

IONIC PROCESSES IN SATURATED SOLUTIONS OF $MgCl_2 \cdot 6H_2O$ IN SOLUTIONS OF OTHER DIVALENT METALS

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Dedicated to the memory of the late Professor Antonín A. Vlček.

Solubility isotherms of $MgCl_2 \cdot 6H_2O$ at 25 °C in solutions of chlorides of bivalent beryllium, calcium, manganese, iron, cobalt, zinc and mercury were treated by the hydration analysis. In addition to the usual procedure, the recently developed modified transfer energy Ξ was used to characterize the situation in saturated solutions. As a result, the following ionic processes were established in the saturated solutions under consideration: competition for water in solutions of $MgCl_2 \cdot 6H_2O$ containing beryllium and calcium chloride, complex formation in solutions of $MgCl_2 \cdot 6H_2O$ containing manganese, cobalt, zinc and mercury ions and formation of ions with heterogeneous coordination sphere in solutions of $MgCl_2 \cdot 6H_2O$ containing iron or copper ions. In the last case, the ability of the formed ions to crystallize from solution was found to be reduced in comparison with the other cases. Activity coefficients of $MgCl_2$ were calculated along the solubility curves under consideration.

Keywords: Solubility; Aqueous solutions; Hydration analysis; Activity coefficients; Magnesium chloride hexahydrate; Divalent metal chlorides; Crystallization.

Recently¹, hydration analysis was developed to yield information about ionic processes in saturated electrolyte solutions on the basis of computational analysis of solubility isotherms. Originally, the method was tested on systems where a competition for water molecules is the main ionic process present. As the next step, the method was used to analyze systems, where complex formation occurs in saturated solutions². Simultaneously, an universal computational program for hydration analysis was developed in Microsoft Visual Basic Version 5.0 (ref.²).

For this treatment, sets of consistent solubility data of constant precision are necessary. In last years, Balarew and co-workers have performed extensive solubility studies in $MX_2 - M'X_2 - H_2O$ ($M, M' = Mg, Ca, Ba, Zn, Fe, Cu; X = Cl, Br$) systems. The aim of these studies was establishing of double

salts formed in the systems under consideration and discussing their existence and/or structure in terms of hard and soft acids and bases. In this paper, hydration analysis of selected Balarew's solubility curves as well as solubility curves of $MgCl_2 \cdot 6H_2O$ in solutions of chlorides of other divalent metals is performed and ionic processes in the saturated solutions under consideration are discussed.

To obtain the most important value used during hydration analysis in these systems, it can be written:

$$P = (w_0^B)_{\text{changed}} / (M_r)_{H_2O} (n_0^B + n_1^B + n_2^B), \quad (1)$$

where

$$(w_0^B)_{\text{changed}} = w_0^B - \left((w_{MgCl_2}^B)^{1/3} n_0^{A,Mg} / 2^{2/3} n_{MgCl_2}^A \right) \left(2n_{MgCl_2}^B + n_{MgCl_2}^A \right)^{2/3}. \quad (2)$$

Here, superscripts A and B refer to the binary and ternary saturated solutions of the subscript component respectively. The parameter P is plotted relative to one mole of the non-saturating component, *i.e.* P/x_1 .

Besides, the parameter Ξ defined recently³ as

$$\Xi = m_s RT \ln (\gamma_{\pm} / \gamma_0) \quad (3)$$

was calculated along the respective solubility curves and the behaviour of this value in individual cases is discussed. Without detailed consideration of the pertinent standard states, this quantity can be assigned the significance of the residual Gibbs energy of the transfer of m_s moles of electrolyte I from its saturated solution to a solution containing 1 kg of water and a concentration of electrolyte II such that the ternary solution formed at temperature T is exactly saturated in electrolyte I. As demonstrated in the previous article³, the dependence of this quantity on the concentration of the non-saturating electrolyte brings a more detailed information about the configuration of saturated solutions along the solubility curve.

As demonstrated elsewhere⁴, the hydration analysis parameter P is in close relation to the activity coefficient of the solute, the respective equation being

$$P = x_{\text{H}_2\text{O}} \left(1 - \frac{\gamma_0}{\gamma_{\pm}} \right). \quad (4)$$

Therefore, on the basis of the hydration analysis results, activity coefficients of MgCl_2 will be calculated in a series of systems containing other divalent metal chlorides.

CHOICE OF SYSTEMS AND VARIABLES

From Balarew's material, solubility curves for hydration analysis were chosen with respect to following criteria:

1. The set of isotherms should present a series, within which a reasonable comparison is possible.
2. The isotherms must be of sufficient technical quality, *i.e.*, the scatter of the dependence of parameter P on the concentration should be as small as possible. (Due to not having met this condition, the otherwise interesting data of Oykova⁵ on the $\text{MgCl}_2\text{-NiCl}_2\text{-H}_2\text{O}$ and $\text{MgCl}_2\text{-CoCl}_2\text{-H}_2\text{O}$ systems had to be omitted.)
3. The branch of the isotherm to be analyzed must have sufficient length ($x_l \geq 1$).
4. The solubility branch under consideration must be formed by at least four experimental points.

With regard to the above criteria, Balarew's solubilities of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in solutions of chlorides of divalent copper⁶, zinc⁶ and iron⁶ as well as solubilities of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in solutions of beryllium⁷, calcium⁸, manganese⁹, cobalt¹⁰ and mercury¹¹ chlorides measured by other authors have appeared suitable for the analysis. In all cases, the solubility studies at 25 °C were chosen.

From the values obtained by hydration analysis, the concentration dependence of the relation P/x_l and the total amount of water available per ion of salt components Aq were found as the most suitable for the description of ionic processes¹. Therefore, only these dependences have been depicted on the relevant figures in this paper. Further, the points depicting the values of the variables have not been connected by curves, as no theory exists to describe the shape of the concentration dependence of P/x_l as yet. The same applies to the values of Ξ .

RESULTS AND DISCUSSION

The results of hydration analysis of the solubility branches under consideration are depicted in Figs 1 and 2. The concentration dependence of the modified transfer energy Ξ is depicted in Fig. 3.

As may be seen in Figs 1–3, the systems studied fall into three groups:

A) A positive value of P/x_l , nearly constant over the whole range of concentration of the non-solute component with the only exception of the experimental point closest to binary saturated solution in the $\text{MgCl}_2\text{-BeCl}_2\text{-H}_2\text{O}$ system⁷. The system is eutonic.

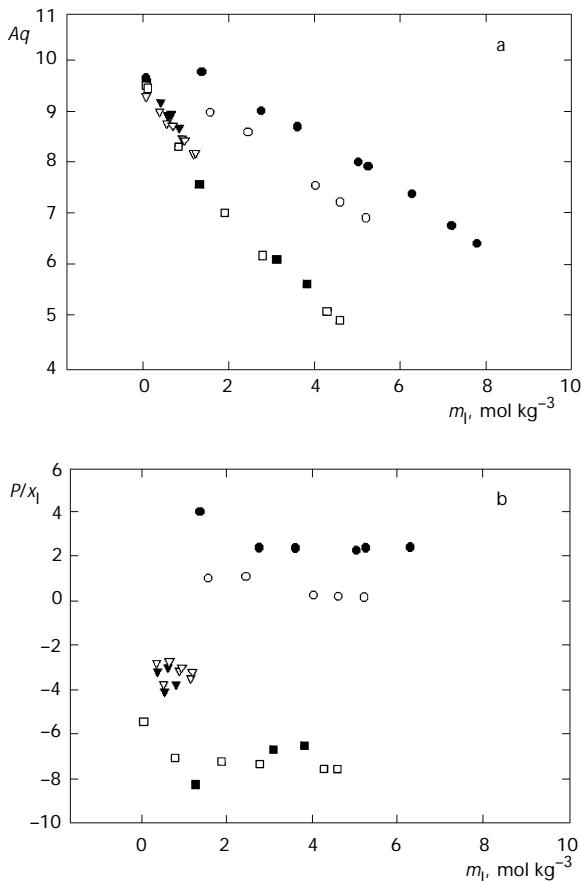


FIG. 1

Hydration analysis in the $\text{MgCl}_2\text{-M(II)Cl}_2\text{-H}_2\text{O}$ systems at 25 °C, (M(II)) = Be (●), Ca (○), Mn (▼), Co (▽), Zn (■), Hg (□): a water available, b concentration dependence of the P/x_l ratio

Positive values of P/x_{I} are found also for the solubility of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in solutions of CaCl_2 reported by Lee and Egerton⁸. Here, the P/x_{I} values seem to be constant up to *ca* 4 mol kg^{-1} of CaCl_2 , then decrease. Tachyhydrite $2\text{MgCl}_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$ was found in the neighbouring crystallization field. The concentration dependence of the Ξ value resembles that discussed³ in the system $\text{KCl}-\text{CaCl}_2-\text{H}_2\text{O}$ exhibiting a break at $m_{\text{Be}} \approx 4 \text{ mol kg}^{-1}$ and $m_{\text{c}} \approx 3 \text{ mol kg}^{-1}$.

B) A negative value, with highest probability independent of the concentration for the $\text{MgCl}_2-\text{MnCl}_2-\text{H}_2\text{O}$ (ref.⁹), $\text{MgCl}_2-\text{CoCl}_2-\text{H}_2\text{O}$ (ref.¹⁰), $\text{MgCl}_2-\text{ZnCl}_2-\text{H}_2\text{O}$ (ref.⁶) and $\text{MgCl}_2-\text{HgCl}_2-\text{H}_2\text{O}$ (ref.¹¹) systems. In these

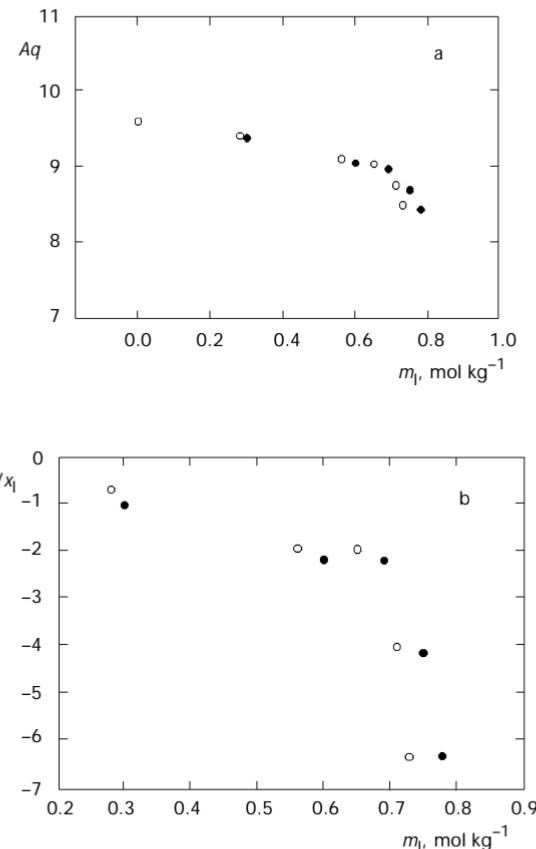


FIG. 2

Hydration analysis in the $\text{MgCl}_2-\text{M(II)Cl}_2-\text{H}_2\text{O}$ systems at 25 °C, (M(II) = Fe (●), Cu (○)): a water available, b concentration dependence of the P/x_{I} ratio

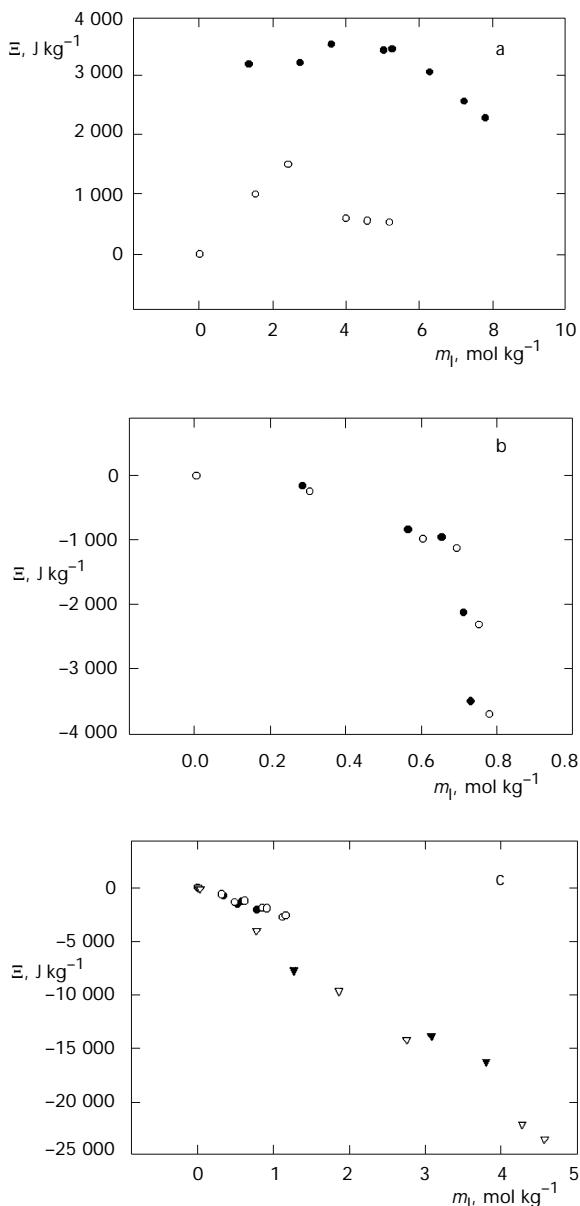


FIG. 3

Concentration dependence of the quantity Ξ in the MgCl_2 -M(II)Cl₂-H₂O systems at 25 °C: a M(II) = Be (●), Ca (○); b M(II) = Fe (○), Cu (●); c M(II) = Mn (●), Co (○), Zn (▼), Hg (▽)

systems, a compound always crystallizes in the crystallization field neighbouring to the crystallization field of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The formulae of the compounds are $2\text{MgCl}_2 \cdot \text{MnCl}_2 \cdot 12\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot \text{CoCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot \text{ZnCl}_2 \cdot 5\text{H}_2\text{O}$ and $\text{MgCl}_2 \cdot \text{HgCl}_2 \cdot 6\text{H}_2\text{O}$. The value Ξ decreases as the concentration of the non-saturated component increases reaching values around -25 kJ kg^{-1} .

C) Concentration-dependent values of P/x_l decreasing as the concentrations of the non-saturating chloride rises. This shape of the hydration analysis curves has been observed in the $\text{MgCl}_2 \cdot \text{FeCl}_2 \cdot \text{H}_2\text{O}$ (ref.⁶) and $\text{MgCl}_2 \cdot \text{CuCl}_2 \cdot \text{H}_2\text{O}$ (ref.⁶) systems. As far as the respective solubility diagrams are concerned, a very narrow crystallization field of the compound $\text{MgCl}_2 \cdot \text{FeCl}_2 \cdot 8\text{H}_2\text{O}$ was found in the FeCl_2 system. The system containing copper chloride is eutonic. The Ξ value decreases as the concentration of the non-saturated component increases exhibiting a break at the concentration of the non-saturating component around 0.7 mol kg^{-1} . When the concentration of the non-saturating component exceeds this value, the decrease in the modified transfer energy Ξ becomes substantially more intensive.

Based on these results, following statements may be formulated about the ionic processes in the above systems:

Addition of BeCl_2 to saturated solution of MgCl_2 is characterized by hydration of Be^{2+} ions due to water molecules both free and those forming originally the ionic sphere of magnesium and/or chloride ions originally. During such processes, positive values of P/x_l can be expected.

The behaviour observed on the crystallization branch of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ in solutions of CaCl_2 can be described as similar hydration of added ions, for which the amount of water molecules available is no longer sufficient at ca 4 mole % of Ca^{2+} . It looks like the Ca^{2+} ions were not able to strip the water molecules from the entities existing in $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution and therefore the Ca^{2+} ions use only bulk water for its hydration. These statements may be related even to the crystal structure of $2\text{MgCl}_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O}$, which has been established by two groups of authors^{12,13}. In this structure, the $[\text{Mg}(\text{H}_2\text{O})_6]$ octahedra are connected by a network of hydrogen bonds to chlorides. The distances O-Cl range from 312.0 to 360.7 pm. Each calcium ion is then situated in the center of an octahedron formed by chloride ions, the distance Ca-Cl being 275.1 pm.

As shown in ref.², negative values of P/x_l characterize complexing as the main ionic process taking place in the saturated solution. In agreement with that, complexing occurs when MnCl_2 is added to a saturated solution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. Balarew's formulation of the respective double salt is

$[\text{Mg}(\text{H}_2\text{O})_6]_2[\text{MnCl}_6]$ as well. Analogously, some form of chlorozincate ions (most probably $[\text{ZnCl}_4]^{2-}$) can be expected in both $\text{MgCl}_2 \cdot \text{ZnCl}_2 \cdot 5\text{H}_2\text{O}$ and its saturated solutions. In the case of cobalt, chloro ions like $[\text{CoCl}_4]^{2-}$ were observed by Balarew's group¹⁴ in its saturated solutions with the use of spectral methods and the blue colour of the double salt $\text{MgCl}_2 \cdot \text{CoCl}_2 \cdot 8\text{H}_2\text{O}$ was mentioned also by Basset *et al.*¹⁰. It seems that chlorocobaltate(II) ions are substantial in saturated solutions containing divalent magnesium and cobalt in spite of the Balarew's idea of heterogeneous coordination sphere of cobalt in crystalline salt¹⁴.

Heterogeneous coordination sphere and the most complicated sum of processes is involved in the case of the systems where $\text{M(II)} = \text{Cu}$ and Fe . The values of P/x_1 fall as the M(II) concentration increases. Such behaviour may be explained as follows: At low concentrations, the M(II) ions bond some water molecules, both free and those originally belonging to chloride ions, which are involved in the complex dichlorotetraquaanions now. This process goes in the opposite direction to liberating water molecules by complex formation and higher values of P/x_1 are observed. At higher concentrations of the added component, the total amount of available water molecules decreases, the amount of water molecules liberated from the influence of chloride is higher than that entering the newly formed anions and the P/x_1 ratio becomes more negative. This is in full agreement with Balarew's suggestion of the structure formula of the anions in solid double salts formed in the $\text{MgCl}_2 \cdot \text{MCl}_2 \cdot \text{H}_2\text{O}$ ($\text{M} = \text{Co, Fe}$) systems such as $[\text{M}(\text{H}_2\text{O})_2\text{Cl}_4]^{2-}$. Therefore, in contrast to $\text{M(II)} = \text{Co}$, some analogous complex anions can be also expected in saturated solutions of both systems under consideration. The crystallization of the respective double salt does not seem to be energetically favourable. Therefore, in the case of iron, the compound crystallizes in a narrow crystallization field only and the $\text{MgCl}_2 \cdot \text{CuCl}_2 \cdot \text{H}_2\text{O}$ system is eutonic. Support for this statement can be taken from the concentrational dependence of the Ξ values, which is depicted in Fig. 3. With highest probability, the ternary saturated solution containing more than 0.67 mole $\text{M(II)}\text{Cl}_2$ per 1 000 g H_2O adopts a structure principally different from that of saturated solutions of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, as can be seen from the concentrational dependence of the Ξ (ref.²). Relative stability of the ternary solution formed may explain difficult crystallization of new solid phases.

In Table I, mean activity coefficients of MgCl_2 in its saturated solutions in other divalent metal chloride solutions are given. As the value of mean activity coefficient of MgCl_2 in the solution saturated with $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at 25 °C, the value 32.68 reported by Rard and Miller¹⁵ was taken.

TABLE I
Activity coefficients of $MgCl_2$ in solutions containing chlorides of divalent metals

| beryllium | | | | calcium | | | | copper | | | | manganese | | | |
|-----------|-------------------|----------------|----------|-------------------|----------------|----------|-------------------|----------------|----------|-------------------|----------------|-----------|-------------------|----------------|--|
| m_{Be} | γ/γ_0 | γ_{\pm} | m_{Ca} | γ/γ_0 | γ_{\pm} | m_{Cu} | γ/γ_0 | γ_{\pm} | m_{Mn} | γ/γ_0 | γ_{\pm} | m_{Hg} | γ/γ_0 | γ_{\pm} | |
| 0.00 | 1.00 | 32.68 | 0.00 | 1.00 | 32.68 | 0.00 | 1.00 | 32.68 | 0.00 | 1.00 | 32.68 | 0.00 | 1.00 | 32.68 | |
| 1.30 | 1.10 | 36.06 | 1.50 | 1.03 | 33.64 | 1.50 | 1.00 | 32.56 | 0.34 | 0.98 | 32.06 | 0.52 | 0.96 | 31.48 | |
| 2.70 | 1.14 | 37.10 | 2.39 | 1.05 | 34.36 | 2.39 | 0.98 | 32.05 | 0.52 | 0.96 | 31.48 | 0.78 | 0.95 | 31.07 | |
| 3.54 | 1.18 | 38.72 | 3.98 | 1.02 | 33.49 | 3.98 | 0.98 | 31.95 | 0.59 | 0.97 | 31.68 | 0.78 | 0.95 | 31.07 | |
| 4.97 | 1.27 | 41.60 | 4.56 | 1.03 | 33.51 | 4.56 | 0.95 | 31.09 | 0.78 | 0.95 | 30.16 | 0.92 | 0.95 | 30.16 | |
| 5.20 | 1.30 | 42.61 | 5.17 | 1.03 | 33.55 | 5.17 | 0.92 | 30.16 | 0.92 | 0.95 | 30.16 | 0.92 | 0.95 | 30.16 | |
| 6.23 | 1.40 | 45.70 | 7.17 | 1.44 | 47.05 | 7.17 | 1.44 | 47.05 | 0.92 | 0.95 | 30.16 | 0.92 | 0.95 | 30.16 | |
| 7.76 | 1.46 | 47.58 | 7.76 | 1.46 | 47.58 | 7.76 | 1.46 | 47.58 | 0.92 | 0.95 | 30.16 | 0.92 | 0.95 | 30.16 | |
| iron | | | | cobalt | | | | zinc | | | | mercury | | | |
| m_{Fe} | γ/γ_0 | γ_{\pm} | m_{Co} | γ/γ_0 | γ_{\pm} | m_{Zn} | γ/γ_0 | γ_{\pm} | m_{Hg} | γ/γ_0 | γ_{\pm} | m_{Hg} | γ/γ_0 | γ_{\pm} | |
| 0.00 | 1.00 | 32.68 | 0.00 | 1.00 | 32.68 | 0.00 | 1.00 | 32.68 | 0.00 | 1.00 | 32.68 | 0.00 | 1.00 | 32.68 | |
| 0.30 | 0.99 | 32.50 | 0.32 | 0.98 | 32.18 | 1.26 | 0.84 | 27.54 | 0.03 | 1.00 | 32.58 | 0.73 | 0.91 | 29.80 | |
| 0.60 | 0.98 | 31.93 | 0.49 | 0.97 | 31.64 | 3.08 | 0.73 | 23.96 | 0.77 | 0.91 | 29.80 | 0.70 | 0.91 | 29.80 | |
| 0.69 | 0.97 | 31.82 | 0.62 | 0.97 | 31.72 | 3.80 | 0.70 | 22.73 | 1.86 | 0.81 | 26.38 | 2.75 | 0.74 | 24.05 | |
| 0.75 | 0.95 | 30.94 | 0.85 | 0.96 | 31.21 | 0.95 | 31.18 | 0.95 | 4.27 | 0.64 | 20.79 | 4.57 | 0.62 | 20.79 | |
| 0.78 | 0.92 | 30.02 | 0.91 | 0.95 | 31.18 | 1.12 | 0.94 | 30.56 | 1.16 | 0.94 | 30.68 | 1.16 | 0.94 | 30.68 | |

SYMBOLS

| | |
|----------------|--|
| Aq | number of moles of water being at the disposal per ion in saturated solutions |
| $(M_i)_{H_2O}$ | relative molecular weight of water |
| m_i | molality of the saturating component |
| $n_i^{A,B}$ | number of moles of i -th component in 100 g of solution specified by the superscript |
| P | parameter of the hydration analysis (mole fraction of water with altered properties) |
| R | universal gas constant |
| T | temperature |
| $w_i^{A,B}$ | mass % of i -th component in the solution specified by the superscript |
| x_i | mole % of the unsaturating component in ternary solutions |
| x_{H_2O} | mole % of water in ternary solutions |
| γ_z | mean activity coefficient of the solute in ternary solutions |
| γ_0 | mean activity coefficient of the solute in its binary saturated solution |
| Ξ | modified Gibbs energy of transfer |

Subscripts

| | |
|---|---|
| 0 | water |
| 1 | saturating component ($MgCl_2 \cdot 6H_2O$) |
| 2 | non-saturating component |

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