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Vapor–Liquid Equilibria of Water + Triethylene Glycol (TEG) and Water + TEG + Toluene at 85 kPa

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In this study, vapor–liquid equilibria data have experimentally been measured for systems water + triethylene glycol (TEG) and water + TEG + toluene at 85 kPa and various temperatures. The VLE data were determined in a modified Othmer still, and the samples were analyzed using gas chromatography and titration methods. The NRTL, UNIQUAC, and Van Laar models were used to correlate the data. The results demonstrate the enhancement of volatility of water in water + TEG solutions and increasing the purity of the dehydrated TEG by the addition of toluene. Using this method, the more concentrated TEG can be obtained in the stripping columns of the natural gas dehydration systems.

Introduction

Natural gas dehydration is an important operation in the gas processing and conditioning industry. In this process, water vapor is eliminated from natural gas streams for domestic usage or other downstream gas processes. The level of water vapor in natural gas should be maintained below a certain value to prevent hydrate formation and minimization of corrosion in transportation pipelines.^{1–3} The standard method for natural gas dehydration is by the absorption of water using triethylene glycol. The glycols are effective liquid desiccants because of their high hygroscopic property, low vapor pressure, high boiling point, and low solubility in natural gas. The four types of glycols that have been used for natural gas dehydration are ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (T₄EG).⁴ TEG is used in about 95 % of the glycol dehydration units for natural gas streams. Glycol dehydration units conventionally consist of a contactor and a regenerator. An alternate approach for the enhancement of reconcentrator performance is the use of stripping agent. In this approach a volatile hydrocarbon liquid is added to the glycol regeneration system. The hydrocarbon increases the volatility of water in the solution of water + TEG. Smith and Skiff⁵ reported that this type of process can achieve compositions of over 99.99 % with triethylene glycol, resulting in potential dry gas with the water dew points range in (–73.3 to –95.5) °C. Toluene and isooctane (2,2,4-trimethyl pentane) are used as entrainers in the stripping columns of natural gas dehydration units.^{6,7} Knowledge of the vapor–liquid equilibrium (VLE) data is necessary for accurate design and simulation of stripping columns. Therefore, vapor–liquid equilibria for the systems water + TEG and water + TEG + toluene (one of the stripping agents) have been studied in this work.

It is common in industry, such as in extraction and distillation units, to add a third component or extract an agent to alter relative volatilities in the interest of facilitating extraction or distillation. Morrison et al.⁸ investigated the salt effect on the VLE of the water + alcohol system using modified Othmer still. Herskowitz and Gottlieb⁹ determined the activity coefficient of

Table 1. Identifications of Materials Used in This Study

chemical	purity	water	$\rho/\text{g}\cdot\text{cm}^{-3}$	supplier
TEG	> 99 %	< 0.3 %	1.123	Merck
toluene	> 99 %	< 0.01 %	0.866	Merck
distilled water			1.00	Shiraz University

Table 2. UNIQUAC Parameters for Pure Materials

parameter	TEG	toluene	water
r	5.59	3.92	0.92
q	4.89	2.97	1.40

Table 3. Vapor Pressure Constants for Pure Components^{27,28a}

comp	c_1	c_2	c_3	c_4	c_5
water	73.649	–7258.2	–7.3037	4.1653e^{-6}	2
toluene	80.877	–6902.4	–8.7761	5.8034e^{-6}	2
TEG	29.36842	–8897.103	–1.467521	2.126367e^{-6}	2

^a $\ln P_i = c_1 + c_2/T + c_3 \ln T + c_4 T^{c_5}$ (T in K and p in Pa except for TEG in kPa).

Table 4. Physical Properties for Pure Components^{17,25,28,29}

comp	M	T_c	$p_c \cdot 10^{-6}$	v_c	z_c	ω
		K	Pa	$\text{m}^3 \cdot \text{kmol}^{-1}$		
TEG	150.2	769.5	3.320	0.5347	0.2462	1.254
H ₂ O	18.01	647.1	21.94	0.056	0.228	0.343
toluene	92.14	591.8	4.10	0.314	0.262	0.262

water in a water–triethylene glycol solution using an isopiestic method. Gupta et al.¹⁰ determined isobaric vapor–liquid equilibria for the systems TEG–benzene, toluene–TEG and benzene–*N*-methylpyrrolidone. Scauzillo¹¹ presented equilibrium ratios and activity coefficients of water in the systems water + TEG + natural gas. Cartaya et al.¹² evaluated a local composition model (the LCM model) for the VLE of the binary mixtures of triethylene glycol in the presence of methane, water, and benzene. Chung and Luo¹³ investigated the vapor pressures of the aqueous desiccants. Wise et al.¹⁴ determined saturated vapor densities and activities of triethylene glycol–water at low pressures. Dingman and Lebas¹⁵ presented dew point data for the binary solution water + TEG. Chen et al.¹⁶ reported solubility of glycol in water–hydrocarbon systems. Twu et al.¹⁷ developed an advanced equation of state for modeling the TEG + water system for the glycol gas dehydration process.

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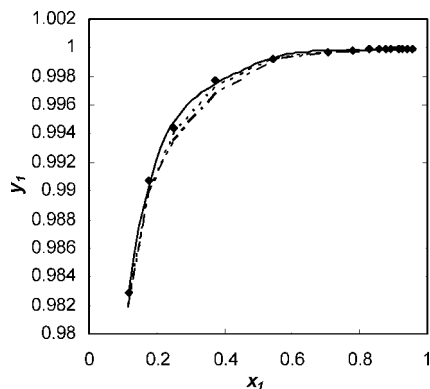


Figure 1. x_1 - y_1 diagram for water (1) in the water (1) + TEG (2) solution at $p = 85$ kPa: ■, this work; —, Van Laar; ---, NRTL; -.-, UNIQUAC models results.

Table 5. Vapor–Liquid Data for the System Water (1) + TEG (2) at $p = 85$ kPa

$t/^\circ\text{C}$	x_1	x_2	y_1	y_2
148.1	0.117	0.883	0.9829	0.0171
141.6	0.176	0.824	0.9908	0.0092
139.4	0.251	0.749	0.9945	0.0055
127.7	0.373	0.627	0.9978	0.0022
117.3	0.543	0.457	0.9992	0.0008
107.0	0.704	0.296	0.9997	0.0003
103.5	0.781	0.219	0.9998	0.0002
101.8	0.826	0.174	0.9998	0.0002
100.8	0.856	0.144	0.9999	0.0001
99.8	0.877	0.123	0.9999	0.0001
99.2	0.893	0.107	0.9999	0.0001
98.4	0.915	0.085	0.9999	0.0001
144.0	0.140	0.860	0.9780	0.0220
143.1	0.161	0.839	0.9833	0.0167
140.5	0.182	0.818	0.9872	0.0128
140.1	0.242	0.758	0.9930	0.0070
130.8	0.325	0.675	0.9965	0.0035
124.8	0.410	0.590	0.9980	0.0020

Table 6. Vapor–Liquid Equilibrium Data for the System TEG (1) + Water (2) + Toluene (3) at $p = 85$ kPa

$t/^\circ\text{C}$	x_1	x_2	x_3	y_1	y_2	y_3
127.7	0.6270	0.3730	0.0000	0.0022	0.9978	0.0000
121.8	0.6197	0.3679	0.0124	0.0015	0.8222	0.1763
117.3	0.6046	0.3590	0.0364	0.0011	0.6564	0.3425
112.4	0.5889	0.3496	0.0615	0.0008	0.5707	0.4285
109.9	0.5834	0.3463	0.0703	0.0007	0.5482	0.4511
106.9	0.5733	0.3403	0.0864	0.0006	0.5180	0.4814
104.0	0.5634	0.3346	0.1020	0.0005	0.4952	0.5043
100.3	0.5479	0.3254	0.1267	0.0004	0.4680	0.5316
97.7	0.5193	0.3084	0.1723	0.0003	0.4396	0.5601
95.7	0.4490	0.2666	0.2844	0.0002	0.4104	0.5894
95.6	0.3954	0.2348	0.3698	0.0002	0.4026	0.5972
139.4	0.7490	0.2510	0.0000	0.0055	0.9945	0.0000
119.9	0.6810	0.2290	0.0900	0.0014	0.4821	0.5165
108.0	0.6308	0.2108	0.1584	0.0008	0.4008	0.5984
100.1	0.5510	0.1990	0.2500	0.0005	0.3673	0.6322
98.4	0.5095	0.1703	0.3202	0.0004	0.3427	0.6569
98.1	0.4595	0.1536	0.3869	0.0003	0.3352	0.6645

Table 7. Binary Interaction Parameters for the System Water (1) + Toluene (2) + TEG (3)

couple of components	interaction parameters (UNIQUAC)		interaction parameters (NRTL)			interaction parameters (Van Laar)	
water + TEG							
water – TEG	$a_{13} = -2.729$ $b_{13} = 0.004$	$a_{31} = 2.112$ $b_{31} = -0.003$	$a_{13} = -0.0015$ $b_{13} = -0.234$	$a_{31} = -1.704$ $b_{31} = 0.004$	$\alpha_{13} = 2.850$	$a_{13} = 1.288$ $b_{13} = -526.887$	$a_{31} = 6.828$ $b_{31} = -257.520$
water + TEG + toluene							
water – toluene	$a_{12} = -2.390$ $b_{12} = 0.004$	$a_{21} = -3.815$ $b_{21} = 0.006$	$a_{12} = 4.374$ $b_{12} = -0.007$	$a_{21} = 2.439$ $b_{21} = -0.004$	$\alpha_{12} = -0.136$	$a_{12} = -3.272$ $b_{12} = 2205.364$	$a_{21} = 6.351$ $b_{21} = 239.429$
water – TEG	$a_{13} = -3.087$ $b_{13} = 0.005$	$a_{31} = 2.304$ $b_{31} = -0.004$	$a_{13} = -12.312$ $b_{13} = 0.020$	$a_{31} = 0.095$ $b_{31} = -0.0002$	$\alpha_{13} = -0.889$	$a_{13} = 40.877$ $b_{13} = 131.318$	$a_{31} = 3.772$ $b_{31} = -2161.730$
toluene – TEG	$a_{23} = 6.537$ $b_{23} = 0.011$	$a_{32} = 2.478$ $b_{32} = -0.004$	$a_{23} = 1.109$ $b_{23} = -0.002$	$a_{32} = 1.359$ $b_{32} = -0.002$	$\alpha_{23} = -2.200$	$a_{23} = -7.415$ $b_{23} = 2078.915$	$a_{32} = -5.910$ $b_{32} = 1955.915$

In this work, an experimental procedure was performed to determine the VLE data for the binary water + TEG and ternary water + TEG + toluene systems. A modified Othmer still was used for taking samples. The samples were analyzed by gas chromatography (GC) and titration methods. This apparatus was already used by Smith and Bonner,¹⁸ Gupta et al.,¹⁰ and Morrison et al.⁸ The results were used to optimize the interaction parameters of the NRTL, UNIQUAC, and Van Laar models.

Experimental Section

Materials. The chemicals were purchased from commercial sources. The nominal purities of the used chemicals are tabulated in Table 1.

Apparatus and Procedure. The VLE data were determined at 85 kPa pressure in a modified Othmer still, which is a continuous-distillation still that recirculates the vapor phase.⁸ The modified Othmer still provides accurate VLE data in a relatively short experimental time. The still comprises a distillation flask, a reflux condenser, and condensate return. For further details, readers are referred to the paper of Morrison et al.⁸ In this research, a sealed glass recirculating still with two magnetic homogenizers was used. The still was slightly modified by providing a magnetic stirrer in condensate and liquid sections. Also, the vacuum was performed by a vacuum pump before any experiments; then, 85 kPa was applied. The temperature sensor model was Pt 100, and the digital temperature detector with ± 0.1 K uncertainty was used.

Sample Analysis. The samples were taken under steady-state conditions. Only the vapor (condensate) samples needed to be analyzed. This method also possesses the advantage of rapidly producing experimental data and of directly giving liquid composition on a single phase. The analysis of samples was carried out by GC on a Varian GC. The GC was equipped with (2 m•0.635 cm) in column packed with Propack Q. Helium was used as a carrier gas. Two different detectors were used to analyze the amounts of components in this work. A flame ionization detector (FID) was applied to obtain the composition of hydrocarbons, and a thermal conductivity detector (TCD) was chosen to detect the water content. The temperatures of the injector and detector were maintained at 300 °C. The column temperature was controlled by programming the temperature. After 1 min of holding at $t = 100$ °C, the column temperature was raised to the final temperature of 220 °C at the rate of 5 °C•min⁻¹. Heterogeneous samples were allowed to remain still for several hours to be sure that two phases were accurately obtained; then, each phase was analyzed. The uncertainty of the mole fractions was within ± 0.0005 . The composition of TEG was determined using a titration method. This method contains the acetylation of the hydroxyl group by acetic anhydride with perchloric acid.¹⁹ Then, the sample was titrated by sodium hydroxide. Liquid compositions were calculated throughout the experiments by overall material balance similar

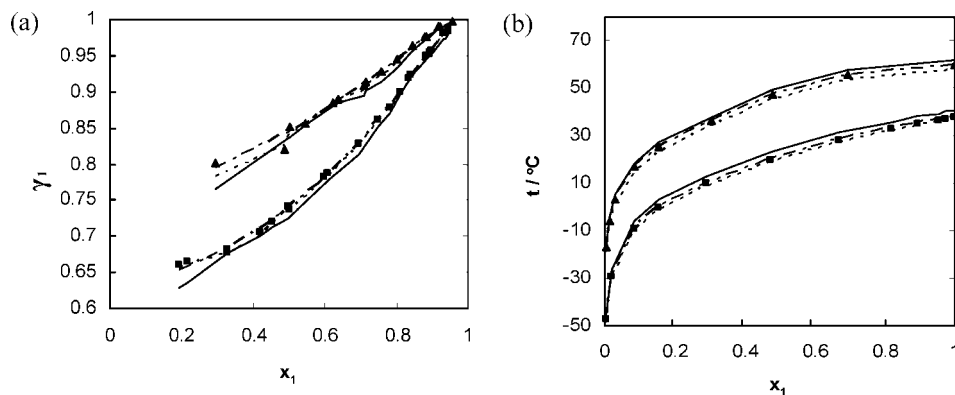


Figure 2. Comparison of correlations with literature data: ---, Van Laar; ···, NRTL; —, UNIQUAC. (a) Activity coefficient of water in the water + TEG solution. Experimental data from ref 9: ■, at $t = 24.5$ °C; ▲, at $t = 59.5$ °C. (b) Water dew points. Experimental data from ref 15: ■, at $t = 37.5$ °C; ▲, at $t = 60.1$ °C.

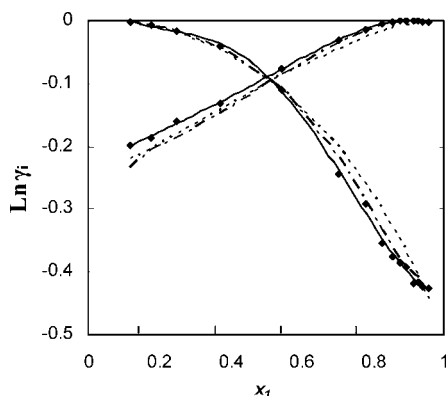


Figure 3. Activity coefficients of water (1) + TEG (2) in their solution at $p = 85$ kPa correlated by: ···, NRTL; ---, UNIQUAC; —, Van Laar equations; ■, experimental data in this work.

to the work of Morrison et al.⁸ The method has sufficient accuracy to determine small traces of glycol. The uncertainty was ± 0.1 % of TEG.

Model Development

For the specific case of multicomponent VLE²⁰

$$\gamma_i = \frac{y_i p \phi_i}{x_i p_i^{\text{sat}} \phi_i^{\text{sat}}} \quad (1)$$

The liquid-phase activity coefficients of the components in the mixtures were calculated from UNIQUAC,²¹ NRTL,²²

and Van Laar²³ equations. Because the pressure was low and this investigation was performed at constant pressure, the virial equation was used to calculate the vapor-phase fugacity coefficients. The UNIQUAC equation for the activity coefficient of component i in a multicomponent mixture is given by²⁴

$$\ln \gamma_i = \ln \frac{\varphi_i}{x_i} + \frac{z_i}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\varphi_i}{x_i} \sum_j x_j l_j - q_i \ln \left[\sum_j \theta_j \tau_{ji} \right] + q_i - q_i \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \quad (2)$$

The NRTL equation²⁴ was also applied for the calculation of activity coefficients of components in the liquid phase

$$\ln \gamma_i = \frac{\sum_j x_j \tau_{ji} G_{ji}}{\sum_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k x_k G_{kj}} \right) \quad (3)$$

where

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (4)$$

In general, the temperature dependence parameters for NRTL and UNIQUAC equations are presented by eqs 5 and 6, respectively

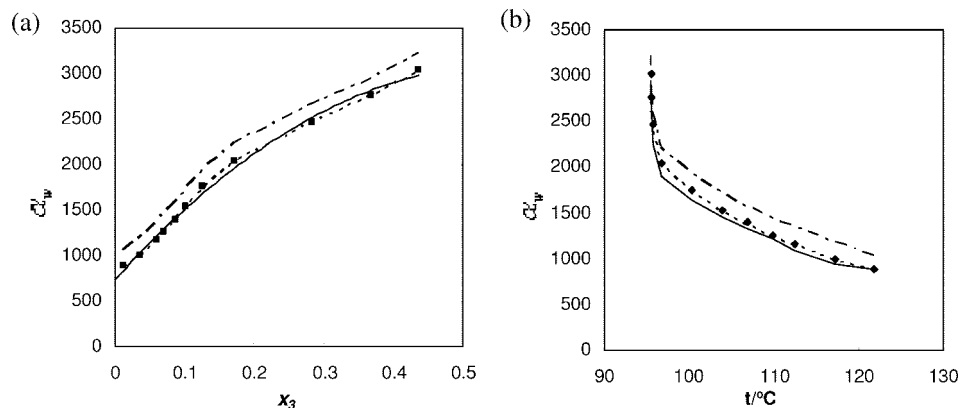


Figure 4. Relative volatility of water to TEG (α_w) in the TEG (1) + water (2) solution with the addition of toluene (3) (a) as a function of toluene (3) mole fraction in liquid phase and (b) as a function of equilibrium temperature correlated by: ···, NRTL; ---, UNIQUAC; —, Van Laar equations; ■, experimental data in this work.

$$\tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + d_{ij}T \quad (5)$$

$$\tau_{ij} = \exp\left(a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T + d_{ij}T\right) \quad (6)$$

The logarithmic term is used only if liquid–liquid equilibria have to be described and because the two parameters usually are used for temperature-dependence binary interaction parameters; therefore, the following equation is applied in to NRTL and UNIQUAC models, and it was observed that the following equation has the most consistency for the mentioned systems

$$\tau_{ij} = a_{ij} + b_{ij}T \quad (7)$$

The simpler model (Van Laar²³) was also correlated for the previously mentioned systems

$$\ln \gamma_i = A_i(1 - z_i)^2 \left[1 + 2z_i \left(\frac{A_i B_i}{|A_i B_i|} - 1 \right) \right] \quad (8)$$

where

$$z_i = \frac{|A_i| x_i}{|A_i| x_i + |B_i|(1 - x_i)} \quad (9)$$

$$A_i = \sum_j x_j A_{ij} / (1 - x_i) \quad (10)$$

$$B_i = \sum_j x_j A_{ji} / (1 - x_i) \quad (11)$$

For the Van Laar equation, the interaction parameter is as follows

$$A_{ij} = a_{ij} + \frac{b_{ij}}{T} \quad (12)$$

The fugacity coefficient of component i in a gas mixture is calculated by the following equation²⁰

$$\ln \phi_i = P/RT \left\{ B_{ii} + \frac{1}{2} \sum_j \sum_k [y_j y_k (2\delta_{ji} - \delta_{jk})] \right\} \quad (13)$$

The second virial coefficient was calculated from the equation

$$B_{ij} = \frac{RT}{P} \left(B_{ij}^0 + \omega_{ij} B_{ij}^1 \right) \quad (14)$$

and B^0 and B^1 were computed as a function of reduced temperature.

In this work, a rigorous method was used for VLE calculations. This method was suggested by Smith et al.²⁰ The UNIQUAC parameters, the vapor pressures, and the physical properties of components are reported in Tables 2, 3, and 4, respectively.

Results and Discussion

The experimental VLE data for system water and TEG are presented in Table 5. Also, the experimental vapor–liquid data for ternary system containing water, TEG, and toluene are given in Table 6. From this table, it is clear that the volatility of water increases in the presence of toluene, and the equilibrium temperature declines when toluene is added to the mixture. The experimental data of the water + TEG and water + TEG + toluene systems were correlated using UNIQUAC, NRTL, and Van Laar equations. The estimation of the binary interactions of the aforesaid models was based on the minimization of the objective function, OF, in terms of the difference between calculated and experimental logarithmic activity coefficients values. The function OF used in this work can be expressed as

$$\text{OF} = \min \sum_{i=1}^n \sum_{j=1}^m (\ln \gamma_{\text{expt}}^{ij} - \ln \gamma_{\text{calcd}}^{ij})^2 \quad (15)$$

where $\gamma_{\text{expt}}^{ij}$ and $\gamma_{\text{calcd}}^{ij}$ are the experimental and calculated activity coefficients of component i , respectively. The subscripts i, j denote the component and data, respectively. The binary interaction parameters in UNIQUAC, NRTL, and Van Laar equations between TEG + water, TEG + toluene, and water + toluene are listed in Table 7.

Figure 1 depicts the y, x diagram of water in the water + TEG solution at 85 kPa. Because there is a large difference between the boiling points of TEG and water, the amount of TEG in the vapor phase is very small. As can be seen from this Figure, the water mole fraction in the vapor phase is greater than 0.98; therefore, water is more volatile relative to TEG. The correlations for this system have very good agreement with experimental data. The correlations have been compared with experimental data from Herskowitz and Gottlieb⁹ and Dingman and Lebas.¹⁵ Figure 2a shows the consistency of the water activity predicted by correlations with experimental data. Also, Figure 2b compares the water dew point predicted by correlations and literature data. The experimental and correlated logarithmic activity coefficients by mentioned equations for water and TEG are shown in Figure 3. Good agreements are observed between model results and experimental data.

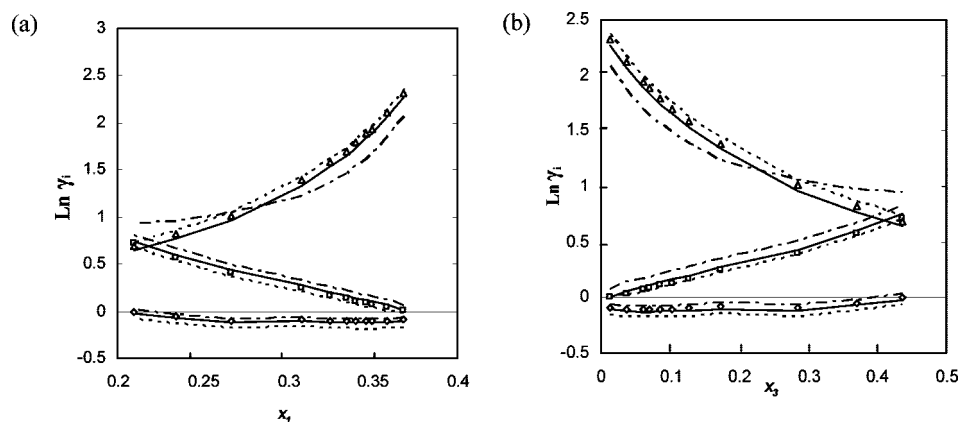


Figure 5. Activity coefficient of water + TEG + toluene in their solution at $p = 85$ kPa (a) as a function of TEG mole fraction and (b) as a function of toluene: \diamond , TEG (1); \square , water (2); Δ , toluene (3). Correlated by: ---, NRTL; —, UNIQUAC; -.-, Van Laar equations.

Table 8. Root-Mean-Square Deviation (RMSD)^a

mixture	NRTL	UNIQUAC	Van Laar
water + TEG	0.032	0.016	0.002
water + TEG + toluene	0.392	0.635	21.913

$$^a \left\{ \sum_i \sum_j m \{ \gamma_{ij}^{\text{exptl}} - \gamma_{ij}^{\text{calcd}} \}^2 / n \right\}^{0.5}$$

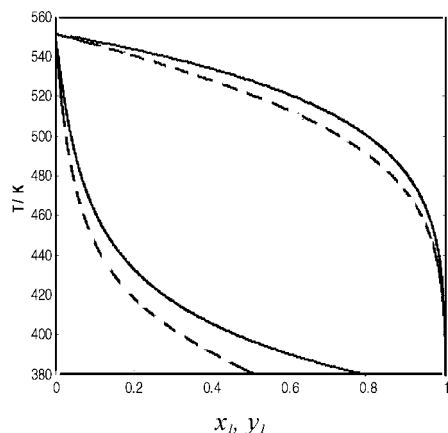


Figure 6. T - x - y diagram of water (1) + TEG (2) solution in the presence and in the absence of toluene using model (UNIQUAC) results at atmospheric pressure: —, water (1) + TEG (2); ---, water (1) + TEG (2) + toluene (3), on a toluene-free basis.

The relative volatility of water to TEG is

$$\alpha_w = \frac{y_w/x_w}{y_{\text{TEG}}/x_{\text{TEG}}} \quad (16)$$

The relative volatility of water to TEG in the ternary system water + TEG + toluene is shown in Figure 4. Figure 4a shows that the relative volatility of water to TEG increases by the addition of toluene. Figure 4b shows that equilibrium temperature declines by the addition of toluene. Moreover, this Figure shows that water volatility increases with decreasing temperature. The equilibrium temperature decreases when the toluene mole fraction increases. Both parts of the Figure show that the Van Laar model has more deviation from experimental data.

The experimental logarithmic activity coefficients of the ternary system water + TEG + toluene for all species are depicted in Figure 5a,b as a function of the TEG and toluene mole fractions, respectively. Water and TEG are soluble together (polar phase), but toluene is present in the other liquid phase (hydrocarbon phase); therefore, the values of the activity coefficients of toluene are higher than those of TEG and water. Also, with increasing TEG mole fraction, the activity coefficient of toluene is enhanced and the activity coefficients of water and TEG decrease; however, with increasing toluene mole fraction, the activity coefficient of toluene decreases and the activity coefficients of water and TEG increase. For reasonably nonideal systems, the NRTL equation proposes no advantages over the simpler Van Laar equation. However, for stoutly nonideal mixtures and especially for partially immiscible systems, the NRTL equations provide a good representation of experimental data.³⁰ In this case, the UNIQUAC, NRTL, and Van Laar equations have good agreement with experimental data for the binary mixture (water + TEG), but for the ternary system, the Van Laar equation does not have good agreement, and the UNIQUAC and NRTL models have good consistency. Therefore, three of the equations are recommended for the binary system and two of them (NRTL and UNIQUAC) are suggested for the ternary system. Root-mean-square deviations (RMSD) in activity coefficients are shown in Table 8.

The composition of water in the liquid phase decreases in the presence of toluene, which is demonstrated in Figure 6. This Figure shows the T - x - y diagram of the mixtures water + TEG and water + TEG + toluene. This Figure shows that by the addition of toluene, the T - x - y diagram of TEG + water shifts to lower compositions of water in the liquid phase (on a toluene-free basis) at the same temperature, which means that by the addition of toluene, the composition of water in the liquid phase is less than its composition without toluene. The effects demonstrate that the toluene is more soluble in the less-volatile component (TEG) and therefore increases the relative volatility of water.

Conclusions

In the natural gas dehydration process, knowledge of thermodynamic behavior of materials is very important for the basic design and operation at industry. Isobaric VLE of water—triethylene glycol (TEG) and the effect of toluene on this solution have been investigated theoretically and experimentally. The VLE data were determined in a modified Othmer still, which is the continuous-distillation still that recirculates the vapor phase, and the samples were analyzed using GC and a titration method. The experimental data of the binary (water + TEG) and ternary systems (water + TEG + toluene) were tuned using Van Laar, quasichemical activity coefficient (UNIQUAC), and nonrandom two liquid (NRTL) activity coefficients models. Good agreements were obtained for the water + TEG system, but only NRTL and UNIQUAC models are suggested for the ternary system. The results demonstrate that the volatility of water increases in the water + triethylene glycol solution, and thus the purity of residual TEG increases by the addition of toluene. By the use of this approach, the separation of TEG and water is achieved with higher performance in the stripping columns of the natural gas dehydration units.

Acknowledgment

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