

## **SOLUBILITY AND PITZER'S IONIC PARAMETERS IN THE SYSTEM $H_2O$ - $NaCl$ - $MgCl_2$**

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### **Abstract**

*The object of this work was to determine Pitzer's ionic parameters,  $\theta$  and  $\psi$ , for the mixed salt solution  $H_2O$ - $NaCl$ - $MgCl_2$  at following temperatures: 273.15, 298.15, 356.15 and 378.15 K in ionic strength interval from 7 to 17.5 mol/kg, using Pitzer-Kim's ionic method. The Pitzer's ionic interaction parameters at all temperatures were evaluated on the bases of solubility data for the system  $H_2O$ - $NaCl$ - $MgCl_2$ , and criterion of diffusion equilibrium. The mean ionic activity coefficient of the  $NaCl$  in heterogeneous system, in which  $NaCl(c)$  was in equilibrium with saturated mixed solution  $H_2O$ - $NaCl$ - $MgCl_2$ , was obtained using solubility data and criterion of diffusion equilibrium. Temperature dependence of the obtained Pitzer's ionic interaction parameters  $\theta$  and  $\psi$ , in temperature range from 273.15 to 378.15 K, were described by the polynom of the forth and second order, respectively.*

*Keywords:* solubility, pitzer's ionic parameters,  $H_2O$ - $NaCl$ - $MgCl_2$  system

### **1. Introduction**

The thermodynamic properties of aqueous electrolyte solutions are of crucial importance in many areas like water desalination, absorption heat pumps, property packages useful in general process simulators, sewage treatment and hydrometallurgical processes. Furthermore, activity and osmotic coefficients of aqueous electrolyte solutions are required for a variety of applications including calculation of Gibbs energies of dilution

and solution, calculation of vapor pressures of water above solutions, and calculation of the e.m.f.s of reversible cells. In addition calculation of thermodynamic diffusion coefficients requires chemical potential derivatives[1, 2].

While aqueous electrolytes have been very extensively studied at room temperature, much less attention has been given to these systems at higher temperatures. This work represents the contribution to this field of investigation.

## 2. Treatment of results and discussion

Criterion of the diffusion equilibrium for the heterogeneous system in which NaCl is in equilibrium with saturated mixed solution H<sub>2</sub>O-NaCl-MgCl<sub>2</sub> is:

$$(\mu_{\text{NaCl(c)}} - \mu_{\text{NaCl}}^{\square})/T = R \ln \left[ \gamma_{\pm \text{NaCl}}^2 m_{\text{NaCl}} (m_{\text{NaCl}} + 2m_{\text{MgCl}_2}) \right]_{\text{sat}}$$

where  $\mu_{\text{NaCl(c)}}$  and  $\mu_{\text{NaCl}}$  present the values of the chemical potential of a NaCl in a crystal state, and chemical potential of the NaCl in ideal, hypothetical solution at  $m = 1$  mol/kg. At the temperature 298.15 K,  $\mu_{\text{NaCl(c)}} = -384.212$  kJ/mol and  $\mu_{\text{NaCl}} = -393.229$  kJ/mol<sup>[3]</sup>. Using the solubility data for the system H<sub>2</sub>O-NaCl-MgCl<sub>2</sub> at temperature 298.15 K and data for the  $\mu_{\text{NaCl(c)}}$  and  $\mu_{\text{NaCl}}$ , the mean ionic activity coefficient of NaCl was calculated.

To obtain the activity coefficients of NaCl in saturated mixed solution H<sub>2</sub>O-NaCl-MgCl<sub>2</sub> at higher temperatures it is necessary to know the temperature dependence of the difference  $[(\mu_{\text{NaCl(c)}} - \mu_{\text{NaCl}})/T]$  which is:

$$\frac{\partial [(\mu_{\text{NaCl(c)}} - \mu_{\text{NaCl}}^{\square})/T]}{\partial T} = \frac{\Delta_{\text{dil}} H^{\infty}}{T^2}$$

where  $\Delta_{\text{dil}} H^{\infty}$  is enthalpy of solution per mole of salt at infinite dilution. From the above equation it is obvious that:

$$\left[ (\mu_{\text{NaCl(c)}} - \mu_{\text{NaCl}}^{\square})/T \right] - \left[ (\mu_{\text{NaCl(c)}} - \mu_{\text{NaCl}}^{\square})/T_r \right] = \int_{T_r}^T \frac{\Delta_{\text{dil}} H^{\infty}}{T^2} dT$$

where  $T_r$  is a referent temperature, which in this case is 298.15 K.

From the common type of enthalpy measurements the temperature dependence of the enthalpy of solution per mol of salt at infinite dilution, is described by<sup>[4]</sup>:

$$\Delta_{\text{dil}}H^\infty = 174\,000.47 - 1321.73T + 3.5623T^2 - (3.4994 \cdot 10^{-3})T^3 \quad (\text{J/mol})$$

Values for the activity coefficient of NaCl in saturated mixed solution calculated from the previous equations, at temperature 298.15 K and at other temperatures, have been taken as experimental activity coefficient of NaCl  $\gamma_{\pm\text{NaCl,sat}}$ , and are given in Table 1.

Table 1. Molalities of NaCl and MgCl<sub>2</sub>,  $m_{\text{NaCl}}$  and  $m_{\text{MgCl}_2}$  respectively, in saturated mixed solution H<sub>2</sub>O-NaCl-MgCl<sub>2</sub>, together with mean ionic activity coefficient of NaCl  $\gamma_{\pm\text{NaCl,sat}}$  at different temperatures.

$m_{\text{NaCl}}$ (mol/kg)	$m_{\text{MgCl}_2}$ (mol/kg)	$\gamma_{\pm\text{NaCl,sat}}$
$T=273.15 \text{ K}$		
0.355	4.167	3.1780
1.422	2.728	1.7850
2.222	2.111	1.4750
4.111	1.050	1.1040
$T=298.15 \text{ K}$		
0.285	4.940	3.6243
0.983	3.581	2.1801
1.816	2.686	1.7074
3.827	1.290	1.2457
4.567	0.885	1.1466
6.202	0.117	1.0242
0.351	4.782	3.3067
0.956	3.553	2.2220
3.787	1.374	1.2399
4.080	1.130	1.2128
0.333	5.277	3.2398
0.456	4.400	3.0026
1.000	3.250	2.2525
1.611	2.689	1.8381
2.166	2.255	1.6222
3.289	1.483	1.3600
4.444	0.889	1.1731

T=328.15 K		
0.257	5.607	3.7455
0.417	4.784	3.1516
1.040	4.363	2.0179
1.199	3.467	2.0594
2.512	2.323	1.5166
4.273	1.186	1.2069
4.500	1.050	1.1800
T=356.15 K		
0.196	5.687	4.1894
0.583	4.843	2.5784
1.872	3.382	1.5690
3.074	2.248	1.3078
4.985	1.151	1.0467
T=378.15 K		
2.250	3.500	1.326
2.900	3.000	1.198
3.500	2.500	1.109
4.350	1.900	1.016
4.750	1.500	0.997
5.400	1.000	0.957

According to Pitzer-Kim's formalism[1], activity coefficient of NaCl  $\gamma_{MX}$ , in mixed salt solution  $H_2O$ -NaCl-MgCl<sub>2</sub> can be expressed in following way:

$$\ln \gamma_{MX} = |z_M z_X| f^\gamma + \frac{2v_M}{v_{MX}} \left\{ m_X [B_{MX} + (\sum m z) C_{MX}] \right\} + \frac{2v_X}{v_{MX}} \left\{ m_M [B_{MX} + (\sum m z) C_{MX}] \right\} +$$

$$m_N \left[ B_{NX} + (\sum m z) C_{NX} + \frac{v_M}{v_X} \theta_{MN} \right] + m_M m_X \left\{ |z_M z_X| B'_{MX} + \frac{1}{v_{MX}} [2v_M z_M C_{MX}] \right\} +$$

$$m_N m_X \left\{ |z_M z_X| B'_{NX} + \frac{1}{v_{MX}} [2v_M z_M C_{NX} + v_M \psi_{MNX}] \right\} + m_M m_N \left\{ \frac{v_X}{v_{MX}} \psi_{MNX} + |z_M z_X| \theta'_{MN} \right\}$$

$$\sum m z = m_X \cdot z_X = m_M \cdot z_M + m_N \cdot z_N.$$

where MX, M, N and X denotes NaCl, Na<sup>+</sup>, Mg<sup>2+</sup> and Cl<sup>-</sup>, respectively;  $m$  present the molality of the appropriate ionic species in mol/kg,  $z$  are

charges of the appropriate ionic species. The parameter  $\theta$  arises from differences in the short range interaction between like and unlike pairs of ions of the same sign. Similarly, parameter  $\psi$  arises from triple interactions.

The quantities  $f^\gamma$ ,  $B$ ,  $C$  and  $B'$  were calculated from appropriate equations, given below:

$$f^\gamma = -A_\phi \left[ \frac{I^{1/2}}{1+bI^{1/2}} + \frac{2}{b} \ln(1+bI^{1/2}) \right]$$

$$B = \beta^{(0)} + (2\beta^{(1)} / \alpha^2 I) \left[ 1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2}) \right]$$

$$B' = (2\beta^{(1)} / \alpha^2 I^2) \left[ -1 + (1 + \alpha I^{1/2} + (1/2)\alpha^2 I) \exp(-\alpha I^{1/2}) \right]$$

$$C = C^\phi / 2 |z_M z_X|^{1/2}$$

where:

- $I$  is the ionic strength of the mixed solution in mol/kg, defined as  $I = m_{MX} + 3m_{NX}$ ,
- parameter  $A_\phi$  is the Debye-Huckel coefficient for the osmotic function characteristic of the solvent,
- $\beta^{(0)}$  and  $\beta^{(1)}$  are parameters characteristic for each substance defining the second virial coefficient,
- $C^\phi$  is the third virial coefficient specific for each substance,
- $b$  and  $\alpha$  are constants.

By the known transformation of equation for the activity coefficient into a linear form and by neglecting the dependence of the  $\theta$  parameter from the ionic strength of the solution  $\theta'$ , the interaction parameters  $\theta$  and  $\psi$  were determined as the intercept and slope.

Parameters for the NaCl (aq) and MgCl<sub>2</sub> (aq) at temperatures other than 298,15 K are calculated from the temperature dependence equations. For the NaCl(aq) [4]:

$$\beta^{(0)} = 0.0765 - 777.03 \left( \frac{1}{T} - \frac{1}{T_r} \right) - 4.470 \ln \left( \frac{T}{T_r} \right) + 0.008946 (T - T_r) - 3.3158 \cdot 10^{-6} (T^2 - T_r^2)$$

$$\beta^{(1)} = 0.2664 + 6.1608 \cdot 10^{-5} (T - T_r) + 1.0715 \cdot 10^{-6} (T^2 - T_r^2)$$

$$C^\circ = 0.00127 + 33.317 \left( \frac{1}{T} - \frac{1}{T_r} \right) + 0.09421 \ln \left( \frac{T}{T_r} \right) - 4.655 \cdot 10^{-5} (T - T_r)$$

where  $T_r$  is referent temperature, 298.15 K. For the  $\text{MgCl}_2(\text{aq})$ :

$$\beta^{(0)} = 0.576066 - 9.31654 \cdot 10^{-4} T + 5.93915 \cdot 10^{-7} T^2$$

$$\beta^{(1)} = 2.60135 - 1.09438 \cdot 10^{-2} T + 2.60169 \cdot 10^{-5} T^2$$

$$C^\circ = 6.57867 \cdot 10^{-2} - 2.89125 \cdot 10^{-4} T + 3.01823 \cdot 10^{-7} T^2$$

In Table 2 are given the calculated Pitzer's parameters for the  $\text{NaCl}(\text{aq})$  at different temperatures.

Table 2. Pitzer's parameters for the  $\text{NaCl}(\text{aq})$  at different temperatures.

Temperature (K)	$A_\phi$	$\beta^{(0)}$	$\beta^{(1)}$	$C^\circ$	$b$	$\alpha$
273.15	0.3770	0.05319	0.2496	0.004411	1.2	2
298.15	0.3920	0.0765	0.2664	0.00127	1.2	2
328.15	0.4142	0.09223	0.2884	-0.00131	1.2	2
356.15	0.4380	0.09928	0.3106	-0.002882	1.2	2
378.15	0.4669	0.1015	0.3293	-0.003701	1.2	2

In Table 3 are given the calculated Pitzer's parameters for the  $\text{MgCl}_2(\text{aq})$  at different temperatures.

Table 3. Pitzer's parameters for the  $\text{MgCl}_2(\text{aq})$  at different temperatures\*.

Temperature (K)	$\beta^{(0)}$	$\beta^{(1)}$	$C^\circ$
273.15	0.36619	1.58319	0.00941
298.15	0.35109	1.6512	0.00641
328.15	0.33421	1.8110	0.00341
356.15	0.31957	2.0043	0.00101
378.15	0.30860	2.1836	-0.00041

\*Parameters  $A_\phi$ ,  $b$  and  $\alpha$  are the same as for  $\text{NaCl}(\text{aq})$  at each temperature (Table 2.)

Treatment of the solubility data give following parameters for the Pitzer-Kim's equation at different temperatures, given in Table 4.

Table 4. Pitzer's ionic interaction parameters  $\theta$  and  $\psi$  for the system  $H_2O$ - $NaCl$ - $MgCl_2$  at different temperatures.

Temperature (K)	$\theta$	$\psi$	Ionic interval (mol/kg)
273.15	0.1496	-0.0140	7.0-13.0
298.15	0.1758	-0.0443	7.0-15.5
328.15	0.1647	-0.0513	7.0-17.5
356.15	0.1453	-0.0363	8.0-17.5
378.15	0.1218	-0.0380	8.0-13.0

The temperature dependence of  $\theta$  parameter can be described by the polinom of the forth order in the form:

$$\theta = -33.27865 + 0.39695(1/T) - 0.001763 \ln T + 3.4777 \cdot 10^{-6} T - 2.575 \cdot 10^{-9} T^2$$

with the standard deviation of the fit 0.003.

This temperature dependance is illustrated at Fig .1.

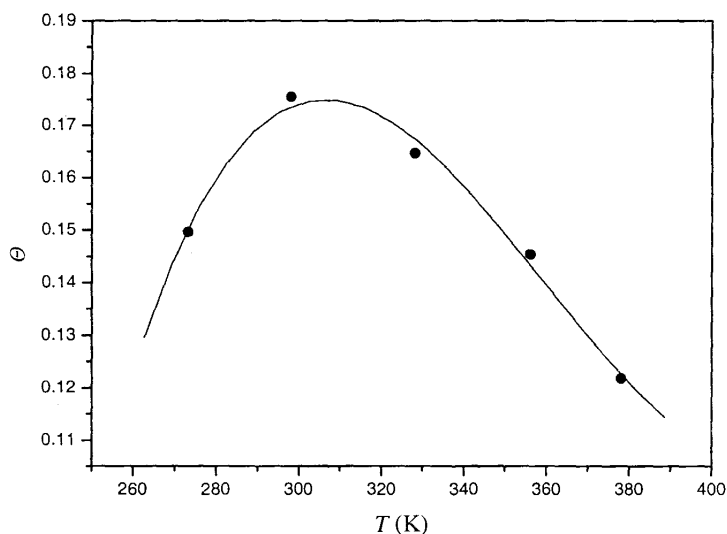


Fig. 1. Temperature dependance of the parameter  $\theta$  for the system  $H_2O$ - $NaCl$ - $MgCl_2$

Parameter  $\psi$  and its temperature dependence, following the polinom of second order, is given by:

$$\psi = 0.252107 - 1.886 \cdot 10^{-3} (1/T) + 2.975 \cdot 10^{-6} \ln T$$

with the standard deviation of the fit 0.006. This temperature dependence is illustrated at Fig.2.

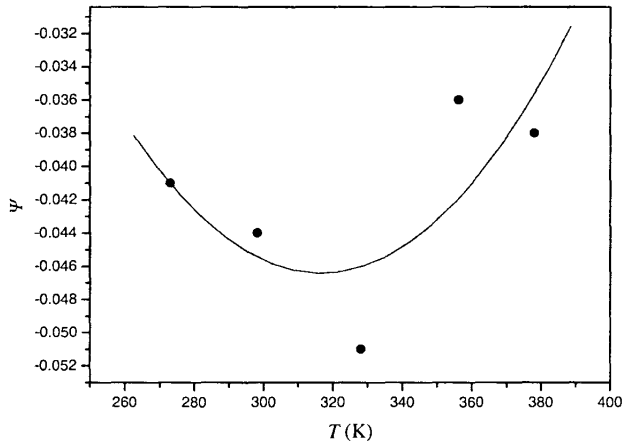


Fig. 2. Temperature dependance of the parameter  $\psi$  for the system  $H_2O-NaCl-MgCl_2$

It should be mentioned that parameter  $\psi$  is usually so small, that can be neglected in calculations of thermodynamic properties.

### 3. Conclusion

Pitzer's ionic interaction parameters for the system  $H_2O-NaCl-MgCl_2$  at temperatures: 273.15; 298.15; 328.15; 356.15 and 378.15 K, in ionic strength interval from 7 to 17.5 mol/kg, were determined together with the temperature dependence of these parameters. It was found that the temperature dependence of the parameter  $\theta$ , in the temperature interval from 273.15 to 378.15 can be described by the polinom of the forth order, while the temperature dependence of the parameter  $\psi$ , in the same temperature interval, by the polinom of the second order.



## References

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