Prediction of Hydrate Formation for the Systems Containing Single and Mixed Electrolyte Solutions

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ABSTRACT: *In this work the effect of electrolytes on hydrate formation was investigated. To do so, a new model was used in predicting the hydrate formation conditions in presence of both single and mixed electrolyte solutions. The new model is based on the van der Waals - Platteeuw hydrate equation of state. In order to evaluate the values for the activity of water in electrolyte solutions the simplified version of the Ghotbi-Vera Mean Spherical Approximation (SGV-MSA) model was used. According to the SGV-MSA model the ions in the solutions are considered as charged hard spheres with different sizes. The values of the parameters for the SGV-MSA model are independent of temperature and depend only on the nature as well as concentration of electrolytes studied in this work. These parameters were obtained using the experimental data for the mean ionic activity coefficient of the single electrolyte solutions at 298.15 K. In the case of the mixed electrolyte solutions a new mixing rule was introduced to obtain the activity of water in aqueous electrolyte solutions. The results show that the proposed model can predict the hydrate formation for the systems containing single or mixed electrolyte solutions with good accuracy compared to the experimental data available in the literature. In addition, the results obtained from the proposed model were favorably compared with those obtained from the previously used models.*

KEY WORDS: *Hydrate formation, Electrolyte solutions, GV-MSA model, Water activity.*

INTRODUCTION

Clathrate hydrates are solid crystalline compounds that generally form in two types of empty lattice structures, i.e., structures I and II. These structures however, in the presence of suitable gas molecules can become stable. In fact, there are two types of cavities, small and large, in each structure that are usually occupied by gas molecules. While small gas molecules like methane and carbon dioxide form structure I, the larger gas molecules such as propane and iso-butane form structure II [1]. Recently the new structure was observed that is called structure H [2]. Formation of gas hydrate is a major problem for the oil and gas industries and it may lead to block the natural gas transmission pipelines, and in turn, causes serious operational problems. Therefore, it is necessary to prevent the

gas hydrate formation in natural gas pipelines. The commonly used method in order to prevent gas hydrate formation is to inject chemicals as inhibitors in the natural gas pipelines [3]. It is customary to use methanol as an inhibitor to lower the hydrate formation temperature [4].

To study the hydrate phase behavior it is necessary to develop an appropriate thermodynamic model. In the presence of pure water, *Parrish* and *Prausnitz* [5] developed a thermodynamic model based on the *van der Waals - Platteeuw* theory [6] to predict the hydrate formation conditions. Many attempts have been made to modify the *van der Waals-Platteeuw* model to accurately predict the gas hydrate formation [7-9]. For prediction of hydrate formation in the systems containing electrolyte solutions a number of models such as *Englezos* and *Bishnoi* [10], *Tohidi et al.* [11], and *Javanmardi et al.* [12] were developed.

In this work, a new model was proposed in predicting the hydrate formation in the presence of both single and mixed electrolyte solutions. The proposed model is based on the *van der Waals - Platteeuw* hydrate equation of state. In order to evaluate the values for the activity of water in electrolyte solutions, the simplified version of the *Ghotbi-Vera* Mean Spherical Approximation (SGV-MSA) model was used [13]. The results obtained from the proposed model were compared with the experimental data available in the literature and with those obtained from the previously used models.

THEORY

For a system containing vapor, hydrate and aqueous phases in equilibrium the following thermodynamic condition can be used for water:

$$\mu_W^H = \mu_W^L \tag{1}$$

where μ_W^L and μ_W^H are the chemical potential of water in aqueous phase and hydrate phase respectively. If the chemical potential of hypothetical empty hydrate phase is denoted by μ_W^β, then equation (1) can be rewritten as:

$$\Delta\mu_W^H = \Delta\mu_W^L \tag{2}$$

where $\Delta\mu_W^H = \mu_W^\beta - \mu_W^H$ and $\Delta\mu_W^L = \mu_W^\beta - \mu_W^L$.

$\Delta\mu_W^H$ was previously given according to the *van der Waals* and *Platteeuw* model [6]:

$$\frac{\Delta\mu_W^H}{RT} = -\sum_i v_i \ln(1 + \sum_j C_{ij} f_j) \tag{3}$$

where v_i is the number of cavity type i per water molecules and f_j is the vapor phase fugacity of hydrate former j. To estimate the values for f_j the *Peng-Robinson* equation of state [14] was used. C_{ij} in equation (3) stands for the *Langmuir* constant of hydrate former i in the cavity type j and can be expressed as [5]:

$$C_{ij} = (\frac{A_{ij}}{T}) \exp(\frac{B_{ij}}{T}) \tag{4}$$

where A_{ij} and B_{ij} are constant parameters and for different gas molecules were given by *Parrish* and *Prausnitz* [5].

In order to evaluate $\Delta\mu_W^L$ the following equation given by *Holder et al.* was used [8]:

$$\frac{\Delta\mu_W^L}{RT} = \frac{\Delta\mu_W^0}{RT_0} - \int_{T_0}^{T} (\frac{\Delta h_W}{RT^2})dT + (\frac{\Delta v_W}{RT})P - \ln a_W \tag{5}$$

where T_0 is considered as reference temperature, i.e. 273.15 K, R is the universal gas constant and T and P are hydrate formation temperature and pressure, respectively. a_W in equation (5) is the activity of water in the aqueous phase. $\Delta\mu_W$ and Δv_W are constant parameters and their values for hydrate structures I and II were given by *Parrish* and *Prausnitz* [5]. The variable Δh_W in equation (5) is a function of temperature and is given by the following equations:

$$\Delta h_W = \Delta h_W^0 + \int_{T_0}^{T} \Delta C_{P,W} dT \tag{6}$$

and

$$\Delta C_{P,W} = a + b(T - T_0) \tag{7}$$

the values of a, b and Δh_W^0 were also provided by *Parrish* and *Prausnitz*.

Combination of Eqs. (2), (3), and (5) leads to the final working equation for prediction of hydrate formation conditions:

$$\frac{\Delta\mu_W^0}{RT_0} - \int_{T_0}^{T} (\frac{\Delta h_W}{RT^2})dT + (\frac{\Delta v_W}{RT})P -$$
$$\sum_i v_i \ln(1 + \sum_j C_{ij} f_j) - \ln(a_W) = \circ \tag{8}$$

It is worth to mention that at a given inhibitor concentration and pressure or temperature, equation (8) can be solved for T or P. Notably, it is necessary to

evaluate the activity of water, a_W, in equation (8). In order to do that *Nasrifar et al.* [4] proposed a simple equation to obtain a_W in the presence of aqueous electrolyte solutions with dissolved gas. They proposed the following simple equation:

$$\ln a_W = \ln a_{W,el} + \ln a_{W,Gas} \tag{9}$$

where $a_{w,el}$ is the activity of water in the solution of single aqueous electrolyte. If the hydrate former is a soluble gas, the activity of water is altered by the amount of dissolved gas. In equation (9) $a_{w,gas}$ is the activity of water in the presence of dissolved gas and can be estimated assuming that the gas is dissolved in the pure water.

In order to evaluate the activity of water in the single electrolyte solutions the simplified version of *Ghotbi-Vera* Mean Spherical Approximation (SGV-MSA) model was used. In the SGV-MSA model, the *Ghotbi-Vera* hard sphere equation of state [15] was coupled with the simplified mean spherical approximation (MSA) model as the reference system. The SGV-MSA model considers the hard-sphere repulsion as well as long-range attraction forces between ions in solution.

The activity of water in electrolyte solutions can be calculated as follows:

$$\ln a_W = (-v_s.m.M_S.\phi)/1000 \tag{10}$$

where M_S, Φ, and m are solvent molecular weight, osmotic coefficient and molality of electrolyte, respectively. v_S is also the total ionic stoichiometric coefficient in aqueous solution.

The values of the mean ionic activity coefficients of electrolytes are directly related to the osmotic coefficient according to the following equation:

$$\phi = 1 + \frac{1}{m}\int_0^m m\left(\frac{\partial \ln \gamma_m}{\partial m}\right)dm \tag{11}$$

where γ_m, is the mean ionic activity coefficient of electrolyte defined as:

$$\gamma_m = (\gamma_+^{v+}.\gamma_-^{v-})^{\left(\frac{1}{v_+ + v_-}\right)} \tag{12}$$

where γ_+ and γ_- are the activity coefficient for cation and anion, respectively. Also v_+ and v_- stand for the cation and anion stoichiometric coefficients.

The mean ionic activity coefficient is calculated using the simplified SGV-MSA model as follows:

$$\ln \gamma_i = \frac{\mu_i^r}{kT} \tag{13}$$

where μ_i^r, T, and k denote the residual chemical potential of ion i, absolute temperature and *Boltzmann* constant, respectively. The residual chemical potential of ion i, μ_i^r, is considered as sum of the hard-sphere and the electrostatic terms as follows:

$$\frac{\mu_i^r}{kT} = \left(\frac{\mu_i^r}{kT}\right)^{hs} + \left(\frac{\mu_i^r}{kT}\right)^{elec} \tag{14}$$

the superscripts hs and elec stand for the hard-sphere and the electrostatic terms, respectively. The electrostatic term of the residual chemical potential is given by:

$$\left(\frac{\mu_i^r}{kT}\right)^{elec} = \frac{Z_i e^2}{DkT}\left(\frac{2\Gamma a_i}{\sigma_i \alpha^2} - \frac{Z_i}{\sigma_i}\right) \tag{15}$$

where:

$$\alpha^2 = \frac{4\pi e^2}{DkT} \tag{16}$$

$$\eta = \frac{\pi}{6}\sum_i \rho_i \sigma_i^3 \tag{17}$$

$$P_n = \frac{1}{\Omega}\sum_{j=1}^N \frac{\rho_j \sigma_j Z_j}{1 + \Gamma\sigma_j} \tag{18}$$

$$\Omega = 1 + \frac{\pi}{2(1-\eta)}\sum_{j=1}^N \frac{\rho_j \sigma_j^3}{1 + \Gamma\sigma_j} \tag{19}$$

$$a_i = \frac{\alpha^2\left[Z_i - \left(\frac{\pi}{2(1-\eta)}\right)\sigma_i^2 P_n\right]}{2\Gamma(1 + \Gamma\sigma_i)} \tag{20}$$

$$\rho_i \frac{mol}{cm^3} = \left(\frac{Z_i.A}{1000}\right)c\frac{mol}{Lit} \tag{21}$$

In the above equations the sums run over all ionic species, σ_i represents the size parameter of the ion i, Z is the charge number, e is the electric charge of the electron, T is the absolute temperature, k is the *Boltzmann* constant, ρ is the number density and Γ is the inverse shielding length. The shielding length represents the long-range electrostatic interactions, which is similar to the *Debye* inverse length.

Since the SGV-MSA is derived in the McMillan-Mayer (MM) framework with temperature, volume, solute mole numbers and solvent chemical potential as independent variables, it is necessary to transform the

activity coefficients calculated with the MSA from the MM framework to the *Gibbs* framework. The *Gibbs* framework uses temperature, pressure and mole numbers as independent variables, and the *Lewis-Randal* (LR) standard state for the chemical potentials. While the transformation of the mean ionic activity coefficients from MM to LR is theoretically necessary, it has been shown that it does not affect the numerical results and for the practical applications, it can be neglected to a very good approximation [13].

The hard-sphere residual chemical potential of SGV-MSA model is calculated using the *Ghotbi-Vera* EOS as a reference system [13]:

$$Z_p = \frac{\beta P}{\rho} = 1 + 2.9619\,\xi + 5.4831\,\xi^2 + 7.4564\,\xi^3 + \qquad (22)$$

$$8.4856\,\xi^4 + \frac{8.85\,\xi^5}{1-\xi} - \frac{0.62\,\xi^7}{(1-\xi)^2} + \frac{0.04\,\xi^{10}}{(1-\xi)^3}$$

Where:

$$\xi_i = \frac{1}{\sqrt{2}}\sum_j \rho_j \sigma_j^i \quad (i = 0,1,2,3), \quad \xi = \xi_3 \qquad (23)$$

$$\eta_i = \frac{\pi\sqrt{2}}{6}\xi_i \qquad \eta = \eta_3 \qquad (24)$$

$$Y_1 = \frac{\xi_1 \xi_2}{\xi_0 \xi} \qquad (25)$$

$$Y_2 = \frac{\xi_2^3}{\xi_0 \xi^2} \qquad (26)$$

and the hard-sphere residual chemical potential of the SGV-MSA model is calculated as:

$$\left(\frac{\mu_i^r}{kT}\right)^{hs} = \begin{bmatrix} \dfrac{A^r}{NkT} + \dfrac{3M_{1,i}}{4}K_1 \\ + \dfrac{3}{2}(\dfrac{2M_{2,i} - M_{1,i}}{4})K_2 \\ + (\dfrac{1+3Y_1}{4})(\dfrac{\partial K_1}{\partial \rho_i})_{T,V,\rho_{j\neq i}} \\ + \dfrac{3}{2}(\dfrac{2Y_2 - Y_1 - 1}{4})(\dfrac{\partial K_2}{\partial \rho_i})_{T,V,\rho_{j\neq i}} \end{bmatrix} \qquad (27)$$

$$\frac{A^r}{NkT} = (\frac{1+3Y_1}{4})K_1 + \frac{3}{2}(\frac{2Y_2 - Y_1 - 1}{N4})K_2 \qquad (28)$$

$$M_{1,i} = Y_1(R_2 + R_1 - R_3 - R_0)_i \qquad (29)$$

$$M_{2,i} = Y_2(3R_2 - R_0 - 2R_3)_i \qquad (30)$$

$$R_{k,i} = \frac{\sigma_i^k}{\sum_j x_j \sigma_j^k} \qquad (31)$$

$$(\frac{\partial K_1}{\partial \rho_i})_{T,V,\rho_{j\neq i}} = R_{3,i}(Z_p - 1) \qquad (32)$$

$$(\frac{\partial K_2}{\partial \rho_i})_{T,V,\rho_{j\neq i}} = R_{3,i}\xi(Z_p - 1) \qquad (33)$$

$$K_1 = \begin{bmatrix} -10.11\xi - 3.34\xi^2 - 1.28\xi^3 - 0.50\xi^4 \\ -0.17\xi^5 - 0.02\xi^6 - 0.006\xi^7 \\ -14.01\ln(1-\xi) \\ -\dfrac{0.98}{1-\xi} + \dfrac{0.02}{(1-\xi)^2} + 0.96 \end{bmatrix} \qquad (34)$$

$$K_1 = \begin{bmatrix} -14.01\xi - 5.05\xi^2 - 2.23\xi^3 \\ -0.96\xi^4 - 0.40\xi^5 - 0.14\xi^6 \\ -0.02\xi^7 - 0.005\xi^8 \\ -14.99\ln(1-\xi) - \dfrac{1.02}{1-\xi} \\ +\dfrac{0.02}{(1-\xi)^2} + 1.00 \end{bmatrix} \qquad (35)$$

In the SGV-MSA model, the hydrate diameter of cation changes with concentration as:

$$\sigma_+ = \sigma_{+0} + \sigma_{+1}c + \sigma_{+2}c^2 \qquad (36)$$

where σ_+ is the hydrate diameter of the cation and c is the concentration in the molarity scale. The parameters σ_{+j} (j=0, 1, 2) are considered to be adjustable parameters. The diameter of anions was considered constant and equal to the pauling diameter [16]. The values of the adjustable parameters were obtained by fitting the experimental data of the mean ionic activity coefficients available in the literature by minimizing the following average absolute relative deviation (AARD) of the calculated mean activity coefficients from the experimental data:

$$AARD(\%) = \frac{1}{NP}\sum_i^{NP} \frac{\left|\gamma_m^{exp} - \gamma_m^{calc}\right|}{\gamma_m^{exp}} \qquad (37)$$

In the above equation, NP refers to the number of the experimental points. While the experimental data for the mean ionic activity coefficients available in the literature are based on the molality scale, the activity coefficients

calculated from the MSA model are based on the molarity scale. Thus, the following conversion criterion is used to change the concentration scale of the activity coefficients [14]:

$$\ln \gamma_i^c = \ln \gamma_i^m + \ln \frac{m_i d_o}{c_i} \qquad (38)$$

in equation (38) the superscripts m and c stand for the molality and molarity scales, d_0 is density of water; m and c are the molality and molarity of the ions or the electrolyte in the solution, respectively. The values of adjustable parameters in equation (36) were obtained by minimizing equation (37).

In order to calculate the activity of water in the mixed electrolyte solutions, $a_{W,mix}$, a new mixing rule was proposed. The theoretical basis of the proposed mixing rule is similar to that proposed by *Patwardhan* and *Kumar* [17] and *Nasrifar et al.* [4]. Notably, in the present work the effects of the other factors such as Ionic Strength, I, on the activity of water have been also considered.

The activity of water in the mixed electrolyte solutions was calculated using the following equation:

$$\ln a_{W,mix} = (-v_{s,mix} . m_T . M_S . \phi_{mix})/1000 \qquad (39)$$

where M_S denotes water molecular weight. In equation (39) m_T and $v_{s,mix}$ are respectively represented as:

$$m_T = \sum_{i=1}^{N} m_i \qquad (40)$$

$$v_{s,mix} = \sum_{i=1}^{N} (\frac{m_i}{m_T}) v_{s,i} \qquad (41)$$

where subscripts i denotes the electrolyte i in the mixed electrolyte solution, m is the molality and sums run over all electrolytes in the solution. In equation (41), $v_{s,i}$ is the stoichiometric number of electrolyte i. In order to calculate Φ_{mix} the following equation was used.

$$\phi_{mix} = \sum_{i=1}^{N} (\frac{v_{s,i} m_i + I_i}{v_{s,i} m_T + I_T}) \phi_i^* \qquad (42)$$

with

$$m_i^* = \frac{1}{v_{s,i}} \sum_{j=1}^{N} v_{s,j} m_j \qquad (43)$$

In the above equations, I_T, I_i are the total ionic strength of the solution and ionic strength of electrolyte i in the solution, respectively. Also Φ^*_{mix} is the osmotic coefficient in a single

electrolyte solution, containing the electrolyte i with the molality m^*_i. The osmotic coefficients in the single electrolyte solution were calculated using the SGV-MSA model.

The results for the systems containing the mixed electrolyte solutions using the proposed mixing rule were compared with two other mixing rules proposed by *Patwardhan* and *Kumar* [17], and *Nasrifar et al.* [4].

Finally to obtain the values for the activity of water in electrolyte solutions, the effect of dissolved gas should be taken into account. Considering the low solubility of gases in the water, according to the *Lewis-Randall* rule, the activity of water is assumed to be equal to the water mole fraction, x_W. For soluble gases, x_W can be calculated using *Krichewsky* and *Kasarnovesky* equation:

$$x_W = 1 - x_{CO_2} = 1 - \frac{f_{CO_2}}{\eta_3 \text{Exp}[(P^{\eta_1} - \eta_2)/RT]} \qquad (44)$$

Where f_{CO_2} is the fugacity of CO_2 in the gas phase. The values for η_1, η_2 and η_3 for CO_2 were reported by *Nasrifar et al.* [4]. Also P is the gas phase pressure and R is the universal gas constant.

RESULTS AND DISCUSSION

Table 1 reports the values of the adjustable parameters in equation (36) together with the average absolute relative deviation (AARD) of the calculated activity coefficients from the experimental data for the mean ionic activity coefficients. As seen from Table 1 the SGV-MSA model can accurately correlate the experimental data for the mean ionic activity coefficients of the single electrolyte solutions. Fig. 1 shows the mean ionic activity coefficient, osmotic coefficient and activity of water for aqueous $CaCl_2$ electrolyte solution as a function of molality. This figure also confirms the accuracy of the SGV-MSA model in correlating the experiment data for the mean ionic activity coefficient of $CaCl_2$ solution. Also Fig. 1 shows the capability of the SGV-MSA model in calculating the osmotic coefficient and the activity of water directly from the values for the mean ionic activity coefficients. As shown in Fig. 1 the results obtained for the osmotic coefficient and the activity of water are in good agreement with the experimental data.

Table 2 presents the AARD for the activity of water obtained from the SGV-MSA model for the systems containing the mixed electrolyte solutions using the proposed mixing rule. Table 2 also compares the results

Table 1: The SGV-MSA parameters for cations and the average absolute relative deviations percent (AARD%) of the calculated mean activity coefficients from the experimental data at 298.15 K.

Electrolyte	GV-MSA parameters			m_{max}	AARD (%)	Source of Exp. Data
	σ_{+0} (Å)	σ_{+1} (Å mol^{-1} L)	σ_{+2} (Å mol^{-2} L^2)			
NaCl	3.3497	-0.2823	0.0277	6	0.63	[23]
KCl	2.8397	-0.4382	0.0556	4.5	0.35	[23]
NH$_4$Cl	2.8792	-0.3565	0.0286	6	0.42	[23]
KBr	2.8144	-0.4747	0.0587	4	0.21	[24]
NaF	3.7307	-1.1583	0.4478	1	0.02	[25]
CaCl$_2$	5.3195	-0.1420	-0.0051	6	1.45	[23]
MgCl$_2$	5.8436	-0.2272	0.0040	6	0.84	[23]
SrCl$_2$	5.5279	0.0457	0.0269	4	0.85	[23]
Cd(NO$_3$)$_2$	6.9839	-0.9058	0.1617	2	0.14	[24]
Cu(NO$_3$)$_2$	6.5075	-0.2724	0.0142	7.8	0.78	[26]
Ca(NO$_3$)$_2$	5.738	-0.4737	0.067	2	0.27	[24]
Na$_2$SO$_4$	3.7800	-1.1257	0.2121	4.4	1.44	[27]
BaCl$_2$	5.2921	-0.9263	0.1826	1.8	0.29	[23]
FeCl$_2$	5.4818	-0.2117	-0.0138	2	0.49	[26]
ZnBr$_2$	6.7329	-1.7215	0.1997	4	0.62	[24]

Table 2: The average absolute relative deviation percent of the SGV-MSA model from the experimental data [28-29] in calculating the activity of water using the three different mixing rules studied in this work.

| System	$r = m_{NaCl}/m_{Salt}$	No. of Points	m_T range	AARD (%)		
				This Model	Nasrifar et al.[4]	Patwardhan et al.[17]
NaCl-KCl	0.2	7	0.60-6.0	0.287	0.287	0.287
NaCl-KCl	0.5	9	0.60-5.4	0.096	0.096	0.096
NaCl-KCl	1.0	9	0.20-6.0	0.256	0.256	0.256
NaCl-KCl	2.0	7	0.30-6.0	0.150	0.150	0.150
NaCl-KCl	3.0	8	0.40-5.0	0.248	0.248	0.248
NaCl-KCl	4.0	7	0.50-4.0	0.077	0.077	0.077
NaCl-MgCl2	1.5	7	0.25-3.0	0.060	0.186	0.158
NaCl-MgCl2	3.0	6	0.40-4.0	0.032	0.186	0.273
Overall		60		0.151	0.185	0.193
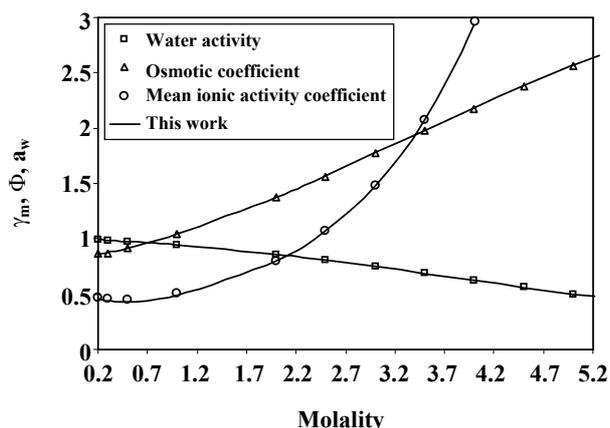
Fig. 1: Plot of the mean ionic activity coefficient, the activity of water, and the osmotic coefficient of CaCl₂ electrolyte solution versus molality using the SGV-MSA model at 298.15 K. □; experimental data for the activity of water [23], △; experimental data for the osmotic coefficient [23], ○; experimental data for the mean ionic activity coefficient[23], —; results of the SGV-MSA model.
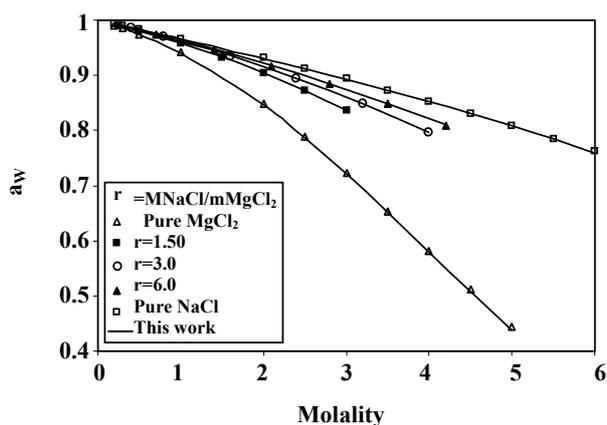

Fig. 2: Plot of the activity of water versus molality for mixed NaCl+ MgCl₂ electrolyte solution using the SGV-MSA model with the proposed mixing rule at different molality ratios (r=m$_{NaCl}$/m$_{MgCl2}$). △; experimental data for the activity of water for MgCl₂ electrolyte solution [29], ■; experimental data in r=1.50 [29], ○; experimental data in r=3.0 [29], ▲; experimental data in r=6.0 [29], □; experimental data for the activity of water for NaCl electrolyte solution [29], —; results of the SGV-MSA model with the proposed mixing rule.

of the SGV-MSA model with those obtained using mixing rules proposed by *Patwardhan* and *Kumar* and *Nasrifar et al.* Going through Table 2 it can be found out that the results obtained from the SGV-MSA model with the proposed mixing rule are exactly similar to those

obtained from the SGV-MSA model using the mixing rules proposed by *Patwardhan* and *Kumar* and *Nasrifar et al.* for uni-uni valent electrolyte solutions. It should be mentioned that the results for the asymmetric electrolyte solutions at the molality ratios studied in this work are more accurate, using the proposed mixing rule, than those obtained using the mixing rules proposed by *Patwardhan* and *Kumar* and *Nasrifar et al.*

Fig. 2 shows the results for the activity of water in the mixed electrolyte solution studied in this work obtained from the SGV-MSA model with three different mixing rules. Again it can be seen that the results obtained from the SGV-MSA model using the proposed mixing rule are in good agreement with experimental data available in the literature [28,29].

Fig. 3 shows the methane hydrate dissociation pressure for the system containing aqueous NaCl solution. As seen from Fig. 3 the results obtained from the proposed model are in good agreement with the experimental data. Also Fig. 3 shows the effect of presence of the electrolyte on the hydrate formation conditions. It can be inferred from Fig. 3 that the dissociation pressure increases as the salt concentration increases. This is plausibly due to the so-called hydration phenomenon and the salting out effect.

Fig. 4 shows the methane hydrate dissociation pressure for the systems containing aqueous mixed electrolyte solution of NaCl+KCl, using the proposed model. It can be seen from Fig. 4 that the proposed model can accurately predict the hydrate dissociation pressure at different electrolyte concentration. As shown in Fig. 4 the concentrations for both NaCl and KCl vary from 3 to 15 in weight percent. It would be worth noting that in obtaining the results shown in Figs. 3 and 4 the nonlinear equations 1-43 were simultaneously solved.

Table 3 presents the results obtained from the proposed model in comparison with those obtained from the model proposed by *Kharrat et al.* [20] along with the average absolute deviation on temperature (AADT) of the model from the experimental data. For both models the working equation, i.e., equation (11) was solved at given pressure and electrolyte concentration for T. As found the result of the proposed model produce less error comparing with those of the model proposed by *Kharrat et al.* [20].

Table 4 represent the results for methane hydrate formation temperature obtained from the proposed model

Table 4: Comparisons of the results obtained from the proposed model with those obtained from three other different models along with the AADT of the models from the experimental data [18] in predicting the methane hydrate formation temperature for different mixed electrolyte systems.

System	No. Points	P/Mpa	AADT (K)			
			This work	NM [4]	EB [10]	JMM [12]
Na3K3	7	2.704 to 5.857	0.12	0.16	0.16	0.08
Na5K5	7	2.829 to 9.379	0.14	0.13	0.13	0.24
Na5K10	4	2.569 to 9.046	0.13	0.23	0.23	0.46
Na5K15	4	2.914 to 8.689	0.07	0.35	0.35	0.84
Na10K12	5	2.989 to 8.819	0.22	0.57	0.57	1.09
Na15K8	4	3.614 to 8.839	0.28	0.50	0.50	1.04
Na3Ca3	4	2.504 to 8.159	0.12	0.35	0.37	0.18
Na6Ca3	4	3.134 to 7.839	0.03	0.20	0.25	0.06
Na10Ca3	4	3.214 to 7.444	0.31	0.14	0.06	0.46
Na10Ca6	4	2.819 to 6.899	0.27	0.24	0.16	0.45
Na3Ca10	4	3.019 to 9.664	0.09	0.12	0.21	0.15
Na6Ca10	4	3.689 to 9.514	0.18	0.11	0.17	0.30
Overall	55		0.15	0.26	0.26	0.45

Table 3: Comparisons of the results obtained from the proposed model with those obtained from the model proposed by Kharrat along with the AADT of the models from the experimental data [20] in predicting the methane hydrate formation temperature for different systems.

Electrolyte	Electrolyte Wt %	No. of Points	A.A.R.D.T (K)	
			This Work	Kharrat et al. [20]
Pure Water	---	3	0.04	0
NaCl	11.89	3	0.09	0.37
NaCl	17.13	3	0.41	0.47
CaCl$_2$	4.99	5	0.29	0.32
CaCl$_2$	10.15	4	0.14	0.13
CaCl$_2$	14.52	4	0.60	0.63
CaCl$_2$	19.78	4	0.27	0.35
CaCl$_2$	23.01	5	0.47	0.42
CaCl$_2$	25.76	4	0.69	0.95
Overall	---	35	0.33	0.40

Table 5: The values of AADP from the experimental data [30] in prediction of CO$_2$ hydrate dissociation pressure in the presence of pure water and different electrolyte solutions.

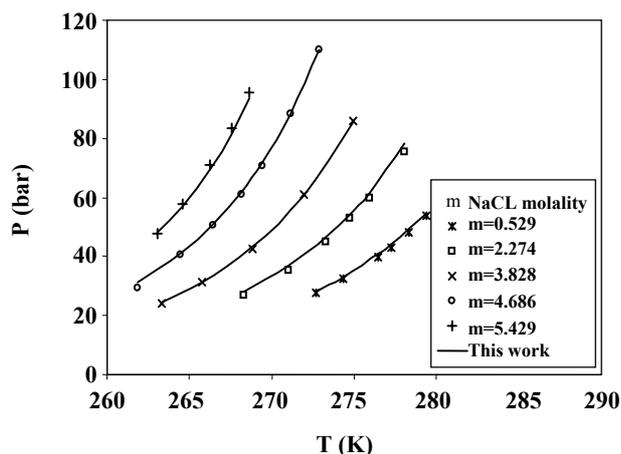| Solutions	Wt % Range	No. of Points	AADP (%)
Pure Water	---	10	2.51
NaCl	3 - 20	25	4.46
KCl	3 - 20	21	4.40
CaCl2	3 - 20	23	3.56
NaCl-KCl	---	17	3.00
NaCl+CaCl2	---	22	3.76
Sea water	---	5	2.78
Overall	---	123	3.50

Fig. 3 : Plot of the methane hydrate dissociation pressure versus temperature for the systems containing aqueous NaCl solution at different molality using the proposed model. ∗; m=0.529, □; m=2.274, ×; m=3.528, ○; m=4.686, +; m=5.429, —; results of the proposed model. Symbols introduce the experimental data for the methane dissociation pressure and given by [18, 19].
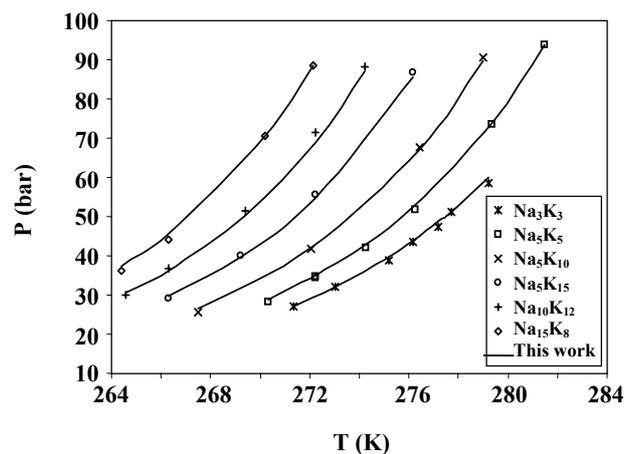

Fig. 4 : Plot of the methane hydrate dissociation pressure versus temperature for the systems containing aqueous mixed electrolyte solution of NaCl-KCl at different weight percents using the proposed model. ∗; Na3K3, □; Na5K5, ×; Na5K10, ○; Na5K15, +; Na10K12, ◇; Na15K8, —; results of the proposed model. Symbols introduce the experimental data for the methane dissociation pressure and given by [18].

along with the AADT of the model from the experimental data. As compared, the results of the proposed model are in better agreement with the experimental data than those obtained from the *Nasrifar et al.*, the *Englezos* and *Bishnoi*, and the *Javanmardi et al.* models.

Table 5 presents the average absolute deviation on pressure (AADP) in predicting CO_2 hydrate dissociation pressure for different systems containing pure water, electrolyte solutions and the synthetic sea water, respectively. As shown in Table 5 the results obtained from the proposed model are in good agreement with the experimental data [30].

CONCLUSIONS

In this work, a model was proposed to predict the hydrate formation conditions for the systems containing aqueous electrolyte solutions. The proposed model is based on the *van der Waals* and *Platteeuw* hydrate equation of state. In order to obtain the values for the activity of water in the electrolyte solutions the simplified version of the *Ghotbi-Vera* Mean Spherical Approximation model (SGV-MSA) was used. The values of the parameters for the SGV-MSA model are independent of temperature and depend only on the nature as well as the concentration of the electrolyte. The parameters were obtained using the experimental data for the mean ionic activity coefficient

of the single electrolyte solutions at 298.15 K. A mixing rule was presented to obtain the activity of water in aqueous mixed electrolyte solutions. The results show that the proposed model can predict the hydrate formation conditions for the systems containing single and mixed electrolyte solutions with good accuracy in comparison with the experimental data available in the literature. Also, the results obtained from the proposed model were favorably compared with those obtained from the previously used models.

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