

Liquid - Liquid Equilibrium of (Methylcyclohexane + Methanol + Ethyl Benzene): Experimental Data and UNIQUAC Model

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ABSTRACT: *The determination region of solubility of methanol with gasoline of high aromatic content was investigated experimentally at temperature of 288.2 K. A type 1 liquid-liquid phase diagram was obtained for this ternary system. These results were correlated simultaneously by the UNIQUAC model. The values of the interaction parameters between each pair of components in the system were obtained for the UNIQUAC model using the experimental result. The root mean square deviation (RMSD) between the observed and calculated mole percents was 3.57 % for methylcyclohexane + methanol + ethylbenzene. The mutual solubility of methylcyclohexane and ethylbenzene was also investigated by the addition of methanol at 288.2 K.*

KEY WORDS: *Liquid-liquid equilibria, Phase equilibria, Plait point, Ternary system, UNIQUAC model.*

INTRODUCTION

The precise liquid-liquid equilibria (LLE) data is necessary to rational design of many chemical processes and optimize extraction processes. Many researchers have investigated various kinds of multi-component systems in order to understand and provide further information about the phase behavior and the thermodynamic properties of such systems [1-8].

In order to be able to predict LLE in multi-component systems, we need an adequate equilibrium model. Several LLE systems can be correlated with the solution model of the UNIQUAC [9,10]. This model depends on optimized interaction parameters between each pair of components

in the system, which can be obtained by experiments. The UNIQUAC equation can be fitted to the experimental composition by optimizing the interaction parameter.

In recent years, there is increasing attraction in adding a range of oxygenated compounds, mainly alcohols and ethers, to gasoline due to their octane enhancing [11]. In some countries, the oxygenated compounds such as, methyl tert-butyl ether (MTBE), tert-amyl methyl ether (TAME) and ter-amyl alcohol (TAOH) have been used. Methanol is one of the most appropriate oxygenated compounds for this purpose because of its physical-chemical properties. Methanol can be easily produced

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Table 1: The UNIQUAC binary interaction parameters (u_{12} and u_{21}) optimized for the system methylcyclohexane + methanol + ethyl benzene.

Components	Methylcyclohexane	methanol	ethylbenzene
Methylcyclohexane	0.000	425.760	32.675
methanol	-112.337	0.000	-54.406
ethylbenzene	9.17	135.369	0.000

from a variety of organic materials [12], petroleum, and coal. However, phase separation and the high vapor pressure of methanol in gasoline had been a restriction for achieving a wide application. Therefore, thermodynamic studies and the precise liquid-liquid equilibria data for Methanol and representative compounds of the gasoline are necessary in order to determination region of solubility of methanol and plait point of the interest system.

Present study is an to show experimentally that methanol can be used as an appropriate oxygenated compound in gasoline formulations. In view of this, we will apply for the first time, the liquid-liquid phase equilibria data are presented for three different ternary systems: methylcyclohexane + methanol + ethyl benzene at 288.15 K. Where the paraffin is methylcyclohexane a representative component of the gasoline, methanol, is the oxygenated compound, and the aromatic hydrocarbons are benzene and ethyl benzene. A high aromatic gasoline (35.4 vol % aromatic, 60.4 vol % saturates, and 4.2 vol % olefins) having density of 0.738 g/mL was used in this study. The UNIQUAC model was used to correlate the experimental liquid-liquid equilibria data. The values for the interaction parameters were obtained for the UNIQUAC model. The effect of aromatic compounds on mutual solubility of methylcyclohexane and methanol was also investigated at 288.2 K.

EXPERIMENTAL

Materials

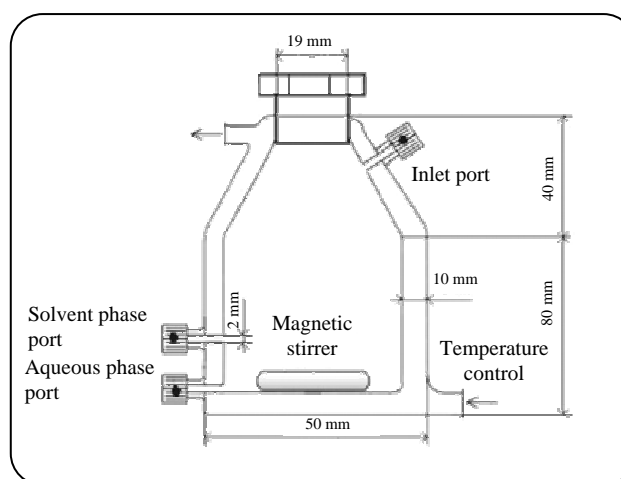
Methanol, toluene, methylcyclohexane and ethylbenzene were obtained from Merck at a purity of about 99.5 % and used without further purification. The purity of these materials was checked by gas chromatography.

Apparatus and procedure

The liquid-liquid phase equilibria measurements under ambient pressure and temperature (288.15 K) were carried out using an apparatus of a 300 mL glass cell that

Table 2: The UNIQUAC structural parameters.

Components	r	q
Ethybenzene	4.600	3.510
Methylcyclohexane	4.640	3.550
methanol	1.4311	1.4720

**Fig. 1: Liquid-liquid equilibrium cell.**

schematic diagram of the apparatus is shown in Fig. 1. The temperature of the cell was controlled by a water jacket and measured with a copper-constantan thermocouple and was estimated to be accurate within ± 0.1 K. A series of liquid-liquid equilibria measurements were performed by changing the composition of the mixture. The prepared mixtures were placed in the extraction vessel, and stirred for 2 h and then left to settle for 4 h. All mixtures were prepared by weighing with a Mettler scale accurate to within $\pm 10^{-4}$ g. All visual experiments were repeated at least three times in order to acquire high accuracy. This procedure gave consistent and reproducible results.

Samples were taken by a syringe (gas chromatography's Hamilton 0.4 μ L) from both the upper (methylcyclohexane) phase and lower layers (aromatic phase).

Both phases were analyzed using Konik gas chromatography (GC) equipped with a thermal conductivity detector (TCD) and Shimadzu C-R2AX integrator. A 2 mm (i.d.) Porapak QS packed column was used to separate the components.

RESULTS AND DISCUSSION

Fig. 1 compares graphically the observed and calculated phase behavior (liquid-liquid equilibria data) for three ternary systems: methylcyclohexane + methanol + ethylbenzene) at temperature of 288.2 K.

The liquid-liquid phase diagrams exhibit type 1 systems and as expected for these type systems, the diagrams show plait point (where the two phases in equilibrium become experimentally miscible). Due to the variation of tie-line, the measuring of plait point is really difficult. The value of the plait point is important and it is a necessary value to define the interval of solubility that present in components of a system. On other hand, this point can define the appropriate quantity of oxygenated compound that can be added to gasoline without phase separation. The plait points were determined using a graphic method [14]. The values of the plait point for these systems are presented in table 3.

As it can be seen from Fig. 2, the ternary systems present a small region of partial miscibility that limited by the plait point. It means that, methanol is totally miscible with the gasoline in a wide interval. The experimental results show, although, in representative compounds of the gasoline, the region of completely miscibility and also the plait point values are nearly the same and independent of the type of aromatic hydrocarbon (see Fig. 2 and table 4). This provides an advantage as it can define the appropriate quantity of oxygenated compound (methanol) that can be added to the gasoline.

The UNIQUAC model was used to correlate the experimental liquid-liquid equilibria data. As it can be seen from Fig. 2, the predicted tie lines (dashed lines) are in good agreement with the experimental data (solid lines). In other words, the UNIQUAC equations adequately fit the experimental data for this multi-component system.

The optimum UNIQUAC interaction parameters u_{ij} between methylcyclohexane, methanol, and ethylbenzene were determined using the observed liquid-liquid data,

Table 3: Experimental and predicted values of the plait point and the percentage of relative error.

Components	Experimental	Uniquac	Relative error %
Methylcyclohexane + Methanol + Ethylbenzene	0.5996	0.6480	0.917

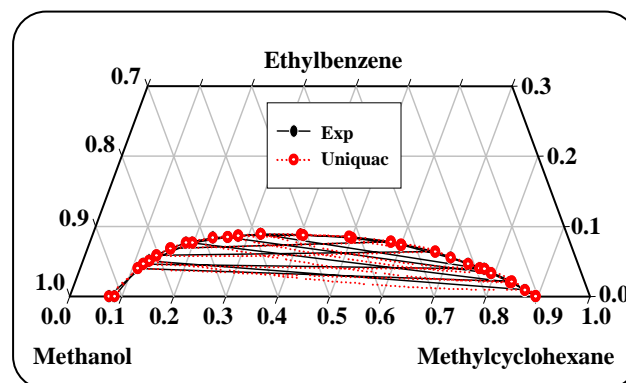


Fig. 2: Experimental (—) and predicted UNIQUAC (---) LLE data at 288.2 K.

where the interaction parameters describe the interaction energy between molecules i and j or between each pair of compounds. Table 4 shows the calculated value of the UNIQUAC binary interaction parameters for the mixture methanol + ethylbenzene using universal values for the UNIQUAC structural parameters. The equilibrium model was optimized using an objective function, which was developed by *Sorensen* [15].

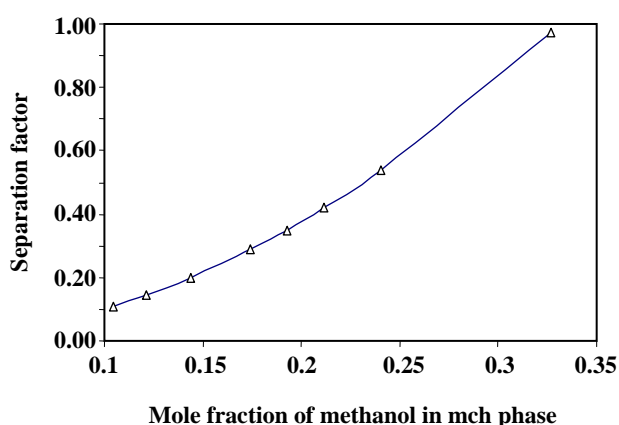
The objective function obtained by minimizing the square of the difference between the mole fractions calculated by UNIQUAC model and the experimental data. The UNIQUAC structural parameters r and q were calculated from group contribution data that has been previously reported [14,15]. The values of r and q used in the UNIQUAC equation are presented in Table 4. The goodness of fit, between the observed and calculated mole fractions, was calculated in terms root mean square deviation (RMSD) [1]. The RMSD values were calculated according to the following equation:

$$\text{RMSD} = 100 \sqrt{\frac{\sum_{k=1}^n \sum_{j=1}^2 \sum_{i=1}^3 (x_{ijk}^{\text{exp}} - x_{ijk}^{\text{cal}})^2}{6n}} \quad (1)$$

Where n is the number of tie lines, x indicates the experimental mole fraction and the calculated mole

Table 4: Experimental and predicted LLE for the ternary system (methylcyclohexane + methanol + ethylbenzene) at 288.2 K.

Methylcyclohexane (upper phase)				Ethylbenzene (lower phase)			
Mole fraction methylcyclohexane		Mole fraction methanol		Mole fraction methylcyclohexane		Mole fraction methanol	
Exp.	Uniquac	Exp.	Uniquac	Exp.	Uniquac	Exp.	Uniquac
0.8224	0.8386	0.1270	0.1260	0.1211	0.1102	0.8698	0.8810
0.7262	0.7600	0.1970	0.2000	0.1438	0.1181	0.8360	0.8659
0.6565	0.7229	0.2610	0.2532	0.1740	0.1371	0.7930	0.8360
0.5845	0.6621	0.3220	0.3221	0.1925	0.1591	0.7675	0.8040
0.5122	0.5586	0.3998	0.4108	0.2115	0.1851	0.7420	0.7699
0.4167	0.4049	0.4999	0.5010	0.2407	0.2328	0.7040	0.7070
0.3269	0.2801	0.5996	0.6100	0.3269	0.2801	0.5996	0.6480
RMSD %	4.83		4.40		2.40		2.67

**Fig. 3: Factor separation (s) of methanol as a function of the mole fraction of methanol in MCH phase.**

fraction, and the subscript i indexes components, j indexes phases and $k=1, 2, \dots, n$ (tie lines). The average root mean square deviation between the observed and calculated mole percents with a reasonable error was 3.57 % methylcyclohexane + methanol + ethylbenzene (see table 4). The percentage of relative error between the experimental and predicted values of the plait point for these systems has been also compiled in table 4. The experimental result shows that the existence of aromatic compound (ethyl benzene) in gasoline increases the solubility of methanol in methylcyclohexane.

Recently, Trejo *et al.* [13] have reported liquid-liquid equilibria measurements for methanol and representative

compounds of the gasoline, and their investigation may be important in gasoline reformation with methanol.

In Fig. 3 the separation factor (S) of methanol as a function of the mole fraction of methanol in the MCH phase, indicate that the factor of separation increase, as the methanol solubility increases in methylcyclohexane. the experimental result shows that the existence of aromatic compound (ethylbenzene) in gasoline increase the solubility of methanol in methylcyclohexane.

CONCLUSIONS

An experimental investigation of equilibrium behavior of the systems composed of methylcyclohexane + ethylbenzene + methanol was carried out at 288.2 K. The liquid-liquid phase diagrams exhibit type 1 systems and indicate that methanol is totally miscible with the gasoline in a wide interval. Therefore, methanol may be considered as a good candied in gasoline formulations for vehicular fuels.

The optimum UNIQUAC interaction parameters between methyl cyclohexane, methanol and ethylbenzene were determined using the experimental liquid-liquid data. The average RMSD value between the observed and calculated mole percents with a reasonable error for these systems was methylcyclohexane + methanol + ethyl benzene for the UNIQUAC model.

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REFERENCES

- [1] Ghanadzadeh, H. and Ghanadzadeh, A., *Fluid Phase Equilibria*, **202**, 339 (2002).
- [2] Ghanadzadeh, H. and Ghanadzadeh, A., *J. Chem. Thermodyn.*, **35**, 1393 (2003).
- [3] Arce, A., Blanco, A., Martinez-Ageitos, J. and Vidal, I., *Fluid Phase Equilibria*, **109**, 291 (1995).
- [4] Fernandez-Torres, M. J., Gomis-Yagues, V., Ramos-Nofuentes, M. and Ruiz-Bevia, F. *Fluid Phase Equilibria*, **164**, 267 (1999).
- [5] Alkandary, J. A., Aljimaz, A. S., Fandary, M. S. and Fahim, M. A., *Fluid Phase Equilibria*, **131**, 187 (2001).
- [6] Pesche, N.S. and Sandler, I., *J. Chem. Eng. Data*, **40**, 315 (1995).
- [7] Wisniewska-Gocłowska, B. and Malanowski, S.K., *Fluid Phase Equilibria*, **130**, 180 (2001).
- [8] Fabries, J.F., Gustin, J.L. and Renon, H., *Chem. Eng. Data*, **22**, 303 (1977).
- [9] Abrams, D.S. and Prausnitz, J.M., *AIChE J.*, **21**, 116 (1975).
- [10] Prausnitz, J.M., Anderson, T.F., Grens, E.A., Eckert, C. A., Hsien, R. and Oconnell, J.P., "Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria", Prentice-Hall, Inc, Englewood, (1980).
- [11] Higashiuchi, H., Sakuragi, Y., Arai, Y. and Nagatani, M., *Fluid Phase Equilibria*, **58**, 147 (1990).
- [12] Velo Garcia, E., "Cinetica Equilibria y Transport De Materia En La Hidratacion Catalitica Directa De Isobuteno a Tert-Butanol", Ph.D. Thesis, Universitat Politecnica De Catalunya Barcelona, Spain (1992).
- [13] Trejo, A., Garcia-Flores, B.E., Galicia-Aguilar, G., Eustaquio-Rincon, R., *Fluid Phase Equilibria*, **185**, 275 (2001).
- [14] Ghanadzadeh, H. "Eleccion De Disolventes Selectivos Para La Extraccion En Fase Liquida De Alcoholes C₄ (ABE) a Partir De Biomasa, Ph.D. Thesis, Universitat Politecnica De Catalunya Barcelona, Spain (1993).
- [15] Sorensen, J. M., "Correlation of Liquid-Liquid Equilibrium data", Ph.D. Thesis, Technical University of Denmark, Lyngby, Denmark, (1980).