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Liquid - Liquid Equilibria of Methanol + Toluene + Hexane Ternary System at 278.15, 283.15, 288.15 and 293.15K

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Abstract

Liquid-liquid equilibria of methanol + ethylbenzene + methylcyclohexane ternary system at 278.15, 283.15, and 293.15K are reported. The effect of the temperature on liquid-liquid equilibrium is discussed. All chemicals were quantified by gas chromatography using a thermal conductivity detector. Experimental data for the ternary system are compared with values calculated by the NRTL and UNIQUAC equations. It is found that the UNIQUAC equation fitted to the experimental data is more accurate than the NRTL model for this ternary system.

Keywords: Liquid- liquid; Methanol; Toluene; Hexane; Equilibria

Introduction

There are increasing demands for use oxygenated compounds to produce reformulated gasoline. For this reason, we are studying the phase equilibrium of systems containing hydrocarbons and oxygenated compounds. Within the oxygenated compounds, ethers and alcohols are the most important, and among these, methanol is receiving much current attention [1-6]. Methanol presents partial miscibility with aliphatic hydrocarbons, but not with aromatic hydrocarbons. Therefore, it is of great importance to study systems composed by methanol and representative hydrocarbon of gasoline, establishing the concentration ranges and the temperature of hydrocarbons and methanol in which the two-phase region does not exist [7].

In order to obtain the behaviour of blends of hydrocarbons and methanol at four temperatures, liquid- liquid equilibrium data have been obtained for methanol + toluene + hexane ternary system at 278.15, 283.15, 288 [8]. 15 and 293.15K with constancy in temperature of ±0.05K. The equilibrium concentration for each component was determined by gas chromatography, using the internal standard method. The plait point coordinates at each temperature are reported. The experimental results were compared with those correlated with the NRTL [9] and UNIQUAC [10] models fitted to those experimental results.

Experimental Sections

Materials

Methanol, toluene and hexane were supplied by Merck. The purity of the chemicals was verified chromatographically using a HP 6890 gas chromatograph with a TCD detector coupled to a Chem Station and nitrogen as gas carrier, showing that their mass fractions were higher than 0.99. Therefore, they were used without further purification.

Apparatus and Procedures

The experimental procedure used is the same as that reported in a previous work [11]. All components in the conjugated phases were quantified by chromatography applying the internal standard method. Acetone (Merck, chromatographic quality) with a mass fraction purity >0.999(GC) was the standard compound used for this purpose. A Hewlett Packard 6890 gas chromatograph with an automatic injector (Agilent G2613A) directly connected to a Chem Station (HP G2070AA) was used. Good separation of the three components was obtained on a 30m longµ 0.25mm idµ0.5µm film thickness capillary column (INNO Wax, cross-linked polyethylene glycol, HP 19091N-233). The temperature program used was: initial temperature 343K for two minutes, ramp 50Kmin^{-1}, and final temperature 473K for another one minute. The nitrogen carrier gas flow rate was electronically kept constant working with a split ratio of 20:1 and with the injector maintained at 453K. Detection was carried out by a thermal conductivity detector at 523K. Three analyses were performed for each sample in order to obtain a mean mass fraction value with repeatability better than one percent.

We prepare several ternary mixtures with very well known concentrations by mass in order to obtain the uncertainty in the equilibrium mass fraction values. These mixtures were analysed with the chromatographic method, and their chromatographic concentrations were compared with those obtained by mass. This comparison shows that the reported mass fraction values have an uncertainty o ϕ ±0.004.

Results and Discussion

Table 1: Experimental data of (w_1 methanol+w_2 toluene+w_3 hexane) ternary system at four temperatures; wi denotes mass fraction.

T/K	Overall Compositions			Methanol - Rich Phase			Hexane - Rich Phase		
	w_1	w_2	w_3	w_1	w_2	w_3	w_1	w_2	w_3
278.15	0.4603	0	0.5397	0.775	0	0.225	0.049	0	0.951
	0.4294	0.0421	0.5285	0.717	0.036	0.247	0.058	0.05	0.892
	0.4213	0.058	0.5207	0.703	0.046	0.251	0.069	0.073	0.858
	0.4119	0.0809	0.5072	0.669	0.065	0.266	0.083	0.101	0.816
	0.3895	0.1233	0.4872	0.577	0.116	0.307	0.113	0.134	0.753
	0.355	0.153	0.492	0.52	0.145	0.335	0.148	0.163	0.689
PP[a]				0.296	0.202	0.502	0.296	0.202	0.502
PP[b]				0.303	0.201	0.496	0.303	0.201	0.496
283.15	0.3354	0	0.6646	0.731	0	0.269	0.062	0	0.938
	0.3042	0.0362	0.6595	0.696	0.023	0.281	0.076	0.044	0.88
	0.2886	0.0645	0.6469	0.674	0.037	0.29	0.098	0.079	0.823
	0.2657	0.0947	0.6396	0.588	0.067	0.346	0.113	0.109	0.779
	0.2536	0.1232	0.6232	0.533	0.108	0.359	0.119	0.131	0.75
	0.2414	0.154	0.6046	0.44	0.143	0.418	0.167	0.158	0.675
PP[a]				0.267	0.184	0.549	0.267	0.184	0.549
PP[b]				0.271	0.168	0.561	0.271	0.168	0.561
288.15	0.3111	0	0.6889	0.702	0	0.298	0.074	0	0.926
	0.3184	0.0347	0.6469	0.66	0.023	0.317	0.093	0.043	0.864
	0.2939	0.066	0.6401	0.625	0.045	0.33	0.119	0.076	0.805
	0.2937	0.0918	0.6145	0.582	0.071	0.347	0.145	0.103	0.752
	0.2725	0.1236	0.6039	0.503	0.106	0.391	0.189	0.13	0.681
PP[a]				0.327	0.151	0.522	0.327	0.151	0.522
PP[b]				0.328	0.151	0.521	0.328	0.151	0.521
293.15	0.3237	0	0.6763	0.66	0	0.34	0.084	0	0.916
	0.3031	0.0244	0.6725	0.628	0.017	0.355	0.098	0.029	0.873
	0.2995	0.0451	0.6554	0.587	0.036	0.377	0.116	0.051	0.833
	0.2778	0.054	0.6682	0.57	0.042	0.388	0.13	0.06	0.81
	0.2976	0.0782	0.6242	0.493	0.071	0.436	0.169	0.083	0.748
PP[a]				0.31	0.105	0.585	0.31	0.105	0.585
PP[b]				0.307	0.106	0.587	0.307	0.106	0.587

“Zero” means that the component is absent.

aEstimated plait point by the UNIQUAC model.

bEstimated plait point by the NRTL model.

(Table 1) report the liquid - liquid equilibrium (LLE), expressed in mass fraction, of (w_1 methanol+ w_2 toluene+w_3 hexane) ternary system at (278.15, 283.15, 288.15 and 293.15 ± 0.05) K. Figure 1 shows experimental ternary equilibrium data at the four temperatures studied here. As can be seen, a good trend agreement is achieved among all temperatures. In this plot binodal curve and tie lines were omitted in order to avoid confusion. Experimental, correlated results at 283.15K are shown in Figure 2 for comparison. For the other temperatures, similar plots were obtained. Therefore, they were not shown.

Figure 1 shows that this ternary system can be classified as type1 in the Treybal's classification [12].

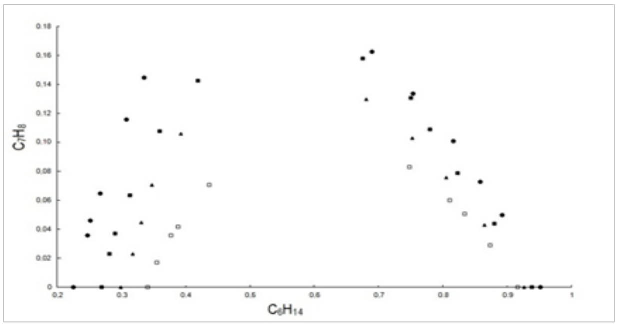

Figure 1: (Liquid + liquid) equilibrium of {w_1 CH_4O + w_2 C_7H_8 + w_3 C_6H_{14}} ternary system at T = {278.15 (●), 283.15 (■), 288.15(▲), 293.15(□)}K.

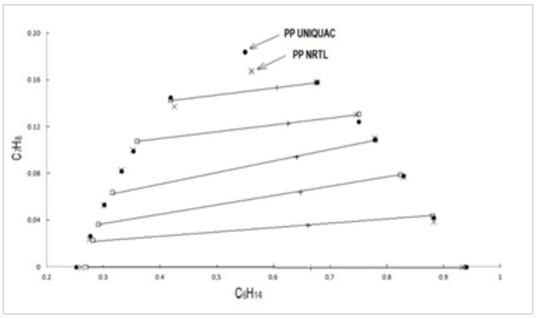

Figure 2: (Liquid + liquid) equilibrium of {w_1 CH_4O + w_2 C_7H_8 + w_3 C6H_{14}} ternary system at T =283.15 K. ■–■, Experimental; X, NRTL; ●, UNIQUAC; +, global compositions.

Since the concentrations of the three components were individually determined, the sums of the mass fractions for each phase in Table 1 may slightly differ from unity. Material balances [13] were performed for each tine line at each temperature in order to check the consistency of the equilibrium experimental data reported in Table 1. These calculations show that our data satisfy the mass balance within an average absolute deviation of 1.8, 2.0, 1.8 and 0.3 percent at (278.15, 283.15, 288.15 and 293.15) K with a greatest deviation of 2.3, 2.8, 2.4 and 0.5 percent, respectively.

The LLE data for the ternary system studied here were correlated by the UNIQUAC and NRTL activity coefficient models, using an iterative computer program developed by Sørensen [14] that minimizes the values of the following objective functions:

$$F_a = \sum^{k}\sum^{i}\left\{\left(a_{ik}^{I} - a_{ik}^{II}\right)/\left(a_{ik}^{I} + a_{ik}^{II}\right)\right\}^2 + Q\sum^{n} P_n^2 \quad ....(1)$$

$$F_x = \sum^{k}\min\sum^{i}\sum^{j}\left(x_{ijk} - \hat{x}_{ijk}\right)^2 + Q\sum^{n} P_n^2 \quad .... (2)$$

Here, $a_{ik}^{I,II}$ are the activities obtained from the experimental concentrations, I and II are the phases, x_{ijk} and $\hat{x}_{ijk}$ are the experimental mole fraction values of the liquid phase and of the calculated tie line lying close to the considered experimental line, respectively, where i represents the components, j the phases, and k the tie lines. P_n and Q are the parameter and the constant values in the penalty term, respectively.

This penalty term was established to reduce the risk of multiple solutions associated with high parameter values. The values of the penalty terms were chosen taking into account Sorensen's recommendation [14]. Table 2 shows the structural parameters of the pure components taken from literature [15] and the optimised binary interaction parameters of the UNIQUAC and NRTL models, for the ternary system. The non-randomness parameter for the NRTL equation is also given.

Goodness of fit, as measured by the r.m.s. deviation in mole fraction F, is given by

$$F = 100\left\{\sum_{k}\sum_{i}\sum_{j}(x_{ijk} - \hat{x}_{ijk})^2 / 2nM\right\}^{1/2} \quad (3)$$

Where n is the number of components in the system. The r.m.s. relative error in the solute distribution ratio Δm is given by

$$\Delta m = 100\sum_{k}\left[\left\{\left(m_k - \hat{m}_k / m_k\right)^2\right\}/M\right]^{1/2} \quad (4)$$

Table 2: Residuals F and Δm for UNIQUAC and NRTL models, optimised parameters of the UNIQUAC and NRTL equations, and non-randomness parameter (i^{th}), of the ternary system (w1 methanol+w_2 toluene+ w_3 hexane at T = (278.15, 283.15, 288.15 and 293.15)K^a.

F%	%Δm	i,j	aij ^{b}/K	aji ^{b}/K	$a_{\iota\varphi}$
T= (278.15±0.05)K					
UNIQUAC					
0.3	9.8	1.2	216.42	98.078	
		1.3	21.889	636.69	
		2.3	224.34	-31.41	
NRTL					
0.2	11.5	1.2	552.6	-1141.3	0.1
		1.3	394.45	424.43	
		2.3	-856.88	-658.88	
T= (283.15±0.05)K					
UNIQUAC					
0.6	18.4	1.2	274.31	205.19	
		1.3	21.601	586.2	
		2.3	1301.4	-123.13	
NRTL					
0.6	18	1.2	-68.795	2506.4	0.3
		1.3	515.76	430.57	
		2.3	-569.32	372.79	
T= (288.15±0.05)K					
UNIQUAC					
0.1	5.7	1.2	-428.31	114.27	
		1.3	9.582	593.57	
		2.3	-211.16	-302.51	
NRTL					
0.1	7.8	1.2	49.276	-482.29	0.2
		1.3	450.8	367.88	

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		2.3	-772.96	-109	
T= (293.15±0.05)K					
UNIQUAC					
0.1	2,6	1.2	-352.42	133.69	
		1.3	5.2664	601.32	
		2.3	-262.2	-84.49	
NRTL					
0.1	7.7	1.2	-1047.9	-1.3223	0.3
		1.3	484.92	435.17	
		2.3	-548.73	-738.08	

These residuals are listed in Table 2 for these two models. Here, x_{ijk} is the experimental mole fraction of the i^{th} component in the j^{th} phase on the kth tie line, $\hat{x}_{ijk}$ is the corresponding calculated value, m_k and $\hat{m}_k$ and are the experimental and calculated solute distribution ratios, respectively, given by w_2'' / w_2'. The goodness of fit in terms of the residuals F and Δm was satisfactory for the UNIQUAC and NRTL models, although this last residual shows relatively high values due to the large relative error associated with low concentrations of some compounds in both phases. Taking into account both residuals, the UNIQUAC equation fitted to the experimental data is more accurate than the NRTL model for this ternary system, as can be seen in Table 2.

Conclusion

LLE of the ternary system methanol + toluene + hexane was investigated at 278.15, 283.15, 288.15 and 293.15K. From LLE results, we conclude that the mutual solubility of methanol in hexane is larger than that of hexane in methanol at four temperatures. This ternary system also shows that the solubility increases when temperature increases as can be seen in Figure 1. Consequently, this blend could be used as a summer reformulated gasoline since it would not show separation of phases.

As can be seen, the solubility of this ternary system is sensitive to changes in a short range of temperature. The UNIQUAC and NRTL models show low values of both residuals, particularly for the residual F, although for Δm is high at 283.15K (Table 1) due to low concentrations of some compounds in both phases. Furthermore, taking into account both residuals, the UNIQUAC equation is more accurate than the NRTL one, except at 283.15K.

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