*Bull. Chem. Soc. Jpn.*, **55**, 2771—2778 (1982)

# Estimation of Compressibility and Volume of Electrostriction Layer in Water–Methanol System and Its Application to the Partial Molar Volumes of LiCl, KCl, and CsCl in This System

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(Received January 25, 1982)

A theory of electrostriction based on the spherical symmetry of electric field around ion and the dielectric continuum of solvent has been applied to the mixed solvent of water–methanol. The isothermal compressibility, $\kappa_T$, and the volume decrease, $\Delta V$ of primary solvation layer have been calculated for univalent ions. Calculation procedure consists of two steps; 1) calculation of the variation of electric field strength and dielectric constant with the distance from ion, 2) calculation of the compressibility and the volume decrease of electrostriction layer. In step 2), the calculation method proposed by Desnoyers *et al.* (*J. Chem. Phys.*, **43**, 243 (1965)) was used. Parameters necessary for the calculation were estimated in an appropriate manner and the results of calculation are shown as plots of $\kappa_T$ and $\Delta V$, *vs.* the distance from the center of ion. Partial molar volumes of LiCl, KCl, and CsCl in water–methanol system have been measured and the disordered part of partial molar volume has been determined after taking account of the values of $\kappa_T$ and $\Delta V$ of the primary solvation layer.

The problem of electrostriction in solutions of electrolyte has an intimate relation to those of ionic hydration and partial molar volume of ion. Since the pioneering work of Webb,[1] numerous investigators have discussed the theories of electrostriction of aqueous solutions, most important of which are, in our opinion, those proposed by Padova[2] and Desnoyers *et al.*[3] The electrostriction is a universal phenomenon and it is not inherent to aqueous media. However, only a few works[4,5] have been reported dealing with the theoretical estimation of electrostriction effects in nonaqueous solution.

On the other hand, in recent years much progress has been achieved in the determination of various physicochemical properties of ion in nonaqueous solvent. The data obtained are now summarized in the form of review.[6,7] For the discussion of these data, the consideration on the effects of electrostriction in nonaqueous solvents should be required. Generally speaking, the interpretation of the differences among the data found in different solvents is often disputable. The sound comparison of the data on the behavior of ions in different solvents or different compositions of the solvent system can only be possible after the electrostriction effects are subtracted from what has been observed in each solvent. This is one of our fundamental points of view. The purposes of this work consist of two parts; one is to develop a method to estimate the electrostriction effects in mixed solvent system for which the reliable physical constants necessary for the estimation are often lacking, while the other is to discuss the numerical values obtained by applying the results of the present calculation to the actual system. In this study we have chosen the mixed solvent consisting of water and methanol and have estimated the compressibility and the volume decrease of the primary solvation layer in this system at 25 °C. The study of the solution properties in mixed aqueous solvents leads to the firm interpretation of the behavior of the ion in nonaqueous solvents. In addition, this mixed solvent system is widely used for inorganic solute species and a limited number of physical constants are known.

Desnoyers *et al.*,[3] concentrating attention on the local behavior of the solvent itself, assumed that the only role of the ions is to provide the polarizing electrostatic field which acts on the solvent and that an ion is a hard incompressible sphere surrounded by a spherical primary coordination shell whose thickness is equal to the diameter of the solvent. In their treatment the volume decrease due to the electrostriction was given as a function of the distance from the center of ion and the total electrostriction volume was evaluated for some particular ions such as $Na^+$ and $F^-$ after considering the number of the coordinated (hydrated) water. The validity of the present calculation of the electrostriction effects in the mixed solvent system is limited in the frame of the idea and the procedure proposed by Desnoyers *et al.*[3] It should be stressed that this work is a macroscopic approach for the elucidation of the solute-solvent interactions. In addition to the calculation, the partial molar volumes of three kinds of alkali chlorides, LiCl, KCl, and CsCl in water–methanol mixture have been measured and the results of the present calculation have been applied to obtain the disordered part of the partial molar volumes. The reason for the choice of these alkali chlorides will be mentioned in the section of the discussion of this paper.

## Theory and Calculation

The calculation of the electrostriction effects will be divided into two part; one is the calculation of the dielectric saturation effects, namely the variation of field strength and dielectric constant with the distance from the center of ion, while the other is that of the compressibility and volume decrease of the electrostriction layer. In what follows, each part will be described separately.

Throughout the calculation, the spherical symmetry of the electric field around ion and the dielectric continuum of the solvent are assumed. A controversy may exist for the application of the dielectric continuum model to the mixed solvent such as water-methanol mixture, as the preferential hydration is often observed in mixed aqueous solvent. If the preferential hydration (more generally, solvation) occurs in a mixed solvent system, this obviously contradicts the basic assumption of the dielectric continuum of the solvent. Nevertheless, we would like to employ the spherical symmetry of the electric field and continuum model of solvent on the ground of the conviction that the *macroscopic* approach can give information on the *microscopic* level of solute-solvent interactions, as for the case of the application of the Debye-Hückel theory to the evaluation of association constant and interionic distance parameter from the conductivity data.

*Calculation of Dielectric Saturation Effects.* Calculation procedure is the same as given by Laidler.[8] The dielectric behavior in the vicinity of ions can be expressed in terms of differential dielectric constant, $\varepsilon_d$, which is defined and given by the relation[3,8,9]

$$\begin{aligned}\varepsilon_d &\equiv \mathrm{d}\boldsymbol{D}/\mathrm{d}E \\ &= [(\varepsilon_0-n^2)/(1+bE^2)] + n^2, \end{aligned} \tag{1}$$

where $\boldsymbol{D}$ is the dielectric displacement, $E$, the field strength, $\varepsilon_0$, the dielectric constant at zero field strength, $n^2$, the square of refractive index, and $b$ a constant as described below. The electric displacement $\boldsymbol{D}$ at a distance $r$ from the center of an ion of charge $ze$ is $ze/r$, which should be equal to $\boldsymbol{D}$ obtained by the integration of Eq. 1. It follows then that

$$\frac{ze}{r^2} = n^2E + [(\varepsilon_0-n^2)/b^{1/2}]\tan^{-1}b^{1/2}E. \tag{2}$$

Equation 2 can not give the explicit solution of $E$ as a function of $r$, but it can afford tabulated values of $r$ for assumed values of $E$. Then, the substitution of the numerical values of $E=E(r)$ into Eq. 1 permits to show the variation of $\varepsilon_d$ with the distance from the center of ion. Values used in calculation are as follows:

$\varepsilon_0$; given or estimated from the data found in Ref. 10.

$b$; $1.08\times10^{-8}$ e.s.u. for water[3,8] and $2.2\times10^{-8}$ e.s.u. for methanol.[5] Values in the mixture are calculated on the assumption of linear variation of $b$ with mole fraction of the component in the solvent.

$n^2$; determined by the present authors.

Results of calculation are illustrated as a series of curves in Fig. 1 ($E$ *vs.* $r$) and Fig. 2 ($\varepsilon_d$ *vs.* $r$) for univalent ion at various compositions of water–methanol system at 25 °C. Figure 1 shows that the field strength at a certain distance from the center of the ion becomes higher with the content of methanol. Figure 2 is essentially the same as Fig. 1 but it has an advantage to give us an explicit image of the dielectric saturation effects and the extent of the dielectric saturation layer. In Fig. 2, the smallest values of $\varepsilon_d$ is determined by the relation that $\varepsilon_d=n^2$, which is approximately 1.8 for both water and methanol at 25 °C. If the distance at which $\varepsilon_d$ begins to be effectively field-dependent is determined on the criterion of $\varepsilon_d=1.9$, following values are obtained: 1.68, 1.74, 1.96, 2.19, 2.52, 2.87, and $3.00\times10^{-8}$ cm for the contents of methanol equal to 0, 10, 30, 50, 70, 90, and 100 mol%, respectively. The dielectric saturation layer becomes larger with the content of methanol in the mixed solvent. The distinction between bulk solvent and dielectric saturation layer is less clear in methanol than in water as is seen in Fig. 2.

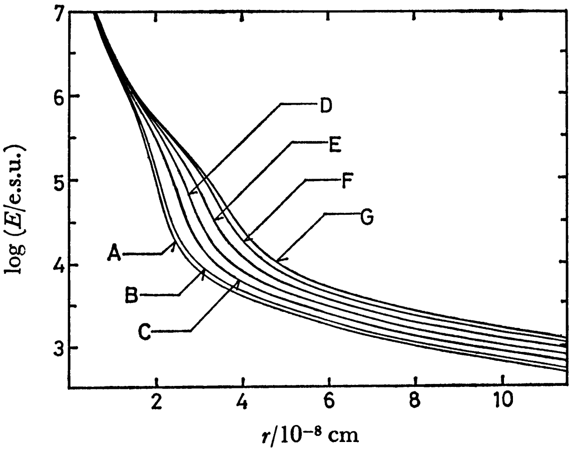

Fig. 1. Relation between the logarithm of the field strength, $E$, and the distance from the center of univalent ion in water–methanol system at 25 °C. Symbols A, B, C, D, E, F, and G correspond to the mole per cent of methanol equal to 0, 10, 30, 50, 70, 90, and 100, respectively.

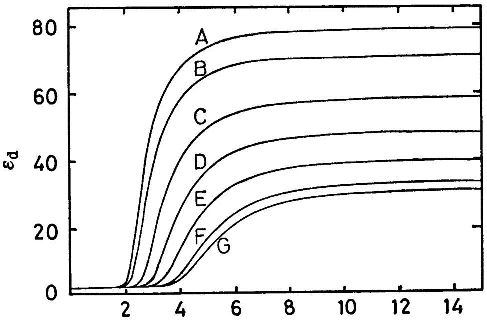

Fig. 2. Variation of differential dielectric constant with the distance from univalent ion in water–methanol system at 25 °C.
Symbols A—G are the same as in Fig. 1.

*Calculation of the Compressibility of Electrostriction Layer.* According to Desnoyers *et al.*,[3] the relation between the field strength and the effective pressure, defined as the pressure which, in the absence of the field $E$, would produce the same volume change of the solvent that $E$ produces is expressed as (Eq. 13 in Ref. 3),

$$\begin{aligned}\mathrm{d}P &= [4\pi D(1+bE^2)]^{-1} \\ &\quad\times\left[\varepsilon_0A\left(1+\frac{P}{B}\right)^A - n^2C\left(1+\frac{P}{B}\right)^C\right]E\mathrm{d}E \\ &\quad+\frac{n^2C}{4\pi D}\left(1+\frac{P}{B}\right)^C E\mathrm{d}E, \end{aligned} \tag{3}$$

where parameters, $A$, $B$, $C$, and $D$ are the constants involved in the following equations:

$$\frac{1}{\varepsilon}\left(\frac{\partial\varepsilon}{\partial P}\right)_{T,E} = \frac{A}{B+P}, \tag{4}$$

$$\frac{1}{n^2}\left(\frac{\partial n^2}{\partial P}\right)_{T,E} = \frac{C}{B+P}, \tag{5}$$

$$\kappa_T = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_{T,E} = \frac{D}{B+P}. \tag{6}$$

In other words, the pressure dependence of dielectric constant, square of the refractive index, and isothermal compressibility can be represented in terms of so-called Tait equation.[11] The use of the Tait-form equation and the adoption of the same value of $B$ through Eqs. 4—6 for such high pressures as in the electrostriction layer are the two essential points employed by Desnoyers *et al.* in deriving Eq. 3 which made the calculation very tractable. The expression of pressure dependence of dielectric constant and square of refractive index in terms of Tait-form equation is understandable if we consider that the variation of these properties with pressure is mainly ascribed to the variation of volume with pressure, as seen by Clausius-Mosotti and Lorenz-Lorentz equations.

In order to carry out the integration of Eq. 3 values of the parameters $A$, $B$, $C$, and $D$ must be known for the solvent composition under consideration. However, in water-methanol mixture, limited data are available on the pressure dependence of the dielectric constant,[12] and for the $(P, n)$ and $(P, \kappa_T)$ relations, no reliable data can be found at present. Therefore, we are obliged to do much effort for the estimation of the values of these parameters in the mixture. A rather expounded description of the estimation procedure may be permitted in the light of the future application for other solvent systems.

*Parameter B*: In the first step of the estimation procedure, the parameter $B$ is to be considered. As $B$ is assumed to be the same in Eqs. 4—6, its value can be otained from any one of the three sets of relationships, $(P, \varepsilon)$, $(P, n)$, and $(P, \kappa_T)$. Even with excellent data, to obtain a set of unique parameter $(A, B)$, $(C, B)$, and $(D, B)$, is not an easy task. Several sets of parameters may equally well represent the available data for a fluid. For example, as shown in Table 1, values of $B$ and $D$ have been known for water,[3,13] and methanol.[13] But this value of $B$ for water differs considerably from the value reported by other investigators from the variation of dielectric constant with pressure ($B=4.547\times10^8$ Pa and $A=0.1916$).[14] As it will be shown later, the parameter $A$ plays only a minor role in the calculation of the electric field of practical interest ($E\geqq5\times10^5$ e.s.u.). On considering this factor along with the fact that the Tait equation was originally derived to express the volume change with pressure, the value of $B$ in the set $(B, D)$ was preferred.

For mixture of water and methanol, Schadow and Steiner[12] have given the data of the pressure dependence of dielectric constant at 30 °C for weight per cent of methanol equal to 0, 20, 40, 60, 80, and 100. Their data are, however, not accurate enough to be usable for the simultaneous determination of the parameters $B$ and $A$. No theory has been proposed for the estimation of the value of $B$ in mixture from its value in pure component. Therefore, values of $B$ in mixture were estimated on the simple assumption of the linear variation of parameter $B$ with mole fraction of the component in the mixed solvent system, without taking account of the values of other parameters.

*Parameter D*: Values of $D$ in the mixed solvent were calculated from the data of isothermal compressibility. Under the condition of $B\gg P$, Eq. 6 should lead to the compressibility at ordinary pressures. In fact, the relation $\kappa_T(P=10^5\,\text{Pa})=D/B$ holds for the reported values of $B$ and $D$ for water and methanol, as seen in Table 1. It is remembered that errors involved in the estimated values of $B$ are largely compensated for by the evaluation process of the parameter $D$.

Values of $\kappa_T$ necessary for the estimation of $D$ were obtained by the aid of the thermodynamic relation,

$$k_T = \kappa_s + \left(\frac{Tv\alpha^2}{C_p}\right). \tag{7}$$

Meaning of the symbols used in Eq. 7 and the values used are;

$\kappa_s$; adiabatic compressibility, whose values are given from the measurements of ultrasonic propagation velocity and density. For the measurements of ultrasonic velocity, an ultrasonic interferometer was used.

$v$; volume.

$\alpha$; thermal expansion coefficient. The value at 25 °C is calculated from the density at 20 and 30 °C.

$C_p$; specific heat capacity, whose values are found in the literature.[15]

*Parameter A*: Slightly different values of $B$ have been given for water and methanol for the pressure dependence of dielectric constant.[17] Therefore, the parameters $A$ in water and methanol were recalculated using the value of $B$ obtained from the pressure dependence of the isothermal compressibility. For mixture, values of parameter $A$ were determined by the fitting of experimental results of $(P, \varepsilon)$ relation[12] using the estimated values of $B$. Average values of $A$ determined for pressures higher than $7\times10^7$ Pa were adopted. Surprisingly values of $A$ thus determined vary linearly with mole fraction of the component. To illustrate the validity of the estimated values of $A$ and $B$ in the mixture, the comparison between $(P, \varepsilon)$ relation determined experimentally and that calculated from Eq. 4 using the estimated values of A and B is represented in Table 2. The agreement is satisfactory.

*Parameter C*: Two reports have been published on the pressure dependence of the refractive index of water.[18,19] These results were combined and recalculated to obtain the parameter $C$ in Eq. 5, irrespective of the difference in the experimental conditions in two works (in Ref. 18, at 25 °C and up to $1.50\times10^8$ Pa, while in Ref. 19, at 24.8 °C and *ca.* to $1.1\times10^8$ Pa). Recalculation yields $C=0.0678$ for $B=2.996\times10^8$ Pa. This value is in fair accordance with the one used by Desnoyers *et al.* ($C=0.0685$).[3] Data on methanol[20] were similarly recalculated as for the case of water. Values of $C$ in the mixture were estimated on the assumption of the linear variation of parameter $C$ with the mole fraction of the component. This assumption seems reasonable in view of the linear variation of parameter $A$ and the small difference in the value of $C$ in water and methanol.

Final results of the numerical values of the parameters $A$, $B$, $C$, and $D$ as well as $\kappa_T$ are summarized in Table 1. Once the values of these parameters are determined, the integration of Eq. 3 reduces to a problem of mathematics.

At low field intensities ($bE^2\ll1$) or at high field

TABLE 1. VALUES OF THE PARAMETERS $A$, $B$, $C$, AND $D$ USED IN CALCULATION AND THE ISOTHERMAL COMPRESSIBILITY OF WATER–METHANOL MIXTURE AT 25 °C

| MeOH / mol % | $\kappa_T$ / $10^{-11}$ Pa$^{-1}$ | $B$ / $10^8$ Pa | $A$ | $C$ | $D$ |
|---|---|---|---|---|---|
| 0 | 45.23, 45.7[15) | 2.996[3,13) | 0.1818 | 0.0678 | 0.1368[3,13) |
| 10 | 43.54 | 2.773 | 0.175 | 0.0671 | 0.1207 |
| 30 | 50.60 | 2.327 | 0.159 | 0.0656 | 0.1177 |
| 50 | 66.10 | 1.880 | 0.142 | 0.0641 | 0.1243 |
| 70 | 83.86 | 1.434 | 0.126 | 0.0626 | 0.1201 |
| 90 | 110.30 | 0.987 | 0.110 | 0.0611 | 0.1088 |
| 100 | 124.50, 125.5[15) | 0.764[3,13) | 0.0998 | 0.0604 | 0.09589[3,13) |

TABLE 2. COMPARISON BETWEEN EXPERIMENTAL (30 °C) AND CALCULATED ($P$, $\varepsilon$) RELATIONS OF WATER–METHANOL MIXTURE

| MeOH | $P$/10$^5$ Pa | | | | | |
|---|---|---|---|---|---|---|
| wt% | 0.980 | 257 | 505 | 717 | 913 | 1107 |
| 20 | 69.01 | 69.75 | 70.50 | 71.52 | 72.73 | 73.51 |
| | | 69.97 | 70.84 | 71.55 | 72.17 | 72.79 |
| 40 | 60.48 | 61.10 | 61.75 | 62.72 | 63.71 | 64.69 |
| | | 61.38 | 62.18 | 62.84 | 63.40 | 63.94 |
| 60 | 53.02 | 53.60 | 54.28 | 55.13 | 56.10 | 57.00 |
| | | 53.96 | 54.80 | 55.46 | 56.03 | 56.56 |
| 80 | 43.72 | 44.20 | 44.75 | 45.61 | 46.54 | 47.52 |
| | | 44.68 | 45.50 | 46.14 | 46.68 | 47.18 |

Values in upper and lower rows correspond respectively to experimental[12) and calculated results.

($bE^2 \gg 1$), Eq. 3 can be simplified and the integration leads to low-field limit (Eq. 6 of Ref. 3) and high-field limit solutions (Eq. 14 or Ref. 3), respectively. In high-field limit solution, the parameter $A$ has little effect. Low-field limit corresponds to Born approximation in which dielectric saturation effects are neglected. It has been shown that the field near ordinary ions in water is of such value as to make the simplification of Eq. 3 inapplicable.[3) In the present work dealing with water–methanol system, Eq. 3 was directly integrated by means of a digital computer FACOM M-200 of Nagoya University Computer Center. Runge-Kutta-Gill method was used. Results of the integration of Eq. 3 are represented in Fig. 3, where the curves related to 10, 30, 70, and 90 mol% of methanol are eliminated for the sake of simplicity. The slope in low-field limit is independent of the composition of the solvent, taking the value of 2, while the slope in high-field limit depends weakly on the properties of the solvent concerned.

## Experimental

The determination of the partial molar volumes of LiCl, KCl, and CsCl which was done as a part of the present study is briefly mentioned here. Salts used are of guaranteed grade reagent supplied from Nakarai Chemicals and they were used without further purification. Densities of solutions containing the salt were measured with pycnometer of 20 cm$^3$.

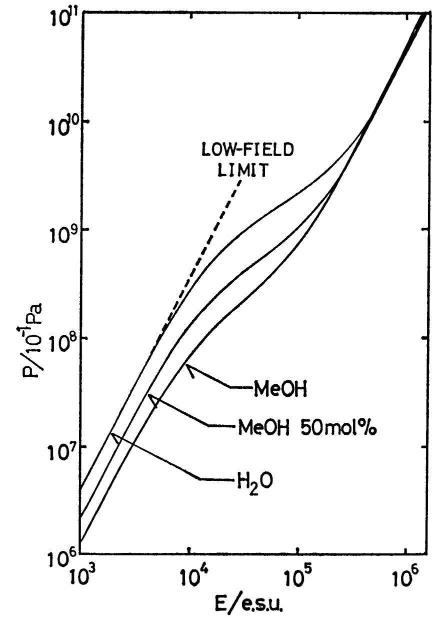

Fig. 3. Numerical solutions to pressure-field relationships in Eq. 3 for univalent ion in water, 50 mol% of methanol, and pure methanol.

## Results and Discussion

*Results of Calculation.* In Fig. 3, the high-field limit approximation holds for $E > 4 \times 10^5$ e.s.u., which corresponds to $r < 2.5 \times 10^{-8}$ cm in methanol in Fig. 1. It follows then that the calculation of electrostriction effects in methanol must at least be done on high-field approximation for the familiar alkali metal and halide ions. Figure 3 also indicates that in methanol the low-field approximation which corresponds to the simple Born approximation holds only for $E < 10^4$ e.s.u., a value equivalent to $r >$ *ca.* $5 \times 10^{-8}$ cm in Fig. 1, namely, the Born approximation is generally unacceptable in the solvent methanol. On the other hand, the combination of the results shown in Figs. 1 and 3 enables $P$ to be expressed as a function or $r$. Substitution of the pressure given as $P(r)$ along with the numerical values of parameters $B$ and $D$ into Eq. 6 can offer the relation between $\kappa_T$ and the distance from the ion, which is represented in Fig. 4. Desnoyers *et al.*[3) have shown the variation of $\kappa_T$ with the field strength in water, but to discuss the dependence of ionic hydration on the dimension of ion, the relation

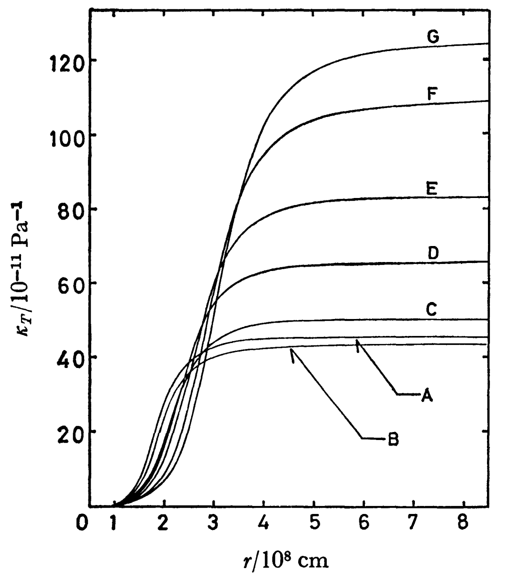

Fig. 4. Variation of the compressibility of solvent with the distance from the center of univalent ion in water–methanol system.
Symbols A—G are the same as in Fig. 1.

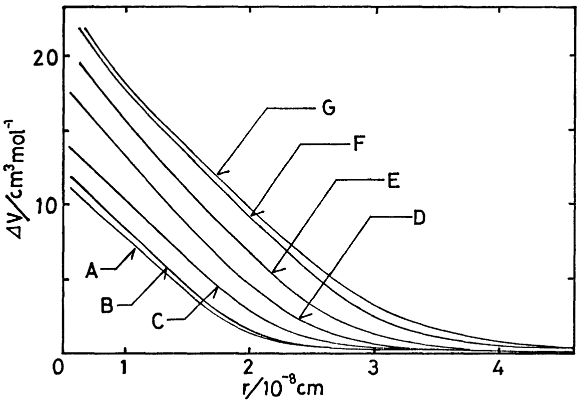

Fig. 5. Volume decrease of one molar of solvent expressed as a function of the distance from the center of univalent ion in water–methanol system at 25 °C.
Symbols A—G are the same as in Fig. 1.

as shown by Fig. 4 is preferable. As a consequence of the estimation procedure of the parameters $B$ and $D$, the value of $\kappa_T$ approaches asymptotically that of the pure solvent with increasing distance from the center of ion.

The volume decrease of solvent defined as $\Delta V = v^\circ - v(P)$, where $v(P)$ is the molar volume of the solvent at the effective pressure $P$, can be evaluated from the relation,

$$\ln(v^\circ/v(P)) = D\ln\left(1+\frac{P}{B}\right). \tag{8}$$

This equation derives from the integration of Eq. 6. It should be noted that the quantity $\Delta V$ does not refer to the absolute amount of volume decrease of the solvent but to the relative decrease of volume assigned to one molar of solvent at distance $r$ from the center of the univalent ion. The variation of the volume decrease $\Delta V$ for univalent ion in mixed solvent system of water–methanol at 25 °C is illustrated in Fig. 5.

Table 3. Partial molar volumes of CsCl, KCl, and LiCl in water-methanol system at 25 °C

| MeOH | $\overline{V}_2^\circ$/cm$^3$ mol$^{-1}$ | | |
|---|---|---|---|
| mol% | CsCl | KCl | LiCl |
| 0 | 39.1 | 26.8 | 18.2 |
| 30 | 39.2 | 27.7 | 15.9 |
| 50 | 37.5 | 27.3 | 13.4 |
| 70 | 32.6 | 22.4 | 8.5[a)] |
| 90 | 25.3 | 13.4 | 4.2[a)] |
| 100 | 23.6[b)] | 5.9[b)] | −4.9[b)] |

a) Owing to the limited solubility of LiCl, uncertainties are larger than the other cases. b) Values found in Ref. 21.

At this point it seems worth while to sum up ambiguities involved in the estimation and the results obtained:

I) Can Tait-form equation containing only two parameters really represent the pressure dependence of $\varepsilon$, $n^2$, and $\kappa_T$ in such high pressure regions as in electrostriction layer with the same accuracy?

II) Even if the Tait-form equation is correct, should the parameter $B$ be the same for three physical quantities? Nearly the same numerical values have been found for $B$ associated with $\varepsilon$ and that associated with $\kappa_T$.[17)] But is the fact a mere coincidence?

III) Parameters A, B, C, and D have not been known with the same precision. Moreover, errors involved in estimating the values of these parameters in the mixed solvent differ for each parameter.

Authors admit that the present treatments of electrostriction are not free from the controversy on the ambiguities mentioned just above. None the less, the result of calculation can afford much information on the order and the magnitude of electrostriction in the mixed solvent system as described below. For example, Fig. 4 shows that for many ordinary univalent ions the compressibility of the primary solvation layer in methanol can be neglected in comparison with that of bulk solvent if the electrostriction layer is assumed to correspond to the primary solvation layer.

*Application of the Calculated Results to the Partial Molar Volumes of LiCl, KCl, and CsCl.* As mentioned at the begining of this paper, the partial molar volumes of ions are discussed in their relation to electrostriction effects. In order to apply the results of the calculation, the partial molar volumes, $\overline{V}_2^\circ$, of salts LiCl, KCl, and CsCl have been determined in water–methanol system. The reasons for the choice of these salts are as follows: Throughout the present work, the continuum model of the solvent has been assumed. This assumption does not hold well for transition metal ions in mixed aqueous solvent, because the ligand-field is generally strong for these ions and the preferential hydration occurs, which contradicts our basic assumption. For alkali metal, in particular for lithium, and chloride ions, preferential hydration may occur, but to much lesser extent than for the case of transition metal

TABLE 4. EFFECTIVE RADIUS AND VOLUME DECREASE OF ONE MOLAR OF SOLVENT FOR IONS $Cs^+$, $K^+$, $Li^+$, AND $Cl^-$ IN WATER-METHANOL SYSTEM AT 25 °C

| MeOH | $r_e/10^{-8}$ cm | | | | $\Delta V/\text{cm}^3\ \text{mol}^{-1}$ | | | |
|---|---|---|---|---|---|---|---|---|
| mol% | $Cs^+$ | $K^+$ | $Li^+$ | $Cl^-$ | $Cs^+$ | $K^+$ | $Li^+$ | $Cl^-$ |
| 0 | 1.91 | 1.42 | 1.10 | 2.15 | 1.6 | 4.6 | 7.0 | 0.8 |
| 10 | 1.94 | 1.47 | 1.18 | 2.17 | 1.9 | 4.6 | 6.9 | 1.0 |
| 30 | 1.99 | 1.58 | 1.31 | 2.20 | 2.9 | 5.7 | 7.8 | 1.8 |
| 50 | 2.05 | 1.68 | 1.47 | 2.23 | 4.3 | 7.0 | 8.9 | 3.2 |
| 70 | 2.10 | 1.78 | 1.60 | 2.27 | 5.9 | 8.4 | 9.9 | 4.6 |
| 90 | 2.15 | 1.89 | 1.74 | 2.30 | 7.9 | 10.1 | 11.3 | 6.7 |
| 100 | 2.18 | 1.94 | 1.81 | 2.32 | 8.3 | 10.1 | 11.2 | 7.2 |

ions, and ionic associations are seldom observed for alkali chlorides. Thus alkali chlorides are considered to be the best salts for the present work. In pure methanol, the determination of the reliable values of $\bar{V}_2^\circ$ was difficult on account of the low solubility of the salts and the values in the literature[21] were adopted. Results of the determination of $\bar{V}_2^\circ$ are given in Table 3. For three alkali chlorides investigated, the variation of $\bar{V}_2^\circ$ is small up to 50 mol% of methanol but in concentration of methanol above 70 mol%, $\bar{V}_2^\circ$ decreases remarkably with the content of methanol in the solvent.

In the application of the theoretically estimated electrostriction effects to the actual ions in solution, a problem of crucial importance is how to evaluate the effective radius of the solvated ion. This problem is inherent to any theory dealing with the electrostriction effects. It is not the ion but the solvent around ion which contracts under electrostrictive pressures. Therefore, the effective radius of the solvated ion concerned in the present treatment must be larger than the crystallographic radius, $r_c$. In this respect, the use of Stokes radius, $r_s$, derived from the hydrodynamic consideration of ion in solution, is inappropriate, as $r_s/r_c<1$ has been observed for large alkali and halide ions. On the same ground, Gourary-Adrian radii[22] are rejected, though sometimes they have been used. Desnoyers *et al.*[3] considered the distance from the center of ion to the center of a neighboring water molecule. Their consideration, however, is not free from the disputation. We have evaluated the effective ionic radius, $r_e$, by the aid of the relationship between $\bar{V}^\circ_{\text{ion}}$ and $r_e$ given by Padova.[2,5] In his papers,[2,5] $r_e$ was defined as the intrinsic radius of ion and the intrinsic volume of the ion in solution $\bar{V}_{\text{int}}$, was expressed as $\bar{V}_{\text{int}}=4/3\pi N_0 r_e^3$, where $N_0$ is the Avogadro number. On the contrary, we have used the value of $r_e$ as a *literal* effective radius of the solvated ion, without taking account of the original physical significances of $r_e$ in the Padova's model for the calculation of $\bar{V}^\circ_{\text{ion}}$. As Padova used incorrect values of $\bar{V}^\circ_{\text{ion}}$,[2,5] effective ionic radii have been determined using the generally accepted values of $\bar{V}^\circ_{\text{ion}}$ in water[23] and methanol.[21] The estimated values of $r_e$ are given in Table 4. In both solvents values of $r_e$ are larger than those of $r_c$ and the variation of $r_e$ with the ionic species seems to be reasonable. In the mixed solvent system, it was assumed that $r_e$ varies linearly with the mole fraction of the component. Corresponding to each value of $r_e$, the amount of volume decrease of one molar of solvent, $\Delta V$, is determined from Fig. 5. Table 4 shows the numerical values of $r_e$ and $\Delta V$ thus determined for ions $Cs^+$, $K^+$, $Li^+$, and $Cl^-$ in water–methanol system. Padova,[5] using the theoretical coefficients of the concentration dependence of the partial molar volume and partial molar compressibility, estimated the average theoretical electrostriction volume per mole of solvent methanol, which is equal to 7.54 $\text{cm}^3\ \text{mol}^{-1}$. In comparison with this value, the results of the present calculation are larger by 1—4 $\text{cm}^3\ \text{mol}^{-1}$ for cations, while the agreement is satisfactory for $Cl^-$ ion. The total electrostriction volume arising from the addition of one molar of 1-1 type salt into solvent, expressed as $\bar{V}_e$, is given by the relation,

$$\bar{V}_e = \Delta V(M^+)n_s(M^+) + \Delta V(X^-)n_s(X^-), \tag{9}$$

where $n_s(M^+)$ and $n_s(X^-)$ are solvation numbers for cation and anion, respectively. However, the solvation number is experimentally determined for salt MX and the assignment of solvation number to cationic and anionic components requires further assumptions. Accordingly, instead of Eq. 9 we have adopted the following relation to calculate $\bar{V}_e$ of the salt MX:

$$\bar{V}_e = [\Delta V(M^+)+\Delta V(X^-)]\bar{n}_s(M^+, X^-), \tag{10}$$

where $\bar{n}_s(M^+, X^-)$ is the solvation number averaged over cation and anion and it is assumed to be equal to a half of $n_s$ for the salt MX. The determination of solvation number in taking account of the volume decrease and the compressibility of the primary solvation layer can be attained by the use of an expression,[24]

$$\bar{\kappa}_2^\circ = \kappa_2 + \frac{n_s v_s}{\bar{v}_2}(\kappa_{\text{sol}}-\kappa_1) \tag{11}$$

In Eq. 11, $\kappa$ stands for the compressibility and $\bar{v}_2$ is the partial specific volume of solute, and the subscripts s and sol (to avoid the confusion with $\kappa_s$ used in Eq. 8) refer to the solvation layer, while subscripts 1 and 2 refer to solvent and solute, respectively. The derivation of Eq. 11 and the determination of the value of $\bar{\kappa}_2^\circ$ from the data of compressibility and density of solution is described elsewhere.[24] For the measurements of the compressibility of solutions, an ultrasonic interferometer was used.[25]

In the calculation of $n_s$ of salt MCl from Eq. 11, the compressibility of the solvation layer, $\kappa_{\text{sol}}$, was not considered for each ion but a mean value of $\kappa_{\text{sol}}$ for salt MCl was considered and a value of $\kappa_T$ at $r$ equal

TABLE 5. COMPRESSIBILITY OF SOLVATION LAYER, SOLVATION NUMBER, TOTAL ELECTROSTRICTION VOLUME, $\bar{V}_e$, AND DISORDERED PARTIAL MOLAR VOLUME, $\bar{V}_d$, OF CsCl, KCl, AND LiCl IN WATER-METHANOL SYSTEM AT 25 °C

| MeOH | $\kappa_{sol}/10^{-11}$ Pa$^{-1}$ | | | $n_s$/mol mol$^{-1}$ | | | $\bar{V}_e$/cm$^3$ mol$^{-1}$ | | | $\bar{V}_d$/cm$^3$ mol$^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| mol% | CsCl | KCl | LiCl | CsCl | KCl | LiCl | CsCl | KCl | LiCl | CsCl | KCl | LiCl |
| 0 | 29.0 | 19.1 | 12.4 | 1.3 | 2.8 | 4.6 | 1.6 | 7.6 | 18.0 | 13.6 | 13.6 | 20.8 |
| 10 | 25.1 | 15.6 | 10.7 | — | — | — | — | — | — | — | — | — |
| 30 | 21.9 | 13.7 | 9.4 | 0.6 | 1.4 | 3.2 | 1.4 | 5.3 | 15.4 | 13.5 | 12.2 | 15.9 |
| 50 | 22.4 | 14.9 | 11.2 | 0.6 | 1.8 | 3.7 | 2.3 | 9.2 | 22.4 | 12.7 | 15.7 | 20.4 |
| 70 | 20.4 | 14.2 | 11.4 | 0.8 | 2.6 | 4.7 | 4.2 | 16.9 | 34.1 | 9.7 | 18.5 | 27.2 |
| 90 | 16.2 | 12.1 | 9.7 | 1.3 | 3.5 | 5.9 | 9.5 | 29.4 | 53.1 | 7.7 | 22.0 | 41.9 |
| 100 | 13.0 | 9.9 | 8.6 | 1.6 | 3.5 | 5.8 | 12.4 | 30.3 | 53.4 | 8.9 | 15.4 | 33.1 |

The numerical values of $\bar{V}$(crystal)/cm$^3$ mol$^{-1}$ for CsCl, KCl, and LiCl are 27.1, 20.8, and 15.4 respectively.

to $1/2(r_e(M^+)+r_e(Cl^-))$ was taken. This step of calculation corresponds to the use of Eq. 10 in place of Eq. 9. As mentioned above, it has been assumed that no preferential solvation occurs in the mixed solvents, $n_s$ being the average solvation number.

It is generally admitted that the partial molar volume of an ion at infinite dilution, $\bar{V}_{ion}{}^\circ$, can be attributed to the following components:

$$\bar{V}^\circ_{ion} = \bar{V}(\text{crystal}) - \bar{V}(\text{electrostriction}) + \bar{V}(\text{disordered}) \tag{12}$$

$\bar{V}$(crystal) can be evaluated using the radius of the ion. Pauling radius was used in the evaluation of $\bar{V}$(crystal). Upon substituting into Eq. 12 the values of $\bar{V}$(crystal) and $\bar{V}$(electrostriction) obtained in the present calculation, the $\bar{V}$(disordered) is evaluated. According to the treatment of Padova,[2,5] the following relation should hold and the amount of $\bar{V}$(disordered) is calculated without recourse to Eq. 12;

$$\bar{V}(\text{disordered}) = \bar{V}_{int} - \bar{V}(\text{crystal}) = \frac{4}{3}\pi N_0(r_e{}^3 - r(\text{crystal})^3), \tag{13}$$

However, we do not calculate $\bar{V}$(disordered) in this manner. As mentioned earlier, the numerical value of $r_e$ was evaluated as to be a mere effective radius of the solvated ion. Moreover, the fundamental point of the present study lies to see to what extent the consideration of the electrostriction effects can explain the observed fact, and for this purpose the contribution of the electrostriction effects must be substracted from the values determined by experiments. If the consideration of the electrostriction term suffices to the interpretation of $\bar{V}^\circ_{ion}$, then the contribution of $\bar{V}$(disordered) disappears, otherwise it will appear as a correction term.

Final results are shown in Table 5 along with the value of $n_s$. In Table 5, three significant figures are used to express the values of $\bar{V}_e$ and $\bar{V}_d$. But apart from the problem related with the estimation procedure of the effective radius of the solvated ion, $r_e$, on account of the cumulation of various kinds of assumptions and ambiguities involved in the present calculation, physical significance of the figures of $\bar{V}_e$ and $\bar{V}_d$ is not so much reliable. However, we can mention and discuss the general features of the variation of $\bar{V}_e$, $\bar{V}_d$, and $n_s$ with the composition of the solvent system as follows.

1) The variation of partial molar volume with composition of the solvent is rather small up to 50 mol% of methanol but in methanol-rich regions partial molar volume decreases rapidly with the content of methanol in the solvent (see Table 3). Corresponding to this fact, the amount of total electrostriction volume increases remarkably in the same concentration ranges of methanol for three chlorides investigated.

2) Values of $\bar{V}_d$ are smaller for CsCl and larger for LiCl than the corresponding values in water, while values of $\bar{V}_d$ for KCl are comparable in both solvents. Smaller value of $\bar{V}_d$ of CsCl in methanol than in water is compatible with the finding of Kawaizumi and Zana[21] that the void space around ions appears to be smaller in methanol than in water. Results related to KCl and LiCl may be interpreted as follows: In an early paper[21] and in many other references[26] the contributions of electrostriction volume and void space to the partial molar volume of ions are evaluated as the parameters A and B of Hepler equation,[27]

$$\bar{V}^\circ_{ion} = Ar^3 - \frac{B}{r}, \tag{13}$$

and $A$ and $B$ are determined independently, while in the present estimation the disordered part of the partial molar volume of the salt is determined through the subtraction of $\bar{V}$(crystal) and $\bar{V}_e$ from the value of $\bar{V}^\circ_{ion}$. For $K^+$ and $Li^+$ ions, the present estimation of electrostriction effects seems to give somewhat larger electrostriction volume than the actual volume decrease in solutions, as is seen from the comparison of the values of $\Delta V$ of Table 4 with the value of 7.54 cm$^3$ mol$^{-1}$ estimated by Padova.[5] The small differences of $\Delta V$ can affect largely the values of $\bar{V}_d$ as a result of the multiplication of $\Delta V$ by $n_s$, this being especially the case for LiCl. It is noteworthy that the value of $\bar{V}^\circ_{ion}$ allotted to $Li^+$ ion in methanol clearly departs from the relationships given by Hepler equation and observed for all small univalent ions.[21] Also we would like to say that the result relative to CsCl seems to support the conclusion drawn by Kawaizumi and Zana,[21] but one should retain prudence in discussing $\bar{V}_d$ and $\bar{V}_e$ separately, as they are essentially interrelated in the present treatment.

3) Values of $\overline{V}_e$ and $\overline{V}_d$ are the largest for LiCl, then for KCl, and the smallest for CsCl at any compositions of the solvent system. In other words, the quantities $\overline{V}_e$ and $\overline{V}_d$ are inversely proportional to the cationic size.

4) For three alkali chlorides investigated, the average solvation number of the salt, $n_s$, first decreases, then increases, with increasing amount of methanol in the solvent and finally in pure methanol values of $n_s$ are larger than those in water.

5) As for $\overline{V}_2°$ of LiCl, the contribution of $\overline{V}$(crystal) is minor than that of $\overline{V}_e$ and $\overline{V}_d$ in the solvents containing more than 50 mol% of methanol.

To be free from the speculation, further discussion of the results of present study is postponed until more data are available on this mixed solvent system.

The authors wish to express their thanks to Professor Keizo Suzuki of Ritsumeikan University and Associate Professor Takashi Moriyoshi of Tokushima University for their kindness of informing them the source of the pressure dependence of dielectric constant and refractive index of the system concerned in the present work.

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11) In some cases, expressions somewhat different from Eqs. 4—6 are cited as Tait equation:

$$1-\frac{\varepsilon^\circ}{\varepsilon}=A\ln\left(1+\frac{P}{B}\right) \tag{4'}$$

$$1-\frac{v}{v^\circ}=D\ln\left(1+\frac{P}{B}\right), \tag{6'}$$

where superscript ° indicates the value at ordinary pressure. Equations 4′ and 6′ are respectively equivalent to Eqs. 4 and 6 under the condition that $\varepsilon^\circ \simeq \varepsilon$, and $v^\circ \simeq v$. The differences between values of dielectric constant and volume calculated from two different forms of Tait equation become gradually significant with increase in pressure. However, the errors arising from two different forms of Tait equation are within the uncertainties arising from various kinds of physical assumption used in the present calculation.

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