

## Application of ESD and PR+Wong Sandler Mixing Rule Equations of State to Study Methane Hydrate Formation in the Presence of Different Inhibitors

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### Abstract

Due to existing inhibitors in capable hydrate forming mixture, extra intermolecular interactions affect hydrate formation conditions. Predicting hydrate formation conditions is not possible without considering these interactions. In this work, two different equations of state (EOS) are used and compared to predict the hydrate formation pressure in the presence of inhibitors. The EOSs applied are Elliot-Suresh-Donohue (ESD) EOS and Peng-Robinson (PR) EOS with Wong-Sandler (WS) mixing rules. Parrish and Prausnitz hydrate formation algorithm is coupled with flash calculations to predict hydrate formation pressure at different temperatures and different concentrations of polar inhibitors. Pure and binary interaction parameters are obtained for ESD EOS. On the other hand, necessary unknown parameters which should be used in applying PR with WS mixing rules are adjusted on experimental hydrate formation condition data. Number of water hydrogen bonding sites, which are used in calculations, is also determined. Hydrate formation pressure for different polar inhibitors (methanol, ethanol, 1-propanol, ethylene glycol and diethylene glycol) in various concentrations is predicted with applying the two EOSs. To investigate the ability of the ESD EOS in predicting gas mixture hydrate formation conditions, four different gas mixtures are considered in the absence and presence of hydrate inhibitor. Generally, ESD EOS shows better results in comparison with PR EOS + WS mixing rule.

**Keywords:** Gas Hydrate, Methane, ESD EOS, PR EOS+WS Mixing Rule, Flash Calculation

### 1- Introduction

Gas hydrates may form when suitable size gases come into contact with water molecules under certain conditions of temperature and pressure. For example, in the natural gas industries hydrate formation

is a major problem in transportation as well as processing equipment. In order to reduce gas hydrate formation risks, several techniques are used in different situations [1]. Injection of chemical inhibitors such as thermo-dynamic and kinetic inhibitors are

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the most applicable and usual techniques. By using thermodynamic inhibitors, it is possible to change hydrate formation conditions; temperature is decreased and the pressure is increased. Several works have been published [2-4] in literature for the prediction of hydrate formation conditions. However, in the presence of chemical inhibitors and in the industrial conditions, only a few of their number demonstrate acceptable accuracy. Despite extensive previous works, developing a reliable and general method is still an open research field, especially for prediction of the effects of inhibitors. To model these systems two different groups of approaches are used in literature: empirical methods [5,6] and statistical thermodynamic based methods [7]. Most of the empirical methods are based on experimental data and, as a result, they are applicable only for small ranges of concentration and temperature and a small number of inhibitors. On the other hand, only the depression of the hydrate formation temperature can be calculated using these correlations [1]. Hammerschmidt [5] and Nielsen-Bucklin [6] methods are involved in this group. The second group of procedures are based on the well known statistical thermodynamic theories and the equality of water chemical potential in coexisting phases [1,4,7]. In this method, two general approaches are common, the  $\gamma$ - $\phi$  and the  $\phi$ - $\phi$ . In both approaches Van der Waals-Platteeuw algorithm is applied for the calculation of water chemical potential in the hydrate phase [7].

In the  $\gamma$ - $\phi$  approach, an activity coefficient model is used for calculating the fugacity of water in the liquid phase and an equation of

state (EOS) is used to obtain the fugacity of water in the vapor phase. Anderson and Prausnitz [8], Munck and Jørgensen [9], and Du and Guo [10] used UNIQUAC model for calculating water fugacity in the liquid phase. The Redlich-Kwong (RK) EOS, Soave-Redlich-Kwong (SRK) EOS, and modified Peng-Robinson (m-PR) EOS were used, respectively, to obtain the fugacity of water in the vapor phase. In the presence of polar inhibitors, the  $\gamma$ - $\phi$  approach presents acceptable results in the low pressure region [11,12]. In this approach the standard state for calculation of the chemical potential of species in the liquid phase is an ideal solution, however, in gas phase the ideal gas is considered as the standard state; this fact poses a thermodynamic consistency problem, especially at high pressures. In addition, for components like methane with low critical temperature, the standard-state has a hypothetical definition. Therefore, this approach fails in its description of mixtures containing supercritical components. Moreover, the number of parameters which have to be adjusted are generally more than the required adjustable parameters in the  $\phi$ - $\phi$  approach. The  $\phi$ - $\phi$  approach can be applied in wider ranges of temperature and pressure; and only pure component properties are required to adjust the existing parameters. The main weak point of using the  $\phi$ - $\phi$  approach lies in choosing a proper EOS capable of predicting the liquid phase behavior, especially for mixtures of polar and associating fluids which are commonly encountered in hydrate formation processes (water+alcohols/glycols+gas).

In order to improve the ability of the  $\phi$ - $\phi$

approach in the prediction of hydrate formation conditions, several works have been published in recent years [13-17]. Trebble-Bishnoi EOS is used by Englezos et al. [13]. Extended Fürst-Renon electrolyte EOS is applied by Zuo et al. [14], Ma et al. [15] have used Patel-Teja EOS coupled with Kurihara mixing rules. In the presence of inhibitors, like alcohols and glycols in the aqueous phase, molecular association occurs. Based on this phenomena, some researchers have used Statistical Associating Fluid Theory (SAFT) EOS. Li et al. [16] used SAFT EOS and Kontogeorgis et al. [17] used cubic plus association model. Their results show considerable improvement in prediction of hydrate formation conditions. It is observed that the introduction of association contribution proposed by Wertheim in EOSs, has shown acceptable results [16,17]. In this work, Elliott-Suresh-Donohue (ESD) EOS [18,19] which is based on thermodynamic perturbation theory (TPT), is utilized. This equation, in the simplest form, consists of ideal (*id*), repulsive (*rep*), and attractive (*att*) terms. For mixtures containing associated and polar substances other contributions can be added to the existing terms [18-20]. In the first version of ESD EOS [18] chemical theory has been used for describing association effects. However, in the latter version of this EOS [19], similar to SAFT EOS, association contribution is applied by using Wertheim theory [21].

In the present work, two different EOSs (ESD and PR+Wong Sandler mixing rule) coupled with Van der Waals and the Platteuw model [7] have been applied to predict gas hydrate formation conditions in

the presence of inhibitors like alcohols and glycols. Also, hydrate formation conditions of four different gas mixtures are calculated by using ESD EOS. Two of these calculations are performed in the absence of inhibitors and the others are considered in the presence of thermodynamic inhibitors (methanol and ethylene glycol). The results are compared in the results and discussion section.

## 2- Theoretical basis

In the incipient hydrate formation condition, the chemical potential (or fugacity) of water in the coexisting phases is equal, hence;

$$\mu_w^H = \mu_w^\alpha \quad (1)$$

In this equation,  $\mu_w^H$  and  $\mu_w^\alpha$  are the chemical potential of water in the hydrate phase and in the water phase, respectively. In this work, equilibrium conditions between hydrate (H), aqueous (L) and vapor (V) phases are considered.

### 2.1- Gas hydrate phase model

Chemical potential of gas hydrate is obtained from the Van der Waals and Platteuw model introduced by Parrish and Prausnitz [4]. In this model, gases with suitable size are considered as adsorbed in water molecule cavities. Van der Waals and Platteuw, on the basis of Langmuir adsorption concept and considering water molecule cavities as adsorbent, presented the following expression.

$$\Delta\mu_w^H = \mu_w^\beta - \mu_w^H = -RT \sum_m v_m \ln(1 - \sum_j \theta_{mj}) \quad (2)$$

$\mu_w^\beta$ , is the chemical potential of water in the hypothetical unoccupied hydrate lattice,  $v_m$

is the number of cavities of type  $m$  per water molecule in the lattice, and  $R$  and  $T$  express universal gas constant and absolute temperature, respectively. In Equation (2)  $\theta_{mj}$  is defined as the fraction of type  $m$  cavities occupied by gas molecules of type  $j$ ;

$$\theta_{mj} = \frac{C_{mj} f_j}{(1 + \sum_j C_{mj} f_j)} \quad (3)$$

where  $f_j$ , is the fugacity of component  $j$  in the vapor phase and  $C_{mj}$  is the Langmuir constant which is presented by equation (4) [4]:

$$C = \frac{4\pi}{kT} \int_0^{\infty} \exp\left[\frac{-\omega(r)}{kT}\right] r^2 dr \quad (4)$$

$k$ , is Boltzmann's constant, and  $\omega(r)$  is spherically symmetric cell potential which is the result of a summation over all gas-water interactions in the cavity. Kihara potential function is applied for describing  $\omega(r)$ :

$$\omega(r) = 2z\varepsilon \left[ \frac{\sigma^{12}}{R^{11}r} \left( \delta^{10} + \frac{a}{R} \delta^{11} \right) - \frac{\sigma^6}{R^5 r} \left( \delta^4 + \frac{a}{R} \delta^5 \right) \right] \quad (5)$$

where

$$\delta^N = \frac{\left[ \left( 1 - \frac{r}{R} - \frac{a}{R} \right)^{-N} - \left( 1 + \frac{r}{R} - \frac{a}{R} \right)^{-N} \right]}{N} \quad (6)$$

In this equation  $N$  takes the values of 4, 5, 10 or 11.

Calculation of the chemical potential difference of water in unoccupied hydrate lattice and the aqueous phase is a two step procedure which has been proposed by Parrish and Prausnitz [4].

In the first step, using a reference hydrate, defined in [4], chemical potential difference is calculated from  $P_0$  (dissociating pressure of the reference hydrate at  $T_0$ , the ice-point temperature), up to reference hydrate dissociating pressure  $P_R$  at the desired temperature,  $T$ .

$$\Delta\mu_w^L(T, P_R) = RT \left( \frac{\Delta\mu_w^{0,L}(T_0, P_0)}{RT_0} + \int_{T_0}^T \frac{\Delta v_w^L}{RT} \left( \frac{dP}{dT} \right) dT - \int_{T_0}^T \frac{\Delta h_w^L}{RT^2} dT \right) \quad (7)$$

$\Delta\mu_w^{0,L}(T_0, P_0)$  stands for chemical potential difference of water between unoccupied hydrate lattice and the aqueous phase at a reference temperature and pressure.  $\Delta v_w^L$ , and  $\Delta h_w^L$ , are molar volume and enthalpy differences between unoccupied hydrate lattice and the aqueous phase, respectively. Table (1) presents the thermodynamic properties of the unoccupied hydrate lattice. In the second step  $\Delta\mu_w^L(T, P)$  is obtained as follows,

$$\Delta\mu_w^L(T, P) = \Delta\mu_w^L(T, P_R) + \Delta v_w^L(P - P_R) - RT \ln a_w \quad (8)$$

The last term on the right side of Equation (8) takes into account the non-idealities of the aqueous phase resulted from the impurities.

**Table 1.** Thermodynamic properties of empty hydrate lattice ( $\beta$ -phase) at 0°C and zero pressure [9].

Property	Unit	Structure I	Structure II
$\Delta\mu_w$	J/mol	1264	883
$\Delta h_w^L$	J/mol	-4858	-5201
$\Delta v_w^L$	cm <sup>3</sup> /mol	4.6	5
$\Delta C_p^L$	J/mol.K	38.12 - 0.141(T - 273.15)	

## 2.2- Liquid and gas phase model

Two different procedures are common for calculation of water activity;  $\gamma$ - $\phi$  and  $\phi$ - $\phi$  procedures. In this work the  $\phi$ - $\phi$  approach is applied. Hence, according to classical thermodynamics,

$$a_i = \frac{f_i}{f_i^{pure}} = \frac{x_i\phi_i}{\phi_{i,pure}} \quad (9)$$

$\phi_i$  and  $x_i$  stand for fugacity coefficient and mole fraction of component  $i$ , respectively. In order to predict equilibrium values of  $T$  and  $P$ , the activity coefficient of water is needed in the presence of an inhibitor. In these mixtures, non-idealities due to association and/or polarity effects, has a considerable effect on hydrate formation conditions. For this reason, ESD EOS and PR+ $G^{ex}$  mixing rule EOS, have been used in the present work. ESD EOS is a perturbation based model which consists of ideal, attractive, repulsive and association contributions in order to consider the effects of different intermolecular interactions on fluid properties [18,19].

$$\frac{PV}{RT} = 1 + Z^{rep} + Z^{att} + Z^{assoc} \quad (10)$$

A more detailed description of ESD EOS can be seen in Appendix A.

In order to compare the result of ESD equation of state with conventional EOSs, PR EOS coupled with Wong-Sandler (WS) mixing rule [22] is used for calculation of water activity in the liquid and gas phases. PR EOS [23] is;

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (11)$$

In which, by using the WS mixing rule, the EOS parameters in the mixture can be defined as;

$$b = \frac{RT \sum_i \sum_j x_i x_j (b - \frac{a}{RT})_{ij}}{RT - \left[ \sum_i x_i \frac{a_i}{b_i} + \frac{G_\gamma^{ex}(T, x_i)}{C^*} \right]} \quad (12)$$

$$a = bRT \left[ \frac{G_\gamma^{ex}(T, x_i)}{C^* RT} + \sum_i x_i \frac{a_i}{b_i RT} \right] \quad (13)$$

$$\left( b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[ \left( b_i - \frac{a_i}{RT} \right) + \left( b_j - \frac{a_j}{RT} \right) \right] (1 - k_{ij}) \quad (14)$$

where  $G_\gamma^{ex}$  is the molar excess Gibbs free energy for which we have used the NRTL model.  $C^*$  is an EOS-dependent constant. Its value for the PR EOS is -0.62323.

## 3- Estimation of parameters

For ESD EOS five adjustable parameters for each associating pure component, along with binary interaction parameters for mixtures are fitted. Pure component parameters are

adjusted using vapor pressure and liquid density data [24]. The procedure of parameter estimation is the same as reference [20]. These parameters have been adjusted for water, alcohols, and glycols which have been considered to be present in the solutions. The adjusted parameters are listed in Table (2). The three pure component parameters for gas components (methane, ethane, propane, nitrogen and carbon dioxide) have been obtained from equations (A-9, A-10, and A-11) [18]. Another important factor that must be specified carefully is the number of hydrogen bonding

sites on each associating molecule. As can be seen in Table (2), 2 and 4 associating sites are considered for alcohols and glycols, respectively. The number of associating sites on water molecule is commonly considered to be 2 or 4. Considering water as a component with 2 or 4 sites, its adjustable parameters are estimated. Also, binary interaction parameters between water and gas components are obtained by using experimental hydrate formation condition data obtained from literature. These parameters are listed in Table (3).

**Table 2.** Values of  $C$ ,  $v^*$ ,  $\varepsilon^{Disp}/k$ ,  $\varepsilon^{HB}/RT_c$ ,  $K_{AB}/v^*$  and the number of associating sites for associating compounds considered in this work.

Component	No. of association sites	$C$	$v^* (cm^3/mol)$	$\varepsilon^{Disp}/k (K)$	$\varepsilon^{HB}/RT_c$	$K_{AB}/v^*$
water	2	1.6288	6.5405	332.34	2.3998	0.5644
water	4	1.6283	7.4040	336.72	1.1320	0.3265
methanol	2	1.5017	14.5431	284.49	4.0016	0.0825
ethanol	2	3.0085	17.3271	235.05	1.5368	0.1561
1-propanol	2	2.7265	23.3967	250.90	2.8598	0.0379
Ethylene glycol	4	1.2827	26.4025	296.37	3.9275	0.0395
Diethylene glycol	4	2.0588	37.0696	392.87	2.1357	0.0355

**Table 3.** Binary interaction parameters for the ESD EOS.

	methane	ethane	propane	nitrogen	carbon dioxide	water	methanol	ethanol	1-propqnl	EG	DEG
methane	0	0	0	0	0	-0.1004	0.0322	-0.0551	-0.1738	-0.003	0.0019
ethane		0		0	0	-0.0714	---	---	---	0	---
propane	0	0	0	0	0	0.0268	---	---	---	---	---
nitrogen	0	0	0	0	0	-0.0372	---	---	---	0	---
carbon dioxide	0	0	0	0	0	-0.0063	0	---	---	0	---
water	-0.1004	-0.0714	0.0268	-0.0372	-0.0063	0	-0.0381	0.0468	0.1462	0.0028	0.0107
methanol	0.0322	---	---	---	0	-0.0381	0	---	---	---	---
ethanol	-0.551	---	---	---	---	0.0468	---	0	---	---	---
1-propqnl	-0.1738	---	---	---	---	0.1462	---	---	0	---	---
EG	-0.003	0	---	0	0	0.0028	---	---	---	0	---
DEG	0.0019		---	---	---	0.0107	---	---	---	---	0

When applying the PR+WS EOS, the value of the non-randomness factor of the NRTL model ( $\alpha$ ) is set equal to 0.3, as it is chosen conventionally. The NRTL parameters ( $\tau_{ij}$  and  $\tau_{ji}$ ) are obtained by adjusting the calculated hydrate formation conditions to their respective experimental values. All of the binary interaction parameters ( $k_{ij}$ ), in the PR EOS, are considered zero. The values of the parameters  $\tau_{ij}$  and  $\tau_{ji}$  are presented in Table (4).

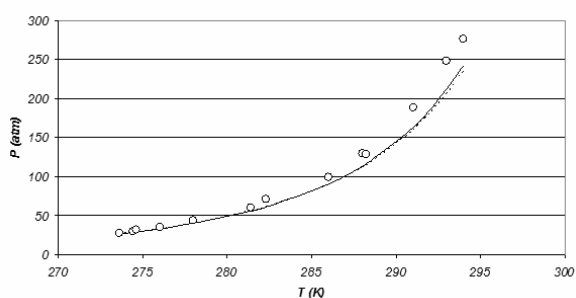
#### 4- Results and discussion

Incipient equilibrium methane hydrate formation pressure is calculated at a given temperature and overall concentration of inhibitor (methanol, ethanol, 1-propanol, ethylene glycol (EG) and diethylene glycol (DEG)) by using Parrish and Prausnitz algorithm. In order to calculate the concentration of the components in the aqueous phase (methane and inhibitor), flash calculation is coupled with hydrate formation pressure calculation algorithm. As mentioned in [25], at the incipient hydrate formation condition the amount of hydrate phase is near zero and the formed hydrate does not have a considerable effect on the mass balance of coexisting phases. Hence, two phase flash calculations can be applied to obtain hydrate

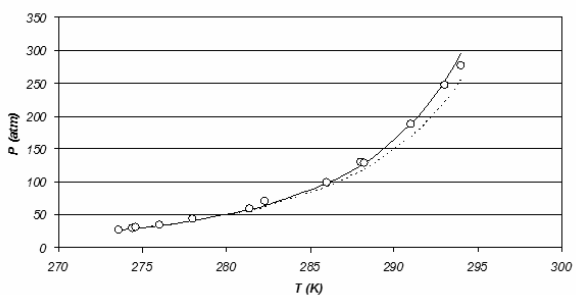
formation pressure in the related temperature and certain concentration of inhibitor. However, for prediction of composition of components present in the hydrate phase, three phase flash calculation is needed [25]. Polar inhibitors such as alcohols and glycols in the aqueous phase are considered to have 2 and 4 hydrogen bonding sites [16,17,19], respectively. Different number of associating sites has been considered on water molecule in literature. Li et al. [16] and Kontogeorgis et al. [17], have considered water as a 4-site component and Suresh and Elliot [19] have determined water as a 2-site molecule. Fig. 1 shows incipient methane hydrate formation pressure as a function of temperature for a system containing methane and water in a temperature range of 263.3-280.2 K. The results are obtained with ESD EOS by considering water as a 2-site and 4-site associating component. In this figure, binary interaction parameter for water-methane is set equal to zero. The same calculations have been repeated by adjusting binary interaction parameters between methane and water, and the results are presented in Fig. 2. It is observed from Figs. 1 and 2 that considering 2 association sites on the water molecule exhibits better results in comparison with considering 4 hydrogen bonding sites on this molecule.

**Table 4.** Binary interaction parameters used in PR+WS mixing rules for NRTL model ( $\tau_{ij}$ ).

	methane	water	methanol	ethanol	1-propanol	EG	DEG
methane	0	-0.0011	-3.5560	3.4424	-0.3003	1.6514	0.8811
water	8.6996	0	-0.7162	-0.3669	7.4573	-1.1307	-2.5333
methanol	3.5293	-0.2455	0	---	---	---	---
ethanol	-1.2789	1.9806	---	0	---	---	---
1-propanol	0.6023	-2.6589	---	---	0	---	---
EG	1.3507	5.6964	---	---	---	0	---
DEG	8.5436	34.4180	---	---	---	---	0



**Figure 1.** Methane hydrate formation pressure as a function of temperature,  $\circ$ : experimental data [1]; calculated results obtained by ESD EOS ( $k_{H_2O-CH_4} = 0$ ), — considering water as a 2-site component, .... considering water as a 4-site component.



**Figure 2.** Methane hydrate formation pressure as a function of temperature,  $\circ$ : experimental data [1]; calculated results obtained by ESD EOS, — considering water as a 2-site component ( $k_{ij} = -0.1004$ ), .... considering water as a 4-site component ( $k_{ij} = -0.1157$ ).

This is the same result that has been confirmed in reference [19] for ESD EOS. Consequently, we considered water to have two hydrogen bonding sites in all the calculations that follow. The value of binary interaction parameter of water-methane, by considering water as a 2-site component, is -0.1004 and by considering it as a 4-site component is -0.1157.

In Table 5 and Fig. 3 the performance of the ESD, PR and SRK equations of state in the prediction of methane hydrate formation pressure are compared. In Table 5 the

average absolute percent deviations of the predicted pressure (AAD%(P)) using different EOSs is presented for methane-water hydrate formation systems. In applying ESD EOS water has been considered as a 2-site and 4-site associating component with and without binary interaction parameters. Ordinary Van der Waals mixing rules have been used for PR and SRK EOSs, both with binary interaction parameters. Values of binary interaction parameters are obtained for ESD and PR EOSs. For SRK EOS the value of binary interaction parameter is obtained from reference [9]. The results show that by applying ESD EOS the accuracy of the prediction is increased in comparison with PR and SRK EOSs, even with smaller values of binary interaction coefficients. Smaller values of binary interaction coefficients can be attributed to the more predictive ability of ESD EOS, which is mainly due to the presence of association contribution in this EOS. In Fig. 3 the hydrate formation pressure is drawn as a function of temperature for ESD (2-site), PR and SRK equations of state with considering binary interaction coefficient. The more accurate prediction of ESD EOS is obvious in this Figure. SRK EOS fails to predict the correct incipient hydrate formation condition, especially at higher pressures and, as a result, this EOS was not used in further calculations. Also, in order to increase the accuracy of the prediction of PR EOS it was coupled with the WS mixing rule.

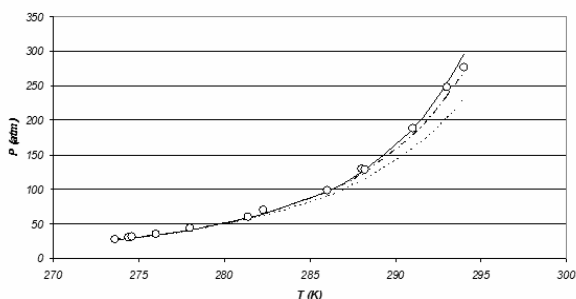
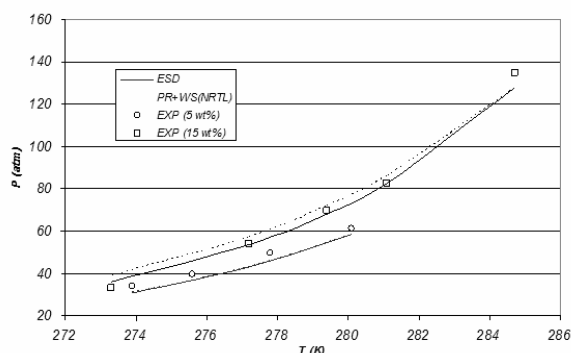
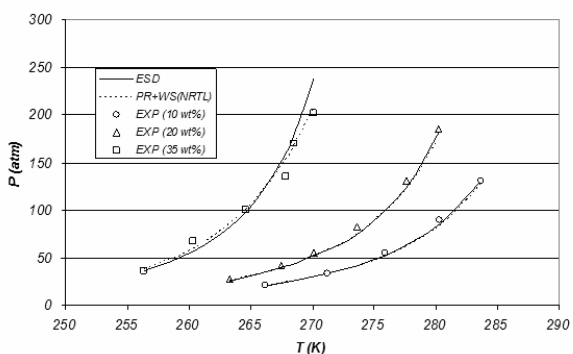
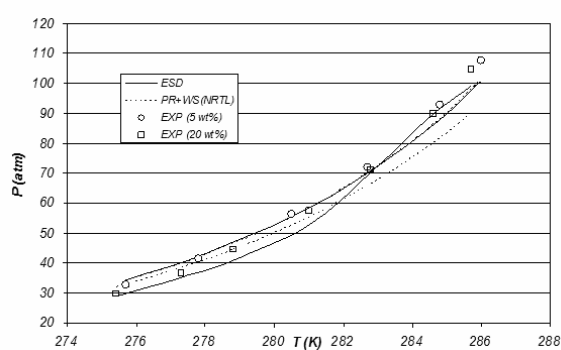
In Figs. (4-8) the results of prediction of the incipient methane hydrate formation conditions at different concentrations of various inhibitors are presented. Inhibitors



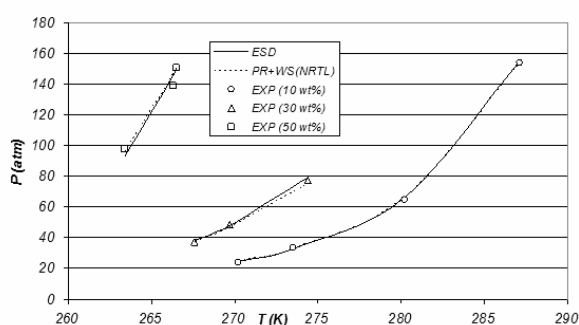
**Table 5.** Average absolute percent deviation in the prediction of hydrate formation pressure in the absence of inhibitor by different equations of state.

Equation of state	Temperature range (K)	Pressure range (atm)	AAD (P)%*
ESD,2-site, $k_{ij}=0$	273.6-294	26-242	9.53
ESD,4-site, $k_{ij}=0$	273.6-294	25.9-234.7	10.59
ESD,2-site, $k_{ij}=-0.1004$	273.6-294	26.5-296.5	3.71
ESD,4-site, $k_{ij}=-0.1157$	273.6-294	26.1-254.5	7.77
PR, $k_{ij}=0.5$	273.6-294	26.4-268.5	5
SRK, $k_{ij}=0.55$	273.6-294	26-229.9	10.59

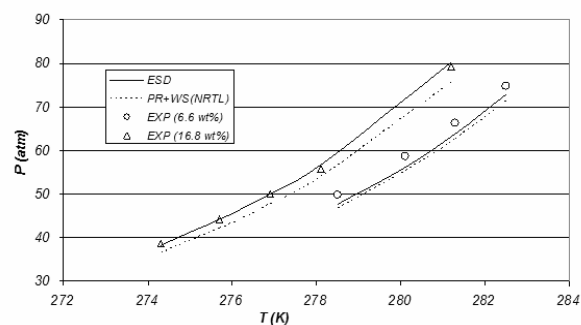
$$* \text{AAD}\%(P) = \frac{1}{N} \sum_{i=1}^N \left| \frac{P_{\text{cal}} - P_{\text{exp}}}{P_{\text{exp}}} \right| \times 1001$$

**Figure 3.** Methane hydrate formation pressure as a function of temperature,  $\circ$ : experimental data [1], — calculated results obtained by ESD EOS (2-site) ( $k_{ij}=-0.1004$ ), ... calculated results obtained by SRK EOS ( $k_{ij}=0.55$ ) [9], --- calculated results obtained by PR EOS ( $k_{ij}=0.5$ ).**Figure 5.** Methane hydrate formation pressure as a function of temperature in the presence of ethanol: data (available in [1], [26]) and predictions based on ESD EOS (—) and PR EOS by using WS mixing rules (....).**Figure 4.** Methane hydrate formation pressure as a function of temperature in the presence of methanol: data (available in [1]) and predictions based on ESD EOS (—) and PR EOS by using WS mixing rules (....).**Figure 6.** Methane hydrate formation pressure as a function of temperature in the presence of 1-propanol: data (available in [27]) and predictions based on ESD EOS (—) and PR EOS by using WS mixing rules (....).

like methanol, ethanol, 1-propanol, EG and DEG in water are used in this work. The results for ESD EOS are compared with PR+WS(NRTL) EOS. As discussed above, in applying the ESD EOS water and alcohols are considered as 2-site and glycols as 4-site associating compounds. Binary interaction parameters are adjusted in mixing rules for both EOSs by using the hydrate formation pressure data. Two adjustable interaction parameters in each mixture are needed for ESD EOS, which is presented in Table 3.



**Figure 7.** Methane hydrate formation pressure as a function of temperature in the presence of ethylene glycol (EG): data (available in [1]) and predictions based on ESD EOS (—) and PR EOS by using WS mixing rules (.....).



**Figure 8.** Methane hydrate formation pressure as a function of temperature in the presence of diethylene glycol (DEG): data (available in [28]) and predictions based on ESD EOS (—) and PR EOS by using WS mixing rules (.....).

In the case of PR+WS(NRTL) EOS, generally 6 adjustable parameters related to NRTL energy parameters must be fitted based on experimental hydrate formation condition data, while two of these parameters (methane-water) are fitted separately and are used as constants in further fittings. Binary interaction coefficients in Equation (15) have been considered zero for all the binaries present in the solution. The adjusted parameters are presented in Table 4. Average absolute percent deviation of hydrate formation pressure are presented in Table 6.

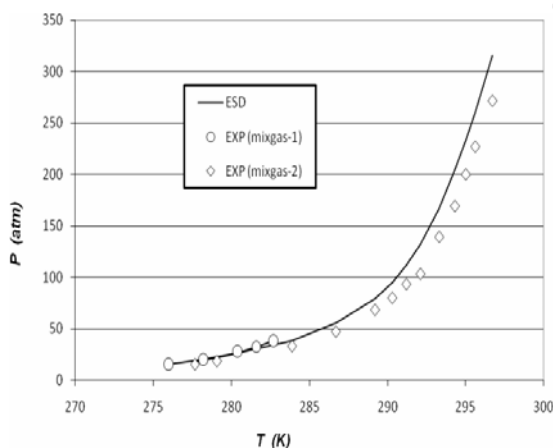
**Table 6.** Average absolute percent deviation in the prediction of hydrate formation pressure in the presence of inhibitor by ESD and PR+WS(NRTL) equations of state.

Gas	Concentration of inhibitor in the aqueous phase (wt %)	T range (K)	P range (atm)	ADD% (P) for ESD EOS	ADD% (P) for PR+WS(NRTL)*
methane	10 % methanol	266.2-283.7	20.3-130.6	3.15	4.21
	20% methanol	263.3-280.2	25.8-181.2	5.84	6.11
	35% methanol	256.3-270.1	36.4-238.2	9.79	5.77
	5 % ethanol	273.9-280.1	31-58.4	7.14	6.76
	15% ethanol	273.3-284.7	36-128.1	3.15	7.2
	5% 1-propanol	275.7-286	34.2-100.8	3.78	3.47
	20% 1-propanol	275.4-285.7	28.9-99.1	4.10	6.77
	10% EG	270.2-287.1	24.7-154.8	2.12	2.61
	30% EG	267.6-274.4	37.9-78.9	2.13	2.64
	50% EG	263.4-266.5	93.1-150.4	3.10	2.17
	6.6% DEG	278.5-282.5	47.6-72.9	3.79	5.53
	16.8% DEG	274.3-281.2	38.3-80	0.8	4.44

$$* \text{AAD} \% (P) = \frac{1}{N} \sum_{i=1}^N \left| \frac{P_{\text{cal}} - P_{\text{exp}}}{P_{\text{exp}}} \right| \times 100$$

As it is observed from the results in Figs 4-8 and Table 6, both models can predict hydrate formation pressure with reasonable accuracy, however, generally the results obtained by ESD EOS are more accurate than PR+WS (NRTL). In the case of glycol as an inhibitor, the superiority of ESD EOS is more evident.

In order to evaluate the ability of the ESD EOS in predicting gas mixture hydrate formation conditions, different gas mixture data are used in the presence and absence of inhibitors (methanol and EG). Required binary interaction coefficients for ESD EOS are used from Table 3. Figures 9 and 10 and Table 7 present the results of these calculations. As it is observed from these results, very good prediction is obtained by ESD EOS.

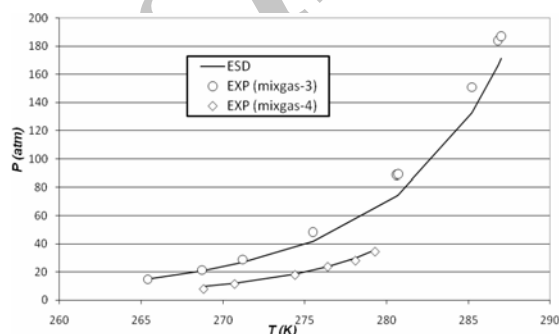


**Figure 9.** Hydrate formation pressure as a function of temperature in the absence of thermodynamic inhibitors:  $\circ$ : experimental data of mixgas-1 [1],  $\diamond$ : experimental data of mixgas-2 [30] and predictions based on ESD EOS (—).

## 5- Conclusions

In this work, Elliot-Suresh-Donohue and Peng-Robinson+Wong-Sandler mixing rule

equations of state have been used to calculate hydrate formation pressure at different temperatures in the presence of polar inhibitors. Parrish and Prausnitz hydrate formation algorithm coupled with two phase flash calculations have been carried out. The pure component parameters for the ESD EOS and all the binary interaction parameters required are adjusted in this work. The inhibitors like methanol, ethanol, 1-propanol, ethylene glycole and diethylene glycole are considered.



**Figure 10.** Hydrate formation pressure as a function of temperature in the presence of thermodynamic inhibitor:  $\circ$ : experimental data of mixgas-3 [1],  $\diamond$ : experimental data of mixgas-4 [1] and predictions based on ESD EOS (—).

In applying the ESD EOS, water is considered as a 2-site component to obtain more accurate results. In the presence of polar inhibitors, ESD EOS has predicted methane hydrate formation pressure with good accuracy. Meanwhile, PR EOS together with WS mixing rule can also predict methane hydrate formation in the presence of inhibitors, however, its accuracy is lower than that of the ESD EOS.

**Table 7.** Average absolute percent deviation in the prediction of gas mixture hydrate formation pressure in the absence and presence of inhibitors by ESD EOS.

Mixture	mol% of inhibitor	Temperature range (K)	ADD(P)%*
Mixed-gas 1 C <sub>2</sub> H <sub>6</sub> (5.31), , CO <sub>2</sub> (94.69) mol%	No inhibitor	276.0-282.7	1.79
Mixed-gas 2 CH <sub>4</sub> (93.2), C <sub>2</sub> H <sub>6</sub> (4.25), C <sub>3</sub> H <sub>8</sub> (1.61), N <sub>2</sub> (0.43), CO <sub>2</sub> (0.51) mol%	No inhibitor	277.7-296.7	17.57
Mixed-gas 3 CH <sub>4</sub> (90.09), , CO <sub>2</sub> (9.91) mol%	Methanol 0.0588 mol%	265.4-287	9.6
Mixed-gas 4 CH <sub>4</sub> (6.83), C <sub>2</sub> H <sub>6</sub> (0.38), N <sub>2</sub> (4.26), CO <sub>2</sub> (88.53) mol%	Ethylene Glycol 0.0312 mol%	268.8-279.3	2.17

$$*AAD\%(P) = \frac{1}{N} \sum_{i=1}^N \left[ \left| \frac{P_{cal} - P_{exp}}{P_{exp}} \right| \right] \times 100$$

For equations like ESD, only combining rules with binary interaction energy parameters are required, while using cubic equations of state with the WS mixing rule require two additional parameters in the  $G^{ex}$  part to be adjusted. This fact is an indication of the more predictive ability of the ESD equation of state.

Our results show that in spite of the simplicity of the ESD EOS, reasonable results are obtained for complex mixtures including alcohols in hydrate formation calculations.

Also, the results revealed that using Parrish and Prausnitz algorithm to predict hydrate formation pressures in the presence of inhibitors has some shortcomings. Due to the definition of the temperature range for reference gas hydrate [4], prediction in temperatures lower than 253 K is not possible with this algorithm.

## 6- Appendix A

Elliot-Suresh-Donohue (ESD) EOS in terms of compressibility factor is defined as the

sum of three terms [18].

$$\frac{PV}{RT} = 1 + Z^{rep} + Z^{att} \quad (A-1)$$

Or equally;

$$\frac{PV}{RT} = 1 + \frac{\langle 4c\eta \rangle}{1 - 1.9\eta} - \frac{z_m \langle q\eta Y \rangle}{1 + k_1 \langle \eta Y \rangle} \quad (A-2)$$

In this equation,  $\eta$  is the reduced number density,  $z_m$  and  $k_1$  are 9.49 and 1.7745, respectively. Other terms in equation (A-1) are defined as;

$$\eta = \frac{N}{V} \sum x_i v_i^* \quad (A-2a)$$

$$\langle 4c\eta \rangle = \frac{4N}{V} \sum \sum x_i x_j (c v^*)_{ij} \quad (A-2b)$$

$$\langle q\eta Y \rangle = \frac{N}{V} \sum \sum x_i x_j (q v^*)_{ij} Y_{ij} \quad (A-2c)$$

$$(c v^*)_{ij} = \frac{(c_i v_j^* + c_j v_i^*)}{2} \quad (A-2d)$$

$$(qv^*)_{ij} = \frac{(q_i v_j^* + q_j v_i^*)}{2} \quad (\text{A-2e})$$

$$\varepsilon_{ij} = (\varepsilon_{ii} \varepsilon_{jj})^{0.5} (1 - k_{ij}) \quad (\text{A-2f})$$

$$Y_{ij} = \exp(\beta \varepsilon_{ij}) - k_2 \quad (\text{A-2g})$$

$$\langle \eta Y \rangle = \frac{\langle q \eta Y \rangle}{\sum x_i q_i} \quad (\text{A-2h})$$

$c, v^*, \varepsilon, k_2, k_3$  are shape factor, characteristic size parameter, potential energy well depth, 1.0617 and 1.90476, respectively.

In order to consider association effect, one extra term is added to equation (A-1). This extra term is based on Wertheim's theory [19].

$$\frac{A^{assoc}}{RT} = \sum_i x_i \left[ \sum_{A_i} \left[ \ln X_i^A - \frac{X_i^A}{2} \right] + \frac{1}{2} M_i \right] \quad (\text{A-3})$$

where  $M_i$  is the number of associating sites on a molecule,  $X_i^A$  is defined as the mole fraction of molecules  $i$  not bonded at site A and is given by,

$$X_i^A = \left[ 1 + N_{av} \sum_j \sum_{B_j} x_j \rho_0 X_j^B \Delta_{A_i B_j} \right]^{-1} \quad (\text{A-4})$$

The summation on  $j$  is over all molecules and the summation on  $B_j$  is over all sites on molecules  $j$ . An expression for  $Z^{assoc}$ , with respect to the definition of excess Helmholtz energy, can be obtained;

$$Z^{assoc} = \eta \left[ \frac{\delta(A^{assoc}/N_0 kT)}{\delta \eta} \right]_{N_0, T} \quad (\text{A-5})$$

In Equation (A-4),  $\Delta_{A_i B_j}$ , the cross-associating term is assumed as follow;

$$\Delta_{A_i B_j} = \Delta_{B_i A_j} = (\Delta_{A_i B_i} \Delta_{A_j B_j})^{0.5} \quad (\text{A-6})$$

In Equation (A-6)  $\Delta_{AB}$  is defined as;

$$\Delta_{AB} = \frac{1}{\rho_0} \left( \frac{\eta_0 F_{AB} K_{AB}}{1 - 1.9 \eta_0 v^*} \right) \quad (\text{A-7})$$

where,

$$F_{AB} = \exp\left(\frac{\varepsilon_{HB}}{RT}\right) - 1 \quad (\text{A-8})$$

In Equations (A-7) and (A-8)  $K_{AB}$  and  $\varepsilon_{HB}$  are defined as measure of bonding volume available to the molecule and hydrogen-bonding square-well depth, respectively. ESD parameters are similar to SAFT EOS in number and nature. For associating components there are five parameters ( $c, v^*, \varepsilon^{disp}, \varepsilon^{HB}$  and  $K_{AB}$ ) which should be adjusted for each component with experimental data. But for non-associating components there are three necessary parameters ( $c, v^*$  and  $\varepsilon$ ) which can be defined by some relations based on critical pressure and temperature of each component [18].

$$c = 1 + 3.535\omega + 0.533\omega^2 \quad (\text{A-9})$$

$$\frac{\varepsilon}{k} = T_c \frac{1 + 0.945(c-1) + 0.13(c-1)^2}{1.023 + 2.225(c-1) + 0.478(c-1)^2} \quad (\text{A-10})$$

$$v^* = \frac{kT_c}{P_c} \frac{0.0312 + 0.087(c-1) + 0.008(c-1)^2}{1 + 2.455(c-1) + 0.732(c-1)^2} \quad (\text{A-11})$$

## References

- [1] Sloan, E. D. and Koh, C. A., Clathrate hydrates of natural gases; Taylor and Francis Group, 3<sup>rd</sup> ed., 643-679 (2008).
- [2] Ng, H.J., and Robinson, D.B. "A Method for Predicting the Equilibrium Gas Phase Water Content in Gas-Hydrate Equilibrium", *Ind. Eng. Chem. Fundam.*, 15, 293-298, (1976).
- [3] Klauda, J. B. and Sandler, S. I., "A Fugacity Model for Gas Hydrate Phase Equilibria", *Ind. Eng. Chem. res.* 39, 3377-3386, (2000).
- [4] Parrish, W. R. and Prausnitz, J. M., "Dissociation Pressures of Gas Hydrate Formed by Gas Mixtures", *Ind. Eng. Chem. Process. Des. Develop.* 11; 1, 26-35., (1972).
- [5] Carroll, J., *Natural gas hydrate: A guide for engineers*; Elsevier Science & Technology Books, 1<sup>st</sup> ed., P. 50 (2002).
- [6] Nielsen, R.B. and Bucklin, R.W, "Why not use methanol for hydrate control?", *Hydro. Proc.* 62; 4, 71-78, (1983).
- [7] Van der waals, J. H., and Platteeuw, J. C. "Clathrate Solutions", *adv. Chem. phys.* 2(1), 1-60, (1959).
- [8] Anderson, F. E. and Prausnitz, J. M. "Inhibition of gas hydrates by methanol", *AIChE J.* 32(8), 1321-1333, (1986).
- [9] Munck, J. and Jørgensen, S. S., "Computations of the formation of gas hydrates", *Chem. Eng. Sci.* 43; 10, 2661-2672, (1988).
- [10] Du, Y. and Guo, T. M., "Prediction of hydrate formation for systems containing methanol", *Chem. Eng. Sci.* 45; 4, 893-900, (1990).
- [11] Orbey, H. and Sandler, S. I., *Modeling Vapor-Liquid Equilibria: cubic equations of state and their mixing rules*; Cambridge University Press, 1<sup>st</sup> ed., P. 17 (1998).
- [12] Patel, N. C., Abovsky V. and Watanasiri S. "Calculation of vapor-liquid equilibria for a 10-component system: comparison of EOS, EOS-G<sup>E</sup> and G<sup>E</sup>-Henry's law models", *Fluid Phase Equilib.* 185; 397-405, (2001).
- [13] Englezos, P., Huang, Z. and Bishnoi, P. R. "Prediction of Natural Gas Hydrate Formation Conditions in the Presence of Methanol Using the Trebble-Bishnoi Equation of State", *J. Can. Pet. Technol.* 30, 148-155, (1991).
- [14] Zuo, J. Y., Zhang, D., and Ng, H. J. "Representation of Hydrate Phase Equilibria in Aqueous Solutions of Methanol and Electrolytes Using an Equation of State", *Energy & Fuels* 14, 19-24, (2000).
- [15]. Ma, Q. L., Chen, G. J. and Guo, T. M. "Modeling the gas hydrate formation of inhibitor containing systems", *Fluid Phase Equilib.* 205, 291-302, (2003).
- [16] Li, X. S., Wu H. J. and Englezos P. "Prediction of Gas Hydrate Formation Conditions in the Presence of Methanol, Glycerol, Ethylene Glycol, and Triethylene Glycol with the

- Statistical Associating Fluid Theory Equation of State", *Ind. Eng. Chem. Res.* 45, 2131-2137, (2006).
- [17] Kontogeorgis, G. M., Folas G. K., Muro-Sūné, N., Solms N. V., Michelsen M. L. and Stenby E. H., "Modelling of associating mixtures for applications in the oil & gas and chemical industries", *Fluid Phase Equilib.* 261, 205–211, (2007).
- [18] Elliott, J. R., Suresh, S. J. and Donohue, M. D., "A simple equation of state for non-spherical and associating molecules", *Ind. Eng. Chem. Res.* 29, 1476-1485, (1990).
- [19] Suresh, S. J. and Elliott, J. R., "Multiphase equilibrium analyses of complex mixtures via an association-based equation of State", *Ind. Eng. Chem. Res.* 31, 2783-2794, (1992).
- [20] Alavi, F. and Feyzi, F., "Extension of the Elliott-Suresh-Donohue Equation of State to Dipolar Systems", *Ind. Eng. Chem. Res.* 48, 5035–5045, (2009).
- [21] Chapman, W. G., Gubbins, K. E., Jackson, G. and Radoz, M., "New Reference Equation of State for Associating Liquids", *Ind. Eng. Chem. Res.* 29, 1709-1721, (1990).
- [22] Wong, D. S. H. and Sandler, S. I. A., "A theoretically correct mixing rule for cubic equations of state", *AIChE J.* 38(5), 671–680, (1992).
- [23] Peng, D. Y. and Robinson, D. B., "A New Two-constant Equation of State", *Ind. Eng. Chem. Fundam.* 15, 59-64, (1976).
- [24] Buford, D. S. and Srivastava R. Thermodynamic data for pure compounds A&B; Elsevier Science & Technology Books, (1986).
- [25] Cole W. A. and Goodwin S. P., "Flash calculations for gas hydrates: A rigorous approach", *Chem. Eng. Sci.* 45, 569-573, (1990).
- [26] Mohammadi, A. H., Afzal, W. and Richon D. J., "Experimental Data and Predictions of Dissociation Conditions for Ethane and Propane Simple Hydrates in the Presence of Distilled Water and Methane, Ethane, Propane, and Carbon Dioxide Simple Hydrates in the Presence of Ethanol Aqueous Solutions", *Chem. Eng. Data* 53, 73–76, (2008).
- [27] Maekawa, T., "Equilibrium conditions for clathrate hydrates formed from methane and aqueous propanol solutions", *Fluid Phase Equilib.* 267, 1–5, (2008).
- [28] Afzal, W., Mohammadi, A. H., and Richon, D. J., "Experimental Measurements and Predictions of Dissociation Conditions for Methane, Ethane, Propane, and Carbon Dioxide Simple Hydrates in the Presence of Diethylene Glycol Aqueous Solutions", *Chem. Eng. Data*, 53, 663–666, (2008).
- [29] Ross, M. J., and Toczykint, L. S. J., "Hydrate Dissociation Pressures for Methane or Ethane in the Presence of Aqueous Solutions of Triethylene Glycol", *Chem. Eng. Data* 37, 488-491, (1992).
- [30] Wilcox, W. I., Carson, D. B. and Katz, D. L., 1941. Natural gas hydrates, *Ind. Eng. Chem.* 33, 662-665.