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Separation of *para*-xylene and *meta*-xylene by extraction process using aqueous cyclodextrins solution

Haofan Yang, Yufeng Hu*

State Key Laboratory of Heavy Oil Processing and High Pressure Fluid Phase Behavior & Property Research Laboratory, China University of Petroleum, Beijing 102249, China

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ABSTRACT

The separation of *para*-xylene (*p*-xylene) from its mixtures with *meta*-xylene (*m*-xylene) using aqueous hydroxypropyl- β -cyclodextrin (HP- β -CD) solution by a two-step liquid–liquid extraction process has been experimentally investigated. The results show that HP- β -CD can form inclusion complexes of different strengths with *p*-xylene and *m*-xylene. It is shown that the different strengths stem from the differences in size, relative alkalinity and dipole moment between the two xylene isomers. The optimum separation condition has been determined as follows: the concentrations of HP- β -CD and initial xylene mixture are $0.1448 \text{ g}(\text{g H}_2\text{O})^{-1}$ and $0.4 \text{ g}(\text{g H}_2\text{O})^{-1}$, respectively. Under this condition, the separation factor α , which is the most important evaluation index in extraction process, is 1.469. The ratio of the formation constants, K_{PX}/K_{MX} , has been determined to be slightly greater than α , consistent with the theoretical prediction. Moreover, a new method for calculation of α has been developed. The experimental results demonstrate the almost perfect reusability of aqueous HP- β -CD solution. For the experiment that begins with a 1:1 mixture of *p*-xylene and *m*-xylene, the *p*-xylene concentration in the extraction phase is 59.71 wt%. After repeating the extraction process 4 times, the concentration of *p*-xylene in the extraction phase can reach 81.48 wt%.

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1. Introduction

Xylenes are one of the most important chemicals, which are mainly used for the production of motor fuels and many other chemicals such as terephthalic acid, phthalic anhydride and isophthalic acid, etc [1]. Since xylene mixtures are produced from naphtha cracker, it is very important to separate xylene isomers, especially *p*-xylene and *m*-xylene. However, it is very difficult to separate them by conventional distillation or rectification due to the close proximity of their boiling points. The effective separation method widely used in industrial production is by absorption, but the expensive cost due to damage and consumption of absorbents is an inevitable disadvantage.

On the other hand, selective liquid–liquid extraction was known as an effective method for the separation of isomers and azeotrope or liquid mixtures having close boiling temperatures [2,3]. The liquid–liquid extraction process has proven to be energy-saving and not time-consuming [4,5]. If an extractant which has high selectivity and recycling efficiency is developed, the extraction

method will hold the potential to replace the widely used absorption approach for the separation of xylene isomers.

Cyclodextrins (CDs), water-soluble oligosaccharides consisting of 6, 7 and 8 glucose units corresponding to α -, β - and γ -CD, respectively, are extensively used in separation due to their remarkable property to accommodate molecules in their cavity. The cavity diameter of α -, β - and γ -CD is 0.47–0.53 nm, 0.60–0.65 nm, 0.75–0.83 nm, respectively [6]. The internal structure of CD is formed by the carbon backbones, making the interior relatively hydrophobic, while most of the CD protons are located outside the CD cavity devoted to the hydrophilic surface. The detailed structure of β -CD is shown in Fig. 1. As a consequence of these features, CDs can encapsulate a wide variety of hydrophobic molecules, or part of them inside their cavity through non-covalent interactions to form host–guest type inclusion complexes [7]. The driving forces to form inclusion complexes include electrostatic and van der Waals interactions as well as hydrogen bonding [8].

Selective liquid–liquid extraction of xylene isomers and ethylbenzene by glucosyl- α -cyclodextrin was reported twenty years ago [9]. This method has yet not been used due to the high price and the complex processes for the synthesis of glucosyl- α -cyclodextrin. β -CD is the most frequently used one due to its readily availability and low cost among CDs. Moreover, the cavity

* Corresponding author.

E-mail address: huyf3581@sina.com (Y. Hu).

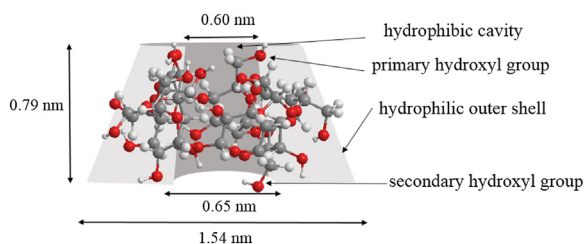


Fig. 1. Structure of β -CD.

diameter of β -CD is similar to the kinetic diameter of xylene isomers. The main disadvantage of native β -CD is its low solubility in water (0.18 g L^{-1}) [10,11]. However, with the conjugation of hydroxypropyl (HP), β -CD not only becomes much more water-soluble (750 g L^{-1}) [12] (because its intermolecular hydrogen bonds among the secondary hydroxyl groups of native CDs are disrupted) [13,14], but also keeps its original characteristics and properties. Because of this, Du et al. [15] have reported the experimental results for separation of xylene isomer mixtures in DMF solution of β -CD by extraction process. The xylene isomers considered included the *p*-/*o*-xylene system and the *o*-/*m*-xylene system. However, these authors did not report the data for the *p*-/*m*-xylene system. It is notable that several attempts have been made to separate xylene isomers using CD-containing membranes [16–18]. However, the long-term instability and a large amount of CDs required may limit their industrial applications. Furthermore, the techniques on the basis of membranes are still in the early development stage. Few experimental data are available in literature and no evaluation of reusability has been reported so far. Nevertheless, these results [16–18] served as examples to show that aqueous solutions of CDs are suitable to be used to separate xylene isomers [19–21].

The above-mentioned theoretical argument shows that aqueous HP- β -CD solution is suitable for separation of *p*-xylene from its mixture with *m*-xylene. The objective of this research is to provide experimental evidences. Therefore, the effects of the concentration of HP- β -CD and the composition of xylene mixtures will be investigated. The separation factor α will be determined to illustrate the separation efficiency under different compositions of xylene mixtures and, then, will be compared to the ratio of the formation constants K . A new method for calculation of α will be developed. And the reusability of aqueous HP- β -CD solutions will be determined. All our measurements will be made using the HP- β -CD that has a relative molecular weight of 1448.

2. Materials and methods

2.1. Materials

HP- β -CD (molecular weight of 1448) was purchased from KunShan technology Co., Ltd. *p*-Xylene (purity 98 wt%), *m*-xylene (purity 98 wt%), cyclohexane (purity 98 wt%) and ethylalcohol (purity ≥ 99.5 wt%) were obtained from Aladdin. Deionized water was distilled in a quartz still, and its conductivity was $0.8\text{--}1.2 \times 10^{-6} \text{ S cm}^{-1}$.

2.2. Extraction process

HP- β -CD was dissolved in deionized water (50 g) in a conical flask. Then a known amount of xylene mixture was added and the thus-obtained aqueous solution was vigorously stirred in a thermostated bath. The solution separated into two layers after standing for a few minutes. The lower was the aqueous phase in which *p*-xylene and *m*-xylene were selectively incorporated into

the cavity of HP- β -CD, whilst the upper was the xylene mixture. The lower aqueous phase was obtained by the first step of extraction.

In order to acquire the separated *p*-xylene and *m*-xylene, cyclohexane [$0.3 \text{ g (g H}_2\text{O)}^{-1}$] was added to the aqueous phase. After it was adequately shaken in a little volumetric flask (100 mL), the solution was transferred to a separating funnel. Two layers were formed after standing for a few minutes. The upper was the organic phase of xylene isomers and the lower was the aqueous HP- β -CD solution. The objective products in the organic phase were collected by the second step of extraction. Another extraction experiment from aqueous HP- β -CD solution was conducted to measure the amount of xylene isomers in aqueous HP- β -CD solution. It was shown by GC measurements that the amount of xylene isomers in aqueous solutions was negligible.

2.3. Separation factor α and formation constant K

The extraction efficiency can be described by the separation factor α :

$$\alpha = \frac{y_p/y_m}{x_p/x_m} \quad (1)$$

where y_p and y_m are the weight percents of *p*-xylene and *m*-xylene in the extraction phase, respectively. x_p and x_m are their weight percents in the feed, respectively.

The formation constant K can be used to better understand the strength of the binding between host and guest molecules. Several researchers have obtained the K values for the binding interactions between various CDs derivatives and xylene isomers by various methods. The relationship between K and α was studied in the following section. Our results showed that the K values can be used to estimate the α value.

2.4. Analytical technique

Samples were analyzed by the BeiFen Gas chromatograph instrument equipped with a FID detector. An Agilent capillary column (HP-INNOWAX length: 60 m, diameter: 0.32 mm, film thickness: 0.25 μm) was used. Analysis conditions were the following: Injection port temperature 473 K; FID temperature 493 K; column temperature holding at 323 K for 24 min; splitting ratio 1:20; sample size 0.2 μL ; carrier gas nitrogen of 0.4 MPa; reagent gases air of 0.4 MPa; hydrogen of 0.3 MPa. Under these conditions, quantification of the components was carried out with the help of an internal standard (ethylalcohol).

3. Results and discussion

3.1. Separation mechanism

CDs and their derivatives can selectively incorporate several organic compounds owing to their function of molecular recognition. Here, our expectation that HP- β -CD is suitable for the separation of *p*-xylene and *m*-xylene by extraction process is based on the following three reasons (the main distinctions between *p*-xylene and *m*-xylene are summarized in Table 1). First, HP- β -CD

Table 1
Distinctions between *p*-xylene and *m*-xylene.

Name	Kinetic diameter/nm	Relative alkalinity	Dipole moment/Debye
<i>p</i> -Xylene	0.58	1 ^a	0.0801 (0.02 ^b)
<i>m</i> -Xylene	0.68	100 ^a	0.3825 (0.30 ^b)

^a Ref. [24].

^b Calculated by the Frohlich equation [25].

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