



The application of a modified dissolving model to the separation of major components in low-temperature coal tar



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ABSTRACT

The selectivity of organic solvent extraction for separating non-aromatic hydrocarbons, aromatic hydrocarbons and polar components in low-temperature coal tar was enhanced by applying the Hansen Solubility Parameters theory. The relationship between solubility parameter “distance” (R_d) and solubility was obtained by turbidimetric titration, thus allowing an approximate comparison of dissolving properties between different solvents and the typical model compound (solute). A modified dissolving model in terms of the Hansen solubility sphere was established in order to select the extraction solvent. In practice, the low-temperature coal tar was successfully divided into three parts (i.e., enriching non-aromatic hydrocarbons, aromatic hydrocarbons and polar components) by a three-step extraction-precipitation process at 298 K and 1 atm. Experimental results demonstrated a high correlation with the estimation made by the ellipsoidal model. The mass percentage of non-aromatic hydrocarbons, aromatic hydrocarbons and polar components in their separation products were all ca. 90 wt.%. The mass percentages of the three products in total feedstock were around 12%, 46% and 36%, respectively. The mass loss during the entire separation process was from 4.5% to 6.0%.

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1. Introduction

Generally speaking, the efficient utilization of coal tar always requires a proper pre-separation process, e.g. the preparation of liquid fuel from low-temperature coal tar. Different components in coal tar (i.e. aromatics and non-aromatics) demand different optimized conditions in the catalytic hydrogenation and/or cracking process [1,2], while other components (e.g. phenols and heterocyclic compounds) could harm catalytic processing and affect the utilization of refined oil [3–5]. In addition, phenols and heterocyclic compounds are high value-added materials in the chemical industry. Thus, an effective separation process would not only advantage tar processing but also bring additional economic benefits by rationally using each component in the feedstock.

As one of the most common methods used in tar separation, extraction is suitable for large-scale treatment and can deal with compounds with high burning points or that are unstable under high temperature. To enhance the selectivity of coal-tar extraction, the Hansen Solubility Parameters theory was adopted. The Hansen Solubility Parameters theory is based on the well-known principle of chemistry that “like dissolves like” [6]. The theory divides cohesive energy into three parts,

according to intermolecular forces [7,8], and thus can be appropriate for both polar and non-polar compounds. Wide applicability and high accuracy make the theory quite useful for solvent selection [9,10], and it has already been widely used in coating chemistry [11,12], medicinal chemistry [13], and polymeric chemistry [14], among other areas. There are also applications of the Hansen Solubility Parameters in the fields of petroleum and coal chemistry. Hansen Solubility Parameters theory was used to study dissolution and swelling property of coal [15], evaluate the solubility of coal tar pitch [16,17], and to perform the removal of n-Alkanes from diesel fuels [18]. Besides, there are also applications of 2-dimensional solubility parameter in the study of dissolving capacity of petroleum [19,20]. The theory also presents strong potential to enhance the selectivity of the extraction process for coal tar; however, this application is still uncommon due to the complexity of coal tar composition and insufficient basic data (i.e., Hansen Solubility Parameters and dissolving radius) for coal tar compounds [21,22].

This study sought to selectively separate major components in low-temperature coal tar by extraction. Because of the compositional complexity of low-temperature coal tar, several model compounds with representative dissolving properties were studied. The solubility parameter “distance” (R_d) was related directly to solubility by turbidimetric titration, and a modified ellipsoidal model taking the form of a Hansen Solubility Parameters sphere was provided. A three-step extraction-precipitation process was conducted using the dissolving

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model. In practice, the feedstock was separated into three parts: i.e., enriching non-aromatic hydrocarbons, aromatic hydrocarbons and polar components. The high selectivity presented in the extraction process revealed that the modified ellipsoidal model has good applicability.

2. Materials and methods

2.1. Materials

The feedstock used in this study was low-temperature coal tar obtained from a semi-coking smelting plant in Shanxi Province, China. The ultimate analysis of the feedstock used in this study is presented in Table 1.

The solvents used in this study are dimethylformamide (DMF, AR), 1-Methyl-2-pyrrolidinone (NMP, >98%), Dimethyl sulfoxide (DMSO, AR), Sulfolane (>98%), Diglycol (>98%), Triglycol (>98%). They were obtained from Aladdin Industrial Corporation (shanghai), and used without further purification.

2.2. Separation process

A three-step extraction-precipitation process was proposed as shown in Fig. 1. First, aromatic hydrocarbons and polar components were extracted from the feedstock using a solvent with strong polar and hydrogen-bonding force, while at the same time keeping non-aromatic hydrocarbons in the residue (aromatics extraction process). Next, aromatic hydrocarbons were separated from the solution by adding anti-solvent to weaken the dissolving capacity of the solution (aromatics precipitation process). Finally, the solvent was removed and the polar components were collected (solvent recovering process).

2.3. Analytical methods

The composition of coal tar distillate and separation products was qualitatively analyzed by GCMS (multistage ion-trap chromatography mass spectrometry apparatus, VARIAN 4000, US), and then quantitatively analyzed by total ion chromatogram (TIC spectrum) using the area normalization method. Even though the response value might have varied between different components, the comparative analysis of a specific component was considered to be reliable. The solvent was trichloromethane and the column of GC was VF-5 ms (diameter: 0.25 mm × 60 m). Injection temperature was 290 °C, and injection volume was 3 µl. Electron energy of the EI source was 70 eV, scanning range was from 50 to 1000 amu, and scanning time was 1.64 s.

2.4. Model compounds

Considering the complexity of the low temperature coal tar, this study discusses the dissolving capacity of model compounds by the theory of Hansen solubility parameter instead of an investigation on the Hansen solubility parameter of the whole coal tar feedstock. The substance of this study is to precipitate major coal tar components selectively by changing the polarity of the solution phase, so the solubility of the chosen model compound in polar solvents should be relatively high compared with other compounds with the similar structure. Thus, n-octadecane and toluene/naphthalene were used to represent the non-aromatic hydrocarbons and aromatic hydrocarbons in coal tar feedstock, respectively. Compared with non-aromatic hydrocarbons

and aromatic hydrocarbons, polar components, such as phenols and heterocyclic compounds are supposed to stay in the solution, rather than in the residual. Those components (the polar components) would not be obtained by the precipitation induced by adding anti-solvent to the solution, but by just removing the mixed solvent in solvent recovering process; therefore we only select the model compounds of non-aromatic hydrocarbons and aromatic hydrocarbons. If the solvent can't dissolve the model compounds, other compounds with the similar structure would also prefer to stay in the residual. The dissolving properties of model compounds were discussed by turbidimetric titration and a modified ellipsoidal model. The optimized solvent composition was estimated and then modified by the three-step extraction-precipitation process mentioned in Section 2.2.

2.5. Turbidimetric titration and establishment of the dissolving model

The turbidimetric titration conducted in this study was similar to that used in previous researches [23–27]. Firstly, the compound under investigation was dissolved in certain amount of good solvent, and the detailed composition of the solution can be found in Table 2 and the Supplementary information (Table s1 and s2). Then the solution was titrated with an anti-solvent (i.e., a solvent with weak or little dissolving capacity for the solute) until precipitation occurred. For one compound under investigation, a series of solutions with concentration gradients was studied by the titration process. At the moment of precipitation, the concentration of solute could be regarded as its solubility in the mixed solvent, calculated in Eq. (1):

$$X = n_2 / (n_{\text{total}} + n_2) = n_2 / (n_1 + n_1' + n_2) \quad (1)$$

where X is the solubility (molar fraction) of solute in the mixed solvent, n_2 is the molar number of the solute, n_{total} is the total molar number of solvents, n_1 is the molar number of good solvents, and n_1' is the molar number of anti-solvent added in the solution until turbidity occurred. The Hansen Solubility Parameters of the mixed solvent when precipitation occurred were calculated by Eq. (2):

$$\delta_{\text{blend}} = \varphi_{\text{comp1}} \delta_{\text{comp1}} + \varphi_{\text{comp2}} \delta_{\text{comp2}} + \dots \quad (2)$$

where δ_{blend} is the partial solubility parameter (δ_d , δ_p or δ_{hb}) of the mixed solvent, and (δ_{comp1} , δ_{comp2} ...) and (φ_{comp1} , φ_{comp2} ...) are the partial solubility parameters and volume fractions of individual solvents, respectively.

The solubility parameter “distance” (R_a) between the solute and the mixed solvent at the moment precipitation occurred was calculated as follows:

$$R_a = \sqrt{4(\delta_{d1} - \delta_{d2})^2 + (\delta_{p1} - \delta_{p2})^2 + (\delta_{\text{hb1}} - \delta_{\text{hb2}})^2} \quad (3)$$

where δ_{d1} , δ_{p1} , and δ_{hb1} refer to the Hansen Solubility Parameters of the solute; and δ_{d2} , δ_{p2} , and δ_{hb2} refer to the Hansen Solubility Parameters of the mixed solvent. The subscripts “d”, “p” and “hb” means the contributions of “dispersion force”, “polarity force” and “hydrogen bonding force”, respectively. The constant 4 is an empirical constant developed from plots of experimental data suggested by [28]. It can also be theoretically predicted by the Prigogine corresponding states theory when the geometric mean is used to estimate the interaction in mixtures of dissimilar molecules [29]. An attempt to relate solubility (X) to the solubility parameter “distance” (R_a) was made in order to achieve a convenient estimation of dissolving properties between solvents and solute.

The dissolving model of certain model compound was established based on the relationship between R_a and the solubility. For certain solute, a set of R_a and solubility can be found by turbidimetric titration as shown in Table 2 and the Supplementary information (Table s1 and s2). Regression analysis among this data was carried out, and thus a relationship between R_a and solubility was found (Eq. (4), Section 3.1).

Table 1
Ultimate analysis of feedstock.

C	H	N	S	O*	H/C
81.42	6.93	1.65	1.66	8.34	1.02

* by difference

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