

Isobaric vapor–liquid equilibria of three aromatic hydrocarbon-tetraethylene glycol binary systems

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Abstract

Isobaric vapor–liquid equilibrium data have been determined at 101.33 kPa for the binary mixtures of benzene-tetraethylene glycol (TeEG), toluene-TeEG and *o*-xylene-TeEG. The vapor-phase fugacity coefficients were calculated from the virial equation. The thermodynamic consistency of the data has been tested via Herington analysis. The binary parameters for four activity coefficient models (van Laar, Wilson, NRTL and UNIQUAC) have been fitted with the experimental data. A comparison of model performances has been made by using the criterion of root mean square deviations in boiling point and vapor-phase composition. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Experiments; Vapor–liquid equilibria; Activity coefficient; Aromatic hydrocarbon; Tetraethylene glycol

1. Introduction

In the past few years, tetraethylene glycol (TeEG) has been more and more employed as extractant to produce high-purity aromatics from catalytic reformates because of its high selectivity for aromatics, high capacity, capability to form two phases at reasonable conditions and its physical and chemical stability. In addition, the use of triethylene glycol (TEG) or TeEG for the dehydration of gases is also a common process. Hazardous compounds such as benzene, toluene and the xylenes together with water may be removed from the gas stream by the glycol. When the glycol is reconcentrated, these compounds are released to the atmosphere along with the water vapor [1]. Knowledge of liquid–liquid and vapor–liquid equilibrium data is required for the design of these processes.

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Herskowitz and Gottlieb [2] measured the water activity in TeEG solution by an isopiestic method. Liquid–liquid equilibria in some binary and ternary mixtures with TeEG have been studied by several authors [3–5]. Al-Sahhaf and Kapetanovic [6] measured the phase equilibrium data in the extraction of aromatics from actual naphtha reformat by TeEG. But for the mixtures of aromatic hydrocarbon–TeEG, the vapor–liquid equilibrium data are not available in the literature.

In this paper, we generated isobaric vapor–liquid equilibrium data for the three binary aromatic hydrocarbon–TeEG mixtures. The data were treated thermodynamically, considering the non-ideality of both phases and verifying their thermodynamic consistency. The van Laar [7], Wilson [8], NRTL [9] and UNIQUAC [10] equations were fitted with the experimental data of each binary mixture for their optimum parameters. These experimental data may be used as a data base to optimize the design of TeEG dehydration units or extractive distillation and solvent recovery columns in the separation processes of aromatics.

2. Experimental

2.1. Material

Pure benzene, toluene and *o*-xylene were obtained from Beijing Chemical Engineering Plant, China. TeEG was procured from Beijing Yanshan Petrochemical, China. All the chemicals were repurified by distillation (TeEG distilled under vacuum) and their middle fractions were collected. They were used after reduction of water with molecular sieves with a pore diameter of 0.5 nm. The purity of all the above chemicals were checked by gas chromatography, which indicated a minimum purity of 99.8% for benzene, toluene and TeEG, and 98.7% for *o*-xylene. The normal boiling point and refractive index values were measured in this work and reported in Table 1 in comparison with the literature data in order to demonstrate the purity of the compounds.

2.2. Apparatus and procedure

In this work, an inclined ebulliometer with a pump-like stirrer (CP-I) developed by Zhou et al. [13] was used. The diagram of the apparatus is shown in Fig. 1. It is of the recirculation type, in which both liquid and vapor recirculate continuously, and the equilibrium compositions of both phases can

Table 1
Boiling points at 101.33 kPa and refractive indexes at 298.15 K, of the compounds

Substance	Boiling points (°C)		Refractive index	
	Experiment	Literature	Experiment	Literature
Benzene ^a	80.18	80.094	1.4979	1.49792
Toluene ^a	110.65	110.630	1.4941	1.49413
<i>o</i> -Xylene ^a	144.41	144.429	1.5029	1.50295
TeEG ^b	307.2	307.8	1.4570	1.4577 ^c

^aThe literature data were taken from Ref. [11].

^bThe literature data were taken from Ref. [12].

^cAt 293.15 K.

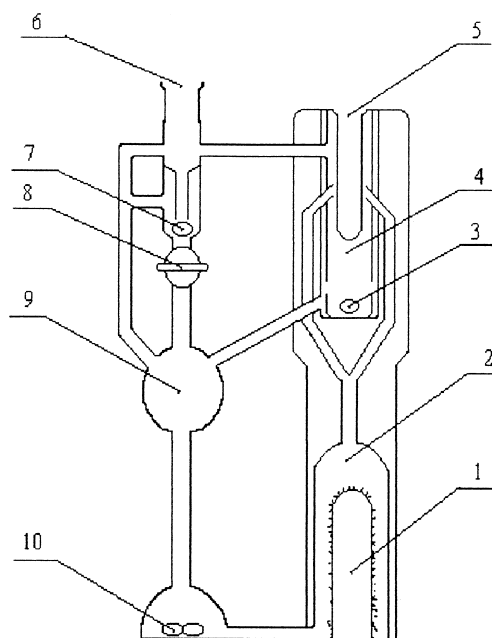


Fig. 1. Diagram of the ebulliometer: 1. heating coil; 2. boiling chamber; 3. liquid-phase sampling port; 4. equilibrium chamber; 5. where the thermometer was inserted; 6. connected to the condenser; 7. vapor-phase sampling port; 8. valve; 9. mixing chamber; 10. magnetic stirrer.

be determined. In operation of the CP-I, about 80 cm³ of solution is introduced into the still. The mixture of liquid and vapor are carried upward to the equilibrium chamber, where the two phases after striking directly against the thermometer stem, separate into a liquid and a vapor stream. The vapor is condensed in condenser and passed through the vapor-phase condensed sampling port to the mixing chamber. The liquid is cooled and passed through the liquid-phase sampling port to the mixing chamber, where it mixes with the condensate, returning to boiling room for recirculation.

Table 2

Vapor–liquid equilibrium data for benzene(1)-TeEG(2) system at atmospheric pressure

t (°C)	x_1	y_1	γ_1	γ_2
81.09	0.9631	0.999998	1.008	9.952
81.58	0.9291	0.999998	1.030	4.954
81.98	0.8846	0.999997	1.069	4.316
82.48	0.8110	0.999997	1.149	2.519
82.81	0.7625	0.999997	1.211	1.946
83.18	0.7230	0.999997	1.263	1.614
83.69	0.6767	0.999996	1.330	1.770
84.50	0.6163	0.999996	1.427	1.387
86.23	0.5300	0.999995	1.579	1.218
87.94	0.4697	0.999994	1.698	1.117
103.96	0.2384	0.99997	2.186	1.019
121.02	0.1516	0.99988	2.292	1.005
168.18	0.0565	0.99730	2.467	1.000

Table 3

Vapor–liquid equilibrium data for toluene(1)-TeEG(2) system at atmospheric pressure

t (°C)	x_1	y_1	γ_1	γ_2
113.18	0.8571	0.99996	1.089	3.580
113.98	0.6935	0.99995	1.318	1.965
114.49	0.6297	0.99995	1.432	1.565
115.64	0.5402	0.99994	1.619	1.389
116.62	0.4526	0.99993	1.883	1.264
120.92	0.3934	0.99990	1.939	1.190
124.79	0.3171	0.99987	2.182	1.042
131.62	0.2531	0.99977	2.315	1.049
142.13	0.1826	0.99951	2.519	1.016
157.83	0.1219	0.99860	2.701	1.021
161.40	0.1074	0.99825	2.853	1.017
171.11	0.0871	0.99692	2.916	1.005
181.74	0.0691	0.99442	3.026	1.002

The ebulliometer was operated at atmospheric pressure (101.33 kPa). The steady state was usually reached after 1.5 h of operation. The temperature in the equilibrium chamber was measured by using a mercury thermometer. The uncertainty in the temperature measurement is ± 0.05 K.

The compositions of the sampled liquid-phase were analyzed with an HP5890A gas chromatography, after calibration with gravimetrically prepared standard solutions. A flame ionization detector was used together with a fused silica capillary column. Because toluene-TeEG and *o*-xylene-TeEG are partly miscible system at ambient temperature, ethanol was added into the samples of liquid-phase in order to form a completely miscible liquid. The uncertainty in the molar fraction measurement of liquid-phase was estimated to ± 0.005 .

Since there is a large difference between the boiling points of TeEG and of the aromatic hydrocarbons used, the amount of TeEG present in the vapor-phase was so small that it was not detected by a gas chromatography. Therefore, a titration method [14] was used to determine the compositions of the vapor-phase condensate samples. This procedure involved perchloric acid-cata-

Table 4

Vapor–liquid equilibrium data for *o*-xylene(1)-TeEG(2) system at atmospheric pressure

t (°C)	x_1	y_1	γ_1	γ_2
145.78	0.9582	0.99978	1.009	7.028
146.20	0.9021	0.99960	1.060	5.313
149.46	0.6258	0.99931	1.409	1.955
149.86	0.5349	0.99928	1.632	1.601
151.40	0.4775	0.99919	1.761	1.458
153.24	0.3924	0.99907	2.050	1.286
155.99	0.3360	0.99886	2.242	1.222
159.35	0.2988	0.99858	2.330	1.180
167.37	0.2112	0.99761	2.748	1.110
181.61	0.1197	0.99443	3.575	1.061
188.59	0.1009	0.99188	3.681	1.053

Table 5
Physical properties of the components used in calculating the second virial coefficients

Components	P_c (MPa)	T_c (K)	Z_c	RD (nm)	μ (D)	η
Benzene ^a	4.898	562.16	0.271	0.3004	0.00	0.00
Toluene ^a	4.109	591.79	0.264	0.3443	0.36	0.00
<i>o</i> -Xylene ^a	3.733	630.37	0.263	0.3789	0.62	0.00
TeEG	2.581 ^b	772.42 ^b	0.225 ^b	0.5054 ^c	5.84 ^d	1.55 ^c

^aThe properties were taken from Ref. [16].

^bCalculated by using the method of Hakuta and Hirata [17].

^cCalculated by using the method of Fredenslund et al. [18].

^dTaken from Ref. [12].

lyzed acetylation of the organic hydroxyl groups in ethyl acetate solution. About 2 ml of the collected vapor sample was titrated according to the procedure described by Fritz and Schenk [14]. This method is sensitive enough to determine small traces of glycols to an accuracy of about $\pm 0.4\%$.

3. Results and discussion

The isobaric vapor–liquid equilibrium data for the benzene-TeEG, toluene-TeEG and *o*-xylene-TeEG systems are shown in Tables 2–4. The liquid-phase activity coefficients of the components in the mixtures were calculated from:

$$\phi_i y_i P = \gamma_i x_i \phi_i^S P_i^S \exp\left[v_i^L (P - P_i^S)/RT\right] \quad (1)$$

The vapor-phase fugacity coefficients were calculated from the virial equation. The second virial coefficients were obtained by using the method of Hayden and O'Connell [15] and the physical properties of the pure components required in this calculation are presented in Table 5. The liquid molar volumes of the pure components were calculated from the Rackett equation [21]. The vapor pressures of the pure components were determined by using Antoine equation with its constants given in Table 6. Figs. 2–4 showed the activity coefficients for the systems of benzene-TeEG, toluene-TeEG and *o*-xylene-TeEG, respectively. All the three systems satisfactorily passed the thermodynamic

Table 6
UNIQUAC structural parameters and Antoine constants of the compounds

Component	UNIQUAC parameters ^a		T (K)	Antoine constants ^b		
	r	q		A	B	C
Benzene	3.19	2.40	353–422	6.06832	1236.034	–48.990
			420–502	6.36070	1466.083	–15.440
Toluene	3.92	2.97	383–445	6.12072	1374.901	–49.657
			440–531	6.40851	1615.834	–15.897
<i>o</i> -Xylene	4.66	3.54	333–419	6.13132	1480.155	–58.804
			416–473	6.15921	1502.949	–55.725
TeEG	7.19	6.21	426–581	9.44760	4051.160	–36.521

^aCalculated from Ref. [19].

^bAntoine equation is $\log_{10} P^S = A - B/(T + C)$, where unit of P^S is kPa and constants were taken from Ref. [20].

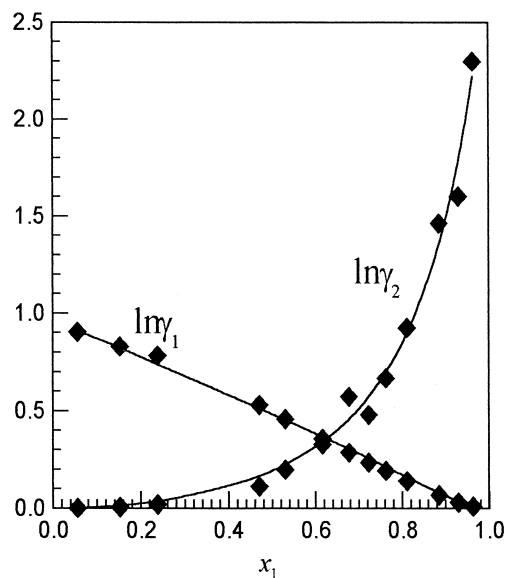


Fig. 2. Activity coefficients for the benzene(1)-TeEG(2) system at 101.33 kPa: \blacklozenge , experimental value; —, smoothed value by using the NRTL equation.

consistency test by using Herington analysis [22]. The values of $(D - J)$ for the test were found to be -96.0 , -73.9 and -54.8 for the benzene-TeEG, toluene-TeEG and *o*-xylene-TeEG systems, respectively.

The experimental data of the three binary systems were correlated by using van Laar, Wilson, NRTL and UNIQUAC equations. Estimation of the energy parameters of all the models was based on

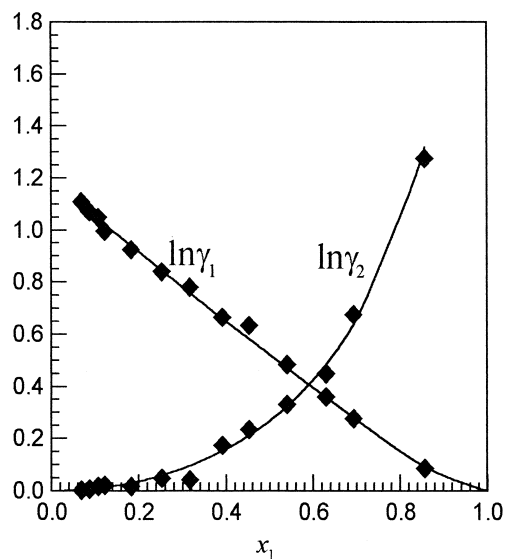


Fig. 3. Activity coefficients for the toluene(1)-TeEG(2) system at 101.33 kPa: \blacklozenge , experimental value; —, smoothed value by using the NRTL equation.

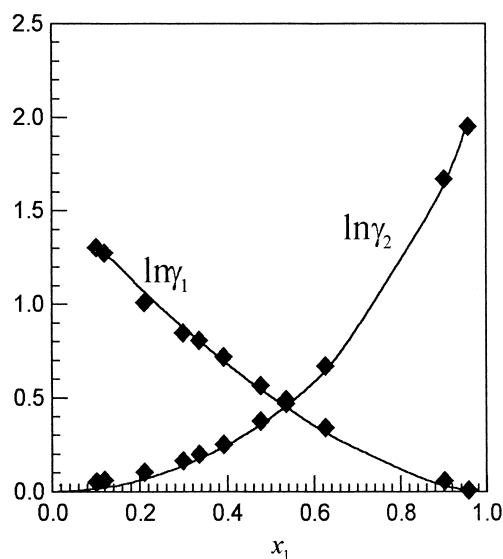


Fig. 4. Activity coefficients for the *o*-xylene(1)-TeEG(2) system at 101.33 kPa: \blacklozenge , experimental value; —, smoothed value by using the NRTL equation.

minimization of the objective function F in terms of calculated and experimental activity coefficient values. The function F used in this work can be expressed as:

$$F = \sum_{k=1}^N \left[(\ln \gamma_1^c - \ln \gamma_1^e)_k^2 + (\ln \gamma_2^c - \ln \gamma_2^e)_k^2 \right] \quad (2)$$

Table 7

Optimized binary parameters and root mean square deviations for the systems studied

System	Parameter ^a	Van Laar	Wilson	NRTL	UNIQUAC
Benzene(1)-TeEG(2)	A_{12}	0.8959	1669.78	7617.62	721.20
	A_{21}	2.7162	8953.07	1077.91	685.23
	α_{12}			0.5399	
	δ_t (°C)	1.13	0.68	0.73	3.98
	δ_y	0.00011	0.00001	0.00001	0.00083
Toluene(1)-TeEG(2)	A_{12}	1.1621	2120.53	7336.52	-33.441
	A_{21}	2.3550	8789.69	1697.09	1460.22
	α_{12}			0.4914	
	δ_t (°C)	0.94	0.96	0.92	2.31
	δ_y	0.00014	0.00011	0.00011	0.00062
<i>o</i> -Xylene(1)-TeEG(2)	A_{12}	1.5302	4026.10	5738.74	-315.40
	A_{21}	2.1838	5426.51	3166.37	1882.05
	α_{12}			0.4297	
	δ_t (°C)	1.40	1.38	1.28	1.78
	δ_y	0.00026	0.00029	0.00022	0.00030

^aWilson: $A_{12} = \lambda_{12} - \lambda_{11}$, $A_{21} = \lambda_{21} - \lambda_{22}$; NRTL: $A_{12} = g_{12} - g_{22}$, $A_{21} = g_{21} - g_{11}$; UNIQUAC: $A_{12} = U_{12} - U_{22}$, $A_{21} = U_{21} - U_{11}$.

The fitted parameters along with the root mean square deviations in boiling point, δ_r , and in vapor-phase mole fraction, δ_y , are listed in Table 7. As seen from Table 7, the results of benzene-TeEG mixture can be best represented by the Wilson equation, and the data of toluene-TeEG and *o*-xylene-TeEG mixtures can be best represented by the NRTL equation. To our surprise, the UNIQUAC equation gives the largest deviations among the four activity coefficient equations. Considering the large differences in boiling points of the binary systems, the deviations are within an acceptable range.

4. Conclusion

Experimental vapor–liquid equilibrium data on three binary systems of benzene-TeEG, toluene-TeEG and *o*-xylene-TeEG are determined at atmospheric pressure. All the three systems satisfied thermodynamic consistency as validated by using Herington analysis with $D - J < 0$. Analysis of the experimental data for the three binary systems by using the van Laar, Wilson, NRTL and UNIQUAC equations shows that all the four equations generally give satisfactory results. Surprisingly, the UNIQUAC method exhibits the largest deviations in boiling point and vapor-phase composition for all the three systems.

5. List of symbols

A_{12}, A_{21}	Parameters of the liquid activity coefficient model
A, B, C	Antoine constants
$D - J$	Herington's criterion
F	Objective function
g	NRTL parameter (J/mol)
N	Number of experimental points
p	Pressure (Pa)
q	UNIQUAC area parameter
R	Universal gas constant, 8.3144 J/(mol K)
RD	Mean radius of gyration (nm)
r	UNIQUAC volume parameter
t	Boiling temperature (°C)
T	Absolute temperature (K)
U	UNIQUAC parameter (J/mol)
v	Molar volume (cm ³ /mol)
x	Mole fraction in the liquid-phase
y	Mole fraction in the vapor-phase
z	Compressibility factor
<i>Greek letters</i>	
α	NRTL parameter
γ	Liquid-phase activity coefficient
δ	Root mean square deviation

ϕ	Vapor-phase fugacity coefficient
λ	Wilson parameter (J/mol)
η	Association parameter
μ	Dipole moment (D)
<i>Superscript</i>	
c	Calculated value
e	Experiment value
L	Liquid state
S	Saturated state
<i>Subscript</i>	
c	Critical state
1, 2, i	Components
t	Boiling point
y	Vapor-phase mole fraction

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