A COMPARATIVE STUDY OF THERMODYNAMIC ELECTROLYTE MODELS APPLIED TO THE SOLVAY SODA SYSTEM

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Fast development of computation techniques for electrolyte activities contributed recently to introduction of a few substantial programmes for thermodynamic computing of multiphase systems. The presented study comprises useful information for practical computing using selected thermodynamic models of aqueous electrolyte solutions. Those models enable quantitative description of both phase and ionic equilibria and provide values of activity coefficients. The carried out analysis of individual models involved a comparison of their practical effectiveness features along with problems encountered in evaluation of the coefficients. The authors conclude that for the Solvay soda system the exUNIQUAC model for an in-house code or the MSE model for a commercial one can be used.

Keywords: thermodynamic models, electrolytes, activity coefficients, soda system

1. INTRODUCTION

The subject literature offers several models dedicated to mathematical description of electrolyte solutions, starting from fundamental models to multiparameter ones. These models can be classified as those using the excess Gibbs energy and equations of state based on the Helmholtz energy (Liu and Watanasiri, 1999), fundamental and engineering models (Loehe and Donohue, 1997), empirical and molecular models (Renon, 1986), and models dependent on the dissociation degree (Anderko et al., 2002). In particular, to the fundamental models belong those based on integral equations, perturbation theories and on fluctuation solution theories. The physical models, models of local composition and of solvation belong to the engineering ones (Prausnitz et al., 1999).

Development of methods for calculation of electrolyte activity coefficients was initiated by the theory of electrolytic dissociation developed by Arrhenius (1887), who introduced the concept of negative and positive particles and the technique of deriving the dissociation degree. Debye and Hückel (1923) published their concept and definition of features characteristic for strong and weak electrolytes. Basic elements of their approach are applied in almost all known thermodynamic models of electrolytes. Bromley (1973) introduced a model, which was used for the first time to electrolytes of relatively high ionic strength. The model consists of two constituents responsible for inter-ionic forces at short and long distances. The Bromley-Zemaitis model, called also Aqueous (AQ), was enhanced by introducing additional coefficients, which resulted in its application to solutions of ionic strength up to 30 mol/kg. At more or less the same time, Pitzer (1973) developed a complex virial model with numerous parameters, which accounts for interactions between all particles present in electrolyte.

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A fast development of techniques used for computing values of thermodynamic activities of electrolyte components took place in the last decade. Semi-empirical thermodynamic models for electrolyte solutions are based on the concept of local composition. They were developed from models for non-electrolytes. UNIQUAC by Abrams and Prausnitz (1975), NRTL of Renon and Prausnitz (1968) and also the model of Wilson (1964) provide typical examples.

Sander (1984) extended validity of equations of the model called universal quasi–chemical (UNIQUAC) model on electrolyte solutions. The expanded model was applied to equilibrium conditions of vapour-liquid and liquid-solid systems. Thomsen et al. (1999) presented details of the extended UNIQUAC (exUNIQUAC) model based on the previous model of Sander et al. (1986). The exUNIQUAC model is composed of three parts. It uses parameters of pure components to describe thermodynamics of mixtures of broadly varying molecule sizes (Walas, 1985). Other authors also proposed models stemmed from the basic model of Sander et al. (1986). For instance, Haghtalab i Makhtarani (2001) developed the UNIQUAC–NRF model for polymer solutions and Balaban et al. (2002) incorporated the Pitzer-Debye-Hückel expression in the UNIQUAC model and accounted for hydration and solvation. The newest modification of UNIQUAC is the Mixed–Solvent Electrolyte (MSE) model introduced by Wang et al. (2002). The model includes elements of the exUNIQUAC model with the virial approach used in the Pitzer model.

Two general types of thermodynamic models were used in the methods just outlined. They are based either on empirical extensions of the initial Debye–Hückel model (e.g. the Pitzer and Aqueous models) or on the local composition concept which accounts for the Debye–Hückel model and its modifications (exUNIQUAC, MSE). A comparison of basic features of the two model types has been the main aim of the presented study.

The system of $NaCl - NH_3 - CO_2 - H_2O$ used in the Solvay soda technology was selected for the evaluation. However, no results for the application of the MSE model to the full soda system were found in the literature. Lin et al. (2010) compared results for solubility of NaCl in H_2O as computed from the el-NRTL, MSE and exUNIQUAC models.

Concise information on model accuracy obtained from 21 published papers is listed in Table A in Appendix for full and partial soda systems. Wide ranges of experimental conditions along with the prediction accuracy for different models are also depicted in the table. Molality [mol/kg_{H2O}] in two-component systems of Table A ranged from 0.002 to 14.5 for CO_2, from 0.3 to 80 for NH_3 and from 1.0 to 7.0 for NaCl. However, molality of salts in three-component systems varied from 0.2 to 7.2 mol/kg_{H2O}, and of NH_3 from 0.5 to 21.2 mol/kg_{H2O}. On the other hand, molality in $CO_2 - NH_3 - H_2O$ ranged from 0.1 up to 40 mol/kg_{H2O}, from 0.3 to 14 mol/kg_{H2O} for NH_3 and CO_2, respectively. Kurz et al. (1996) presented both experimental data and those derived from the Pitzer model for the $NaCl - CO_2 - NH_3 - H_2O$ system at 4 temperature levels in the range 313–393K, pressure from 0.02 to 3MPa and the following concentrations: 4.0 mol/kg_{H2O} of NaCl, 0.3–4.1 mol/kg_{H2O} of CO_2 and 1.6–4.1 mol/kg_{H2O} of NH_3.

In the case of two-component systems, the average deviation of modelling results from experimental ones ranged from 0.5% for NH_3 and the Pitzer model up to until 7% for CO_2 and the Duan model (Duan and Sun, 2003). For three-component systems with salt, however, the deviation extent was from 1.2% for the Pitzer model up to 15% for the Duan model. In three component system of $CO_2 - NH_3 - H_2O$ the model results differed from the experimental ones by 5.6–15% for the Pitzer model, by 3.5–7.8% for UNIQUAC–NRF, by 8.9% for exUNIQUAC as proposed by Sander (1984) or by 4.6% as reported by Thomsen et al. (1996). The relative error of the Duan model for $NaCl - CO_2 - H_2O$ occupied the range of 8 – 15%. For all the three systems, i.e. two-, three- and four-component, the total range of deviations was 0.5 - 15%, 3.6 - 11%, 7 - 15% and 3.5 - 7.8% for the Pitzer, exUNIQUAC, Duan and UNIQUAC-NRF, respectively.

Computing conditions of thermodynamic equilibrium requires a database with model constants for activity coefficients. Model complexity depends on the required number of model parameters and has some impact on the model's accuracy. Four different thermodynamic models are evaluated in this study from the point of view of both the required number of parameters and accuracy of modelling results. The possibility of applying available commercial programmes for computing activity coefficients was also taken into account following the conclusion of Jaworski et al. (2010). One such code was used in this study. A comparison of computing results for equilibrium conditions using different models and programmes was carried out to assess suitability of the models for the complete and partial soda system.

2. THERMODYNAMIC MODELS OF ELECTROLYTE SOLUTIONS

The concept of chemical potential, μ, is usually employed for analysis of thermodynamic properties of solutions. A real solution of components with concentration, x_i, fulfils only roughly relationships for ideal mixtures in all phases. Departure from the ideal state of real mixtures is usually accounted for by an activity coefficient, γ_i, for the i-th component. The coefficient is also applied to ions present in electrolyte solutions. Mathematical relationship describing the chemical potential of component "*i*" in a real solution takes then the following form:

$$\mu_i = \mu_i^o(T,p) + RTln\gamma_i x_i \tag{1}$$

The potential for a real solution differs from that for an ideal mixture by a quantity, μ_i^E, which is called the excess potential.

$$\mu_i^E = RTln\gamma_i \tag{2}$$

Individual activity coefficients characterise respective Gibbs excess free energies and allow for strict quantitative description of the empirically derived excess of free energy by means of a mathematical model.

Significant features of four representative models for determining activity coefficients of solution components are presented in the following. Perhaps historically the first models proposed by Debye and Hückel and Bromley have considerable limitations due to their applicability only to solutions of low ionic strength and therefore are of little practical use. Important progress was also achieved in the model by Pitzer (1973). Two other models are also outlined, i.e. exUNIQUAC and MSE, which include standardised parameters. Calculation of values of activity coefficients involves gathering literature data and solving complex sets of mathematic equations.

2.1. Models of Debye –Hückel, Bromley, Bromley-Zemaitis (Aqueous)

The model of Debye – Hückel was developed for diluted strong electrolytes. However, due to its assumption of incomplete dissociation it can be applied also to weak electrolytes, up to 0.1 mol/kg of ionic strength. The model assumes that only electrostatic forces act between ions and that every ion is surrounded by other ions of the total charge equal to that of the central ion. The general equation (Zemaitis et al., 1986) for average activity coefficient of ions originated from dissociated salt reads:

$$\log\gamma_{\mp} = -\frac{A|z_+ z_-|\sqrt{I}}{1+\beta a\sqrt{I}} \tag{3}$$

Equation (3) is usually adopted as a part of future models that account for long-range interactions.

Bromley (1973) introduced a modification of the β coefficient of the Debye-Hückel model. The coefficient was replaced by the Bromley coefficient, B, defined in Eq. (4).

$$B = B_+ + B_- \qquad (4)$$

As a final result, the general model equation was transformed to Eq. (5), (Bromley, 1973):

$$\log \gamma_\mp = -\frac{A|z_+ z_-|\sqrt{I}}{1+\sqrt{I}} + \frac{(0.06+0.6B)|z_+ z_-|I}{\left(1+\dfrac{1.5}{|z_+ z_-|}I\right)^2} + BI \qquad (5)$$

The model is applicable to electrolytes of the ionic strength, I, even above 6 mol/kg. It should be also mentioned that Meissner and Kusik (1978) proposed a further modification of the model resulting in prediction of activity coefficients for higher ionic strength (Sander, 1984).

In the Bromley – Zemaitis model, also called "Aqueous", two other components were added, which contain the C and D coefficients, hence significant increase in the model accuracy was achieved. The temperature dependence of the coefficients was expressed by quadratic equations. The general form of the model is an expansion of Eq. (5), Zemaitis et al. (1986):

$$\log \gamma_\mp = -\frac{A|z_+ z_-|\sqrt{I}}{1+\sqrt{I}} + \frac{(0.06+0.6B)|z_+ z_-|I}{\left(1+\dfrac{1.5}{|z_+ z_-|}I\right)^2} + BI + CI^2 + DI^3 \qquad (6)$$

Introduction in Eq. (6) of additional elements to Eq. (5) resulted in widening the applicability extent of the Bromley – Zemaitis model up to the ionic strength of 30 mol/kg. The model was incorporated in a commercial code OLI Analyzer Studio as the Aqueous model.

2.2. Pitzer model

The Pitzer model was chronologically the first one which could be applied both to weak and strong electrolytes of high ionic strength. A number of interaction types can be accounted for in the model such as double relations: anion-anion, anion-cation, cation-cation and also triple interactions that comprise cross-interactions between all ions present in a solution. Those interactions are represented by relevant virial parameters included in mathematical relationships representing the model.

The basic relationships of the Pitzer model (Pitzer, 1973) for deriving activity coefficients for cations (M) and anions (A) are presented in Eqs. (7, 8).

$$\ln \gamma_M = z_M^2 F + \sum_a m_a \left(2 B_{Ma} + Z C_{Ma}\right) + \sum_c m_c \left(2 \Phi_{Mc} + \sum_a m_a \Psi_{Mca}\right) +$$
$$+ \sum_{a=1} \sum_{a'=a+1} m_a m_{a'} \Psi_{aa'M} + z_M \sum_{c=1} \sum_{a=1} m_c m_a C_{ca} \qquad (7)$$

$$\ln \gamma_X = z_x^2 F + \sum_{c=1} m_c \left(2 B_{cX} + Z C_{cX}\right) + \sum_{a=1} m_a \left(2 \Phi_{Xa} + \sum_{c=1} m_c \Psi_{Xac}\right) +$$
$$+ \sum_c \sum_{c'} m_c m_{c'} \Psi_{cc'M} + z_X \sum_c \sum_a m_c m_a C_{ca} \qquad (8)$$

Individual coefficients of the model are obtainable exclusively from experiments. Although the coefficient values were published for a relatively broad set of ion groups, they are however still far

from being complete. Activity of water is calculated from the osmotic coefficient that is dependent on the dual and triple coefficients in a similar way to that in Eqs. (7, 8). The model was employed in free-software VMINTEQ (Gustafsson, 2004) licensed by Jon Petter Gustafsson of KTH and the code is mainly used for studying geochemical equilibria. The Pitzer model was also used in a commercial software ChemApp from GTT-Technologies (Eriksson and Königsberger, 2008), mostly applied to studying multiphase equilibria in metallurgical industry.

2.3. Extended UNIQUAC model

The extended UNIQUAC model (exUNIQUAC) was developed by Thomsen et al. (1996) and it contains the Debye–Hückel expression along with two components representing energetic parameters, which are dependent on the chemical structure of solution components. Two parameters, r and q, are incorporated in the model and they are characteristic for given species and independent of temperature. The basic model equation, that is described in detail by Thomsen (1997), for unsymmetrical activity coefficients reads:

$$\ln \gamma_i^* = \ln \frac{\gamma_i^K}{\gamma_i^{K,\infty}} + \ln \frac{\gamma_i^R}{\gamma_i^{R,\infty}} + \ln \gamma_i^{D-H} \tag{9}$$

Its individual components, combinatorial (K) and residual (R) and Debye–Hückel (D-H), are defined by the following equations:

$$\ln \gamma_i^K = \ln \left(\frac{\phi_i}{x_i} \right) + 1 - \frac{\phi_i}{x_i} - \frac{z}{2} q_i \left[\ln \left(\frac{\phi_i}{\theta_i} \right) + 1 - \frac{\phi_i}{\theta_i} \right] \tag{10a}$$

$$\ln \gamma_i^{K,\infty} = \ln \frac{r_i}{r_w} + 1 - \frac{r_i}{r_w} - \frac{z}{2} q_i \left[\ln \frac{r_i \, q_w}{r_w q_i} + 1 - \frac{r_i \, q_w}{r_w q_i} \right] \tag{10b}$$

$$\ln \gamma_i^R = q_i \cdot \left[1 - \ln \left(\sum_j \theta_j \cdot \Psi_{ji} \right) - \sum_j \left(\frac{\theta_j \cdot \Psi_{ij}}{\sum_k \theta_k \cdot \Psi_{kj}} \right) \right] \tag{11a}$$

$$\ln \gamma_i^{R,\infty} = q_i \left[1 - \ln \Psi_{wi} - \Psi_{iw} \right] \tag{11b}$$

$$\ln \gamma_i^{D-H} = -\frac{z_i^2 A\sqrt{I}}{1 + 1.5\sqrt{I}} \tag{12}$$

The Debye–Hückel component for water is different and expressed by Eq. (13).

$$\ln \gamma_w^{D-H} = M_s \frac{2A}{1.5^3} \left[1 + 1.5\sqrt{I} - \frac{1}{1+1.5\sqrt{I}} - 2\ln \left(1 + 1.5\sqrt{I} \right) \right] \tag{13}$$

The exUNIQUAC model is distinguished from the Pitzer one by a significantly lower number of temperature dependent parameters (Jaworski et al. 2010), which have to be derived experimentally. The model encompasses superficial, r, and volumetric, q, parameters that account for the shape of ions. The parameters are constants characteristic for each chemical species and directly define model coefficients, ϕ i θ, as specified in Thomsen et al. (1996). Energetic parameters, Ψ_{ji}, are functions of u_{ij} coefficients, which are linearly dependent on temperature. Nearly all coefficient values were given by Thomsen and Rasmussen (1999) for the $NH_3 - CO_2 - NaCl - H_2O$ system.

2.4. MSE model

The only thermodynamic model that remains for description in this study is called Mixed-Solvent Electrolyte (MSE). It was developed by Wang et al. (2002) specifically for concentrated electrolyte solutions. The basic model equation also encompasses three components, which explain long-range (LR), middle-range (MR) and short-range interactions (SR).

$$\ln \gamma_i = \ln \gamma_i^{LR} + \ln \gamma_i^{MR} + \ln \gamma_i^{SR} \tag{14}$$

The component accounting for long-range relations (LR) is defined in a similar way to that in the classic Debye–Hückel models, although differing by accounting for dependence of the dielectric constant on the composition of electrolyte solutions. It results in a complex relationship used in calculating the γ_i^{LR} value as described in Wang et al. (2002).

The equation describing the long-range interactions can be presented in the following form:

$$\ln \gamma_i^{LR} = -A_x \left[\frac{2z_i^2}{\rho} \ln \left(\frac{1+\rho\sqrt{I_x}}{\sum_k x_k \left[1+\rho\sqrt{I_{x,k}^0}\right]} \right) + \frac{\sqrt{I_x}\left(z_i^2 - 2I_x\right)}{1+\rho\sqrt{I_{x,k}}} \right] +$$
$$-\frac{4A_x I_x}{\rho} \left\{ \ln \frac{1+\rho\sqrt{I_x}}{\sum_k x_k \left[1+\rho\sqrt{I_{x,k}^0}\right]} \left(\sum_l n_l \right) \left[\frac{1}{2 \cdot d_s} \frac{\partial d_s}{\partial n_i} - \frac{3}{2 \cdot \varepsilon_s} \frac{\partial \varepsilon_s}{\partial n_i} \right] - \frac{1+\rho\sqrt{I_{x,k}^0}}{\sum_k x_k \left[1+\rho\sqrt{I_{x,k}^0}\right]} + 1 \right\} \tag{15}$$

Eq. (15) explains the activity coefficient depends on ionic charge and on composition of a studied system by means of the dielectric constant, ε_s, molar concentration, d_s, and an empirical constant, ρ, which is characteristic for the system studied. The other interactions between two ions or ion-molecule, which were not explained by the γ_i^{LR} coefficient are described by a middle-range function that uses virial coefficients.

The second component of the middle-range type (MR) includes binary coefficients, *B*, that are dependent on ionic strength and temperature, and it is expressed by Eq. (16).

$$\ln \gamma_i^{MR} = \sum_k \sum_j x_k x_j B_{kj}(I_x) - \left(\sum_i n_i \right) \sum_k \sum_j x_k x_j \frac{\partial B_{kj}(I_x)}{\partial n_i} - 2\sum_k x_k B_{ki}(I_x) \tag{16}$$

That part of the activity coefficient depends on composition and ionic charge. $B_{ij}(I_x)$ is a symmetrical parameter, i.e. $B_{ij} = B_{ji}$ and $B_{ii} = B_{jj} = 0$. The parameter accounts for binary interactions, both ionic and molecular. The relationship is expressed by means of a, b, c model coefficients and on ionic strength, which is explained in detail by Wang et al. (2002).

The third part responsible for short-range (SR) interactions is similar to that in the exUNIQUAC model and it consists of combinatorial and residual terms.

The reference states for ions and solvent are different in the MSE model, unlike those in the UNIQUAC. In case of ions, the reference state is a state on infinite dilution and for solvents it is the pure solvent. Molality is generally assumed as the concentration type for ions and molar ratio as that for solvents. The MSE model has the advantage of full spectrum of applicability ranging from solutions of infinite dilution up to saturated solution of salts.

3. NUMBER OF MODEL PARAMETERS

The four thermodynamic models just presented, i.e. Pitzer, exUNIQUAC, AQ and MSE, were compared from the point of view of parameter quantity. A detailed list of the type and corresponding number of model parameters (coefficients) is presented in Tables B, C and D, for the singular, double and triple parameters, respectively. The parameters are to be considered for calculating activity coefficients for the analysed system based on each of the models. The required parameter number were compared for the $NH_3 - NaCl - H_2O$ system, which comprises the following interacting particles: 1 non-dissociated species – $NH_{3(aq)}$, 3 cations – NH_4^+, Na^+, H^+, 2 anions – Cl^-, OH^- and water. A summary of the types and the maximum numbers of various parameters is presented in Table 1 for that system.

Table 1. Maximum number of different parameters and other data used in the selected models for the $NH_3 - NaCl - H_2O$ system

Model parameters	Thermodynamic models							
	exUNIQUAC		AQ		Pitzer		MSE	
Singular	r_i, q_i	14	none	0	α_1, α_2	2	r_i, q_i, ρ, a_1	16
Double	u^0_{ij}, u^T_{ij}	56	$\beta_{ij}^{(0)}$, $\beta_{ij}^{(1)}$, B_{ij}, C_{ij}, D_{ij},	30	$a_{0\text{-}2,ij}$, $a_{0\text{-}2,ji}$, $b_{0\text{-}2,ij}$, $c_{0\text{-}2,ij}$,	51	$\beta_{ij}^{(0\text{-}2)}$, θ_{ij}, C_{ij}	252
Triple	none	0	none	0	μ_{ijk}, ζ_{ijk}, Ψ_{ijk}, η_{ijk}	27	none	0
Other data	z_i, m_i	12	z_i, m_i	12	z_i, m_i	12	z_i, m_i	12
Total number of parameters	82		42		92		280	

The Mixed-Solvent Electrolyte (MSE) model requires knowing the values of theoretically highest number of parameters. However in some applications many coefficients quantifying temperature influence, as in other models, can be neglected.

4. CHARACTERISTIC FEATURES OF COMPUTER PROGRAMMES

Perhaps chronologically first of broadly available computer programmes for estimating values of activity coefficients in electrolyte solutions was PHREEQC that focused on compounds characteristic for geological applications. It employed the Debye-Hückel method in the source code of the programme (Parkhurst and Appelo, 1999), and the application range was rather narrow due to its intrinsic limitation to low values of ionic strength. Its follower, PHRQPITZ, used the Pitzer model, which broadened its application to more concentrated solutions up to ionic strength of 30 mol/kg. The two programmes require a special file of input data and this requires considerable effort on the part of users and knowledge of the code convention. The latter programme may be used in computations for the studied $NaCl - NH_3 - H_2O$, $NaCl - NH_3 - CO_2 - H_2O$ systems provided the correct input files are constructed.

Another freely accessible programme is VMINTEQ, which uses the PHRQPITZ code for deriving activity coefficients and the code encompasses databases for several dozen of chemical species. Availability of the databases is of major significance to a user since to compute activity coefficients one needs to input information on the concentration of the studied system along with the process conditions. That programme contains parameters for all the ions forming all the systems investigated in this study.

Other two considered computational programmes were commercial FactSage and Chemapp. The two codes are dedicated to calculate equilibrium conditions in multiphase systems where chemical reactions and/or phase transitions can proceed. FactSage is based on the model presented by Königsberger and Eriksson (1995) and is composed of three computing modules: for minimisation of the Gibbs energy, creation of phase diagrams and optimisation of the Gibbs energy. Chemapp is a programme based also on the module for minimalisation of the Gibbs energy that was used in FactSage. However, Chemapp is used for computing multiphase systems containing a high number of different phases. Its database encompasses parameters of the Pitzer model for 49 different cations and 36 anions. The two programmes are designed for computing systems of the metallurgical industry, but it is also possible to perform effective calculations for selected inorganic systems. The code also contains parameters for ions present in the soda system investigated in this study.

The third commercial code considered for thermodynamic analysis of multiphase and multicomponent systems was OLI Analyzer Studio from OLI Systems Inc. The program uses two different models, Aqueous and Mixed Solvent Electrolyte (OLI Systems Inc., 2010). To derive values of activity coefficients of solution components, users of the code define a global composition of the studied system and process conditions. A significant advantage of the programme is that it makes it possible to compare results obtained with the use of the two methods. However, in principle the Aqueous model is applicable for ionic strength up to 30 mol/kg, whereas the MSE model can be used in the whole concentration range. Those features significantly prevailed over those of the former models and therefore OLI Analyzer Studio of OLI Systems Inc. was employed for studying the soda system and its subsystems.

5. RESULTS OF MODEL CALCULATIONS

Three systems of different complexity were chosen to compare thermodynamic models regarding their accuracy in predicting experimental data. Calculations began for a two component system, $NH_3 - H_2O$, then for a three component one, $NaCl - NH_3 - H_2O$, and finally the complete Solvay soda system, $CO_2 - NaCl - NH_3 - H_2O$, was used. The composition of all the phases and the concentration of all the components were computed using OLI Analyzer Studio. Four thermodynamic models of electrolyte solutions were tested. Parameters and coefficients of the Pitzer model were adopted from Kurz et al. (1996) and for exUNIQUAC from Thomsen (1997) and Thomsen and Rasmussen (1999). In the AQ and MSE models, computations were conducted using OLI Analyzer Studio.

The first calculation step in the three systems consisted in deriving activity coefficients for ions and neutral species. The next step involved estimation of partial pressure of water, carbon dioxide and ammonia using their saturation pressure values from Piotrowski et al. (1998) along with the Henry constants calculated according to Pazuki et al. (2006a). Total pressure was calculated as the sum of values of partial pressure for all components of the gas phase.

Experimental data for the two-component system, $NH_3 - H_2O$, in the form of mass fractions of ammonia and the total pressure were obtained from Stephen (1963) and Sing et al. (1999). The performed calculations for the two-component system revealed similar, good accuracy in predictions of the total pressure, *P*, by all the tested thermodynamic models, see Fig. 1.

Values of partial pressure of water and ammonia for varied molality of sodium chloride and ammonia in aqueous phase were obtained from the experiments of Sing et al. (1999) for the three-component system of $NaCl - NH_3 - H_2O$. The calculations were carried out for the temperature of 313 K and molality of NaCl at 4 mol/kg_{H_2O} and also for 353 K and NaCl molality of 2 mol/kg_{H_2O}. Thus, the obtained variations of the total pressure both from the experiments, P^{exp}, and modelling, P^{cal}, were graphically shown against molality of ammonia or as a direct comparison of the two pressures for

temperature levels of 313 and 353 K in Figs. 2 and 3, respectively. To present the results in a clear form, the pressure axes were arranged in a logarithmic scale in all the figures.
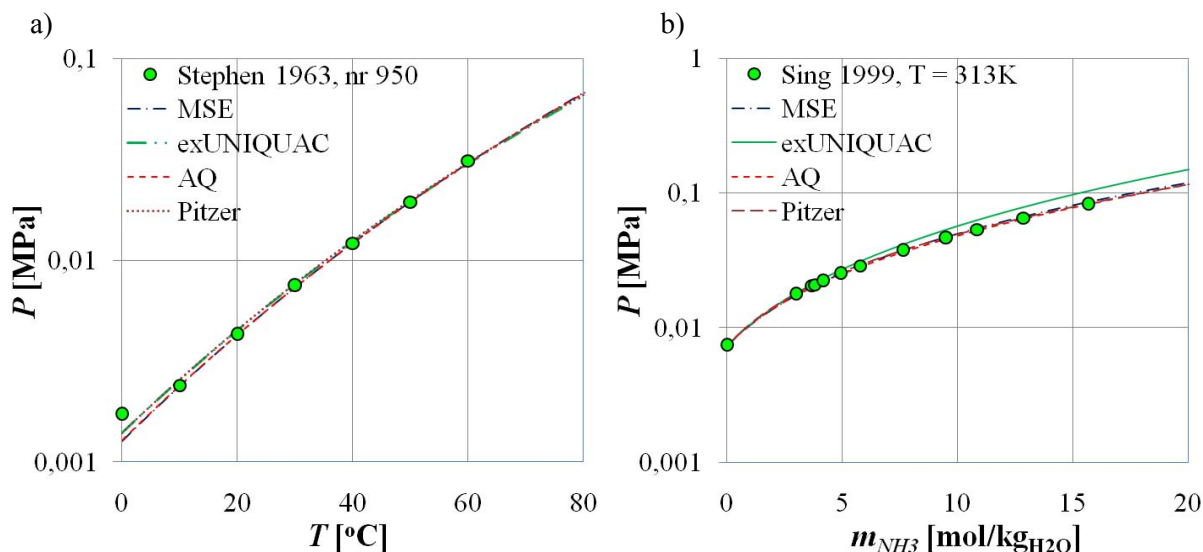

Fig. 1. Variation of the total pressure versus a) temperature, b) NH_3 molality at temperature of 313 K, for the $NH_3 - H_2O$ system
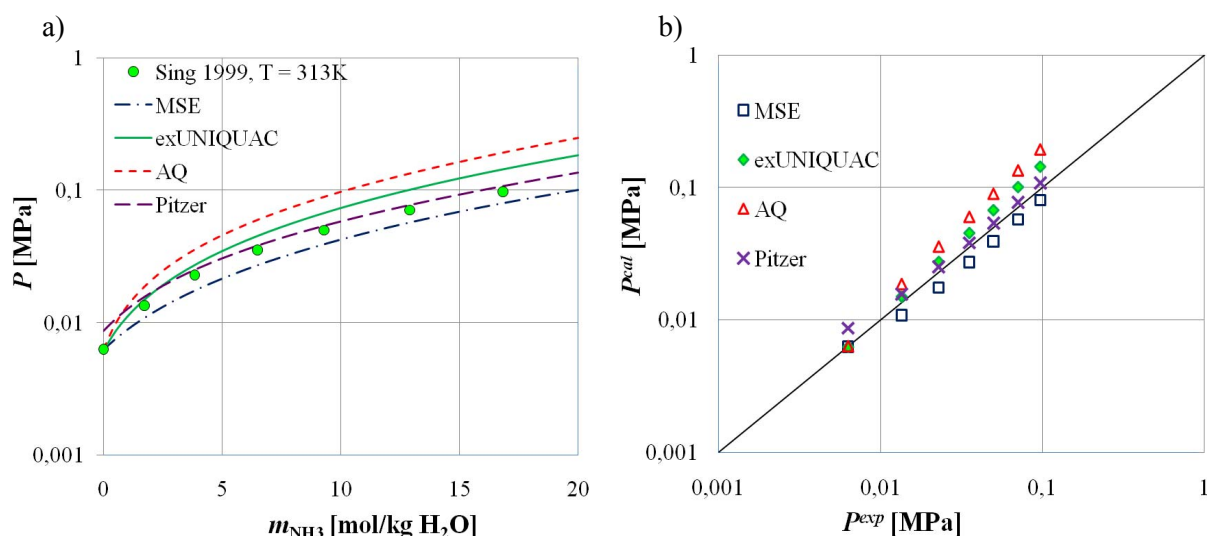

Fig. 2. Variation of a) total pressure versus NH_3 molality, b) calculated pressure vs. experimental pressure for the $NaCl - NH_3 - H_2O$ system at temperature of 313 K and NaCl concentration of 4 mol/kg$_{H2O}$

The variation of ammonia molality in aqueous phase ranged from 0 to 17 mol/kg$_{H2O}$. The performed calculations resulted in a conclusion of the best fit of the Pitzer model predictions to the experiments for the $NaCl - NH_3 - H_2O$ system. The relative error was close to 0.5% for 313K and about 2% for 353K. Low values of the error were found also for the MSE model as compared with deviations of 2.2% and 7% for the exUNIQUAC, and the highest differences of about 5% and 6% for AQ.
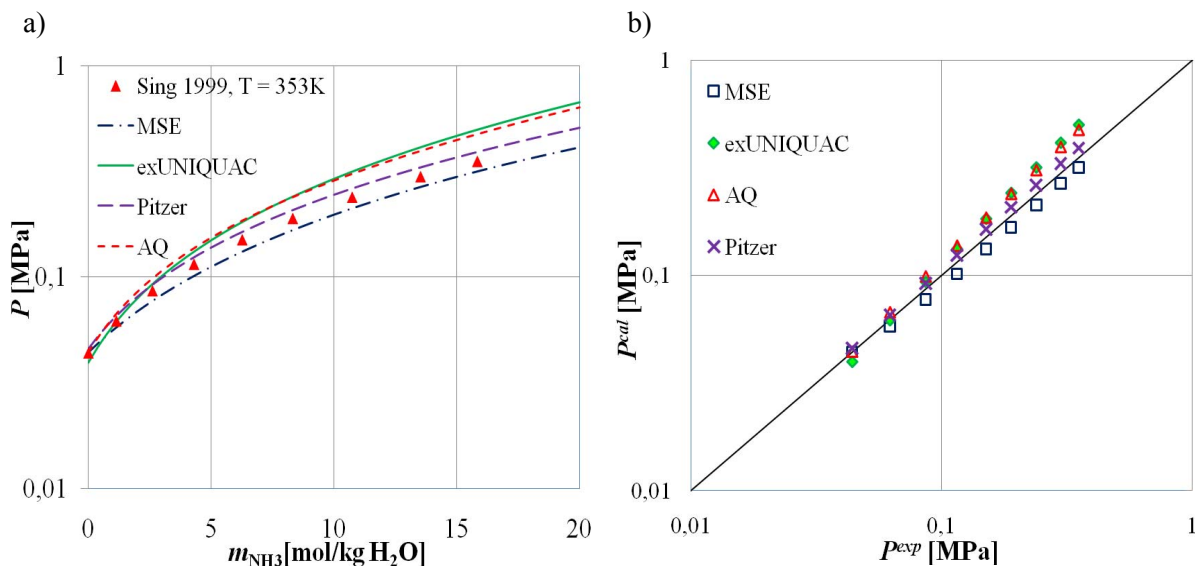
a)

b)

Fig. 3. Variation of a) total pressure versus NH_3 molality, b) calculated pressure vs. experimental pressure for the NaCl – NH_3 – H_2O system at temperature of 353 K and NaCl concentration of 2 mol/kg_{H2O}

Kurz et al. (1996) published experimental data of molality, partial and total pressure for the NaCl – NH_3 – CO_2 – H_2O system at the temperature ranged from 313 to 393 K. The results obtained from the four selected models were compared for two temperature levels of 313 and 353 K at molality both of NaCl and NH_3 of 4 mol/kg_{H2O}. A graphical comparison of the computed total pressure in dependence on the total concentration of carbon dioxide is presented in Figs. 4 and 5.

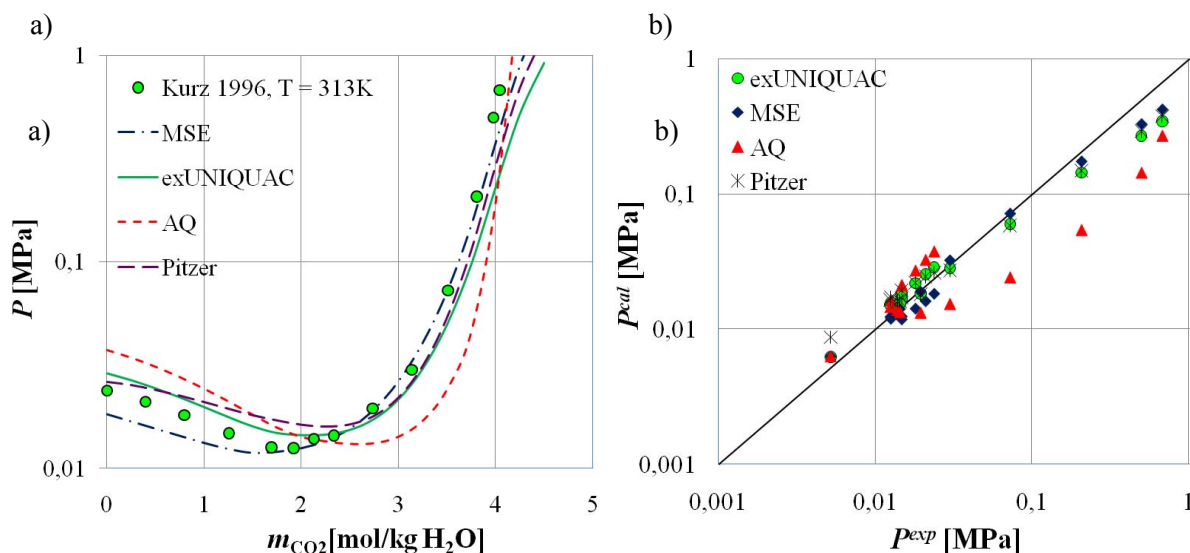a)

b)

Fig. 4. Variation of a) total pressure versus total CO_2 molality, b) calculated pressure vs. experimental pressure for the NaCl – NH_3 – CO2 – H_2O system at temperature of 313 K and molality of NaCl and NH_3 of 4 mol/kg_{H2O}
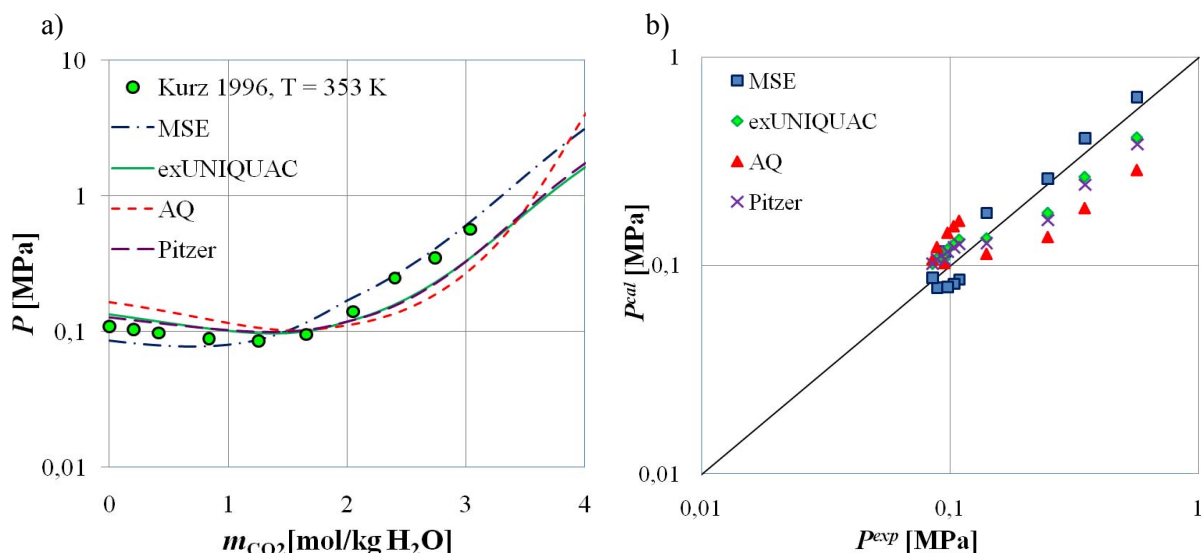
Fig. 5. Variation of a) total pressure versus total CO_2 molality, b) calculated pressure vs. experimental pressure for the $NaCl - NH_3 - CO_2 - H_2O$ system at temperature of 353 K and molality of NaCl and NH_3 of 4 mol/kg$_{H2O}$

The best match of model predictions to experiments for the $NaCl - NH_3 - CO_2 - H_2O$ system was achieved for the MSE model with the mean relative error close to 8% and 3.5% for 313K and 353K, respectively. The Pitzer model led to respectively 9.3% and 7.4% errors, with the exUNIQUAC of 10.2% and 6.2%, and the highest discrepancy close to 14% and 11% for AQ.

Table 2 presents a specification of experimental conditions reported in the literature and of the computed mean values of the relative standard deviation for predictions delivered by the four thermodynamic models applied to two multicomponent systems.

Table 2. Mean standard deviation for tested models for three- and four-component systems

System	T [K]	Molality of CO_2, [mol/kg]	Molality of NH_3, [mol/kg]	Molality of NaCl [mol/kg]	Exper. data from	No. of exper. points N	Mean relative standard deviation S_N [%] for models			
							AQ	MSE	exUNI-QUAC	Pitzer
$NH_3 - H_2O$	273–333		1.5		Stephen et al. (1963)	7	0.04	0.03	0.05	0.04
$NaCl - NH_3 - H_2O$	313		1.7–16.9	4.0	Sing et al. (1996)	7	4.69	0.99	2.24	0.53
$NaCl - NH_3 - H_2O$	353		1.1–15.8	2.0	Sing et al. (1996)	9	6.14	2.10	7.05	2.03
$NaCl - NH_3 - CO_2 - H_2O$	313	0.3–4.0	4.0	4.0	Kurz et al. (1996)	16	14.16	7.66	10.25	9.31
$NaCl - NH_3 - CO_2 - H_2O$	353	0.2–3.0	3.9	4.0	Kurz et al. (1996)	10	11.22	3.51	6.23	7.37

$$S_N = \left(\frac{1}{N} \sum_i^N \left(\frac{P_i^{exp} - P_i^{cal}}{P_i^{exp}} \right)^2 \right)^{0.5} \times 100$$

6. CONCLUDING REMARKS

An attempt of assessing suitability of the main types of thermodynamic models proposed in the last 25 years for concentrated electrolyte solutions was undertaken. The particular goal of this study was first a specification of the required set of model parameters needed for calculations and then a comparison of the calculation results with experimental data for pressure in the studied systems.

Each of the presented models has its advantages and drawbacks associated with its complexity, availability of literature data for model parameters and limitations of the application range. In general, higher accuracy of a model involves more work in preparing a necessary set of input data. On the other hand, the tested programmes are relatively precise and easy-to-use. In that group one can distinguish those free of charge, which either require preparation of a special data set by users or those containing all data is only for a limited number of systems. Commercial packages allow for relatively quick and convenient calculation of activity coefficients and other thermodynamic quantities and their critical use calls for knowledge of their theoretical foundations.

All the four models were correctly predicting equilibrium states for the two-component system of NH_3 – H_2O. With introduction of two additional components, NaCl and CO_2, the number of model parameters significantly increases along with qualitative changes in the influence of the mixture composition on the total pressure However, both in the three-component mixture of NaCl – NH_3 – H_2O and in the four-component one of NaCl – NH_3 – CO_2 – H_2O, the character of modelled variations of the total pressure was similar to the experimental ones for all the thermodynamic models and conditions tested in this study.

The mean values of the standard deviations in Table 2 indicate the Pitzer model delivered best predictions for the three-component system, NaCl – NH_3 – H_2O, with the average error below 2%. However, for the full four-component system a clear advantage of the MSE model over the other three was found. Thus, for the NaCl – NH_3 – CO_2 – H_2O system the average error for the MSE model was minimum and below 8% for all the conditions used in the tests. Other models showed lesser accuracy with the following maximum deviations: 10.3% for exUNIQUAC, 9.3% for the Pitzer and 14.2 for the AQ model.

For creating an in-house programme, it is advisable to employ the exUNIQUAC model instead of the Pitzer one since the former requires to know fewer parameters and their values are more readily available in the subject literature. However, for models available in commercial programmes, Mixed – Solvent – Electrolyte can be recommended as the one that achieved the best accuracy in this study.

Calculation of activity coefficients is usually a preliminary stage in the determination of the conditions of thermodynamic equilibrium. To obtain a full range of information about equilibrium one has to resolve a complex, strongly non-linear set of numerous equations (Bethke, 2008), where highly specialized codes, VMINTEQ, ChemApp and OLI Analyzer are exceptionally helpful.

SYMBOLS

A	constant of Debye- Hückel model, $(dm^3/mol)^{0,5}$
a	parameter defining the effective radius of ionic sphere, nm
a, b, c	adjustable parameters of the MSE model,

B, C, D	coefficients of the Bromley model,
C	coefficient in the Pitzer model, dependent on ion charge,
EOS	equation of state,
F	summation function in the Pitzer method,
I	ionic strength, $mol/kg_{solvent}$
K	constant of chemical equilibrium,
m	molality, $mol/kg_{solvent}$
n	number of moles, mol
P	pressure, Pa
R	universal gas constant, J/mol K
r	parameter of the exUNIQUAC model,
T	temperature, K
u	energetic parameters of the exUNIQUAC model, K
q	parameter of the exUNIQUAC model,
x	molar ratio,
Z	coefficient dependent on composition and charge of ion, $mol/kg_{solvent}$
z	ion charge,
z_i	charge of species,

Greek symbols

Ψ	parameter describing triple interactions in electrolyte solution, $(kg/mol)^2$
Ψ	energetic coefficient of the extended UNIQUAC model,
Φ, *B*	binary coefficients of the Pitzer model, (kg/mol)
β	coefficient of the Debye-Hückel model, $1/nm\ mol^{0,5}\ dm^{1,5}$
γ	activity coefficient,
θ, ϕ	coefficients associated with species shape,
μ	molar chemical potential, J/mol
ρ	parameter of the MSE model,

Superscripts

0	standard state,
cal	calculated from the model,
d	ideal state,
exp	experimental data,
D-H	Debye-Hückel term in the exUNIQUAC model,
K	combinatorial term in the exUNIQUAC model,
LR	long-range interaction,
MR	middle-range interaction,
R	residual term in the exUNIQUAC model,
SR	short-range interaction,

Subscripts

-	refers to anion,
+	refers to cation,
c, a	cation, anion,
i, j	species in ionic or neutral form,
M, X	calculated cation or anion,
S	solvent,
x	quantity determined for molar fraction.

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APPENDICES

Table A. Experimental conditions and accuracy of prediction of selected thermodynamic models for the $NaCl – NH_3 – CO_2 – H_2O$ system

L.p.	System studied	Concentr. of CO_2, mol/kg H_2O	Salt concentr. mol/kg H_2O	Concentr. of NH_3, mol/kg H_2O	Temperature range, K	Pressure range, MPa	Applied model	Accuracy of determination			Literature
								Pressure P	Number of experimental points, N	Deviation %	
1.	$NH_3 – H_2O$	-	-	1.9–19.0	313–393	0.02–0.68	Pitzer	Total NH_3 H_2O	33 33 36	< 0.5[d] 1.4[d] 2.0[d]	Sing et al. (1999)
2.	$NH_3 – H_2O$	-	-	0.3–80	273–383	0.004–3.0	exUNIQUAC	Total	296	AD 4.9	Thomsen and Rasmussen (1999)
3.	$CO_2 – H_2O$	-	-	-	273–383	0–10	exUNIQUAC	Total	104	AD 3.7	Thomsen and Rasmussen (1999)
4.	$CO_2 – H_2O$	0.002–14.5	-	-	273–533	0.1–200	Duan model – EOS & Pitzer	Total	unknown	7	Duan and Sun (2003)
5.	$NaCl – H_2O$	-	3.79–6.94	-	398	0.17–0.20	MSE exUNIQUAC	bubble point P	5 5 5	0.0004[e] 0.0003[e] 0.0034[e]	Lin et al. (2010)
			1.05–6.12		323	0.0093–0.012	MSE exUNIQUAC	bubble point P	10 10 10	0.00011[e] 0.00002[e] 0.00003[e]	
6.	$NaCl – NH_3 – H_2O$	-	2.0–6.0	0.5–21.2	313–393	0.013–0.69	Pitzer	Total NH_3 H_2O	81 56 64	1.2[d] 2.3[d] 1.3[d]	Sing et al. (1999)
7.	$NaCl – NH_3 – H_2O$	-	4.0	1.5–4.0	313–373	0.01–0.2	exUNIQUAC	Total	7	D 11	Thomsen and Rasmussen (1999)
8.	$NaCl – CO_2 – H_2O$	-	0–6.0	-	273–363	0.1–10	exUNIQUAC	Total	224	RD 3.59	Thomsen and Rasmussen (1999)
9.	$NaCl – CO_2 – H_2O$	0.001–7.9	1.0–4.0	-	273–543	0.1–200	Duan model – EOS & Pitzer	Total	unknown	8–15	Duan i Sun (2003)
10.	$NH_4Cl – CO_2 – H_2O$	-	0.2–7.2	-	288–353	0.1–10	exUNIQUAC	Total	89	RD 5.63	Thomsen and Rasmussen (1999)

No.	System						Model				Reference
11.	$NaHCO_3 - CO_2 - H_2O$		0.2–0.9	-	323–373	5.0–10.5	exUNIQUAC	Total	12	D 56	Thomsen and Rasmussen (1999)
12.	$NH_3 - CO_2 - H_2O$	0.5–9.7	-	6.0–12.1	313–353	0.02–0.67	Pitzer	Total NH_3 CO_2	47 13 16	RD 5.6 2.1 10.3	Kurz et al. (1995)
13.	$NH_3 - CO_2 - H_2O$	4.8–6.3	-	9.03	353		UNIQUAC–NRF	Total NH_3 CO_2	unknown	3.5–7.1[a] 4.4–8.7[a] 0.6–7.3[a]	Pazuki et al. (2006b)
								Total	unknown	7.8[b]	
14.	$NH_3 - CO_2 - H_2O$	0.0–13.9	-	3.9–25.9	373	0.01–1.4	exUNIQUAC – Sander	Total	171	8.9[b]	Bernardis et al. (1989)
15.	$NH_3 - CO_2 - H_2O$	0.3–5.4	-	2.6–9.6	373, 423	0.2–3.5	Pitzer	Total	unknown	< 15	Pawlikowski et al. (1982)
16.	$NH_3 - CO_2 - H_2O$	0.5–3.5	-	0.5–2.9	353–360	1.0–7.9	UNIQUAC–NRF	Total	240	7.8	Pahlevanzadeh et al. (2005)
17.	$NH_3 - CO_2 - H_2O$	0.9–5.8	-	1.1-8.1	268–288	0.097	UNIQUAC–NRF	Total	25	4.72[c]	Pazuki et al. (2006b)
18.	$NH_3 - CO_2 - H_2O$	0.0–12.0	-	0.1–40	293–373	0.0–7.0	exUNIQUAC	Total NH_3 CO_2	791 367 632	AD 4,6 12 11	Thomsen and Rasmussen (1999)
19.	$NaCl - NH_3 - CO_2 - H_2O$	0.3–4.1	4.0	1.6–4.1	313–393	0.02–3.0	Pitzer	Total	unknown	unknown	Kurz et al. (1996)
20.	$NaCl - NH_3 - CO_2 - H_2O$	0.3–4	4.0	1.6–4.0	313–373	0.01–3.0	exUNIQUAC	Total NH_3 CO_2	34 28 24	RD 8.3 19 11	Thomsen and Rasmussen (1999)
21.	$NH_4Cl - NH_3 - CO_2 - H_2O$	0.2–3.8	4.0	4.0	313–393	0.02–0.7	Pitzer	Total NH_3 CO_2	29 29 29	ARD 0.97–10.0 9.8–31.4 5.1–16.3	Kamps et al. (2000)

a) $AAD\% = \frac{|P^{exp} - P^{cal}|}{P^{exp}} \times 100$ b) $RMSD(P) = \left(\frac{1}{N} \sum_I^N \left(\frac{|P_i^{exp} - P_i^{cal}|}{P_i^{exp}} \right)^2 \right)^{0.5}$ c) $AAD(m)\% = \frac{100}{N} \sum_i^N \frac{|m^{exp} - m^{cal}|}{m^{exp}}$

d) $AAD(P)\% = \frac{100}{N} \sum_i^N \frac{|p^{exp} - p^{cal}|}{p^{exp}}$ e) Average numerical difference

D – Deviation %;   AD – Average   Deviation %,   RD – Relative   Deviation %;   ARD – Average   Relative Deviation %; AAD – Average Absolute Deviation %; RMSD – Root Mean Squared Deviation %

The type and number of parameters and other data required to calculate activity coefficients from thermodynamic models for species in the system $NH_3 - NaCl - H_2O$ are presented in Tables B, C and D.

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Table B. Maximum number of singular parameters for selected models used for computing activity coefficients for the $NH_3 – NaCl – H_2O$ system

Species i	exUNIQUAC		AQ	Pitzer		MSE			All models		
NH_3	r_i	q_i				r_i	q_i				m_i
NH_4^+	r_i	q_i				r_i	q_i			z_i	m_i
Na^+	r_i	q_i				r_i	q_i			z_i	m_i
Cl^-	r_i	q_i	–	α_1	α_2	r_i	q_i	ρ, a_1	A	z_i	m_i
H^+	r_i	q_i				r_i	q_i			z_i	m_i
OH^-	r_i	q_i				r_i	q_i			z_i	m_i
H_2O	r_i	q_i				r_i	q_i				x_i
Total number of parameters for chosen model	14		0	2		16			13		

Table C. Maximum number of double parameters for selected models used for computing activity coefficients for the $NH_3 – NaCl – H_2O$ system

Species i	Species j	exUNIQUAC		AQ	MSE		Pitzer	
NH_3	NH_3	u^0_{ij}	u^T_{ij}	$\beta_{ij}^{(0)}(T,P), \beta_{ij}^{(1)}$	–	–	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	
	NH_4^+	u^0_{ij}	u^T_{ij}	$\beta_{ij}^{(0)}(T,P), \beta_{ij}^{(1)}$	$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	
					$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	Na^+	u^0_{ij}	u^T_{ij}	$\beta_{ij}^{(0)}(T,P), \beta_{ij}^{(1)}$	$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	
					$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	Cl^-	u^0_{ij}	u^T_{ij}	$\beta_{ij}^{(0)}(T,P), \beta_{ij}^{(1)}$	$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	
					$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	H^+	u^0_{ij}	u^T_{ij}	$\beta_{ij}^{(0)}(T,P), \beta_{ij}^{(1)}$	$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	
					$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	OH^-	u^0_{ij}	u^T_{ij}	$\beta_{ij}^{(0)}(T,P), \beta_{ij}^{(1)}$	$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	
					$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	H_2O	u^0_{ij}	u^T_{ij}		$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$		
					$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
NH_4^+	NH_4^+	u^0_{ij}	u^T_{ij}		–	–		θ_{ij}
	Na^+	u^0_{ij}	u^T_{ij}		$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$		θ_{ij}
					$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	Cl^-	u^0_{ij}	u^T_{ij}	$B_{ij}(T), C_{ij}(T), D_{ij}(T),$	$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	C_{ij}
					$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	H^+	u^0_{ij}	u^T_{ij}		$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$		θ_{ij}
					$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		

		u^0_{ij}	u^T_{ij}						
	OH$^-$	u^0_{ij}	u^T_{ij}		$B_{ij}(T),$ $C_{ij}(T),$ $D_{ij}(T),$	$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	C_{ij}
						$a_{0,ji}, a_{1,ij}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	H$_2$O	u^0_{ij}	u^T_{ij}			$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$		
						$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
Na$^+$	Na$^+$	u^0_{ij}	u^T_{ij}			–	–		θ_{ij}
	Cl$^-$	u^0_{ij}	u^T_{ij}		$B_{ij}(T),$ $C_{ij}(T),$ $D_{ij}(T),$	$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	C_{ij}
						$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	H$^+$	u^0_{ij}	u^T_{ij}			$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$		θ_{ij}
						$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	OH$^-$	u^0_{ij}	u^T_{ij}		$B_{ij}(T),$ $C_{ij}(T),$ $D_{ij}(T),$	$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	C_{ij}
						$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	H$_2$O	u^0_{ij}	u^T_{ij}			$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$		
						$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
Cl$^-$	Cl$^-$	u^0_{ij}	u^T_{ij}			–	–		θ_{ij}
	H$^+$	u^0_{ij}	u^T_{ij}		$B_{ij}(T),$ $C_{ij}(T),$ $D_{ij}(T),$	$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	C_{ij}
						$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	OH$^-$	u^0_{ij}	u^T_{ij}			$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$		
						$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		θ_{ij}
	H$_2$O	u^0_{ij}	u^T_{ij}			$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$		–
						$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
H$^+$	H$^+$	u^0_{ij}	u^T_{ij}			–	–		θ_{ij}
	OH$^-$	u^0_{ij}	u^T_{ij}		$B_{ij}(T),$ $C_{ij}(T),$ $D_{ij}(T),$	$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$	$\beta_{ij}^{(0)}, \beta_{ij}^{(1)}, \beta_{ij}^{(2)}$	C_{ij}
						$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
	H$_2$O	u^0_{ij}	u^T_{ij}			$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$		–
						$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
OH$^-$	OH$^-$	u^0_{ij}	u^T_{ij}			–	–		θ_{ij}
	H$_2$O	u^0_{ij}	u^T_{ij}			$a_{0,ij}, a_{1,ij}, a_{2,ij}$	$b_{0,ij}, b_{1,ij}, b_{2,ij}$		–
						$a_{0,ji}, a_{1,ji}, a_{2,ji}$	$c_{0,ij}, c_{1,ij}, c_{2,ij}$		
H$_2$O	H$_2$O	u^0_{ij}	u^T_{ij}			–	–	–	
Total number of partial parameters		28	28	12	18	6 x 21	6 x 21	3 x 12	9 + 6
Total number of parameters for chosen model		56		30		252		51	

Table D. Maximum number of triple parameters for the Pitzer model and the $NH_3 - NaCl - H_2O$ system

Species i	Species j	Species k	Parameters of Pitzer model
NH_3	NH_3	NH_3	μ_{ijk}
		NH_4^+	μ_{ijk}
		Na^+	μ_{ijk}
		Cl^-	μ_{ijk}
		H^+	μ_{ijk}
		OH^-	μ_{ijk}
	NH_4^+	Cl^-	ζ_{ijk}
		OH^-	ζ_{ijk}
	Na^+	Cl^-	ζ_{ijk}
		OH^-	ζ_{ijk}
NH_4^+	NH_4^+	NH_3	η_{ijk}
		Cl^-	Ψ_{ijk}
		OH^-	Ψ_{ijk}
	Na^+	Cl^-	Ψ_{ijk}
		OH^-	Ψ_{ijk}
Na^+	Na^+	NH_3	η_{ijk}
		Cl^-	Ψ_{ijk}
		OH^-	Ψ_{ijk}
Cl^-	Cl^-	NH_4^+	Ψ_{ijk}
		Na^+	Ψ_{ijk}
		NH_3	η_{ijk}
	OH^-	NH_4^+	Ψ_{ijk}
		Na^+	Ψ_{ijk}
		NH_3	η_{ijk}
OH^-	OH^-	NH_4^+	Ψ_{ijk}
		Na^+	Ψ_{ijk}
		NH_3	η_{ijk}
Total number of parameters			27