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Test for Validity of Constant Ionic Medium Principle. Variation of the Activity Coefficient of Hydrogen Ion in Various Compositions of Medium Cations with 3 M Perchlorate Ions

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Potential changes of cells with a glass electrode and a hydrogen electrode in combination with a reference half-cell were measured in solutions of various compositions of cations at constant concentrations of hydrogen and total perchlorate ions. Measurements were carried out for the systems $LiClO_4$-$NaClO_4$, $LiClO_4$-$AgClO_4$, $NaClO_4$-$AgClO_4$, $NaClO_4$-$TlClO_4$, $LiClO_4$-$Mg(ClO_4)_2$, $LiClO_4$-$Ba(ClO_4)_2$, $NaClO_4$-$Ba(ClO_4)_2$, $AgClO_4$-$Ba(ClO_4)_2$, and $LiClO_4$-$La(ClO_4)_3$. In some cases a remarkable potential change was observed. Part of the change was due to the variation of the liquid junction potential at the interface of a test solution and a solution in a salt bridge. However, the change was attributed in greater part to the electrostatic free energy change of the transfer of hydrogen ion from a ($3/m$ M A^{m+}, 3M ClO_4^-) solution to a (xM A^{m+}, yM B^{n+}, 3M ClO_4^-) solution (where $mx+ny=3$). Variation of the composition of electrolytes gives rise to a significant change of the dielectric constant of a solution, so that the activity coefficient of hydrogen ions varies in different solutions at a constant concentration of perchlorate ions. Potential changes are additive in $A_1(ClO_4)_{m_1}$-$B_1(ClO_4)_{n_1}$, $A_1(ClO_4)_{m_1}$-$B_2(ClO_4)_{n_2}$ and $B_2(ClO_4)_{n_2}$-$B_1(ClO_4)_{n_1}$ solutions for a given replacement of cations in solutions, where A_1, B_1, and B_2 denote cations with charges of m_1, n_1, and n_2, respectively.

When we apply the constant ionic medium principle to reactions in electrolyte solutions, it is essential to choose what variable must be kept constant in the course of the reactions. Often the formal ionic strength is taken as the variable. Sometimes the total equivalent concentration of all ions is chosen, and sometimes the concentration of "inert" cation or anions. A historical review on the application of ionic media and merits of the use of the high concentration of medium salts have been described by Biedermann and Sillén.[1] The assumption of constant ionic activities in a constant ionic medium, however, has not been rigorously tested. The present study was undertaken to examine this by testing the validity of the ionic medium principle by means of emf measurements of cells containing solutions in which concentrations of perchlorate and hydrogen ions were kept constantant and those of "inert" cations were varied.

Experimental

Reagents. All reagents used were prepared from relevant carbonates or oxides and perchloric acid. They have been used for studies of hydrolytic reactions of metal ions in the Laboratory of Inorganic Chemistry of the Royal Institute of Technology, Stockholm.

Apparatus. *Glass electrodes*: Beckman glass electrodes (No. 40498) were used.

Hydrogen electrodes were prepared by the method described by Bates.[2] Emf values obtained were corrected to those at one atmospheric pressure.[3]

Silver chloride electrodes were prepared by Brown's method.[4]

The "Wilhelm" type of half-cell described by Forsling, Hietanen, and Sillén[5] was used as the reference half-cell.

A Leeds and Northrup Type K-3 Universal Potentiometer for measurements with hydrogen electrodes and *a Radiometer PHM 4 pH Meter* with glass electrodes were used. Emf's were read to 0.01 mV with the former and 0.1 mV with the latter.

A Coulometric Analyzer (Leeds and Northrup Co., Philadelphia) was used for coulometric reduction of hydrogen ions.

Hydrogen gas, free from oxygen and carbon dioxide, was preequilibrated with a solution of 3 M perchlorate and was then introduced into a hydrogen electrode. A titration vessel was filled with nitrogen gas, free from carbon dioxide and preequilibrated with a 3 M perchlorate solution, instead of hydrogen gas when we used only glass electrodes for measurements. No essential difference has been found in results obtained with hydrogen and glass electrodes.

Procedure for Potentiometric Measurements. All potentiometric measurements were performed at 25.00±0.01°C in a paraffin oil thermostat which was placed in a room thermostated at 25±2°C. In the course of emf measurements the total concentration of perchlorate ion was kept constant at 3 M. The hydrogen ion concentration was also kept constant at 0.01 M except in the case of $NaClO_4$-$TlClO_4$ solutions in which the total concentration of perchlorate ion was 3 M but the concentrations of hydrogen ion were 0.01 and 0.1 M.

The titration procedure was as follows: Into a solution S_1 titrant S_2 was added. The composition of S_1 was $(3-0.01)/m$ M A^{m+}, 0.01 M H^+, 3 M ClO_4^-, and that of S_2 was $(3-0.01)/n$ M B^{n+}, 0.01 M H^+, 3 M ClO_4^-. All metal ions used were not hydrolyzed in such acid solutions. Titration was performed up to a point where A^{m+} ions of more than half of the total equivalent were replaced with B^{n+} ions, and then the reverse titration, *i.e.*, titration of the S_2 solution with the S_1 solution was carried out with the same set of electrodes. Data obtained with these two titrations were combined by the use of data in the overlapped region.

Emf's of cells

$$\text{Ref}\,|\,\text{Solution}\,|\,\text{GE} \qquad \text{(A)}$$

and

$$\text{Ref}\,|\,\text{Solution}, H_2\,|\,\text{Pt} \qquad \text{(B)}$$

were determined, where the solution has the general com-

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[1] G. Biedermann and L. G. Sillén, *Arkiv Kem.*, **5**, 425 (1953).

[2] R. G. Bates, "Electrometric pH Determinations," J. Wiley and Sons, New York (1954).

[3] W. R. Hainsworth, H. J. Rowley, and D. A. MacInnes, *J. Amer. Chem., Soc.*, **46**, 1437 (1924).

[4] A. S. Brown, *ibid.*, **56**, 646 (1934).

[5] W. Forsling, S. Hietanen, and L. G. Sillén, *Acta Chem. Scand.*, **6**, 901 (1952).

position

$$|x\text{M A}^{m+},\ y\text{M B}^{n+},\ 0.01000\text{ M H}^+,\ 3.000\text{ M ClO}_4^-|$$

$$(mx+ny+0.01=3) \qquad \text{(C)}$$

and Ref denotes the reference half-cell

$$\text{Ag-AgCl}|(3-0.01)/m\text{ M A(ClO}_4)_m,$$

$$0.01\text{ M AgClO}_4|3/m\text{ M A(ClO}_4)_m| \qquad \text{(D)}$$

The value of the emf measured, E, may be given by the following equation at 25°C;

$$E = E^\circ + \frac{RT}{F}\ln a_{\rm H} + E_j$$

$$= E^\circ + 59.15\log[\text{H}^+] + 59.15\log f_{\rm H} + E_j(\text{H, A, B}) \qquad (1)$$

where E° is a constant and $a_{\rm H}$ and $f_{\rm H}$ denote the activity and the activity coefficient of hydrogen ion, respectively. E_j represents the liquid junction potential at the junction

$$3/m\text{ M A(ClO}_4)_m|\text{Solution} \qquad \text{(E)}$$

which is a function of concentrations of H^+, A^{m+}, and B^{n+} at the 3 M perchlorate ions, the junction potential at the junction, $(3-0.01)/m$ M $\text{A(ClO}_4)_m$, 0.01 M $\text{AgClO}_4/3/m$ M $\text{A(ClO}_4)_m$, in the salt bridge in the reference half-cell being assumed constant during the emf measurements.

Equation (1) can be rewritten as

$$E - 59.15\log[\text{H}^+]$$

$$= E^\circ + 59.15\log f_{\rm H} + E_j(\text{H, A, B}) \qquad (2)$$

Since E° is a constant ΔE, the difference of $E-59.15\log[\text{H}^+]$ values in a solution, $(3-0.01)/m$ M A^{m+}, 0.01 M H^+, 3 M ClO_4^-, and in a solution, xM A^{m+}, yM B^{n+}, 0.01 M H^+, $(mx+ny+0.01=3)$, depends on the variation of $f_{\rm H}$ and E_j with the composition of cations in a solution at the constnat perchlorate and hydrogen ion concentrations.

Results and Discussion

Variation of potentials with compositions of electrolytes in a solution can be given by

$$\Delta E = \frac{RT}{F}\Delta\ln f_{\rm H} + \Delta E_j$$

$$= 59.15\Delta\log f_{\rm H} + \Delta E_j(\text{H,A,B}) \qquad (3)$$

where $\Delta\log f_{\rm H}$ and ΔE_j represent differences of $\log f_{\rm H}$ and E_j, respectively, in solutions, $(3-0.01)/m$ M A^{m+}, 0.01 M H^+, 3 M ClO_4^- and xM A^{m+}, yM B^{n+}, 0.01 M H^+, 3 M ClO_4^- $(mx+ny+0.01=3)$. Values of ΔE were determined in nine sets of various combinations of $\text{A(ClO}_4)_m$ and $\text{B(ClO}_4)_n$. Results are graphically shown in Figs. 1 and 2.

Each ΔE could be expressed by an approximate linear function of $[\text{B}^{n+}]$, but in some cases in which ΔE varies markedly, it could be better described with a quadratic function of $[\text{B}^{n+}]$ than a linear function. Equations for variations of ΔE as a function of $[\text{B}^{n+}]$ in various systems of $\text{A(ClO}_4)_m$-$\text{B(ClO}_4)_n$ are summarized in Table 1. Solid lines in Figs. 1 and 2 show curves drawn on the basis of equations for ΔE in Table 1.

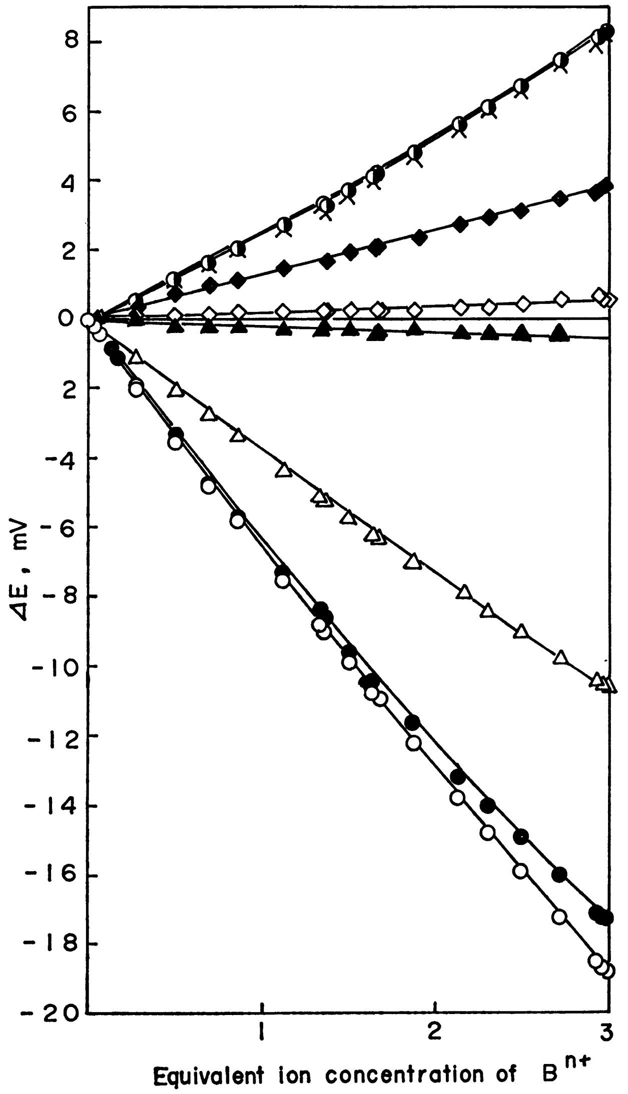

Fig. 1. ΔE in various sets of metal perchlorate media at $[\text{H}^+]=0.010$ M. ◑, NaClO_4-$\text{Ba(ClO}_4)_2$; ×, AgClO_4-$\text{Ba(ClO}_4)_2$; ◆, LiClO_4-$\text{Mg(ClO}_4)_2$; ◇, LiClO_4-$\text{La(ClO}_4)_3$; ▲, NaClO_4-AgClO_4; △ LiClO_4-$\text{Ba(ClO}_4)_2$; ●, LiClO_4-AgClO_4; ○, LiClO_4-NaClO_4

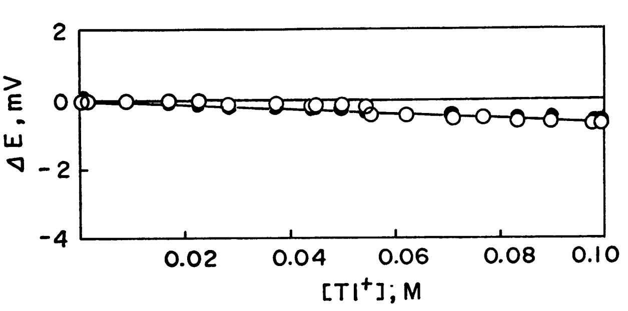

Fig. 2. ΔE in NaClO_4-TlClO_4 solutions : ○, $[\text{H}^+]=0.010$ M; ●, $[\text{H}^+]=0.100$ M.

Liquid junction potentials have been determined in some solutions containing 3 M perchlorate as ionic media. In 3 M LiClO_4 solution, E_j has been evaluated as $-16[\text{H}^+]$ mV/M[6] and in 3 M NaClO_4, $E_j=-16[\text{H}^+]$ mV/M[1] or $-17[\text{H}^+]$ mV/M.[7] When the concentration of hydrogen ion increases, a quadratic function with respect to the hydrogen ion concentration may be more adequate to describe the variation of

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[6] H. Ohtaki and H. Kato, *Inorg. Chem.*, **6**, 1935 (1967).

[7] N. Ingli, G. Lagerström, M. Frydman, and L. G. Sillén, *Acta Chem. Scand.*, **11**, 1034 (1957).

Table 1. Variation of ΔE as a function of the composition of electrolytes in the solution

$A(ClO_4)_m$-$B(ClO_4)_n$	$\Delta E=\alpha[B^{n+}]+\beta[B^{n+}]^2$, mV	ΔE at 1 equiv. $[B^{n+}]$, mV
$NaClO_4$-$Ba(ClO_4)_2$	$\Delta E=4.6[Ba^{2+}]+0.6[Ba^{2+}]^2$	2.6
$AgClO_4$-$Ba(ClO_4)_2$	$\Delta E=4.5[Ba^{2+}]+0.6[Ba^{2+}]^2$	2.5
$LiClO_4$-$Mg(ClO_4)_2$	$\Delta E=2.5[Mg^{2+}]$	1.3
$LiClO_4$-$La(ClO_4)_3$	$\Delta E=0.6[La^{3+}]$	0.2
$NaClO_4$-$AgClO_4$	$\Delta E=-0.2[Ag^+]$	−0.2
$LiClO_4$-$Ba(ClO_4)_2$	$\Delta E=-7.6[Ba^{2+}]+0.3[Ba^{2+}]^2$	−3.7
$LiClO_4$-$AgClO_4$	$\Delta E=-6.7[Ag^+]+0.3[Ag^+]^2$	−6.4
$LiClO_4$-$NaClO_4$	$\Delta E=-6.8[Na^+]+0.2[Na^+]^2$	−6.6
$NaClO_4$-$TlClO_4$	$\Delta E=-7[Tl^+]$ $([Tl^+]\leq 0.1M)$	−7

E_j.[1] About −0.2 mV may be estimated for the liquid junction potential caused by the diffusion of hydrogen ions at the junction (E), which is in the same order of magnitude with the experimental uncertainty of a measurement with a pH meter.

Correction of the junction potential caused by migration of hydrogen ions in solutions were examined in the following way. From a solution containing 3 M $LiClO_4$ and a trace amount of hydrogen ions, the hydrogen ions were removed coulometrically and values of $E-59.15\log[H^+]$ were extrapolated to $[H^+]=0$.[8] The value obtained by extrapolation is denoted as E', which may be given by

$$E' = E^\circ + 59.15\log f_H + E_j(\text{Li}, 0) \tag{4}$$

Since E' was determined in a solution in which concentrations of hydrogen and sodium ions ($Na^+=B^{n+}$ in this case) were zero, E_j is denoted as $E_j(0, \text{Li}, 0)$ or simply $E_j(\text{Li}, 0)$ as in Eq. (4). The composition of electrolytes in the solution was then changed by the addition of the solution S_2 (only a trace amount of hydrogen ions was contained) without removing electrodes from the solution, and the value of E'

$$E' = E^\circ + 59.15\log f_H + E_j(\text{Li}, \text{Na}) \tag{5}$$

was determined with the same procedure as before. The current passed in the course of coulometric titrations was so small that variation of composition of the solution by electrolysis was negligible, $\Delta E'$, the difference of E' values in 3 M $LiClO_4$ and in 3 M $(Li^+, Na^+)ClO_4^-$ solutions, differed from ΔE by only negligible amounts in the whole range of compositions of solutions, as seen in Fig. 3.

Different mobilities of lithium and sodium ions give rise to a liquid junction potential, $E_j(\text{Li, Na})$ at the junction (E). The liquid junction potential may be estimated by Henderson's equation,[9] which can be simplified as[1]

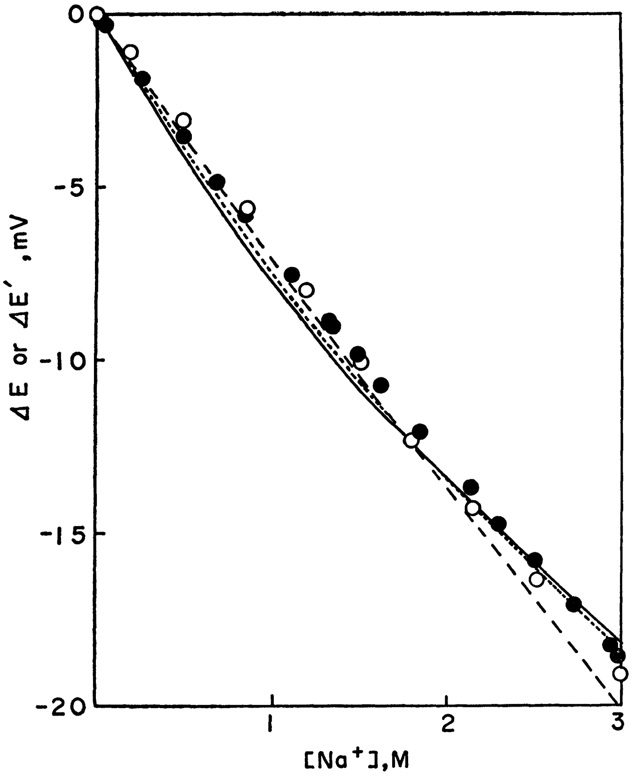

Fig. 3. Relationship between ΔE (●) or $\Delta E'$ (○) and $[Na^+]$. ----, calculated ΔE values by the use of Eq. (13); —— calculated ΔE values by the use of Eq. (13); calculated ΔE_{corr} values by the use of (16) with $r_H=7.0$Å and $\delta_{ClO_4}=-9.0$; ···, calculated ΔE_{corr} by Eq. (16) with $r_H=4.0$Å and $\delta_{ClO_4}=-6.7$.

$$E_j(\text{A, B}) = -59.15\log\left(1+\frac{nd_{B(A)}[B^{n+}]}{3}\right) \tag{6}$$

in 3 equiv./l perchlorate solutions, where $d_{B(A)}$ denotes

$$d_{B(A)} = \frac{\Lambda_{B(ClO_4)_n} - \Lambda_{A(ClO_4)_m}}{\Lambda_{A(ClO_4)_m}} \tag{7}$$

and Λ represents the equivalent conductivity of the relevant electrolyte.

Equation (6) may be approximated as

$$E_i(\text{A, B}) \simeq -19.72nd_{B(A)}[B^{n+}] \tag{8}$$

The value of $d_{B(A)}$ in a 3 M $(Li^+, Na^+)ClO_4^-$ solution may be evaluated from data of Λ in 3 M $LiClO_4$ and in 3 M $NaClO_4$. It can be estimated from data

$$-19.72d_{H(Li)} \simeq -16^{6)} \text{ or } d_{H(Li)} = 0.81 \tag{9}$$

and

$$-19.72d_{H(Na)} \simeq -17^{7)} \text{ or } d_{H(Na)} = 0.86 \tag{10}$$

Since $d_{Na(Li)}$ is derived from Eqs. (9) and (10) as

$$d_{Na(Li)} = \frac{\Lambda_{NaClO_4} - \Lambda_{LiClO_4}}{\Lambda_{LiClO_4}} = \frac{d_{H(Li)}+1}{d_{H(Na)}+1} - 1 = -0.027 \tag{11}$$

provided that Λ_{HClO_4} remains unchanged in 3 M $LiClO_4$ and 3 M $NaClO_4$ solutions, the liquid junction potential, $E_j(\text{Li, Na})$ is obtained as

$$E_j(\text{Li, Na}) = -19.72d_{Na(Li)}[Na^+] = 0.53[Na^+] \tag{12}$$

Thus, ΔE values obtained experimentally may be corrected by the liquid junction potential $E_j(\text{Li, Na})$:

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[8] G. Gran, *Analyst*, **77**, 661 (1952).

[9] P. Henderson, *Z. phys. Chem.* (Leipzig), **59**, 118 (1907); *ibid.*, **63**, 325 (1908).

$$\begin{aligned}\varDelta E_{\text{corr}} &= 59.15\varDelta \log f_{\text{H}} = \varDelta E - E_j(\text{Li, Na}) \\ &\simeq -7.3[\text{Na}^+]\end{aligned} \tag{13}$$

Calculation of Eq. (8) may be oversimplified with neglection of higher terms of $[\text{B}^{n+}]$ and, therefore, the term with $[\text{Na}^+]^2$ is dropped in Eq. (13). The value -17 in Eq. (10) for $E_j(\text{H, Na})$ may be the upper limit of the $-19.72d_{\text{H(Na)}}$ value, so that $\varDelta E_{\text{corr}}$ estimated by Eq. (13) may give the lower limit of $\varDelta E_{\text{corr}}$. Since no essential difference has been observed in the measurements with hydrogen and glass electrodes, the sodium effect on glass electrodes is negligible. In Fig. 3 values of $\varDelta E_{\text{corr}}$ calculated by Eq. (13) are plotted by a broken line.

Liquid junction potentials have not been determined in other solutions but it can be expected that the liquid junction potentials may not be so large that the contribution of the variation of the potentials to $\varDelta E$ values becomes significant, because most ions have similar equivalent conductivities in aqueous solutions except for hydrogen and hydroxyl ions. Thus, it is concluded that the change of the activity coefficient of hydrogen ion is attributed to $\varDelta E$ with varying compositions of electrolytes in solutions.

Reactions of hydrogen ions with metal ions and perchlorate ions are denied from the fact that no association and hydrolytic reactions have been observed in these solutions. Association of lithium or sodium ions with perchlorate ions has not been detected in 3 M solutions. If no association reaction occurs in lithium perchlorate-sodium perchlorate solutions, variation of the activity coefficient of hydrogen ions may be caused by the free energy change of transfer of hydrogen ions from a 3 M LiClO_4 solution to a LiClO_4-NaClO_4 mixture.

According to Hasted, Ritson, and Collie,[10] the dielectric constant of a solution decreases with increasing concentration of an electrolyte. The variation of the dielectric constant is proportional to the concentration of an electrolyte and the contributions of a cation and an anion, δ, to the variation are additive.

$$\varepsilon = \varepsilon_0 + (\delta_c + \delta_a)C \tag{14}$$

where ε and ε_0 represent dielectric constants of a solution and the pure solvent, respectively, and C the molar concentration of an electrolyte, and values of δ are evaluated to be -11 ± 1 for Li^+ and -8 ± 1 for Na^+. However, no value has been given for δ_{ClO_4}. Equation (14) holds for solutions containing about 2—2.5 equiv./l cations and anions, and its application to 3 M solutions should not give rise to serious error making the following discussion worthless. Free energy changes of transfer of ions from one solution to another may be calculated by the simple Born's equation or, more adequately, by other equations with more realistic models of hydrated ions.[11,12] Stokes[11] has calculated hydration energies of various ions with models of hydrated ions taking into consideration the dielectric saturation effect of water in hydration shells. Ohtaki[13] has modified Stokes' model and applied it to hydrated hydronium ion in order to interprete variation of dissociation constants of acids in mixed solvents. Ohtaki assumed a "naked" hydronium ion having an ionic radius of 1.4 Å, the ion being surrounded by the first and the second hydration shells each with thickness of 2.8 Å. In the following considerations, a simple approximation is applicable where the dielectric constants in the first and second hydration shells of a hydronium ion in 3 M LiClO_4 solution are the same as those in 3 M NaClO_4 and 3 M $(\text{Li}^+, \text{Na}^+)$-$\text{ClO}_4^-$ mixtures, and dielectric constants of bulk solutions are given by Eq. (14). With these approximations the electrostatic free energy changes of transfer of 1 mol of hydronium ion from 3 M LiClO_4 to a 3 M $(\text{Li}^+, \text{Na}^+)\text{ClO}_4^-$ mixture can be given by

$$\begin{aligned}\mu_{\text{H}}^{\circ}(m) - \mu_{\text{H}}^{\circ}(s) &= \boldsymbol{RT}\{\ln f_{\text{H}}(m) - \ln f_{\text{H}}(s)\} = \boldsymbol{RT}\varDelta \ln f_{\text{H}} \\ &= \frac{\text{N}e^2}{2r_{\text{H}}}\left(\frac{1}{\varepsilon(m)} - \frac{1}{\varepsilon(s)}\right)\end{aligned} \tag{15}$$

where $\mu_{\text{H}}{}^0$ denotes the standard chemical potential of the hydronium ion and m and s in parentheses represent quantities in a 3 M $(\text{Li}^+, \text{Na}^+)$ ClO_4^- mixture and 3 M LiClO_4, respectively as follows. Since $\varDelta E_{\text{corr}}$ is given by $\boldsymbol{RTF}^{-1}\varDelta \ln f_{\text{H}}$, $\varDelta E_{\text{corr}}$ can be represented

$$\varDelta E_{\text{corr}} = \frac{\text{N}e^2}{2\boldsymbol{F}r_{\text{H}}}\left(\frac{1}{\varepsilon(m)} - \frac{1}{\varepsilon(s)}\right) \tag{16}$$

and

$$\left.\begin{aligned}\varepsilon(s) &= \varepsilon_0 + 3(\delta_{\text{Li}} + \delta_{\text{ClO}_4}) \\ \varepsilon(m) &= \varepsilon_0 + x\delta_{\text{Li}} + y\delta_{\text{Na}} + 3\delta_{\text{ClO}4} \quad (x+y=3)\end{aligned}\right\} \tag{17}$$

If we assume that the radius of the hydrated hydronium ion is 7.0 Å (1.4 Å for the naked hydronium ion and 2.8 Å for each hydration shell), satisfactory agreements were found between $\varDelta E_{\text{corr}}$ (or even $\varDelta E$) values observed and calculated using Eq. (16) when we choose $\delta_{\text{ClO}_4} = -9$. Values of $\varDelta E_{\text{corr}}$ in mV unit thus calculated were plotted by a solid line in Fig. 3. Application of the Hepler's model[12] gave similar results (shown by a dotted line in Fig. 3) with $r_{\text{H}} = 4$ Å and $\delta_{\text{ClO}_4} = -6._7$. $r_{\text{H}} = 7$ Å may be a better assumption than $r = 4$ Å in these calculations because Hasted *et al.*[10] estimated the minimum hydration number of 10 for a proton in their treatment and these hydrated water molecules may possibly be included in the first and second hydration shells.[14] The value $\delta_{\text{ClO}_4} = -9$ assumed in calculations with Stokes' model seems to be reasonable in comparison with values of $\delta_{\text{Cl}} = -3$, $\delta_{\text{I}} = -7$ and $\delta_{\text{OH}} = -13$, and the results show that electrostatic free energy changes caused by the variation of bulk dielectric constants of solutions may play the most important role in variation of the activity coefficient of hydrogen ions.

For magnesium, barium, and lanthanum ions, values of δ have been found to be -24, -22, and -35, respectively.[10] Application of the above arguments to $(\text{A}^+, \text{B}^{n+})\text{ClO}_4^-$ solutions leads to the following conclusions. Replacement of lithium ions with corresponding equivalent quantities of these ions contributes to variation of dielectric constants of solu-

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[10] J. B. Hasted, D. M. Ritson, and C. H. Collie, *J. Chem. Phys.*, **16**, 1 (1948).

[11] R. H. Stokes, *J. Amer. Chem. Soc.*, **86**, 979 (1964).

[12] L. G. Hepler, *Austr. J. Chem.*, **17**, 587 (1964).

[13] H. Ohtaki, This Bulletin, **42**, 1573 (1969).

[14] R. Grahn, *Arkiv Kem.*, **21**, 13 (1962).

tions to a less extent than that with sodium ions. In Li^+–La^{3+} mixtures, the potential variation may be fairly small and in Na^+–Ba^{2+} solutions ΔE varies in the opposite direction with that found in Li^+–Na^+ solutions. Variation of ΔE in Li^+–Ba^{2+} and Li^+–Mg^{2+} solutions may be smaller than that in Li^+–Na^+ solutions.

Experimental results support these considerations. Thus, it can be said that the main part of the variation of potentials measured in this study is interpreted in terms of electrostatic free energy changes of transfer of hydrogen ions from one salt medium to another, the main factor of the variation being caused by the change of the bulk dielectric constant of solutions with varying compositions of medium salts.

This conclusion is supported by the fact that the variation of potential is additive. Potential variations occurring at 1 equivalent-ion replacement of a cation are shown in the last column of Table 1. The equivalent replacement of a highly hydrated cation, such as lithium ion, with strongly hydrated bi- or tervalent cations might be expected to introduce only a small violation of the ionic medium principle of the solution. Replacement of strongly hydrated cations with less hydrated cations, on the other hand, results in a larger variation of activity coefficients of reacting species in the medium. From the viewpoint of δ values, activity coefficients of reacting species may vary to a much larger extent when an anion such as ClO_4^- of a medium salt is replaced by another kind of anion, *e.g.*, Cl^- ion.