Liquid—liquid equilibria for the extraction of phenols from alkane using ethylene glycol

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ABSTRACT

The separation of low temperature coal tar can be carried out using extraction technology, especially for the collection of phenols. Liquid—liquid equilibria data for the ternary mixture of 1-Heptane + phenols + ethylene glycol were obtained at 323.15 K and 343.15 K under atmospheric pressure, where phenols refer to phenol, o-cresol, m-cresol and p-cresol. The tie lines were displayed in ternary phase diagrams. The distribution coefficient and selectivity were calculated according to the measured tie-line data. The calculation results revealed that the selectivity was large enough for the extraction application. The root-mean-square deviation (RMSD) value of the NRTL model was a little lower than that of UNIQUAC, demonstrating NRTL can better fit the experimental data.

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1. Introduction

Coal tar, as a byproduct of coal coking, is an important feedstock for the coal chemical industry due to its numerous and valuable components. In the chemical industry, distillation is widely applied to separate light components of coal tar. After distillation, several fractions of high temperature tar are roughly obtained: BTX, carbolic oil, naphthalene oil, wash oil, anthracene oil and coal-tar pitch [1]. However, the distillation process demands high energy at a high cost. Therefore, it is necessary to find a lower consumption process like the extraction technology to obtain phenols in low-temperature tar. Phenol and phenol derivatives mainly obtained from coal tar are widely used in the production of polycarbonates and phenolic resins [1].

An optimized planning and realization of extraction plants in the chemical industry will require comprehensively qualitative and quantitative phase equilibrium data [2]. Due to the complicated components of tar, it would be an insurmountable task to completely obtain the liquid—liquid equilibrium data of every individual compound and solvent. Therefore, a simplification method is used in this work, as referred to that in Catherine A. Peter's report

[3]. 1-Heptane and phenols are used as the main representative components in low temperature tar. Considering the polarities of these components are different, the polar solvent may be used as the extractant to separate coal tar. Ethylene glycol, as a typical polar solvent, has been used for phenol extract and arenes separation from nonaromatic compounds [4,5].

At present, the liquid—liquid equilibria data of a coal tar system is rarely reported in literature, especially for the system containing phenol. According to Zhang's report [6], phenol, o-cresol, m-cresol, and p-cresol are the main phenols in low temperature coal tar. So, the LLE data for the ternary mixture of 1-Heptane + phenols + ethylene glycol were measured at 323.15 and 343.15 K under atmospheric pressure. Tie-lines are determined for the ternary systems according to the LLE data. The distribution coefficient and separation factor were calculated according to the LLE data and used as the standard to evaluate the separation efficiency. The experimental data are also correlated with Non-Random Two Liquids (NRTL) [7] and Universal Quasi-Chemical (UNIQUAC) [8] activity coefficient models.

2. Experimental

2.1. Materials

The chemicals used were 1-Heptane, phenol, o-cresol, m-cresol,

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Nomenclature

g, u	interaction parameters
K	the distribution coefficient
M	number of tie lines
OF	objective function
q	area parameter in UNIQUAC equation or randomly varying quantity described by a probability distribution
$\bar{q}$	arithmetic mean of n independent repeated observations q_k of randomly-varying quantity q
q_k	kth independent repeated observation of randomly-varying quantity q
r	volume parameter in UNIQUAC equation
RMSD	root mean square deviation
$s(\bar{q})$	experimental standard deviation of the mean q, equal to the positive square root of $s^2(\bar{q})$
$s(q_k)$	experimental standard deviation, equal to the positive square root of $s^2(q_k)$
$s(\bar{X}_i)$	experimental standard deviation of input mean X_i equal to the positive square root of $s^2(\bar{X}_i)$
S	the separation factor
$u(x_i)$	standard uncertainty of input estimate x_i that estimates input quantity X_i
w_i	mass fraction composition of liquid phase
x_i	estimate of input quantity X_i
X_i	i th input quantity on which the measurand depends
$\bar{X}_i$	estimate of the value of input quantity X_i

Greek letter

α	non-randomness factor in NRTL equation

Superscripts

ˆ	calculated

Subscript

i, j	component identification: 1, 2, 3
k	number of the tie line

p-cresol and ethylene glycol, which were purchased from Sinopharm Chemical Reagent. The details about the chemicals are presented in Table 1. The purities of these components were tested by gas chromatography and no appreciable peaks of impurities were found, which indicated no purification methods were needed for the LLE measurements.

2.2. Apparatus and procedure

LLE data for the studied ternary system were obtained at 323.15 and 343.15 K under atmospheric pressure. The details about experimental equipment have been presented in our previous work and the reliability of the experimental system has been evaluated [9]. The set-up is shown in Fig. 1. The agitation and settling time were investigated, demonstrating that the equilibrium could be attained in 1 h. So, this mixture was agitated vigorously for at least 1 h and left for 1 h before GC measurements. Meanwhile, the air in the still was replaced by N_2 in order to prevent the oxidation of phenol. The evaporated compounds were completely condensed by the condenser to ensure the mass balance.

After 1 h of settlement, the liquid−liquid equilibrium was formed. Afterwards, the samples were taken from the still and then analyzed by GC. Agilent GC6820 gas chromatograph equipped with a thermal conductivity detector and Porapak N column (3 mm × 3 m) was used. The carrier gas was hydrogen with a flow rate of 60 mL/min. The temperature of the injector and detector was 523.15 K. The column temperature was kept at 423.15 K for 0.5 min, then increased to 523.15 K at a rate of 20 °C/min and maintained at this temperature for 6.5 min. The calibration area normalization method was used to obtain quantitative results in the analysis. Each
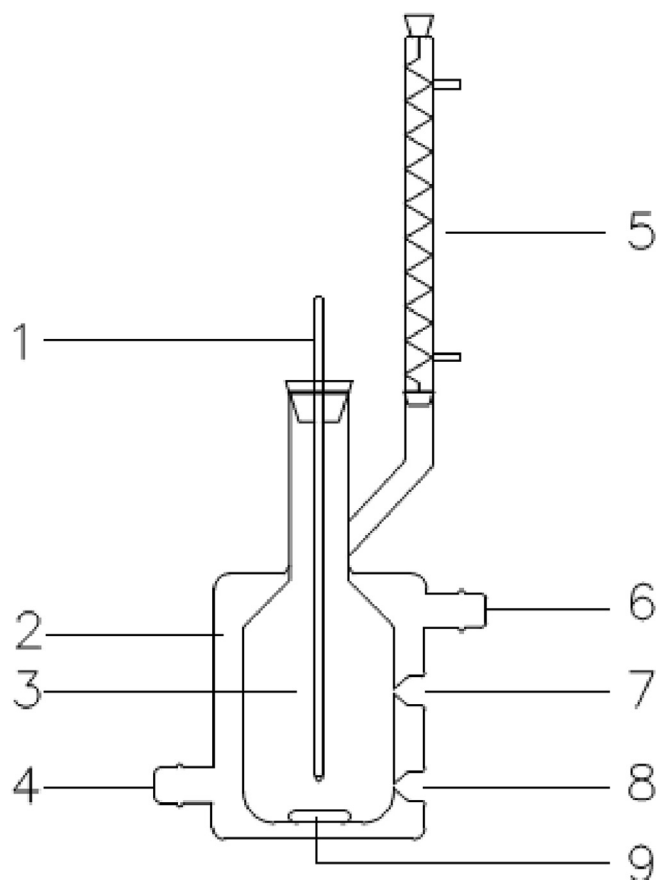
Table 1
Materials description.

Component	CAS	Source	GC purity (mass%)
1-Heptane	142-82-5	Sinopharm	99.97
Phenol	108-95-2	Sinopharm	99.90
o-Cresol	95-48-7	Sinopharm	99.26
m-Cresol	108-39-4	Sinopharm	99.19
p-Cresol	106-44-5	Sinopharm	99.37
Ethylene glycol	107-21-1	Sinopharm	99.59

Fig. 1. (Liquid + liquid) equilibrium still. 1. thermometer; 2. circulating water chamber; 3. equilibrium cell chamber; 4. circulating water inlet; 5. condenser; 6. circulating water outlet; 7.light phase port; 8. heavy phase port 9. magnetic stirrer.

sample was analyzed at least three times and the average value was used as the sample composition. According to GUM standard [10], the standard uncertainty of the liquid phase compositions was