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# Solubility of Calcium Sulfate Dihydrate in the System $Na_2SO_4$–$MgCl_2$–$H_2O$

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**Gypsum solubility in salty water solutions containing $Na_2SO_4$ and $MgCl_2$ has been measured at 40 °C. Experiments were carried out at various concentrations of salts up to an ionic strength of 7 *m*. A model with a firm thermodynamic basis has been applied for the data fitting and the values for the model parameters are given. The results obtained show that gypsum solubility in $Na_2SO_4$ water solutions is strongly increased by the addition of $MgCl_2$ at moderately low sulfate concentrations while the reverse is true in the high sulfate concentration range. This is interpreted in terms of the different polarizability of $SO_4^{2-}$ and $Cl^-$ anions.**

## Introduction

Accurate knowledge about the solubility of calcium sulfate dihydrate is of primary importance for the design and operation of cooling towers and of many industrial processes like reverse osmosis and electrodialysis for water desalination.

Moreover, this knowledge is also of interest to geologists and geochemists because of gypsum and anhydrite conversion occurring in nature (*1*). Many investigators have reported solubility data for calcium sulfate dihydrate at 40 °C in water (*2–6*) and in water solutions of sodium sulfate (*6*), sodium chloride (*3–5*), magnesium chloride (*7*), sodium sulfate and sodium chloride (*6*), and sodium chloride and magnesium chloride (*7*). A larger number of experimental data are also available for the above systems and for the system $CaSO_4$–$MgSO_4$–$H_2O$ (*8*) at 25 °C. However, we did not find any experimental gypsum solubility in mixed $Na_2SO_4$–$MgCl_2$ water solutions.

In a previous paper (*9*) a thermodynamic model for the solubility of gypsum in water solutions of mixed salts was presented and its applicability was shown for brackish water and seawater at several concentration factors and for different magnesium augmentation at 25 °C. By this model the gypsum solubility in water solutions containing sodium chloride and sodium sulfate was also calculated up to an ionic strength of 6 *m*.

Our purpose in this work is to investigate the behavior of calcium sulfate dihydrate solubility in water solutions of sodium sulfate and magnesium chloride with the aid of the above-mentioned model and new experimental solubility data at 40 °C.

We obtained these data during research on the process for the production of magnesium oxide from concentrated seawater brines (*10*, *11*).

Our data should prove useful in the development and evaluation of electrolyte solution models and in providing insight into the nature of intermolecular forces.

In fact, with the quaternary system $CaSO_4$–$Na_2SO_4$–$MgCl_2$–$H_2O$, it is possible to study all the main factors, some competitive, that determine the solubility behavior of calcium sulfate dihydrate even in much more complicated electrolyte solutions. These factors include the following: the presence of the common ion, $SO_4^{2-}$, that decreases solubility, the solubilizing effect of magnesium through the formation of stable magnesium sulfate ion pairs (*12*), and the ionic strength effect with two quite different anions, $Cl^-$ and $SO_4^{2-}$, both at high concentration.

Table I. Density and Molar $MgCl_2$ Concentrations for the Stock Solutions at 25 °C

| density, kg/L | $[MgCl_2]$, M | density, kg/L | $[MgCl_2]$, M |
|---|---|---|---|
| 0.998 18 | 0 | 1.034 29 | 0.4745 |
| 1.016 51 | 0.2452 | 1.049 25 | 0.6897 |

## Experimental Procedure

Double-distilled water and all reagents (p.a. grade, Merck) have been used in performing the experimental solubility measurements reported in this paper.

Weighed amounts (±0.0001 g) of sodium sulfate were added to 500 g of the stock solutions with magnesium chloride concentration and density reported in Table I.

The resulting solution and excess solid $CaSO_4 \cdot 2H_2O$ were then put into a 1-L glass bottle coated with a jacket for circulating water, thermostatically controlled by an ultrathermostat to within ±0.05 °C. The temperature in the equilibrium volume was measured with the aid of a precision Taylor thermometer to within ±0.05 °C. After the solution was stirred with an electrical paddle stirrer for at least 36 h at an automatically controlled temperature of 40 ± 0.05 °C, liquid samples were taken by filtering through a fritted glass filter (porosity 10–15 μm) previously immersed in the solution. The sampling procedure was the same as that described by Shaffer (*13*) and the porosity of the filter was chosen according to his results. The molal concentrations of calcium and magnesium were obtained by tritrating with a standard EDTA solution after the determination of the density on a second portion of the same sample. Finally, we used X-ray analysis to exclude the possibility that the excess solid phase was different from the desired pure gypsum.

## Experimental Results and General Discussion

The experimental results are given in Table II, where the molal solubility of gypsum at 40 °C is reported together with the molal concentrations of sodium sulfate and magnesium chloride. The value of 0.0156 *m* for solubility in water is in excellent agreement with the reported literature values (*2–6*). The data in Table II referring to solutions without $MgCl_2$ are directly comparable with those obtained by Block and Waters (*6*) at the same temperature; the general behavior is the same but the quantitative agreement is not satisfactory.

However, it must be stressed that, for instance, the data at 25 °C reported in ref *6* appear to be of lower accuracy than sets of similar data reported by other authors for the same temperature (*12*, *14*). Therefore, we further compared our data with those of Hill and Wills (*14*) at 35 °C since the gypsum solubility as a function of the temperature is a very flat curve in the range 35–40 °C. Now we find a good agreement over all the concentration range although the values reported in Table II show a slight tendency to be higher for high values of ionic strength. It was impossible to make a direct comparison for the remaining data in Table II but we can observe that our experimental point in a water solution of only magnesium chloride perfectly agrees with the conclusions of Fabuss and Lu (*15*) and it is qualitatively correct when compared with the value at 25 °C reported by Elgquist and Wedborg (*16*) for a

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Table II. Experimental Solubility of $CaSO_4 \cdot 2H_2O$ in Water Solutions of $Na_2SO_4$ and $MgCl_2$ at 40 °C[a]

| $CaSO_4 \cdot 2H_2O$ | $Na_2SO_4$ | $MgCl_2$ | $CaSO_4 \cdot 2H_2O$ | $Na_2SO_4$ | $MgCl_2$ |
|---|---|---|---|---|---|
| 0.0156 | 0 | 0 | 0.0166 | 1.495 | 0.180 |
| 0.0115 | 0.025 | 0 | 0.0184 | 1.977 | 0.159 |
| 0.0109 | 0.050 | 0 | 0.0460 | 0.026 | 0.477 |
| 0.0106 | 0.068 | 0 | 0.0279 | 0.105 | 0.471 |
| 0.0107 | 0.098 | 0 | 0.0189 | 0.201 | 0.462 |
| 0.0111 | 0.193 | 0 | 0.0145 | 0.297 | 0.454 |
| 0.0117 | 0.285 | 0 | 0.0131 | 0.389 | 0.446 |
| 0.0124 | 0.374 | 0 | 0.0123 | 0.478 | 0.438 |
| 0.0130 | 0.459 | 0 | 0.0134 | 0.647 | 0.424 |
| 0.0142 | 0.622 | 0 | 0.0134 | 0.880 | 0.404 |
| 0.0157 | 0.848 | 0 | 0.0134 | 1.225 | 0.374 |
| 0.0174 | 1.184 | 0 | 0.0139 | 1.519 | 0.348 |
| 0.0498 | 0 | 0.247 | 0.0160 | 2.004 | 0.306 |
| 0.0282 | 0.051 | 0.244 | 0.0548 | 0.027 | 0.698 |
| 0.0230 | 0.076 | 0.243 | 0.0460 | 0.053 | 0.695 |
| 0.0223 | 0.100 | 0.242 | 0.0221 | 0.205 | 0.675 |
| 0.0159 | 0.197 | 0.238 | 0.0161 | 0.303 | 0.663 |
| 0.0137 | 0.291 | 0.234 | 0.0148 | 0.397 | 0.651 |
| 0.0136 | 0.381 | 0.230 | 0.0143 | 0.478 | 0.640 |
| 0.0135 | 0.469 | 0.226 | 0.0128 | 0.659 | 0.618 |
| 0.0138 | 0.635 | 0.219 | 0.0126 | 0.895 | 0.588 |
| 0.0144 | 0.864 | 0.208 | 0.0124 | 1.244 | 0.544 |
| 0.0153 | 1.205 | 0.193 | 0.0128 | 1.541 | 0.506 |

[a] All concentrations are in molality.

magnesium chloride concentration close to that of Table II.

Our experimental results show that in the quaternary system $CaSO_4$–$Na_2SO_4$–$MgCl_2$–$H_2O$ the general behavior of the calcium sulfate dihydrate solubility as a function of sodium sulfate concentration is the same as in the ternary system $CaSO_4$–$Na_2SO_4$–$H_2O$. The main effect of adding $MgCl_2$ is a much higher solubility at low concentration of sodium sulfate that strongly decreases as the $Na_2SO_4$ concentration is increased. Furthermore, we see a marked shifting of the minimum solubility point toward higher sodium sulfate concentrations as the $MgCl_2$ concentration is increased.

## Fitting of the Experimental Results

The thermodynamic model presented in a previous paper (*9*) has been used to correlate the experimental solubility data reported in Table II. There are some other models, notably that of Pitzer (*17*), by which it is possible to calculate gypsum solubility in very concentrated multicomponent salt solutions with satisfactory accuracy as has been recently demonstrated (*1*).

The chosen model fits our experimental data well and we believe that the following assumptions, on which it is built, allow us to achieve a better and more realistic understanding about the nature and role of the different intermolecular forces which determine the relationship between composition and solubility: (a) We assume that the excess Gibbs energy, $G^E$, is the sum of three terms: a Debye–Hückel contribution, $G^E_{DH}$; a Debye–McAulay term as correction for the change of dielectric constant of the solvent due to the presence of the ions, $G^E_{BORN}$; and a short-range contribution calculated according to the NRTL (*18*) equation, $G^E_{NRTL}$. The term $G^E_{DH}$ is given by the Debye–Hückel limiting law plus higher order terms of a purely electrostatic nature which are significant for solutions like those investigated in the present study (*19*). (b) We assume that we have the formation of only bivalent metal sulfate ion pairs and the relative dissociation constants can be defined as follows:

$$K_{(ij)^0} = \gamma_{\pm(ij)}{}^2 m_i m_j / \{\gamma_{(ij)^0} m_{(ij)^0}\} \qquad (1)$$

(c) We assume that the thermodynamic solubility product is given by

$$K_{sp}{}^0 = m_{Ca^{2+}} m_{SO_4{}^{2-}} \gamma_{\pm(CaSO_4)}{}^2 a_w{}^2 \qquad (2)$$

All the analytical expressions and the procedure for the calculation of the activity coefficients which appear in eq 1 and 2 are extensively described in ref *9*.

Table III summarizes the full set of parameters recommended for the gypsum solubility calculation in the quaternary system $CaSO_4$–$Na_2SO_4$–$MgCl_2$–$H_2O$ at 40 °C. Most of them, i.e., those related to the NRTL contribution in the excess Gibbs energy function, were obtained from the previous parametrization at 25 °C (*9*) by adopting a temperature dependence similar to that usually accepted for nonelectrolyte solutions (*20*). The only exception was made for $Z_{\pm MgCl_2}$ which we found better to set as equal to zero.

For the binary subsystem NaCl–$H_2O$ we used experimental activity coefficients from the literature at 40 °C (*21*) to determine the $G^E_{BORN}$ contribution parameters, minimizing the following function:

$$S_\gamma = \sum_k (\gamma^{calcd}_{\pm NaCl} - \gamma^{exptl}_{\pm NaCl})_k{}^2 \qquad (3)$$

The summation was extended to 10 experimental points and the corresponding square root of the estimated variance is $\sigma_\gamma = 0.84 \times 10^{-3}$. The remaining parameters were fitted to the experimental data reported in Table II minimizing the function

$$S_{S_{Ca}} = \sum_{1k}^{N} (S_{Ca}{}^{calcd} - S_{Ca}{}^{exptl})_k{}^2 \qquad (4)$$

where $S_{Ca}{}^{calcd}$ and $S_{Ca}{}^{exptl}$ are respectively the calculated and experimental gypsum solubilities and $N$ indicates the number of experimental points. We used the data which refer to solution without $MgCl_2$ first to find the best binary parameters for $CaSO_4$ and then, working on the other data with nonzero concentration of $MgCl_2$, we found the last two parameters. In the last two data fittings the square roots of the estimated variances are respectively $\sigma_1 = 0.21 \times 10^{-3}$ *m* and $\sigma_2 = 0.86 \times 10^{-3}$ *m*. The difference between $\sigma_1$ and $\sigma_2$ is justified when considering that the determination of calcium at high magnesium concentration is quite difficult, but surely it has to be ascribed partly to a lower reliability of the model for high concentrations of $Cl^-$ together with metal earth (*1*, *9*). However, when we consider the comparison of our data with values from the literature, the values of $\sigma_\gamma$, $\sigma_1$, and $\sigma_2$ compared to the absolute values of the quantities that they refer to, and the single deviations between each experimental and calculated quantity, we can state that the experimental accuracy and the general reliability of the used model are satisfactory enough for a deeper analysis of solubility behavior.

To complete the discussion on the fitting of the experimental results it is worth noting that the values for the dissociation constants $K_{(CaSO_4)^0}$ and $K_{(MgSO_4)^0}$ compared to those obtained at 25 °C (*9*) are in good agreement with $\Delta H$ values given by Pitzer (*22*) for the same reactions. This result is more important when we consider that the value of the thermodynamic solubility product is independent of our experimental data. We calculated

Table III. Model Parameters for the System $CaSO_4$-$Na_2SO_4$-$MgCl_2$-$H_2O$ at 40 °C

| NaCl | $CaCl_2$ | $MgCl_2$ | $Na_2SO_4$ | $MgSO_4$ | $CaSO_4$ |
|---|---|---|---|---|---|
| $\bar{\delta} = 2.076$<br>$Z = 0.016$<br>$G = 0.001$<br>$\Delta_{Cl^-} = 0.102$ | $\bar{\delta} = 3.946$<br>$Z = 0.000$<br>$G = 13.915$ | $\bar{\delta} = 6.123$<br>$Z = 0.000$<br>$G = 0.000$ | $\bar{\delta} = 0.000$<br>$Z = 1.627$<br>$G = 20.510$ | $\tau_{(ij)^0 w} = 43.250$<br>$\tau_{w(ij)^0} = -4.806$<br>$\delta_{(ij)^0} = 5.004$<br>$K_{(ij)^0} = 0.00615$ | $\delta_{(ij)^0} = 1.125$<br>$K_{(ij)^0} = 0.00518$ |

Table IV. Calculated Activity Coefficients, $\gamma_{\pm(CaSO_4)} \times 10^3$, at 40 °C as a Function of $Na_2SO_4$ and $MgCl_2$ Molality

| $[MgCl_2]$, $m$ | $[Na_2SO_4]$, $m$ 2.0 | 1.8 | 1.6 | 1.4 | 1.2 | 1.0 | 0.8 | 0.6 | 0.4 | 0.2 | 0.0 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 27 | 30 | 32 | 35 | 39 | 45 | 53 | 65 | 85 | 131 | 446 |
| 0.2 | 51 | 53 | 55 | 58 | 62 | 68 | 75 | 86 | 104 | 134 | 167 |
| 0.4 | 60 | 63 | 65 | 68 | 72 | 78 | 86 | 97 | 114 | 134 | 147 |
| 0.6 | 73 | 75 | 78 | 81 | 86 | 93 | 101 | 113 | 127 | 142 | 149 |

$K_{sp}^0 = 2.39 \times 10^{-5}$ at 40 °C making use of the work of Gardner and Glueckauf (*23*) for the temperature dependence of $K_{sp}^0$ but retaining the value previously adopted at 25 °C (*9*) given by the same authors (*24*).

### Thermodynamic Analysis

Figure 1 shows the molal gypsum solubility vs. $Na_2SO_4$ concentration in solution where the molality of $MgCl_2$ is held constant. The four curves have been calculated by using the thermodynamic model with the parameters obtained in the previous paragraph. Our next objective is to explain the behavior of these curves as an effect of the different forces that act at molecular level and to find a relationship between solubility and some general properties of the species in the solution. Using eq 1 and 2 but with all the activity coefficients equal to 1, we also obtained four dashed curves in the same figure for the same $MgCl_2$ molalities as before. In this way it is possible to observe the common ion and associating effects independently of that related to all the physical forces acting between the different species in the solution.

The first observation is the following: the common ion effect would determine an asymptotic behavior in the gypsum solubility curve whose value is different from zero, in our case, because of the $CaSO_4^0$ ion-pair formation. The $Na_2SO_4$ molality corresponding to the asymptotic value of the solubility is a function of $MgCl_2$ in the solution as a consequence of the finite value of the dissociation constant $K_{(MgSO_4)^0}$ defined in eq 1.

However, as expected, all four dashed lines reach the asymptotic value at the same concentration ($\simeq 0.2$ $m$) of non-associated $SO_4^{2-}$. In the second place we observe that, up to the minimum, the gypsum solubility vs. $Na_2SO_4$ concentration increases with increasing $MgCl_2$ molality and that the shifting of the minima is closely related to the asymptotes of the dashed lines.

Hence, it is possible to state that, at moderately low sulfate concentration, physical and chemical forces act together in determining higher solubility values as $MgCl_2$ concentration is increased while the common ion effect coupled with chemical forces is mainly responsible for the general behavior of the solubility curves shown in Figure 1. We have a completely different situation on the right side of the diagram where at fixed $Na_2SO_4$ molality the gypsum solubility decreases as $MgCl_2$ in the solution is increased.

To understand this behavior we need consider only physical forces since the "chemical model" alone (eq 1 and 2 with all the activity coefficients equal to 1) always drops on the same asymptotic value. Table IV shows the calculated activity coefficients of calcium sulfate, $\gamma_{\pm(CaSO_4)}$. As can be seen this quantity always decreases, at constant $MgCl_2$ molality, when the $Na_2SO_4$ concentration increases, but its behavior vs. $MgCl_2$ molality at fixed $Na_2SO_4$ is more complicated depending on the proportion of the different ions in the solution.

Marshall and Yeatts (*25*) in an excellent experimental study showed the importance of the nature of the anion in determining gypsum solubility and found $NO_3^-$ more solubilizing than $Cl^-$ at the same ionic strength. We can add that the observed behavior of the activity coefficients in Table IV, and consequently that of the solubility curves in the high ionic strength region, is a result of the higher solubilizing capacity of $SO_4^{2-}$ compared to that of $Cl^-$.

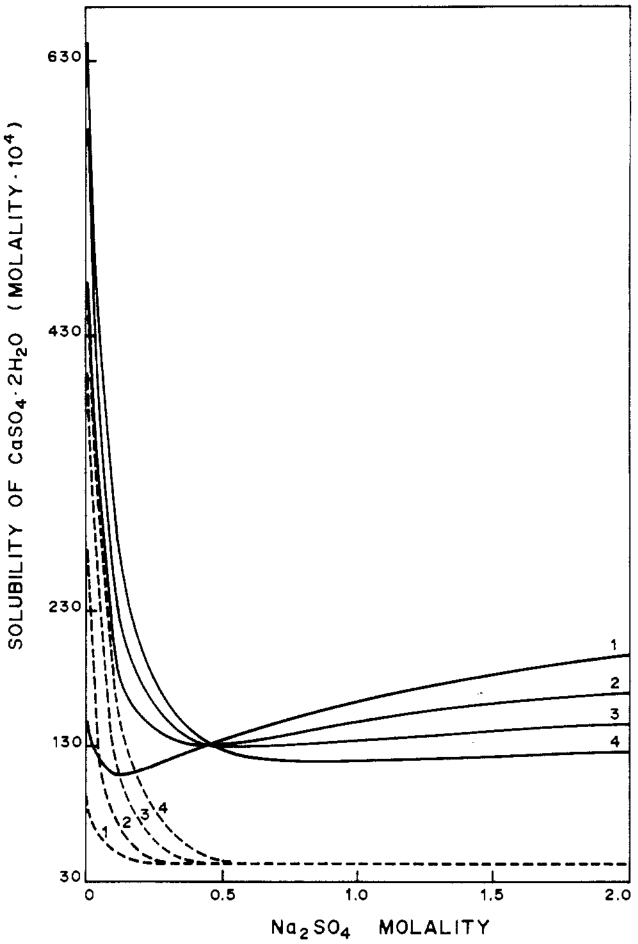

**Figure 1.** Solubility of $CaSO_4 \cdot 2H_2O$ in water solutions of $Na_2SO_4$ and $MgCl_2$ at 40 °C. Dashed lines refer to the "chemical model" alone. Each curve is characterized by a fixed $MgCl_2$ molality: (1) 0, (2) 0.2, (3) 0.4, (4) 0.6.

The above conclusion is in a full agreement with the experimental activity coefficients of sulfate and chloride in single saltwater solutions as a function of the ionic strength at 40 °C (*21*, *26*) and in accordance with the decreasing polarizability of the anions in the order $SO_4^{2-}$–$NO_3^-$–$Cl^-$.

### Conclusions

The reported experimental data on the system $CaSO_4$–$Na_2SO_4$–$MgCl_2$–$H_2O$ at 40 °C show that gypsum solubility is strongly affected by the total amount and proportion of the different salts in the solutions. A previously tested thermodynamic model containing a limited set of adjustable parameters performs satisfactorily for the above system even though we believe that it can be improved with special regard to predictive purposes and for high chloride concentration.

Chemical forces, restricted to the formation of metal earth sulfate ion pairs, appear to be mainly responsible for the special and well-known solubilizing effect of the magnesium which, as a result of this study, has been found to vanish for high sulfate concentration. In fact, under these conditions, the observable solubility of $CaSO_4 \cdot 2H_2O$ decreases with $MgCl_2$ molality at fixed sulfate concentration but increases at constant $MgCl_2$ when the sulfate is increased. We found this behavior to be related to the different polarizability of $Cl^-$ and $SO_4^{2-}$ anions.

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## Glossary

| | |
|---|---|
| $a_w$ | activity of water |
| $G$ | NRTL binary parameter defined in Table III |
| $G^E$ | total excess Gibbs energy, J |
| $K_{sp}{}^0$ | thermodynamic solubility product of $CaSO_4 \cdot 2H_2O$ |
| $K_{(ij)^0}$ | dissociation equilibrium constant for ion pair $(ij)^0$ |
| $m_i$ | true molality of species i |
| $m_{(ij)^0}$ | molality of ion pair $(ij)^0$ |
| $N$ | number of experimental determinations |
| $S_{Ca}$ | solubility of $CaSO_4 \cdot 2H_2O$, $m$ |
| $S_\gamma$, $S_{S_{Ca}}$ | sums of squares |
| $Z$ | NRTL binary parameter defined in Table III |

*Greek Letters*

| | |
|---|---|
| $\gamma_{\pm(ij)}$ | mean ionic molal activity coefficient of electrolyte (ij) |
| $\underline{\gamma}_{(ij)^0}$ | molal activity coefficient of ion pair $(ij)^0$ |
| $\delta$ | Debye–McAulay parameter defined in Table III |
| $\delta_{(ij)^0}$ | Debye–McAulay binary parameter for ion pair $(ij)^0$ |
| $\Delta_{Cl^-}$ | empirical parameter specific for chloride ions |
| $\rho$ | density |
| $\sigma_\gamma$, $\sigma_2$ | square root of estimated variances |
| $\tau_{(ij)^0}$ | NRTL binary parameter for ion pairs |

**Registry No.** $CaSO_4$, 7778-18-9; $Na_2SO_4$, 7757-82-6; $MgCl_2$, 7786-30-3; gypsum, 13397-24-5.

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# Density, Viscosity, and Electrolytic Conductivity of Concentrated Aqueous Electrolyte Solutions at Several Temperatures. Alkaline-Earth Chlorides, $LaCl_3$, $Na_2SO_4$, $NaNO_3$, NaBr, $KNO_3$, KBr, and $Cd(NO_3)_2$

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**The densities, viscosities, and electrolytic conductivities of concentrated aqueous solutions of alkaline-earth chlorides, $LaCl_3$, $Na_2SO_4$, $NaNO_3$, NaBr, $KNO_3$, KBr, and $Cd(NO_3)_2$ have been measured at temperatures from 15 to 55 °C. Temperature dependences of the above-mentioned properties are represented in terms of their thermal coefficients at 25 °C.**

## Introduction

Density, viscosity, electrolytic conductivity, and their thermal coefficients of electrolyte solutions are physicochemically important properties to understand the nature of solute–solute and solute–solvent interactions and the structural change of solvent induced by the solute. Although a number of studies on the above-mentioned properties have been found in the literature (*1*, *2*), experimental data on concentrated solutions are still lacking for the discussion of solute–solute–solvent interactions. This situation has encouraged us to make a series of systematic measurements of density, viscosity, and electrolytic conductivity of aqueous electrolyte solutions at concentrations from 0.05

Table I. Density and Viscosity of Water

| temp/ °C | density[a]/ (kg $m^{-3}$) | viscosity[b]/ (mN s $m^{-2}$) |
|---|---|---|
| 15 | 999.101 | 1.138 |
| 20 | 998.206 | 1.002 |
| 25 | 997.047 | 0.8903 |
| 30 | 995.650 | 0.7975 |
| 35 | 994.036 | 0.7194 |
| 40 | 992.219 | 0.6531 |
| 45 | 990.216 | 0.5963 |
| 50 | 988.038 | 0.5467 |
| 55 | 985.695 | 0.5044 |

[a] Reference *4*. [b] Reference *5*.