Modelling triethylene glycol – water system for natural gas dehydration

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Absorption by means of triethylene glycol is one of the most popular methods for natural gas dehydration. In spite of this popularity, thermodynamic modelling of the system TEG-water is still rather inaccurate, especially with regard to systems at high temperature and high TEG concentration, which are typical conditions in the glycol regeneration unit. Available experimental data were selected and correlated by means of a thermodynamic model based on the Peng-Robinson equation of state. Obtained results show that the model provides a good representation of experimental data and leads to reliable prevision on typical plant data.

1. Introduction

Among methods available for natural gas dehydration, absorption by means of triethylene glycol (TEG) has been used for many decades and remains the most popular. Nowadays very low natural gas dew points are required for gas transmission by pipelines, corresponding to a reduction of water content, on average, down to 70–120 mg/Nm³ (Huffmaster, 2004). In order to attain these strict specifications, TEG regeneration step is the crucial part of the dehydration process. If the water-rich TEG exiting the absorption column is distilled at atmospheric pressure, TEG can not be regenerated to levels above 98.8–98.9 % by weight. This is caused by the reboiler operating temperature, which can not be fixed above 204 °C. In fact, this temperature must be regarded as an upper limit for TEG processing, because of thermal degradation at higher values (Steele et al., 1996; Rajeh and Szirtes, 1991). In order to reach current specifications, it is necessary to regenerate TEG up to levels in the range 99.0–99.95 % by weight. To attain these regeneration levels several alternative processes have been proposed, requiring an accurate representation of TEG–water phase equilibria, especially in the zone close to water infinite dilution and at high temperature.

In spite of this strict requirements, thermodynamic modelling of the system TEGwater is still rather inaccurate, especially with regard to systems at high temperature and very high TEG concentration. For these reasons, improving the accuracy of thermodynamic modelling of the system TEG-water is expected to have a significant effect on dehydration process design and operating parameters selection.

2. Literature review

Phase equilibria for TEG-water system have been investigated since the 50's, but experimental data reported in the literature until the 70's show large discrepancies. Furthermore, data were generally correlated by using empirical equations. In particular,

water infinite dilution data were extrapolated from measurements at low water concentration. Most recent and accurate experimental data on this subject, according to GPSA (1994), are those by Herskowitz and Gottlieb (1984) and Parrish et al. (1986).

Herskowitz and Gottlieb measured water activity coefficient of TEG-water liquid mixtures by means of an isopiestic method. Measurements refer to water molar fraction from 0.2 to 0.95, at 297.6 and 332.6 K. Parrish et al. measured infinite dilution activity coefficient of water by means of the gas-liquid partition chromatography (GLPC) method. Experimental temperature was varied in the range 300-380 K. Obtained data were grouped together with data of Herskowitz and Gottlieb and correlated by an empirical model. Operating in this way the dependence of water activity coefficient on both composition and temperature was expressed. Also Bestani and Shing (1989) studied TEG-water system, measuring infinite dilution activity coefficient of water by means of the GLPC method. Temperature of the measurements ranged from 323.15 to 383.15 K. Obtained values overestimate data of Parrish et al. of about 15 %. Even though Parrish et al. correlation is recommended by GPSA, there are some arguments supporting Bestani and Shing data. For example, if data of Herskowitz and Gottlieb are extrapolated to water infinite dilution, by using van Laar model, values closer to Bestani and Shing than to Parrish et al. data are obtained. For these reasons, neither Parrish et al. nor Bestani and Shing data were excluded a priori in this work.

As for thermodynamic modelling, an approach based on TST cubic equation of state (TST-EOS) is reported in a recent work on this subject (Twu et al., 2005). The proposed model was used for the correlation of Herskowitz and Gottlieb and Parrish et al. data. Good results were obtained, even though a high number of binary parameters were employed for the correlation of experimental data.

3. Thermodynamic modelling

In this work, thermodynamic behaviour of the system TEG–water was represented by means of the Peng and Robinson equation of state (PR-EOS). Models based on cubic equation of state generally guarantee good phase equilibrium predictions over a wide range of temperature and pressure, especially when supercritical components are present in the system. This is important in view of modelling the multicomponent system in the natural gas dehydration units, where it is necessary to account for the presence of gases and for the high operating pressure of the absorption column.

As for mixture properties, van der Waals mixing rules including one binary interaction parameter (k_{12}) were assumed in order to calculate the attractive parameter (a_m) and covolume (b_m) as a function of mixture molar fractions (x_i) . The mixture attractive parameter and covolume are given by:

$$a_m = \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j a_{ij}; \qquad b_m = \sum_{i=1}^2 x_i b_i$$
(1)

where $a_{11}=a_1$, $a_{22}=a_2$, b_1 and b_2 refer to pure components, whereas for $i \neq j$ it is assumed:

$$a_{12} = a_{21} = \sqrt{a_1 a_2 \cdot (1 - k_{12})} \tag{2}$$

Critical properties and acentric factors of pure compounds are required in order to calculate a_i and b_i . Experimental critical temperature, pressure and acentric factor for water were taken from Reid et al. (1988). On the contrary, since TEG critical properties are not available, they must be calculated using a previsional method. In this work, the Ambrose group contribution method, as reported in Reid et al., was employed to estimate TEG critical properties. TEG normal boiling point, required for the application of the Ambrose method, was recently measured and reported by Steele et al. (2002). TEG acentric factor was evaluated according to its definition, using vapour pressure data reported in Steele et al. (2002). Critical parameters, acentric factors, normal boiling temperatures and molecular weights of the two compounds are reported in Table 1.

Prior to employing the thermodynamic model on binary mixture calculations, a comparison between calculated and experimental TEG vapour pressures, which are reported in Steele et al. (2002), was carried out. TEG vapour pressure prediction is quite satisfactory even though the proposed model leads to a slight overestimation.

As for mixture calculations, in order to improve the accuracy of the model in representing phase equilibria over a wide range of temperature, k_{12} was allowed to vary with temperature as a linear function:

$$k_{12} = \alpha \cdot T + \beta \tag{3}$$

The parameters α and β must be calculated from regression of experimental data referred to the binary mixture. On the whole, α and β are the only regression parameters requested by the proposed model

Two different set of data were employed for the parameter calculation. The first set of data, labelled HP, is composed of data from Herskowitz and Gottlieb together with data from Parrish et al., whereas the second, labelled HB, is composed of data from Herskowitz and Gottlieb together with data from Bestani and Shing .

In order to perform data regression, water activity coefficient (γ_1) and water activity coefficient at infinite dilution (γ_1^{∞}) were evaluated by means of the PR-EOS, which contains the optimization parameters in the mixing rules. The following objective function was introduced for the minimization:

$$\phi = \sum_{i=1}^{N} \left(\gamma_{1,\exp}(T_i, x_{1,i}) - \gamma_{1,calc}(T_i, x_{1,i}, \alpha, \beta) \right)^2 + p \cdot \sum_{i=1}^{M} \left(\gamma_{1,\exp}^{\infty}(T_i) - \gamma_{1,calc}^{\infty}(T_i, \alpha, \beta) \right)^2$$
(4)

where *N* and *M* stand for the number of experimental determinations of γ_1 and γ_1^{∞} , respectively, and *p* is a weight of the objective function. With the HP set of data, the optimal expression for k_{12} resulted:

 $P_C(kPa)$ Compound $T_C(K)$ Mw $T_B(K)$ ω Water (1) 373.2 647.3 22120 0.344 18.02 TEG (2) 561.7 806.3 3958 0.563 150.17

Table 1: critical properties, acentric factors and molecular weights

 $k_{12,HP} = 0.000482 \cdot T - 0.3935$

whereas with the HB set of data it was obtained:

$$k_{12 HB} = 0.000710 \cdot T - 0.4605 \tag{6}$$

4. Discussion

Fig. 1 shows the comparison between calculated and experimental γ_1^{∞} , referring both to Parrish et al. and Bestani and Shing. Corresponding continuous lines were calculated by means of the PR-EOS model with optimal parameters calculated from Eq. 5 and Eq. 6, respectively. As it can be seen, PR-EOS model provides a good correlation of both data sets. As reported in Table 2, absolute average deviation (AAD%) for the two sets of data is around 1 % in both cases, which is approximately the same deviation showed by the TST-EOS model on γ_1^{∞} data. Bestani and Shing obtained a good correlation of their data assuming $\ln \gamma_1^{\infty}$ proportional to 1/T. On the other hand, Parrish et al. provided an empirical model that expresses the dependence of γ_1 on both temperature and composition. Their model leads to an AAD% above 3 % on their γ_1^{∞} data.

As for the dependence of water activity coefficient on composition, Fig. 2 shows a comparison between data reported in Herskowitz and Gottlieb and previsions by the model proposed in this work, expressed by both k_{12} correlations. A good representation of data is obtained at 297.6 K, whereas at 332.6 K the correlation is not completely satisfactory in both cases. As it can be seen from Table 2, AAD% obtained averaging on data at both temperatures, is around 2.6 %. This value is only slightly higher than the



Fig. 1: Infinite dilution water activity coefficient data. \triangle *: Experimental data of Parrish et al. compared to calculated curve with* k_{12} *from HP data set.* \Box *: Experimental data of Bestani and Shing compared to calculated curve with* k_{12} *from HB data set.*

Table 2 : AAD % between experimental data and calculated values with different models

Experimental	PR-EOS	PR-EOS	TST-EOS	Van Laar	Bestani and	Parrish et al.
data	$(k_{12} \text{ from Eq. 5})$	(k ₁₂ from Eq. 6)			Shing	
Herskowitz	2.49	2.75	2.33	0.29	-	2.48
and Gottlieb						
Parrish et al.	1.26	-	1.03	23.67	-	3.42
Bestani and	-	0.99	-	11.27	0.60	-
Shing						

one obtained by TST-EOS or Parrish et al. model. If regression is performed according to van Laar model, an excellent result is obtained (AAD% = 0.29 %). According to this model, γ_1^{∞} results equal to 0.616 at 297.6 K and 0.748 at 332.6 K. From these data predicted values of γ_1^{∞} at higher temperatures can be calculated but extremely large deviations from experimental data are found (see Table 2).

Another investigation on model reliability can be carried out on typical data referred to regeneration units of natural gas dehydration plants. Performing an atmospheric distillation it is known from plant experience that operating the reboiler around 200-204 °C, water in the liquid phase results to be around 1-1.2 % by weight at pressure around 1.1–1.2 atm. Since equilibrium pressure can be expressed as:

$$P = p_{s1}\gamma_1 x_1 + p_{s2}\gamma_2 x_2 \tag{7}$$

Since the liquid phase is near to pure TEG, $\gamma_2 \cong 1$ and $\gamma_1 \cong \gamma_1^{\infty}$; therefore Eq. (8) gives:



Fig. 2: water activity coefficient as a function of water molar fraction at two different temperatures. Markers: experimental data (Herskowitz and Gottlieb). \square : 297.6 *K.* \triangle :332.6 *K. Continuous lines:* k_{12} *from Eq.5. Dashed lines:* k_{12} *from Eq. 6.*

Substituting in Eq. (8) typical reboiler operating values and calculating p_{S2} from Steele et al. (2002), it is found that γ_1^{∞} at 200-204 °C can be in the range 0.67-0.95, with more likely values expected to be in the range 0.74–0.86. The model proposed in this work lead to a value equal to 0.7435 or 0.9273 if Eq. (5) or Eq. (6) is employed, respectively. The model based on TST-EOS, with the optimal parameters reported in Twu et al., lead

to γ_1^{∞} equal to 0.7960. On the contrary if the Parrish model is used for extrapolation, at

204 °C it is found γ_1^{∞} equal to 0.9477, whereas the extrapolation of Bestani and Shing gives an unreliable value equal to 1.

5. Conclusions

Models based on cubic equations of state, like TST-EOS and the model proposed in this work, provide the best agreement with existing experimental data and are capable of predicting reliable extrapolation at 204 °C, according to typical plant data. Furthermore, the model proposed in this work leads to better predictions of TEG vapour pressure, with respect to TST model, if parameters reported in Twu et al. are considered. Moreover, the proposed model requires just two binary parameters to be obtained from fitting of experimental data, instead of five as it is required by the model developed by Twu et al. for TEG-water system.

It has to be pointed out that according to the two sets of data taken into consideration, quite different $k_{12}(T)$ functions are obtained for the proposed model, leading to substantial differences in the extrapolation. It is apparent that further experimental analysis is necessary on TEG-water system, especially at higher temperatures and in the zone closer to water infinite dilution.

6. References

Bestani, B. and K.S. Shing, 1989, Fluid Phase Equilbiria, 50, 209.

- GPSA Engineering Data Book, 1994, Tenth Edition, First revision, Gas Processors Suppliers Association, Tulsa, OK.
- Herskowitz, M. and M. Gottlieb, 1984, Journal of Chemical and Engineering Data, 29, 173.
- Huffmaster, M.A., 2004, Gas Dehydration Fundamentals, Proceedings of the Laurance Reid Gas Conditioning Conference.
- Parrish, W.R., K.W. Won and M.E. Baltatu, 1986, Proceedings of the 65th Annual GPA Convention, San Antonio, TX, March 10-12.
- Rajeh, A.O. and L. Szirtes, 1991, Journal of Thermal Analysis, 37, 777.
- Reid, R.C., J.M. Prausnitz and B.E. Poling, 1988, The Properties of Gases and Liquids, Fourth Edition, Mc Graw Hill International Editions.
- Steele, W.V., R.D. Chirico, S.E. Knipmeyer and A. Nguyen, 1996, Journal of Chemical and Engineering Data, 41, 1255.
- Steele, W.V., R.D. Chirico, S.E. Knipmeyer and A. Nguyen, 2002, Journal of Chemical and Engineering Data, 47, 689.
- Twu, C.H., V. Tassone, W.D. Sim and S. Watanasiri, 2005, Fluid Phase Equilbiria, 228-229, 213.