

# **Liquid-Liquid Phase Diagrams of Multicomponent Systems as a Function of Temperature<sup>1</sup>**

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## ABSTRACT

Methanol is used as raw material in many industrial processes and as oxygenate in gasoline formulation. However, it is well known that methanol presents partial miscibility with some hydrocarbons, hence it is very important to establish with accuracy the amount of methanol that can be blended in gasoline formulations without the appearance of a second liquid phase. This can be done through the study of phase diagrams, thus, we have determined experimentally the liquid-liquid equilibrium of the ternary systems isooctane + methanol + o-xylene, + m-xylene, and + ethylbenzene, at 298.15 K, using gas chromatography together with a calibration and the internal standard method. Furthermore, we have studied the effect of temperature on the miscibility of methanol with hydrocarbons through the measurement of the phase diagram of the system isooctane + methanol + o-xylene at 283 and 308 K. The experimental tie-line data obtained defines the binodal curve for each one of the studied systems. Since the presence of water in gasoline formulations greatly modifies the solubility of methanol, we have also obtained experimental "isowater" tolerance curves for the system isooctane + methanol + o-xylene at 283, 298 and 308 K. The experimental tie-line data for the different ternary systems were correlated with the NRTL and UNIQUAC solution models and plait points were derived.

## INTRODUCTION

Presently there is increasing interest in adding oxygenated compounds such as alcohols, to gasoline because of their octane-enhancing and pollution-reducing capabilities. Methanol has been the subject of numerous investigations in the recent years because of its anti-knocking properties and relatively low cost that makes it a good candidate to be used as additive in gasoline. Methanol can be manufactured from a variety of carbon-based feedstocks such as natural gas, coal and biomass (e.g., wood). Methanol because of its physical and chemical characteristics has several advantages as an automotive fuel, however, the phase separation had been a restriction for achieving and extensive use. The availability of the relevant liquid-liquid equilibrium data on methanol and representative compounds of the gasoline, is necessary to determine the range of partial miscibility of this compound. In this work liquid-liquid equilibrium measurements are reported for the ternary systems isooctane + methanol + o-xylene, + m-xylene, and + ethylbenzene, at 298 K. The temperature has a marked effect on the liquid-liquid phase equilibrium, this effect is studied in the system isooctane + methanol + o-xylene, 283 and 308 K; at 283 K, the partial miscibility gap is larger than those at 298 and 308 K. The presence of water in gasoline with methanol raises the phase separation region, hence, in this work we have also determined water solubility limits in a ternary phase diagrams. Isowater tolerance lines are reported at three temperatures for the system isooctane + methanol + o-xylene, 283, 298 and 308 K. The experimental tie-line data for the different ternary systems were correlated with the NRTL (Non Random Two Liquids) and UNIQUAC (Universal Quasi-Chemical

Activity Coefficients) solution models and plait points were derived, both models reproduce the data with similar quality.

## **EXPERIMENTAL**

### *Materials*

All chemicals used were of guaranteed reagent grade and their purities are reported by the supplier to be higher than 99%, they were used without any further purification because no impurities were detected on gas chromatography with a Thermal Conductivity Detector (TCD), except for isooctane which was necessary to distill in a column at high reflux in order to obtain a purity better than 99%. The water used was deionized. The compounds were dried with a molecular sieve or sodium. The amount of water of each reactive, was checked with a Karl Fisher apparatus, Aquatest 8, Photovolt, methanol contained  $8 \times 10^{-3}$  wt% water maximum.

### *Measurements*

The measurements were carried out in the same type of liquid-liquid equilibrium cells reported in the work by Romero-Martínez and Trejo (1995). These cells were thermally controlled with a constant temperature bath-circulator at the temperatures mentioned with a stability of  $\pm 0.01$  K. The sample was stirred by a magnetic bar for four hours, before allowing a 10 hours period for phase separation prior to sampling. The equilibrium samples were obtained from the upper (hydrocarbon-rich) and lower (methanol-rich) phases with disposable syringes as shown in Figure 1. The samples were analyzed in a Varian Model

3400 chromatograph using a TCD and a megaboro column DB-5 for the systems without water, for the isowater lines we used a Porapak Q column.

This method has been successfully used in the Thermodynamics Laboratory of the Mexican Petroleum Institute for several studies (Cruz, 1993; Eliosa, 1995; Peñas, 1995, García-Flores 1998), the results obtained present good accuracy.

The internal standard method was used for the calibration of the TCD's response, in this study the internal standard was toluene. The calibration samples were prepared by weight in an analytical balance Sartorius 2006 MP with a precision and accuracy of  $\pm 0.0001$ g. After the calibration samples were thoroughly stirred and analyzed in the chromatograph, the area percentage was obtained for each substance, then with the area ratio of the *i* component with respect to the area of the internal standard, and the known mass ratio, the calibration function was obtained for each component. A straight line was obtained for each component with a correlation coefficient of 0.999 minimum, which guarantees an accuracy in thousandths in mole fraction.

## **RESULTS AND DISCUSSION**

The equilibrium tie-lines for the upper phase as well as for the lower phase for isooctane + methanol + o-xylene at 298 K are presented in the Figure 2. Equilibrium tie - line results were also obtained for the isooctane + methanol + m-xylene and isooctane + methanol + ethylbenzene systems at the same temperature. Because of space limitations they are not presented in this paper.

The plot in Figure 2 exhibits type 1 liquid-liquid equilibrium behavior, with partial miscibility in a very short range of concentration, respect to the aromatic hydrocarbon its concentration is about 10% in mole fraction, the same occurs with the other two systems, i.e., the change of the aromatic hydrocarbon does not present a significant effect on the behavior of the phase diagrams. For a possible application in gasoline reformulation this result is rather important since the total miscibility region being wide means that the miscibility of methanol with the gasoline covers a large concentration range.

In the work of Higashiuchi et al. (1990), tie-line data were reported for several ternary systems containing methanol and hydrocarbons, their results have a similar behavior to those obtained here. But for the systems in which the alkane number increases, the partial miscibility gap also increases as is shown in the work by Higashiuchi et al. (1987), however, it can be noted too that in these systems the type of aromatic hydrocarbon does not modify the behavior.

The liquid-liquid equilibrium behavior changes as a function of temperature, this is shown for the system isooctane + o-xylene + methanol at the temperatures 283 y 308 K. In Figure 3 we show the corresponding phase diagrams for the three temperatures studied. We can observe from this figure that the partial miscibility zone is smaller the higher the temperature and viceversa. In the papers by Trezoni et al. (1971) and Brigs and Comings (1943), we can appreciate the same behavior.

The influence of water on the phase diagram of the studied systems is large because with a small concentration of water the equilibrium diagram can change notably, so that in this study we also measured water tolerance lines at different concentrations. In Figure 4

we present the phase diagram in weight fraction for the system isooctane + o-xylene + methanol, at 298 K. In this figure we have included the region of two liquid phases and the water tolerance lines, the right hand side of these lines represents total miscibility whereas the left hand side represents partial miscibility.

Works related to tolerance lines of water are very few, in the papers of Terzoni et al. (1971) and Ancillotti and Pescarollo (1977) tolerance lines were determined for the systems methanol - isooctane -benzene and methanol - gasoline (isooctane + toluene) - MTBE. Results from literature and those obtained in this work show that it is important to consider the presence water in gasoline reformulation, particularly with the presence of oxygenates, such as methanol.

## **CORRELATION**

The correlation of the experimental data was carried out, using two activity coefficient models: NRTL (Renon and Prausnitz, 1968) and UNIQUAC (Abrams and Prausnitz, 1975). The algorithms were developed by García-Sánchez et al. (1997). In the present work, for calculation of the plait point we used a similar procedure to that of Novák et al. (1987), which in turn is a modification of the procedure due to Heidemann and Khalil (1980). The procedure used here is described in García-Sánchez et al. (1977). For the NRTL model the parameter  $\alpha$  was set to 0.2.

In Figures 5 and 6 the results from the correlation for the system ( $x_1$ ) isooctane + ( $x_2$ ) o-xylene + ( $x_3$ ) methanol, at 298 K, are shown as a representative of the systems studied, with the models NRTL and UNIQUAC, respectively. In both cases the models fit the

experimental data very satisfactorily with standard deviations of 0.72 mole fraction % and 0.69 mole fraction %, respectively. In the diagrams, there is very little difference between the calculated and the experimental data. In general, both models correlated the data with equal quality.

The parameters  $\tau_{ij}$  for the systems: ( $x_1$ ) isooctane + ( $x_2$ ) o-xylene + ( $x_3$ ) methanol at 283, 298, and 308 K, ( $x_1$ ) isooctane + ( $x_2$ ) m-xylene + ( $x_3$ ) methanol, at 298 K, and ( $x_1$ ) isooctane + ( $x_2$ ) ethylbenzene + ( $x_3$ ) methanol, at 298 K, are given in the Tables I and II for NRTL and UNIQUAC, respectively. The plait point concentrations are reported in Table III, for both models.

## CONCLUSIONS

Liquid-liquid equilibrium data reported in this paper form type I diagrams and present a partial miscibility gap relatively small, this observation may be important in possible gasoline reformulation with methanol, because no phase separation will occur with the aromatic hydrocarbon content that conventional gasolines have.

We see that with an increase of temperature the partial miscibility region is reduced, however, even at low temperatures this zone is small.

We can see that the presence of water produces a great effect on the phase diagrams, the partial miscibility range gets bigger in the presence of water.

We have also found that our experimental data can be accurately correlated with either NRTL or UNIQUAC models.

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Table I. Parameters obtained with the model NRTL, with  $\alpha = 0.2$ .

System	$i,j$	$i,j$	$j,i$	
$(x_1)$ isooctane + $(x_2)$ o-xylene + $(x_3)$ methanol		T = 283 K		
		1,2	-314.06	1452.5
	$\sigma = 0.20$	1,3	351.12	550.17
		2,3	-95.486	880.26
			T = 298 K	
		1,2	-51.397	1301.70
	$\sigma = 0.72$	1,3	262.12	599.57
		2,3	-300.34	1397.1
			T = 308 K	
	1,2	-612.02	-596.09	
$\sigma = 0.73$	1,3	124.29	725.95	
	2,3	-216.46	-625.30	
$(x_1)$ isooctane + $(x_2)$ m-xylene + $(x_3)$ methanol		T = 298 K		
		1,2	429.18	-462.51
	$\sigma = 0.41$	1,3	263.35	583.60
	2,3	-24.538	110.50	
$(x_1)$ isooctane + $(x_2)$ ethylbenzene + $(x_3)$ methano		T = 298 K		
		1,2	-1778.9	1842.8
	$\sigma = 0.54$	1,3	261.91	600.02
	2,3	-486.34	-49.053	

Table II. Parameters obtained with the model UNIQUAC

System	$i,j$	$i,j$	$j,i$	
$(x_1)$ isooctane + $(x_2)$ o-xylene + $(x_3)$ methanol	T = 283 K			
	$\sigma = 0.15$	1,2	218.19	-204.28
		1,3	662.75	-3.4464
		2,3	350.52	-49.626
	T = 298 K			
	$\sigma = 0.69$	1,2	-471.46	841.45
		1,3	620.45	-6.0731
		2,3	266.74	-55.936
	T = 308 K			
$\sigma = 0.78$	1,2	-202.43	-233.63	
	1,3	558.51	3.7984	
	2,3	330.69	-471.85	
$(x_1)$ isooctane + $(x_2)$ m-xylene + $(x_3)$ methanol	T = 298 K			
	$\sigma = 0.36$	1,2	188.81	-151.08
		1,3	622.30	-9.9988
	2,3	263.46	-41.492	
$(x_1)$ isooctane + $(x_2)$ ethylbenzene + $(x_3)$ methanol	T = 298 K			
	$\sigma = 0.59$	1,2	-129.83	298.08
		1,3	616.19	-6.4498
	2,3	111.23	209.38	

Table III. Values of the plait point

System	NRTL		UNIQUAC	
	$x_1$	$x_2$	$x_1$	$x_2$
(x <sub>1</sub> ) isooctane + (x <sub>2</sub> ) o-xylene + (x <sub>3</sub> ) methanol	T = 283 K.			
	0.238	0.167	0.253	0.176
	T = 298 K			
	0.322	0.090	0.326	0.089
	T = 308 K			
	0.287	0.071	0.297	0.067
(x <sub>1</sub> ) isooctane + (x <sub>2</sub> ) m-xylene + (x <sub>3</sub> ) methanol	T = 298 K.			
	0.336	0.098	0.337	0.098
(x <sub>1</sub> ) isooctane + (x <sub>2</sub> ) ethylbenzene + (x <sub>3</sub> ) methanol	T = 298 K			
	0.331	0.065	0.324	0.064

## FIGURE CAPTIONS

Fig. 1 Experimental device for determining the liquid-liquid equilibrium.

Fig. 2 Liquid-liquid equilibrium of the system  $(x_1)$  isooctane +  $(x_2)$  o-xylene +  $(x_3)$  methanol at 298 K.

Fig. 3 Liquid-liquid equilibrium of the system  $(x_1)$  isooctane +  $(x_2)$  o-xylene +  $(x_3)$  methanol at 283, 298, and 308 K.

Fig. 4 Liquid-liquid equilibrium of The system  $(w_1)$  isooctane +  $(w_2)$  o-xylene +  $(w_3)$  methanol, at 298 K.

Fig. 5 Experimental data correlation of the system:  $(x_1)$  isooctane +  $(x_2)$  o-xylene +  $(x_3)$  methanol, at 298 K, with the NRTL model.

Fig. 6 Experimental data correlation of the system:  $(x_1)$  isooctane +  $(x_2)$  o-xylene +  $(x_3)$  methanol, at 298 K, with the UNIQUAC model.





