2014 5th International Conference on Chemical Engineering and Applications
IPCBEE vol.74 (2014) © (2014) IACSIT Press, Singapore
DOI: 10.7763/IPCBEE. 2014. V74. 2

Three-Suffix Margules Model for Liquid-liquid Phase Equilibrium in Phenolic Compound Extraction from Coal Tar

Dewi Selvia Fardhyanti [1+], Megawati [1] and Sri Wahyuni [1]

[1] Department of Chemical Engineering, Faculty of Engineering, Semarang State University, E1 Building, 2nd floor, Kampus Sekaran, Gunungpati, Semarang 50229, Indonesia

Abstract. The focus of this research is to study the liquid-liquid extraction process of the major components of coal tar and to generalize the results of experiments by correlating the data of liquid-liquid equilibrium with thermodynamic model and to obtain the values of the parameters of the model. Variables of the research are composition of the solvent (the mole fraction of water and solvent), the type of solvent, and solvent-feed mass ratio.

This research includes one stage experiment, that is the the liquid-liquid extraction of phenol, *o*-cresol, and *p*-cresol using a aqueous acetone and aqueous methanol. The experiment used artificial coal tar containing phenol, *o*-cresol, *p*-cresol in kerosene, which was prepared in the laboratory with the phenol, *o*-cresol, *p*-cresol content similar to the real coal tar. The extraction process aims to obtain the equilibrium data and parameters of thermodynamic model for this system.

By using visual inspection, it can be concluded that Three-Suffix Margules's model produces the best results for predict the liquid-liquid equilibrium of phenol, *o*-cresol, *p*-cresol system studied.

Keywords: Phenol, *o*-cresol, *p*-cresol, extraction, three-suffix Margules

1. Introduction

Coal has been widely used as energy resource. With a relatively cheap price compared to other fossil fuels and its abundant availability, as well as the reserves which are relatively well-distributed all around the world, coal becomes a promising primary energy resource. In the future, Indonesian coal production is expected to increase. This is not only to meet domestic demand but also to meet export. National coal production in 1992 had reached 22.951 million tons, in 2005 it had subsequently reached 151.594 million tons, and in 2013 it became 332 million tons [1]. Most of coal production is intended to meet the export demand, i.e. about 72.11% and the remaining 27.89% is intended to meet the domestic demand. Due to the high percentage of export, it would be much better if the exported coal can be converted to alternative raw material of synthetic petroleum. Gasification and carbonation are common processes to convert coal into more valuable compounds. One of the products of the coal gasification and carbonation process is tar, which contains the large amount of economically valuable long-chain hydrocarbons. However, tar has sharp and unpleasant odor, so it is often considered as waste. Tar usually contains very complex poly-aromatic compounds, but until now its use in chemical industries is still very limited. Coal tar is also a liquid by-product in some industries such as steel, power plant, cement. The amount of tar produced from coal pyrolysis varied widely. It can reach 15.8% by weight, depending on the temperature of coal pyrolysis process and coal rank [2]. According to Egashira et al (2005), coal tar contains more than 348 types of chemical compounds, which are very valuable. They are aromatic compounds (benzene, toluene, xylene, naphtalene, anthracene, etc.), phenolic compounds (phenol, cresol, xylenol, cathecol, resorcinol, etc.), heterocyclic nitrogen compounds (pyridine, quinoline, isoquinoline, indole, etc.), and oxygen heterocyclic compound (dibenzofuran, etc.), which all have been used as raw materials or intermediates materials in

[+] Corresponding author. Tel.: +62-24-8508101; Fax.: +62-24-8508101.
E-mail address: dewiselvia@yahoo.com.

various chemical industries (as anti-oxidant, anti-septic, resin, softener ingredient in plastic industry, paint, perfume, medicine, etc.).

Although lots of studies related to coal utilization have been conducted, studies concerning coal tar are relatively rare. Some researchers have studied the coal pyrolysis and coal tar component separation [3]-[7]. Eventough extraction is an important process in separating coal tar compounds, they have not analyze the liquid-liquid phase equilibrium of its systems.

This purposes of the research are to separate the phenol compound that have some benefits. For example, phenol can be used as the main component in the production of antiseptic (trichlorophenol), washing oil, gasoline and diesel oil via catalytic hydrogenation, etc. [3]. On the other hand, cresol can be used as disinfectant (the main component of disinfectant trade, lysol), the main component of deodorizer and antiseptic. Phenol and phenolic compound, in fact, can be used in some chemical industries, such as in the production of polymers, pharmaceuticals, explosives, pesticides, stabilizers, and antioxidants [8].

This research investigates thermodynamic modelling of phase equilibria for the separation of phenol, *o*-cresol and *p*-cresol from the coal tar by solvent extraction using activity coefficient approach, in which Three-Suffix Margules equation are applied. The values of the parameter involved are obtained by curve-fitting to the experimental data. The information on activity coefficient equations is expected to be useful for predicting solvent extraction effectiveness.

2. Experimental

2.1. Material

Methanol, acetone, phenol, *o*-cresol and *p*-cresol were purchased from e-Merck (Germany), aquadest and kerosene.

2.2. Experimental

This research uses artificial coal tar solution feed with the composition:

- Solution 1: 92% v/v kerosene (diluent) and 8% v/v phenol (solute).
- Solution 2: 96.5% v/v kerosene (diluent) and 3.5% v/v *o*-cresol (solute).
- Solution 3: 89% v/v kerosene (diluent) and 11% v/v *p*-cresol (solute).

Each solution is extracted with the solvents of aqueous acetone and aqueous methanol to obtain the equilibrium data of each component. The material systems and experimental conditions for the equilibrium extraction are summarized in Table I.

Table 1: Material Systems and Conditions for Equilibrium Extraction

	Quantity
feed	Solution A, B, C
mass, R_o	2.5 mL
Solvent, E_o	aqueous methanol and aqueous acetone
mole fraction of water in solvent (Y_w)	0.2, 0.5, 0,8
solvent-feed mass ratio (E_o/R_o)	1, 2, and 3
shaking time	5 hr
amplitudo of shaking	35 rpm
temperature	308 K [9]

The feed (artificial coal tar), R_o, and the solvent, E_o, were brought into contact in an erlenmeyer flask with a screw cap. The erlenmeyer was shaken in a water bath shaker with the operating conditions as in Table I. After equilibrium attained (5 hours), the mixtures were poured into a separating funnel, settled for an hour and separated into two phases. Then the two phases were weighed. The extract phases were analyzed by Gas-Chromatograph (GC).

2.3. Data Analysis Methods

For the liquid extraction processes of the major components of coal tar, artificial coal tar is used in which the solute (A) is a phenol / *o*-cresol / *p*-cresol, diluent (D) is kerosene, and solvent are water (C) and methanol or acetone (B). Methanol and acetone need to be mixed with water because their polarities are not strong enough to form immiscible mixture with kerosene [4].

The extract phase of the each extraction processes are analyzed by GC to obtain the concentration of each component i in the extract phase ($X_{i,1}$), the concentration of each component i in raffinate phase ($Y_{i,1}$) is obtained from the mass balance of component i as follows [4]:

$$R_o.Y_{i,o} - R_1.Y_{i,1} = E_1.X_{i,1} - E_o.X_{i,o} \quad (1)$$

The calculation of the mass fraction of each component i in raffinate phase ($Y_{i,1}$) by using Equation (1) gets similar results with the analysis result by GC toward the rafinat phase.

Equation (1) is formulated based on the assumption that there is no material loss during extraction. This assumption was laboratorily checked by measuring the amount of extract and raffinate and the results were compared to the amount of initial feed and solvent. It turned out that the assumption is correct. The assumption that after 6 hours the equilibiurm has been attained was checked by analyzing the compositions of the extract and raffinate at various time. The compositions after 4 hours are almost constant. So the assumption of 6 hours for equilibrium time is justified.

In this study, the activity coefficients are calculated using semi-theoretical equation as the Three-suffix Margules equation. This equation is developed by Margules. There are some Margules equation in which the differences among one equation to another depend on the amount of suffix. This equation is giving a good overview for a simple liquid mixture which has the similarity of the molar volume of the component.

Three-Suffix Margules equation [10]:

$$\ln \gamma_A^{\,I} = A_{12}X_B^{\,2}(1-2X_A) + 2A_{21}X_AX_B(1-X_A) + A_{13}X_C^{\,2}(1-2X_A) + 2A_{31}X_AX_C(1-X_A) - 2A_{23}X_BX_C^{\,2} - 2A_{32}X_B^{\,2}X_C + \left[\frac{1}{2}(A_{12}+A_{21}+A_{13}+A_{23}+A_{32}-Q')\right](X_BX_C - 2X_AX_BX_C) \quad (2)$$

Expression for γ_B, and γ_C are similar to that of γ_A and the formulae can be obtained easily by swapping the indexes. To obtain γ_B, index 1 is swapped by 3; 2 is swapped by 3; and 3 is swapped by 1. To obtain γ_C, index 1 is swapped by 3; 3 is swapped by 2; and 2 is swapped by 1.

where: $X_1=X_A$: mole fraction of phenol in extract phase, $Y_1=Y_A$: mole fraction of phenol in raffinate phase
$X_2=X_B$: mole fraction of solvent in extract phase, $Y_2=Y_B$: mole fraction of solvent in raffinate phase
$X_3=X_C$: mole fraction of water in extract phase, $Y_3=Y_D$: mole fraction of kerosene in raffinate phase

3. Results and Discussion

3.1. Equilibrium Extraction of Phenol, *o*-cresol, and *p*-cresol Using an Aqueous Acetone Solvent with Three-Suffix Margules's Model

Fig. 1 shows that the visual comparison of calculated and experimental mole fractions in the extract phase and the raffinate phase by Three-Suffix Margules's model for the acetone solvent system are very good. It indicates that the molar volume of the components in the system is more influential than the molecules size of the component. Three-Suffix Margules's model is good to be used for simple liquid mixture with similarity of the molar volume to its components. Phenol, *o*-cresol, *p*-cresol, and acetone have similarity of the molar volume: 89.09cm^3/mol, 105.20cm^3/mol, 105.20cm^3/mol and 73.93cm^3/gmol although the molar volume of water = 18.1 cm^3/gmol and kerosene = 228.6cm^3/mol has differences. By using the visual inspection in Fig. 1, Three-Suffix Margules's model is suitable for predicting the liquid-liquid phase equilibrium in the extraction process of phenol, *o*-cresol, and *p*-cresol using an aqueous of acetone solvent. It suggests that the molar volume to its components is influential in the system.

Table II shows the activity coefficients which were calculated by Three-Suffix Margules's model and Table III shows optimization of Three-Suffix Margules's parameters for extraction of phenol, *o*-cresol, *p*-cresol using an aqueous acetone solvent.

Table 2: The Activity Coefficients were Calculated by Three-Suffix Margules's Model

	$\gamma_A^{\,I}$	$\gamma_B^{\,I}$	$\gamma_C^{\,I}$	$\gamma_A^{\,II}$	$\gamma_B^{\,II}$	$\gamma_D^{\,II}$
fenol	43.19	4.47	1.09	3.79	6.18	1.03
o-cresol	34.43	5.34	1.07	4.06	4.08	1.02
p-cresol	31.47	5.50	1.06	4.05	3.96	1.03

Table 3: Three-Suffix Margules's Parameter for the Extraction of Phenol, *o*-Cresol, and *p*-Cresol Using an Aqueous Acetone Solvent

	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}	B_{12}	B_{21}	B_{13}	B_{31}	B_{23}	B_{32}
fenol	3.652	3.305	5.068	3.035	2.392	1.768	2.959	3.013	1.322	3.075	2.247	3.311
o-cresol	3.476	3.293	4.767	3.027	2.210	1.801	2.783	2.812	1.217	3.319	1.649	3.180
p-cresol	3.335	3.237	4.474	3.024	2.356	1.885	2.838	2.849	1.266	3.366	1.608	3.056

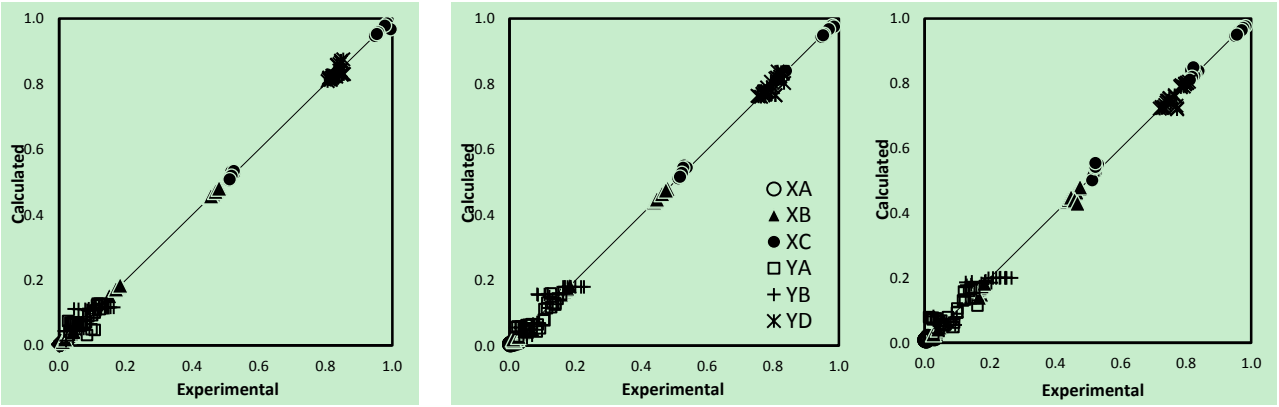


Fig. 1: Comparison of Calculated and Experimental Mole Fractions of the Phenol (a), *o*-Cresol (b), and *p*-Cresol (c) - Acetone Sytem by Three-Suffix Margules's Model

3.2. Equilibrium Extraction of Phenol Using an Aqueous Methanol Solvent with Three-Suffix Margules's Model

Fig. 2 (a), (b), and (c) show that the visual comparison of calculated and experimental mole fractions in the extract phase and the raffinate phase by Three-Suffix Margules's model for the methanol solvent system are good (indicating that the molar volume of the components in the system is more influential than the molecular size of the components), although the results are not as good as acetone solvent system because the molar volume of phenol, *o*-cresol, *p*-cresol are more likely acetone. Phenol, *o*-cresol, *p*-cresol, methanol, water, and kerosene have different the molar volume: 89.09 cm^3/mol, 105.20 cm^3/mol, 105.20 cm^3/mol, 40.50 cm^3/gmol, 18.1 cm^3/gmol, and 228.6 cm^3/mol. By using the visual inspection in Fig. 2, Three-Suffix Margules's model is also suitable for predicting the liquid-liquid phase equilibrium in the extraction process of phenol, *o*-cresol, and *p*-cresol using an aqueous methanol solvent. It suggests that the molar volume to its components is not influential in the system.

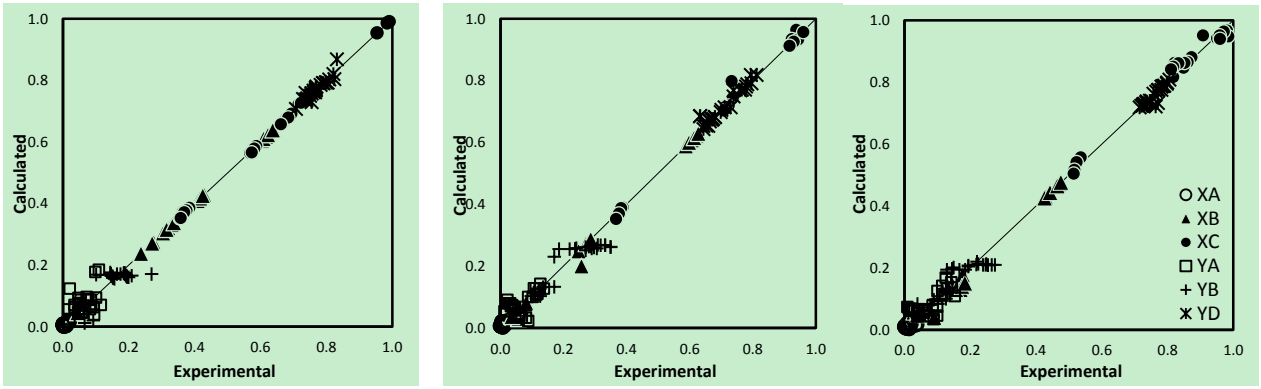
Table IV shows the activity coefficients which were calculated by Three-Suffix Margules's model and Table V shows optimization of Three-Suffix Margules parameters for extraction of phenol, *o*-cresol, and *p*-cresol using an aqueous methanol solvent.

Table 4: The Activity Coefficients were Calculated by Three-Suffix Margules's Model

	γ_A^I	γ_B^I	γ_C^I	γ_A^{II}	γ_B^{II}	γ_D^{II}
fenol	51.49	3.74	1.18	3.82	4.62	1.05
o-cresol	21.47	3.62	1.15	3.77	2.79	1.08
p-cresol	31.94	10.24	1.02	4.60	3.81	1.02

Table 5: Three-Suffix Margules's Parameter for the Extraction of Phenol,*o*-Cresol, and *p*-Cresol Using an Aqueous Methanol Solvent

	A_{12}	A_{21}	A_{13}	A_{31}	A_{23}	A_{32}	B_{12}	B_{21}	B_{13}	B_{31}	B_{23}	B_{32}
fenol	3.832	3.369	5.899	3.036	2.382	1.960	2.891	2.938	1.290	3.073	1.941	3.201
o-cresol	3.198	3.241	4.644	3.024	2.188	1.972	2.581	2.711	1.264	3.392	1.437	2.736
p-cresol	3.250	3.191	4.187	3.016	2.522	1.906	2.896	2.909	1.349	3.389	1.583	2.988



(a) (b) (c)

Fig. 2: Comparison of Calculated and Experimental Mole Fractions of the Phenol (a), *o*-Cresol (b), and *p*-Cresol (c) - Methanol Sytem by Three-Suffix Margules's Model

4. Conclusions

Thermodynamic models for the extraction of phenol, *o*-cresol, and *p*-cresol using an aqueous acetone and an aqueous methanol solvents showed that the Three-Suffix Margules's model is suitable for predicting the liquid-liquid equilibrium in phenol, *o*-cresol, and *p*-cresol extraction.

The activity coefficients of methanol, acetone, phenol, *o*-cresol, and *p*-cresol in the extract phase and raffinate phase are far from unity. It means that they are far from ideal condition. The activity coefficients of water and kerosene in their phases are close to one. It means that they are nearly ideal in their phases.

5. Acknowledgements

The authors would like to acknowledge Directorate General of Higher Education, Indonesia, for financial support of this work through the research grant of "Hibah Bersaing" Universitas Negeri Semarang (UNNES) No. 1.14.5/PPK.3.1/2013.

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