

New numerical model for solubility of light alkanes in triethylene glycol

Alireza Bahadori[†]

National Iranian South Oil Co. (NISOC), Process Engineering Department, Main office, Ahvaz, Iran

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Abstract—A new numerical model, which covers the full range of dehydration-plant operating conditions and wide range of experimental data results, estimates the amount of CH_4 , C_2H_6 and C_3H_8 absorbed per volume of triethylene glycol (TEG) circulated vs. the partial pressure of light alkanes and the absorber temperature. This article shows that the proposed numerical approach is more accurate than routine equation of states in predicting the solubility of light hydrocarbons in TEG. This article also provides comparisons between the results of the proposed model with experimental data and an equation of state results.

Key words: Alkane, Solubility, Gas Dehydration, Numerical Model

INTRODUCTION

TEG has a tendency to remove the hydrocarbons. Hydrocarbon solubility is a major factor when considering the use of a physical solvent. Quantifying this amount of absorption is critical in order to minimize hydrocarbon losses or to optimize hydrocarbon recovery.

Physical solvents all absorb hydrocarbons to some extent. In most cases the hydrocarbon removal is undesirable and should be minimized. In some cases, which includes hydrocarbon recovery [1], the pickup should be maximized or at least optimized. Both temperature and pressure affect hydrocarbon absorption. In general, the lower the temperature and the higher the pressure, the more hydrocarbons will be dissolved in the physical solvent. In some cases, however, the hydrocarbon solubility actually increases with temperature [2].

Glycol dehydration of natural gas employs triethylene glycol (TEG) or diethylene glycol (DEG) to remove water from the gas stream. The most commonly used glycol is triethylene glycol. Diethylene glycol and ethylene glycol may also be used in dehydration applications; however, DEG and EG are often not considered due to dry gas water content requirements. TEG has a higher degradation temperature and can be regenerated to a higher lean concentration with no modifications to the standard regenerator reboiler. However, EG and DEG can meet water content specifications when used with enhanced regeneration systems. Enhanced regeneration is any system that improves glycol regeneration to achieve a “leaner” or more concentrated glycol solution. Enhanced regeneration could be the injection of stripping gas into the reboiler, azeotropic regeneration [2], or other proprietary processes. The costs associated with the use of EG or DEG would be increased glycol makeup and some form of enhanced regeneration to obtain a more concentrated glycol to achieve the dry gas water content [2].

From an industry perspective, the estimation of the air emissions and the development of control technologies to mitigate the impact of these emissions on the environment have become important issues.

More stringent emissions regulations have forced the use of some

methods of minimizing hydrocarbon pickup or disposing of the emissions in glycol dehydration units. When natural gas is dehydrated with TEG some of CH_4 , C_2H_6 and C_3H_8 is absorbed in the TEG. Regeneration of the rich TEG solution liberates the light alkanes components. The amount of these compounds absorbed and consequently liberated from the glycol depends on their concentrations in the wet gas being dehydrated and on the contactor's pressure and temperature.

In an actual dehydration facility, the glycol is regenerated to about 99% purity or higher. The absorbed amount of light alkanes components depends on the amount of glycol circulated. If the glycol is not regenerated to this purity, then the amount of gas absorbed per unit of lean glycol circulated would be slightly less than in the proposed equations.

Fig. 1 illustrates a typical dehydration process train. The regenerated glycol is pumped to the top tray of the contactor (absorber). The glycol absorbs water as it flows down through the contactor counter-currently to the gas flow.

Water-rich glycol is removed from the bottom of the contactor, passes through the reflux condenser coil, flashes off most of the soluble gas in the flash tank, and flows through the rich-lean heat ex-

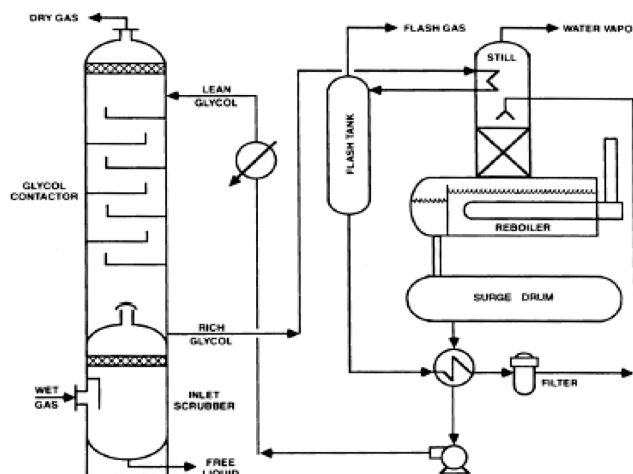


Fig. 1. Schematic of a typical dehydration plant.

[†]To whom correspondence should be addressed.

E-mail: Bahadori.a@nisoc.ir

changer to the regenerator.

In the regenerator, absorbed water is distilled from the glycol at near-atmospheric pressure by application of heat. The regenerated lean glycol leaves the surge drum, is partly cooled in the lean-rich exchanger, and pumped through the glycol cooler before being re-circulated to the contactor.

Glycol will absorb some hydrocarbons at the high pressure of the contactor. Glycol has a special affinity for such cyclic hydrocarbons as benzene, toluene, ethyl benzene, and xylene (BTEX), light Hydrocarbon components as well as polar gases H_2S and CO_2 (acid gases).

Heavier paraffinic hydrocarbons are essentially insoluble in TEG. Aromatic hydrocarbons, however, are very soluble in TEG and significant amounts of aromatic hydrocarbons may be absorbed in TEG at contactor conditions. This may present an environmental or safety hazard when they are discharged from the top of the regenerator.

Upon regeneration of the glycol, all absorbed gases are flashed off. From here they can be routed to fuel, flare, or gas-recovery system [3,4].

A new model, proposed in this article, applies to pure TEG or to lean TEG which is essentially pure. These equations show good agreement with experimental data which were obtained with pure glycol [5].

There are no standard sampling and analytical methods established by regulatory agencies for determining emissions from glycol dehydrators, and the methods initially used by the industry showed significant variability in results [6,7].

To address this lack of method, an effort to develop measurement methods and emission estimation techniques for glycol dehydrators is introduced in this article.

Process engineers currently use commercial software to predict the solubility of light alkanes components in TEG. These software packages use equations of state and need complete process data to simulate wet gas dehydration plants, and consequently calculate the solubility of light Hydrocarbon components in TEG.

It is impossible accurately to predict their solubility in TEG by routine commercial software. Moreover, this commercial software is expensive. Another widely used procedure employs graphics.

Graphs present a convenient visual comparison of the effect of pressure and temperature on the solubility of acid gases in TEG but graphs are less accurate in predicting the solubility of acid gases in TEG especially when they are plotted in log scale. Moreover, process engineers have difficulty reading a graph accurately and modern design techniques are usually based on computer calculations. The benefit of equations is that they can easily be programmed and incorporated in the overall design program, thus bypassing the need for charts or graphs.

The proposed new model has been developed on the basis of experimental data [5]. The solubility of light alkanes components in TEG is a function of temperature and partial pressure. The partial pressure is the product of the operating pressure times the mole fraction of light alkanes components in the gas in the absorber.

The amount of light alkanes components removed by the glycol depends on the following parameters:

- Mole fraction of light alkanes in the feed gas. The effect of composition increases with pressure, particularly for C_2H_6 and C_3H_8 or both.

- Contactor operating pressure and temperature.
- Glycol circulation rate [3,4].

1. New Proposed Model

In previous work [3] new equations were developed for binary systems [8] including H_2S - and CO_2 solubility in TEG.

The model devised in this article is polynomial, which has 16 parameters. In fact, the new model devised in this article is an experimental numerical model.

The required data to use this approach include partial pressure and mole fraction of individual components in liquid phase. At first, the mole fraction of components is correlated vs. partial pressure of components at different constant temperatures; then the calculated coefficients for these polynomials are correlated for different temperatures. In this study a generalized model for multi components system is developed and this new proposed approach is used. A practical case for gas dehydration is evaluated by this new proposed approach. When calculated coefficients are correlated for different temperatures by least squares method in a gas dehydration plant, the tuned coefficients are calculated, which are shown in Table 1. These coefficients are used in Eqs. (1) to (4). These polynomial are used to calculate new coefficients for calculating mole fraction of individual components vs. partial pressure, so finally Eq. (5) is a polynomial which demonstrates the variation of mole fraction vs. individual components partial pressure. This numerical model covers the variation of pressure and temperature in a multi component system accurately.

The principle of the proposed method is based on thermodynamic properties as Tr (reduced temperature), Pr (Reduced Pressure) for individual components and feed composition and experimental data [4].

So the following approach is repeated for components in a multi component system.

- 1-select component (i)
- 2- select temperature (j)
- 3-curvefit xi as a function of partial pressure for experimental

Table 1. New proposed model coefficients to predict absorbed alkanes in TEG

Coefficient	CH_4	C_2H_6	C_3H_8
Aa	-0.0121	-0.3478	-0.0010
Ab	0.0676	1.1514	0.0010
Ac	-0.1254	-1.2654	0
Ad	0.0772	0.4618	0
Ba	0.1077	2.4498	-0.6756
Bb	-0.5942	-7.7630	0.7717
Bc	1.0910	7.9652	0
Bd	-0.6417	-2.5372	0
Ca	-0.0619	-8.0352	-2.9544
Cb	0.3457	26.9224	2.7319
Cc	-0.6381	-29.9186	0
Cd	0.3867	11.0068	0
Da	0.0093	5.2194	9.5330
Db	-0.0524	-17.6989	-8.8886
Dc	0.0972	19.9795	0
Dd	-0.0595	-7.5082	0

Table 2. New model results, experimental data and Peng-Robinson equation of state results for solubility of CH₄ in TEG

Pressure KPa (abs)	Temperature °C	CH ₄ mole fraction at (experimental) [5]	CH ₄ mole fraction (calculated)	Absolute deviation percent (%) (ADP) between model and experimental data	Peng-Robinson equation of state
113.5	25	0.000636	0.00074	14.0541	0.000525
366.1	25	0.002022	0.00200	1.1	0.001676
960	25	0.005212	0.00480	8.5833	0.004288
2320	25	0.01193	0.01110	7.4775	0.009798
4800	25	0.02028	0.02170	6.5438	0.018332
6120	25	0.02776	0.02700	2.8148	0.022177
9240	25	0.03921	0.03820	2.644	0.029682
12840	25	0.04907	0.049	0.1429	0.036176
16280	25	0.05656	0.0573	1.2914	0.040836
19470	25	0.06379	0.0631	1.0935	0.044212
110.7	50	0.000617	0.00057	8.2456	0.000611
335.2	50	0.001859	0.00170	9.3529	0.001835
1010	50	0.005324	0.00510	4.3922	0.005398
2350	50	0.0119	0.01120	6.25	0.011975
4520	50	0.02198	0.02060	6.699	0.021347
7320	50	0.03326	0.03150	5.5873	0.031425
10190	50	0.04302	0.04120	4.4174	0.039818
13140	50	0.05243	0.0498	5.2811	0.046823
16830	50	0.06215	0.061	1.8852	0.053811
109.2	75	0.00059	0.00055	7.2727	0.000708
328.7	75	0.001806	0.00170	6.2353	0.002115
393.4	75	0.002129	0.00204	4.3627	0.002526
905	75	0.004878	0.00469	4.0085	0.005718
2910	75	0.015	0.01465	2.3891	0.017263
5350	75	0.02638	0.02589	1.8926	0.02944
7550	75	0.03505	0.03518	0.3695	0.038893
10540	75	0.04654	0.046531	0.0193	0.049788
13560	75	0.05692	0.0565	0.7434	0.058911
16630	75	0.06586	0.0651	1.1674	0.066631
19690	75	0.07432	0.0721	3.0791	0.073081
112.9	100	0.000627	0.00060	4.5	0.000848
388.8	100	0.002182	0.00210	3.9048	0.002899
940	100	0.005139	0.00500	2.78	0.006900
2510	100	0.01345	0.01300	3.4615	0.017615
5100	100	0.02557	0.02560	0.1172	0.033285
8080	100	0.03923	0.03890	0.8483	0.048628
10340	100	0.04807	0.04830	0.4762	0.058634
12890	100	0.05818	0.058	0.3103	0.068494
15400	100	0.06668	0.0667	0.03	0.076937
19240	100	0.07842	0.0784	0.0255	0.087856
369.9	125	0.002181	0.00200	9.05	0.003173
928	125	0.005305	0.00510	4.0196	0.007849
2510	125	0.01379	0.01370	0.6569	0.020362
3860	125	0.02094	0.02080	0.6731	0.030226
6270	125	0.03321	0.03290	0.9422	0.046151
8750	125	0.04453	0.04450	0.0674	0.060531
11980	125	0.05865	0.0584	0.4281	0.076654
15140	125	0.0708	0.0707	0.1414	0.090032
18920	125	0.084	0.0838	0.2387	0.103494
Average of Absolute Deviation (%)				3.3075	

$$\% \text{ ADP} = \frac{100}{\text{NOP}} \sum_i^{\text{NOP}} \left| \left(\frac{\text{Calculated value}}{\text{Experimental value}} \right)_i - 1 \right| = 3.3075\%$$

mole fraction and partial pressure of component (i) at temperature (j).

4- repeat step 2 and 3 for other data at other temperatures.

5-correlate corresponding polynomial coefficients which were obtained at different temperatures, $A_i=f(T)$, $B_i=f(T)$, $C_i=f(T)$, $D_i=f(T)$ it means Eqs. (1)-(4).

6- Repeat step 1 to 5 for other component (i)

7-calculate xi vs. partial pressure of component (i) from Eq. (5).

Then Eqs. (6) and (7) show the mole fraction conversion of components to volumetric dimensions.

$$A_i = A_{a\bar{ij}} + B_{a\bar{ij}}T_{ri} + C_{a\bar{ij}}T_{ri}^2 + D_{a\bar{ij}}T_{ri}^3 \quad (1)$$

$$B_i = A_{b\bar{ij}} + B_{b\bar{ij}}T_{ri} + C_{b\bar{ij}}T_{ri}^2 + D_{b\bar{ij}}T_{ri}^3 \quad (2)$$

$$C_i = A_{c\bar{ij}} + B_{c\bar{ij}}T_{ri} + C_{c\bar{ij}}T_{ri}^2 + D_{c\bar{ij}}T_{ri}^3 \quad (3)$$

$$D_i = A_{d\bar{ij}} + B_{d\bar{ij}}T_{ri} + C_{d\bar{ij}}T_{ri}^2 + D_{d\bar{ij}}T_{ri}^3 \quad (4)$$

$$x = A_i + B_iP_{ri} + C_iP_{ri}^2 + D_iP_{ri}^3 \quad (5)$$

$$v = \frac{23645x}{(Mx + 150.2(1-x))} \quad (6)$$

$$v_{\text{teg}} = \frac{1 - \frac{Mx}{(Mx + 150.2(1-x))}}{1.126} \quad (7)$$

Std. Cubic meter of light Alkane component in Cubic meter

$$\text{TEG} = \frac{v}{v_{\text{teg}}}$$

The equation box shows the proposed equations for the solubility of CH_4 , C_2H_6 and C_3H_8 in TEG in mole fraction. The pressure limits of applicability are till 12,000 kPa partial pressure, and temperature is limited to 130 °C for CH_4 .

Concerning C_2H_6 , the pressure limits of applicability are up to 7,000 kPa and temperature is limited to 100 °C and for C_3H_8 partial-pressure range is to 1,000 kPa and temperature is limited to 80 °C.

Eqs. (6) and (7) show the mole fraction conversion of light alkanes components to volumetric dimensions.

RESULTS

Table 1 shows the new proposed model coefficients to predict

Table 3. New model results, experimental data and Peng-Robinson equation of state results for solubility of C_2H_6 in TEG

Pressure KPa (abs)	Temperature °C	C_2H_6 mole fraction (experimental) [5]	C_2H_6 mole fraction (calculated)	Absolute deviation percent (%) (ADP) between model and experiental data	Peng-Robinson equation of state
110	25	0.0028	0.0029	3.7037	0.002181
156	25	0.00399	0.004	0.01	0.003079
305	25	0.00772	0.00790	2.2785	0.005938
983	25	0.02348	0.02470	4.9393	0.017942
2840	25	0.06044	0.06050	0.0992	0.042576
116	50	0.002457	0.00250	1.72	0.002302
228	50	0.004919	0.00480	2.4792	0.004486
397	50	0.008381	0.00810	3.4691	0.007712
950	50	0.01769	0.01870	5.4011	0.017678
2100	50	0.03841	0.03850	0.2338	0.035579
3200	50	0.0557	0.05470	1.8282	0.049259
6490	50	0.0866	0.08650	0.1156	0.071394
115	75	0.002121	0.0022	3.5909	0.002313
225	75	0.004044	0.0041	1.3659	0.004494
418	75	0.00761	0.0073	4.2466	0.008248
583	75	0.01036	0.0101	2.5743	0.011382
1010	75	0.01688	0.017	0.7059	0.01918
2130	75	0.03362	0.0339	0.826	0.037525
4280	75	0.06103	0.0611	0.1146	0.06466
7640	75	0.08982	0.0898	0.0223	0.088638
10140	75	0.1002	0.1002	0	0.096393
112	100	0.00183	0.0019	3.6842	0.002305
194	100	0.003205	0.0033	2.8788	0.003976
259	100	0.004074	0.0045	9.4667	0.005291
392	100	0.006103	0.0067	8.9104	0.007951
709	100	0.01068	0.012	11	0.014137
1500	100	0.02182	0.0244	10.5738	0.028629
3950	100	0.05236	0.0547	4.2779	0.065408
5690	100	0.07101	0.069	2.913	0.084731
Average of Absolute Deviation (%)				3.2217	

Table 4. New model results, experimental data and Peng-Robinson equation of state results for solubility of C₃H₈ in TEG

Pressure KPa (abs)	Temperature °C	C ₂ H ₆ mole fraction (experimental) [5]	C ₂ H ₆ mole fraction (calculated)	Absolute deviation percent (%) (ADP) between model and experiental data	Peng-Robinson equation of state
15.9	25	0.001001	9.45E-04	5.9259	0.000738
46	25	0.002667	0.0027	1.2222	0.002125
57	25	0.003475	0.0034	2.2059	0.00263
122.1	25	0.007085	0.0073	2.9452	0.005585
127	25	0.007138	0.0076	6.0789	0.005805
231.6	25	0.01381	0.0138	0.0724	0.010436
378.5	25	0.02275	0.0225	1.1111	0.016707
767	25	0.04654	0.0456	2.0614	0.031922
19.1	50	0.000855	8.94E-04	4.3624	0.000803
35.2	50	0.001525	0.0015	1.6667	0.001478
131.4	50	0.005522	0.0055	0.4	0.00546
289.9	50	0.01231	0.0119	3.4454	0.011833
695	50	0.02939	0.0283	3.8516	0.02703
33.2	75	0.001126	1.30E-03	13.3846	0.001301
134.8	75	0.004374	0.0044	0.5909	0.005234
305	75	0.009931	0.0098	1.3367	0.011656
802	75	0.02548	0.0254	0.315	0.029181
960	75	0.03014	0.0303	0.5281	0.034362
Average of Absolute Deviation (%)				2.8614	

absorbed alkanes in TEG.

Table 2 shows comparisons between the experimental data for CH₄ of Reference 5 with results from the proposed model. As can be seen, the average absolute deviation percent at different temperatures and for CH₄ is 3.3075%. This table also shows the comparison between the proposed numerical model and the Peng-Robinson equation of state results in predicting the solubility of methane in TEG. It shows this model is more accurate for predicting the solubility of methane in TEG.

Table 3 shows comparisons between the experimental data for C₂H₆ of Reference 5 with results from the proposed model. As can be seen, the average absolute deviation percent at different temperatures and for C₂H₆ is 3.139%. This table also shows the comparison between proposed numerical model and the Peng-Robinson equation of state results in predicting the solubility of ethane in TEG. It also shows this model is more accurate for predicting the solubil-

ity of ethane in TEG.

Table 4 shows comparisons between the experimental data for C₃H₈ of Reference 5 with results from the proposed model. As can be seen, the average absolute deviation percent at different temperatures and for C₃H₈ is 2.7903%. This table also shows the comparison between proposed numerical model and the Peng-Robinson equation of state results in predicting the solubility of propane in TEG. It also shows this model is more accurate for predicting the solubility of propane in TEG.

Figs. 2 to 7 show the solubility of CH₄, C₂H₆ and C₃H₈ at different temperatures and partial pressures in TEG. There is a good agreement between the new proposed equations and experimental results.

Methane is main component in the gas stream and it has the highest mole fraction in dehydration plants feed stream, so Fig. 8 shows the results of CH₄ Proposed equations, which have been plotted in the linear scale. It also shows the trend of solubility of CH₄ in TEG

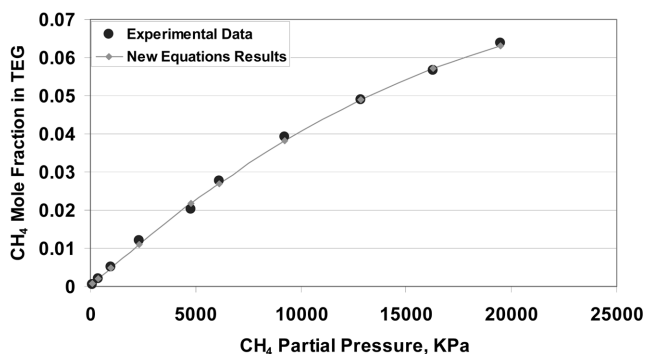


Fig. 2. New equations results and experimental data for solubility of CH₄ in TEG at 25 °C.

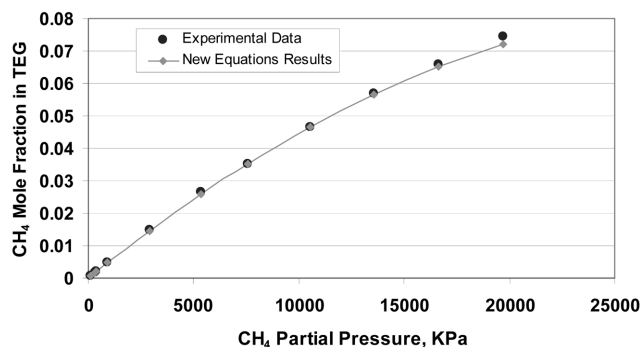


Fig. 3. New equations results and experimental data for solubility of CH₄ in TEG at 75 °C.

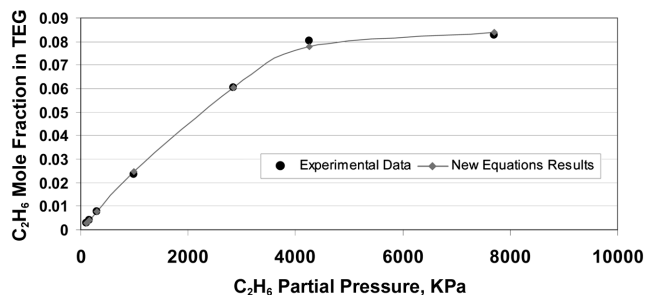


Fig. 4. New equations results and experimental data for solubility of C_2H_6 in TEG at 25 °C.

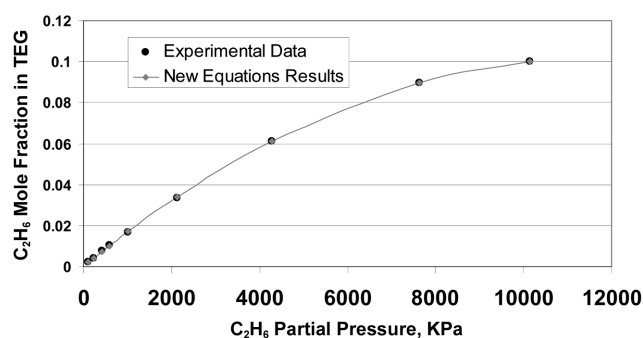


Fig. 5. New equations results and experimental data for solubility of C_2H_6 in TEG at 75 °C.

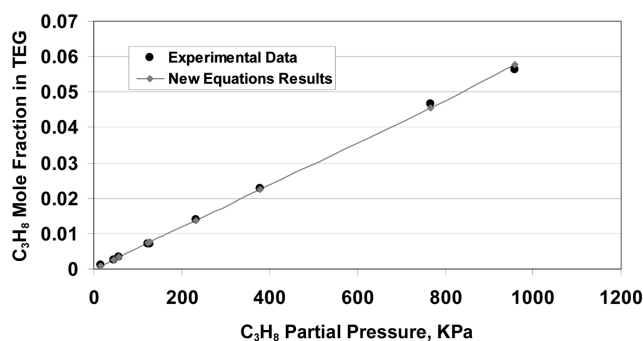


Fig. 6. New equations results and experimental data for solubility of C_3H_8 in TEG at 25 °C.

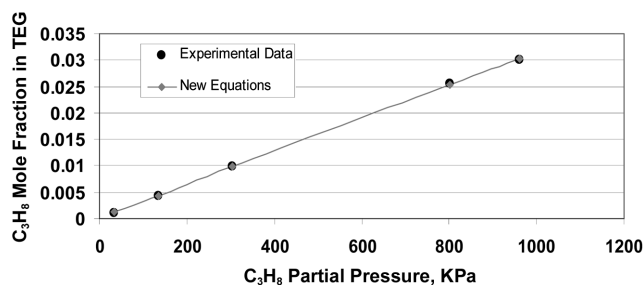


Fig. 7. New equations results and experimental data for solubility of C_3H_8 in TEG at 75 °C.

at different temperatures and partial pressures. The solubility of methane in TEG is almost independent of temperature and at high pres-

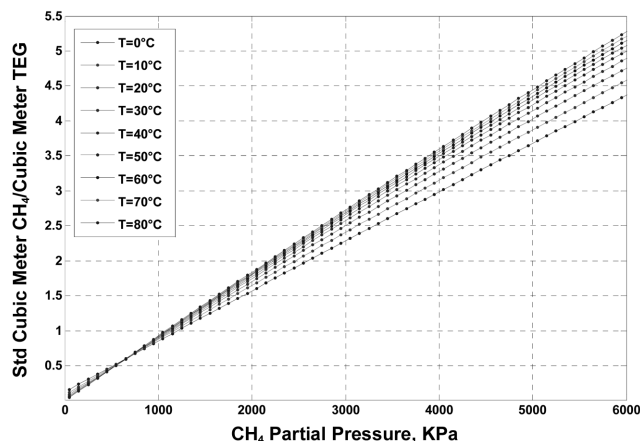


Fig. 8. New equations results for standard cubic meter CH_4 absorbed in TEG vs. contactor temperature and different partial pressure.

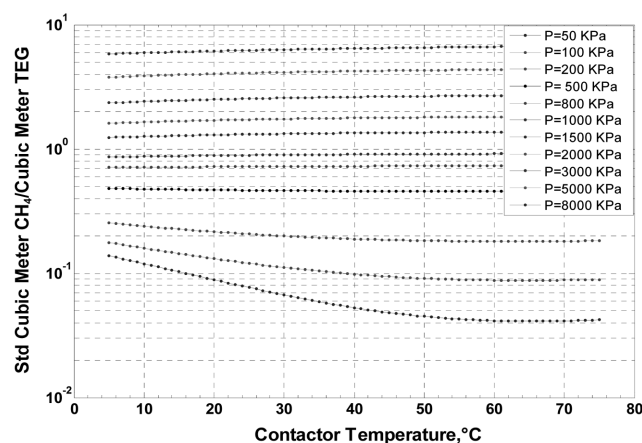


Fig. 9. New equations results for standard cubic meter CH_4 absorbed in TEG vs. Contactor temperature and at different partial pressure.

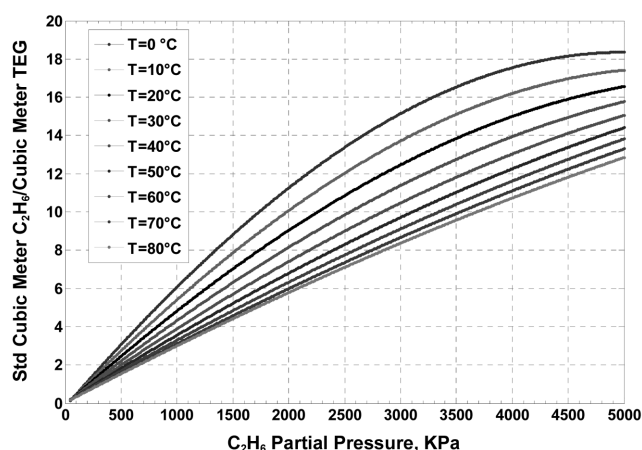


Fig. 10. New equation results for standard cubic meter C_2H_6 absorbed in TEG vs. partial pressure and at different contractor temperature.

ures (pressure greater than about 700 KPa), the solubility increases with increasing temperature. And the trend of solubility is linear.

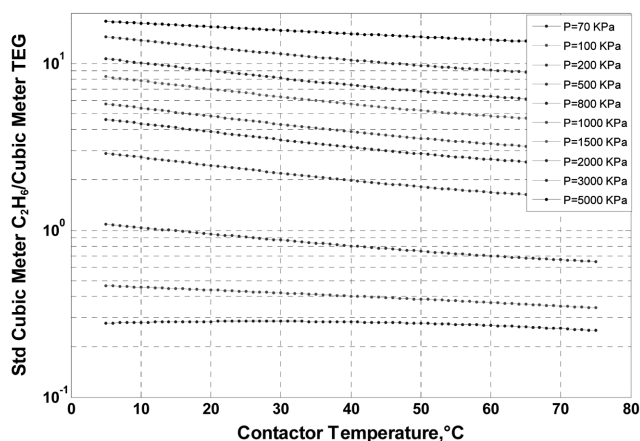


Fig. 11. New equation results for standard cubic meter C_2H_6 absorbed in TEG vs. temperature and different partial pressure.

Fig. 9 shows the results for CH_4 , which have been plotted in the log scale. It also shows the trend of solubility of CH_4 in TEG vs. partial pressures at different temperatures.

Figs. 10 illustrates the solubility of ethane in TEG in linear scale vs. ethane partial pressure at different temperatures; it also shows the solubility of ethane in TEG is more than methane (compare with Fig. 8) and the trend of solubility is not linear. Fig. 11 demonstrates the solubility of ethane in TEG vs. contactor temperature at different partial pressures. In wet gas stream, the mole fraction of ethane is less than methane, so Fig. 11 demonstrates the graph in smaller pressure domain.

Figs. 12 illustrates the solubility of C_3H_8 in TEG in linear scale vs. propane partial pressure at different temperatures; it also shows the solubility of C_3H_8 is more than methane and ethane (compare with Figs. 8 and 10) and the trend of solubility is not linear but different than ethane solubility. Fig. 13 demonstrates the solubility of ethane in TEG vs. contactor temperature at different partial pressures. In wet gas stream, the mole fraction of C_3H_8 is less than methane and ethane so, Fig. 13 demonstrates the graph in a small pres-

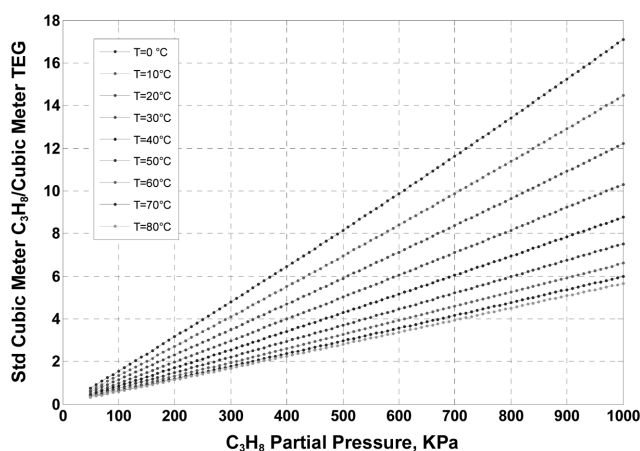


Fig. 12. New equations result for standard cubic meter C_3H_8 absorbed in TEG vs. partial pressure and different temperature.

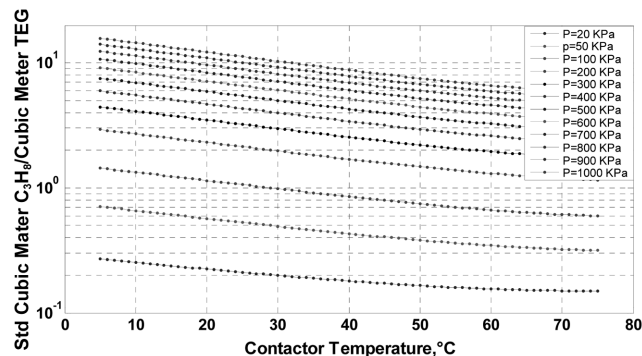


Fig. 13. New equation results for standard cubic meter C_3H_8 absorbed in TEG vs. temperature and at different partial pressure.

sure domain.

Since dehydrators usually operate at temperatures of less than $60^\circ C$, there was no practical need to include temperatures higher than $75^\circ C$ in graphs of this work. And these new proposed equations are very accurate in predicting the solubility of light alkanes in TEG.

The accuracy of the new proposed model is acceptable and much better, simpler, and easier to use than routine graphical methods or conventional commercial software.

NOMENCLATURE

A	: coefficient
B	: coefficient
C	: coefficient
D	: coefficient
x	: alkanes in liquid phase mole fraction
Tr	: reduced temperature
Pr	: reduced partial pressure

Subscripts

a	: an index to show coefficient for A
b	: an index to show coefficient for B
c	: an index to show coefficient for C
d	: an index to show coefficient for D
i	: component index
j	: number of isothermal data sets
V	: standard volume light alkane component in TEG (cubic meter)
M	: light alkane component molecular weight
V _{teg}	: volume of TEG (cubic meter)
NOP	: number of points

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