Change of Mixing. The excess volumes of the pseudo-binary salt solution may be defined as the product of the total molality and the excess apparent molal volume:

$$V^{ex}(x, m) = m\phi_V{}^{ex}(x, m). \tag{10}$$

The excess volume change of mixing $\Delta_m V^{ex}$ has been given as the deviation from the linear relationship between V^{ex} and x at constant molality.[4]

$$\Delta_m V^{ex}(x, m) = V^{ex}(x, m) - xV^{ex}(1, m) - (1-x)\phi_V{}^{ex}(0, m). \tag{11}$$

On substituting Eq. 10 to Eq. 11, we obtain

$$\begin{aligned}\Delta_m V^{ex}(x, m) &= m\{\phi_V{}^{ex}(x, m) - x\phi_V{}^{ex}(1, m) \\ &\quad - (1-x)\phi_V{}^{ex}(0, m)\} \\ &= m\cdot\Delta.\end{aligned} \tag{12}$$

Therefore the Δ in Eq. 9 correspond to $\Delta_m V^{ex}/m$. As shown in Figs. 4 and 5, $\Delta_m V^{ex}$ plotted against x are

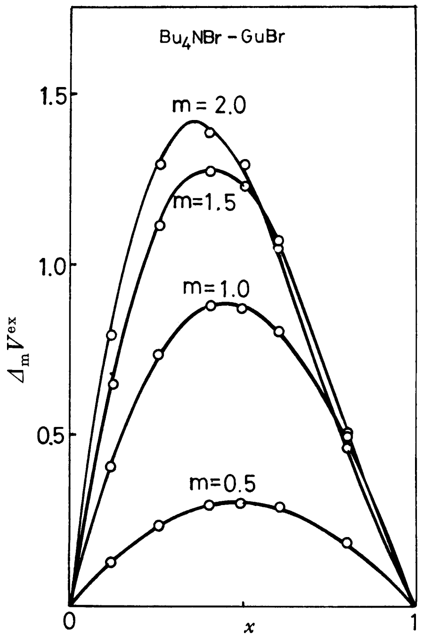

Fig. 4. The relationship between $\Delta_m V^{ex}$ and x at various m of the H$_2$O–GuBr–Bu$_4$NBr system.

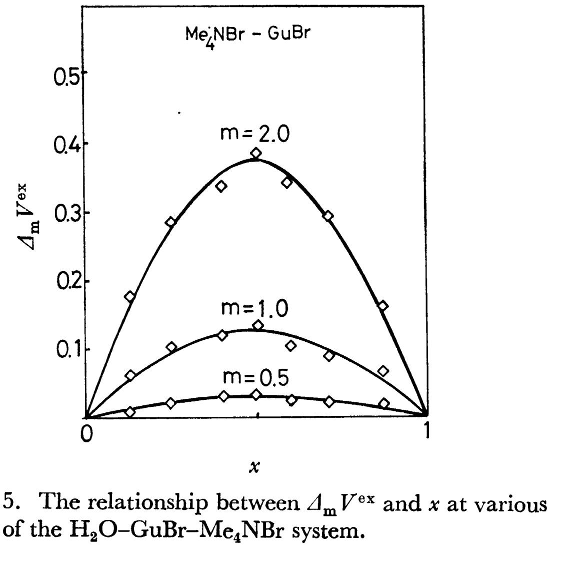

Fig. 5. The relationship between $\Delta_m V^{ex}$ and x at various m of the H$_2$O–GuBr–Me$_4$NBr system.

both positive and nearly parabolic. The maximum points for the system GuBr–Bu_4NBr–H_2O are left from the vertical line of $x=0.5$. The $\Delta_m V^{ex}$ values and the degree of the skewness increased with increasing the total molality. The magnitude of $\Delta_m V^{ex}$ for the system containing Bu_4NBr is six or seven times larger than that for the system containing Me_4NBr. From this experimental result, the observed large values of $\Delta_m V^{ex}$ are considered to be due to the change of the hydration of tetraalkylammonium salts as shown in next section, because the mixing of inorganic salts solution is not accompanied by such a large volume change and the hydration cosphere of the Bu_4N^+ is more extensive than that of the Me_4N^+. In the binary tetraalkylammonium salt solutions in the relatively low concentration range, the decrease of the apparent or partial molal volume was considered to take place because of the formation of cage-like structure around the tetraalkylammonium ion[10] and the overlap of the cage by cation-cation interactions.[11] To interpret the $\Delta_m V^{ex}$ dependences on the ionic strength and/or ionic mole fraction in Figs. 4 and 5, one may introduce the following Friedman's treatment:[2,4]

$$\Delta_m V^{ex}(x, m) = x(1-x)\{v_0+v_1(1-2x)+\cdots\} \qquad (13)$$

where v_0 and v_1 are volumetric interaction parameters. To evaluate v_0 and v_1, the quantities $\Delta_m V^{ex}(x,m)/x(1-x)$ are plotted against x. This relation would be linear if the higher terms are negligibly small. As seen in the upper corner of Fig. 6, v_0 and v_1 has been obtained from the intercept and slopes.

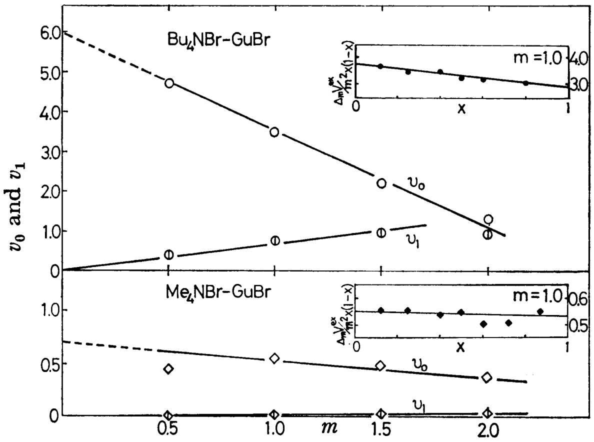

Fig. 6. The concentration dependence of v_0 and v_1 for the ternary systems.

In the common ion mixing, one can easily consider the pairwise and triplet interactions between like-charged ions, which mainly influence the excess function of mixing at relative low concentrations. Applying a treatment similar to the excess free energy of mixing,[1,2] v_0 and v_1 can be described as

$$v_0 = (2v_{B^+C^+} - v_{C^+C^+} - v_{B^+B^+}) + v_0(\text{trip})\cdot m, \qquad (14\text{-a})$$

and

$$v_1 = v_1(\text{trip})\cdot m, \qquad (14\text{-b})$$

where v_{ij} is the concrete interaction parameter of cation i and j, and v_0(trip) and v_1(trip) are the triplet interaction parameters.[1] As predicted from Figs. 4 and 5, the signs and magnitude of $\Delta_m V^{ex}$ are determined mainly by the v_0 values, while the skewness of the curve depends on the v_1 values.

The large excess volume change does not always arise from the volume difference of two kinds of solutes. In the volume changes of mixing of the ternary system KBr–tetrapropylammonium bromide–H_2O and KBr tetrakis(2-hydroxyethyl)ammonium bromide–H_2O, the former system showed large $\Delta_m V^{ex}$, while the latter underwent almost no volume change, although the ion sizes of the two kinds of cations are nearly the same.[4] Based on the above result and the similar properties of Bu_4N^+ and tetrapropylammonium ion($Pr_4(N^+)$), we will discuss the large $\Delta_m V^{ex}$ for the system GuBr–Bu_4NBr–H_2O by focusing on the change of water structure and the structuredness of a hydration cosphere by the interionic interactions.

The curves in Fig. 6 can be expressed by Eq. 13 within experimental error. According to Eq. 13, the contribution of the triplet interaction term(v_0(trip)) become large with increase of total molality, but the pairwise interaction term $(2v_{B^+C^+} - v_{C^+C^+} - v_{B^+B^+})$ contributes more significantly to v_0 in the concentration range studied. Since v_0 decreases almost linearly with m, as seen in Fig. 6, the value of $(2v_{B^+C^+} - v_{C^+C^+} - v_{B^+B^+})$ was obtained by extrapolating Eq. 13 to infinite dilution. Although it is quite difficult to evaluate the v_{ij} from the present approach, the free energy of mixing for the same system will help us in estinating the signs and magnitude of the v_{ij}. Among the three parameters of the pairwise term, $v_{B^+B^+}$ the interaction parameter between Gu^+'s, must be small, because of the weak hydration of the guanidinium cation.[12] Therefore, it is reasonable to neglect the contribution of $v_{B^+B^+}$ to the pairwise term. The $v_{C^+C^+}$ between Bu_4N^+'s has a negative sign, because two cations approach each other at a suitable distance and tend to link up to release water molecules of the cosphere to bulk solution,[11] leading to a small volume. On the other hand, the $v_{B^+C^+}$ between Gu^+ and Bu_4N^+ must be positive, since the hydrophobic hydration originally makes a negative contribution to the solution volume.[10] Indeed the hydration cosphere itself around a hydrophobic ion is more bulky than pure water, but the tight packing based on the formation of cage decreases the void space of liquid water. The latter effect dominate over the former. The guanidinium ion reduces and breaks the cage-like structure around a hydrophobic ion, leading to a large volume. From the consideration above, both parameters, $v_{B^+C^+}$ and $-v_{C^+C^+}$ make positive contributions to the solution volume.

In the free energy of mixing of the system KBr–Pr_4NBr–H_2O,[3] where the mutual salting-out was observed, the formation of like-cation pairs were more favoured than that of mixed cation pairs. On the other hand, the positive value of $\Delta_m V^{ex}$ was obtained from the volume of mixing of the same system and attributed also to the interaction of a like cation pair.

In contrast to the above results, a large mutual salting-in was observed in the free energy of mixing of the system GuBr–Bu_4NBr–H_2O,[1] where the formation of mixed cation pair was preferred to that of the like cation pairs.

These facts strongly suggest that $v_{B^+C^+}$ parameter should contribute more significantly than $v_{C^+C^+}$ parameter to the large $\Delta_m V^{ex}$ of the system GuBr–Bu_4NBr–H_2O. Consequently, the increase of solution volume observed in the above two systems would depend on the different cation-cation interaction, that is, C^+–C^+ interaction for the system KBr–Pr_4NBr–H_2O and B^+–C^+ interaction for the system GuBr–Bu_4NBr–H_2O. This concept is consistent with the general aspects of dissolution of hydrophobic solute in aqueous guanidinium solution, that is, the guanidinium ion breaks the water structure and weakens the water-structure-enforced association of hydrophobic solute. Since the interaction of hydrophobic solute with K^+ and guanidinium ion take place through the structure of water, the difference in the interaction indicates that the guanidinium ion breaks water structure in a different way from K^+.

Partial Molal Volumes, $\bar{V}_i$. Since $\phi_v(x,m)$ are regarded as the apparent molal volumes of the pseudo-binary salt, the partial moal volume of this salt $\xi(x,m)$ may be defined as[13]

$$\xi(x, m) = \left(\frac{\partial V}{\partial m}\right)_x = \phi_v(x, 0) + \frac{\sqrt{m}}{2}\left(\frac{\partial \phi_v(x, m)}{\partial \sqrt{m}}\right), \quad (15)$$

Using Eq. 6, we obtain

$$\xi(x, m) = \phi_v(x, 0) + \sum q_i\left(1+\frac{i}{2}\right)m^{i/2}. \quad (16)$$

$\xi(x,m)$ are computable. As the solution volume is the sum of the partial molal volumes of the individual components,

$$V(x, m) = 55.51\bar{V}_A + (1-x)m\bar{V}_B + xm\bar{V}_C. \quad (17)$$

Differentiating Eq. 17 with m or x, and applying the Gibbs-Duhem relation to the differentiated equation, we have the partial molal volume of solute B and C,

$$\bar{V}_B = \xi(x, m) - x\left(\frac{\partial \phi_v(x, m)}{\partial x}\right)_m \quad (18\text{-a})$$

$$\bar{V}_C = \xi(x, m) - (1-x)\left(\frac{\partial \phi_v(x, m)}{\partial (1-x)}\right)_m \quad (18\text{-b})$$

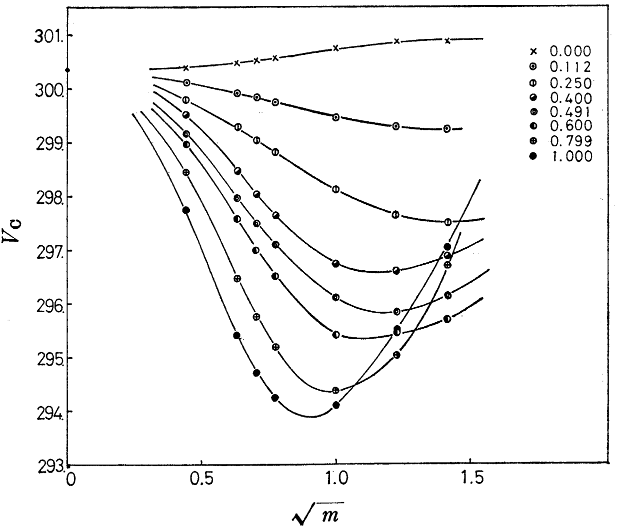

Fig. 7. $\bar{V}_C$ *vs.* $\sqrt{m}$ at various x for the H_2O–GuBr–Bu_4NBr system.

$\bar{V}_A$ values did not change appreciably with m and were nearly the same as $\bar{V}_A^0$ in this experimental method. The partial molal volumes of tetrabutylammonium bromide $\bar{V}_C$ are calculated from Eq. 18-b and are shown in Fig. 7 at various x values. With decreasing x, the curves of $\bar{V}_C$ *vs.* $\sqrt{m}$ become flat, accompanying the shift of the minimum values. However, this figure is not suitable for the comparison of the m_C dependence of $\bar{V}_C$ in water and with that in aqueous GuBr solution. To elucidate the volume change of Bu_4NBr in the GuBr solution, $\bar{V}_C$ at constant rational mole fraction, N_C were calculated and replotted against m_C'. N_C and m_C' are defined as[1]

$$N_C = \frac{2m_C}{55.51+2m_C} = \frac{2m_C'}{55.51+2m_C'+2m_B} \quad (19)$$

where m_C' is the molality of Bu_4NBr in ternary solution

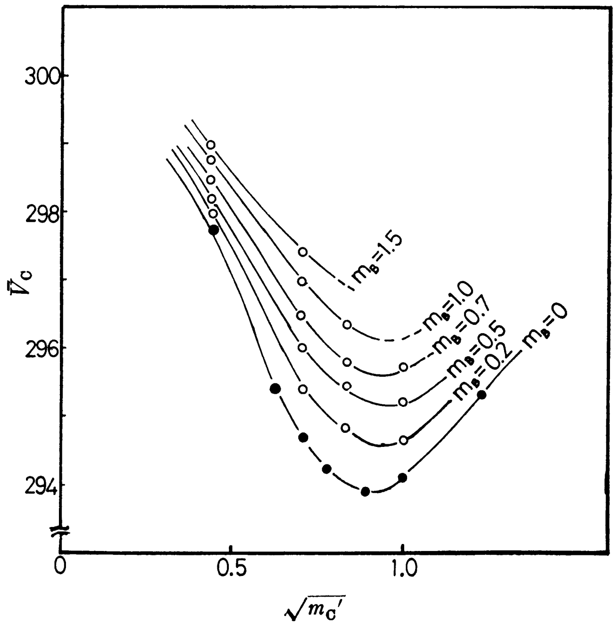

Fig. 8. $\bar{V}_C$ *vs.* $\sqrt{m_C'}$ at various m_B for the H_2O–GuBr–Bu_4NBr system.

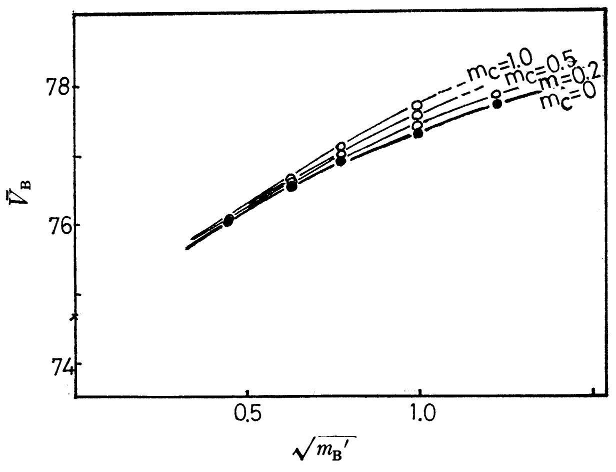

Fig. 9. $\bar{V}_B$ *vs.* $\sqrt{m_B'}$ at various m_C for the H_2O–GuBr–Bu_4NBr system.

having the same N_C in the binary solution. This treatment means that the guanidinium bromide solution is regarded as a solvent. As seen in Fig. 8, the $\bar{V}_C$ *vs.* m_C' curves clearly shift upward with increase of m_B, but the concentrations of Bu_4NBr having the minimum $\bar{V}_C$ value are independent of m_B. $\bar{V}_B$ *vs.* $\sqrt{m_B'}$ curves are shown in Fig. 9. The V_B values change only slightly with increase of m_C. These facts indicate that the large volume change of mixing for this system is due to the change of the hydration of Bu_4N^+ caused by the change of solvent structure.

References

1) K. Miyajima, H. Yoshida, and M. Nakagaki, *Bull. Chem. Soc. Jpn.*, **51**, 2826 (1978).

2) H. L. Friedman, "Ionic Solution Theory," Interscience Pub. New York, N. Y., London (1962), Vol, 3; R. H. Wood and H. L. Anderson, *J. Phys. Chem.*, **70**, 992 (1966).

3) W-Y. Wen, K. Miyajima, and A. Otsuka, *J. Phys. Chem.*, **75**, 2148 (1971).

4) W-Y. Wen and K. Nara, *J. Phys. Chem.*, **71**, 3907 (1967).

5) J. Padava, D. Rosenzweig, and Y. Marcus, *J. Chem. Thermodynamics*, **8**, 431 (1976).

6) K. Miyajima, H. Yoshida, and M. Nakagaki, *Bull. Chem. Soc. Jpn.*, **51**, 2508 (1978).

7) B. E. Conway, R. E. Verrall, and J. E. Desnoyers, *Trans. Faraday Soc.*, **62**, 2738 (1966).

8) T. F. Young and M. B. Smith, *J. Phys. Chem.*, **58**, 716 (1954).

9) F. J. Millero, *Chem. Rev.*, **71** 147 (1971).

10) W-Y. Wen and S. Saito, *J. Phys. Chem*., **68**, 2639 (1964); F. Frank and H. T. Smith, *Trans. Faraday Soc.*, **63**, 2586 (1967).

11) J. E. Desnoyers, M. Arel, G. Perron, and C. Jolicoeur, *J. Phys. Chem.*, **73**, 3346 (1969).

12) K. Miyajima, K. Inari, S. Hamaguchi, H. Yoshida, and M. Nakagaki, *Nippon Kagaku Kaishi*, **1975**, 1447.

13) J. Padova and I. Lewkowicz, *J. Chem. Phys.*, **65**, 3611 (1976).