

The Separation of Benzene and N-Octane by Liquid-Liquid Extraction with DMF/Thiocyanate Salts

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Abstract This work assessed the separation of aromatic and non-aromatic hydrocarbons in gasoline via liquid-liquid extraction, using benzene/n-octane as a model. The separation efficiency was determined at various temperatures and employing N, N-dimethyl formamide (DMF) with potassium, sodium and ammonium thiocyanate (NH₄SCN) as the extraction solvent. DMF with NH₄SCN gave the best results and generated a phase containing 99% mole benzene. A 12 h extraction using 20% NH₄SCN in DMF at 25 °C and atmospheric pressure was found to be optimal. In addition, a solvent ratio of 1 in the mixture being extracted gives the best results. These results include a benzene distribution coefficient of up to 3.88 and a selectivity coefficient above 150.

1. Introduction

Benzene, toluene, xylenes (collectively, BTX) and ethylbenzene are all found in gasoline fractions that also contain various C₅-C₁₁ saturated hydrocarbons^[1-5]. These aromatics, whether they are directly used as petrochemical products or as raw materials for the synthesis of fine products, are more valuable than gasoline when used for fuel purposes. In addition, China has strict regulations that restrict the aromatics content in gasoline^[6-9]. The present study investigated the separation of benzene/n-octane mixtures via liquid-liquid extraction as a means of modelling the separation of aromatics from non-aromatics in gasoline fractions^[10-12].

Compared with other separation methods, the liquid-liquid approach also has several other advantages, such as being highly adaptable and efficient, applicable to the processing of large quantities, highly selective, and applicable to continuous operations^[13-15]. However, the large-scale separation of aromatic/aliphatic mixtures by traditional liquid-liquid extraction techniques has thus far been limited due to reasons related to economics and performance^[15-21].

Data have been reported for the liquid-liquid equilibrium of benzene/n-octane mixtures based on extraction and separation using N, N-dimethyl formamide (DMF) and ethylene glycol/DMF as extractants^[22]. The present study investigated the effects of salts on the distribution coefficient during the extraction and separation of mixtures of benzene and n-octane.

2. Experimental

2.1. Materials and Equipment

Benzene (Tianjin Guangfu Fine Chemical Industry Research Institute), n-octane (Laiyang Economic and Technological Development Zone Fine Chemical Factory), DMF (Tianjin Tianli Chemical Reagent



Co., Ltd.), KSCN, NaSCN, NH₄SCN (Tianjin Fuchen Chemical Reagent Factory) were used in this work. Analyses were performed using a 6890N gas chromatograph (Agilent, U.S.A.).

2.2. Analysis method

Correction factors and extraction efficiencies were calculated based on the peak area normalization method.

2.3. Experimental steps

2.3.1 Comparison of different extractants

Holding the temperature and pressure constant, benzene/n-octane mixtures were extracted with DMF with a thiocyanate salt mass percentages of 5%, 10%, 15%, 20% or 25%.

3. Results and Discussion

3.1. The effect of the salt solution on the extraction

The selection of the solvent is very important to the extraction process, as using the optimal solvent can reduce costs. The extraction results obtained using DMF in conjunction with various thiocyanate salts at a concentration of 20% are shown in Figure 1.

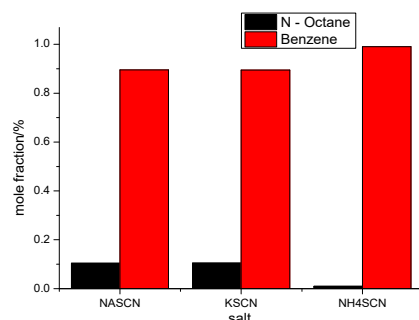


Figure 1. Extraction results obtained with DMF and various thiocyanate salts at a concentration of 20%

The extraction efficiency was found to improve as the thiocyanate salt content was increased. However, KSCN was not completely soluble in DMF at 25%, and so all three salts were used at levels of 5%, 10%, 15% and 20%. Figure 1 demonstrates that, at the same salt content, the DMF/NH₄SCN solvent system was superior, giving a benzene mole fraction of 0.99. As a result, the following experiments were carried out using the DMF/NH₄SCN solvent system.

3.2. The effect of extraction temperature on the separation effect

Figures 2 and 3 demonstrate the effects of varying the temperature.

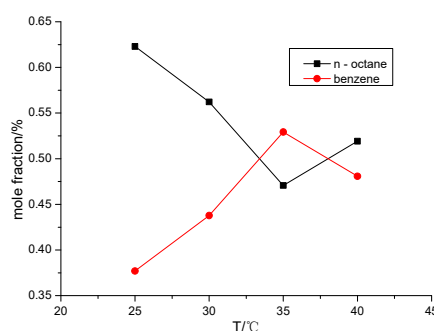


Figure 2. Mole fractions in the raffinate as functions of temperature

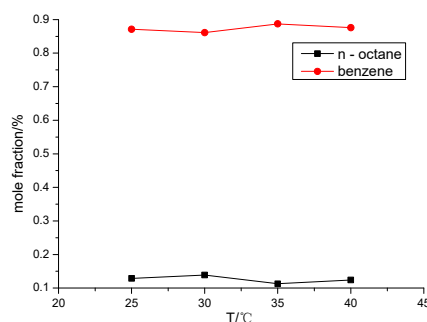
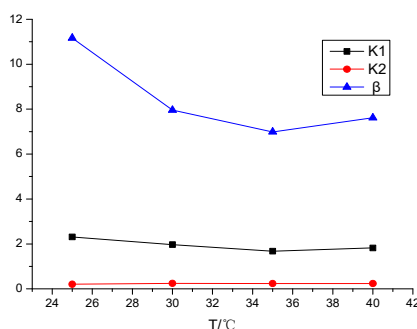


Figure 3. Extraction efficiencies as functions of temperature

From these data, it is evident that the mole fraction of benzene first increases and then decreases with increasing temperature, while the mole fraction of n-octane increases and then decreases. The optimal extraction effect evidently occurs at 25 °C. The mole fraction of benzene in the extraction phase changed only minimally with temperature. Based on these data, the following experiments were performed at 25 °C.

To further investigate the separation effects of the solvents, the above experimental data were processed to determine the partition coefficient, K_1 , the n-octane distribution coefficient and the benzene selectivity coefficient, K_2 . The associated equations are provided below.

Figure 4. K_1 , K_2 and β as functions of temperature

These data show that, with increasing temperature, K_1 and β decrease gradually while K_2 is essentially constant. A higher selectivity coefficient and greater selectivity for benzene will increase the benzene distribution coefficient and improve the benzene extraction. Therefore, these data confirm that extraction at 25 °C is optimal.

3.3. The effect of time on the separation effect

The extraction time was varied while leaving the other conditions unchanged, giving the results summarized in Figures 5 and 6.

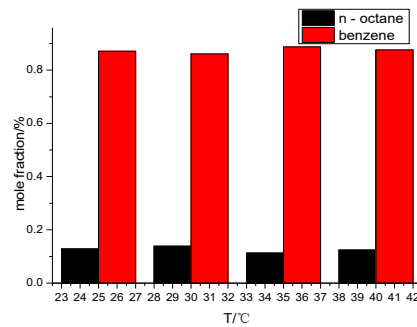


Figure 5. Effect of time on extraction efficiency

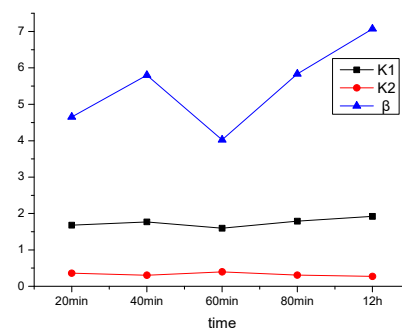
Figure 6. Effect of time on K1, K2 and β

Figure 5 demonstrates that the mole fractions of benzene and n-octane in the extraction phase were essentially constant over time. According to Figure 6, time also had little effect on the partition coefficients of both benzene and n-octane, although the selectivity coefficient did fluctuate between 4.5 and 7. Based on these results, an extraction time of 12 h was selected as optimal.

3.4. Analysis of single stage extraction results

3.4.1 Effect of solvent ratio on separation

The distribution coefficients and selection coefficients obtained at varying salt contents are plotted in the following figures.

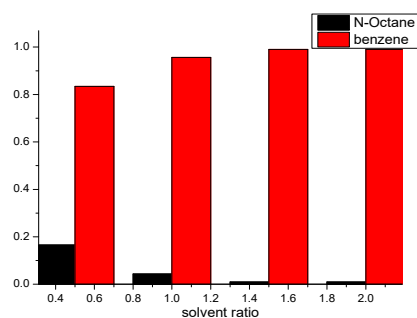
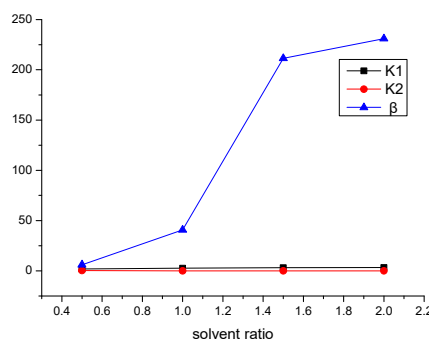
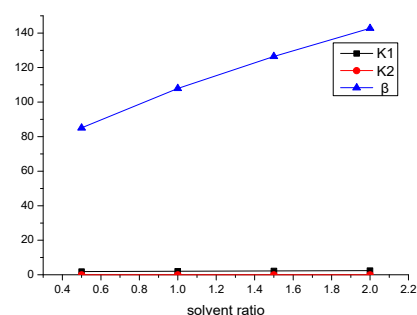


Figure 7. Extraction results at varying solvent ratios with 10% salt content

Figure 8. K1, K2 and β as functions of the solvent ratio with a 10% salt contentFigure 9. K1, K2 and β as functions of the solvent ratio with a 15% salt content

These graphs demonstrate that the benzene mole fraction increased gradually to a maximum of 0.99 as the solvent ratio was increased, while the n-octane fraction decreased to 0.01. This effect plateaued at a solvent ratio of 1.5 (Figure 7). As the solvent ratio increased, at both 10% and 15% salt, the benzene distribution coefficient gradually increased, the n-octane distribution coefficient slowly decreased, and the selectivity coefficient became greater. These data indicate that a higher solvent ratio led to improved selectivity for benzene (Figures 8 and 9), although the associated solvent recovery would be energy-intensive and costly. The DMF/ NH_4SCN solvent system exhibits high selectivity because it is a good solvent for benzene but not for n-octane. However, increasing the solvent ratio only increases the selectivity coefficient at higher levels. Considering the separation rate and other factors, the optimal solvent ratio is believed to be in the range of 0.5 to 1.0.

3.4.2 The effect of NH_4SCN content on the separation effect

In subsequent trials, the solvent ratio was fixed at 1 and the NH_4SCN concentration in the solvent was varied while assessing changes in the extraction phase. The results are shown in Figures 10 and 11 below.

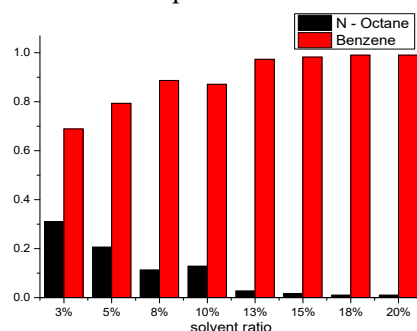
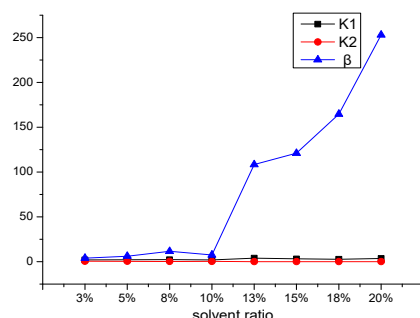


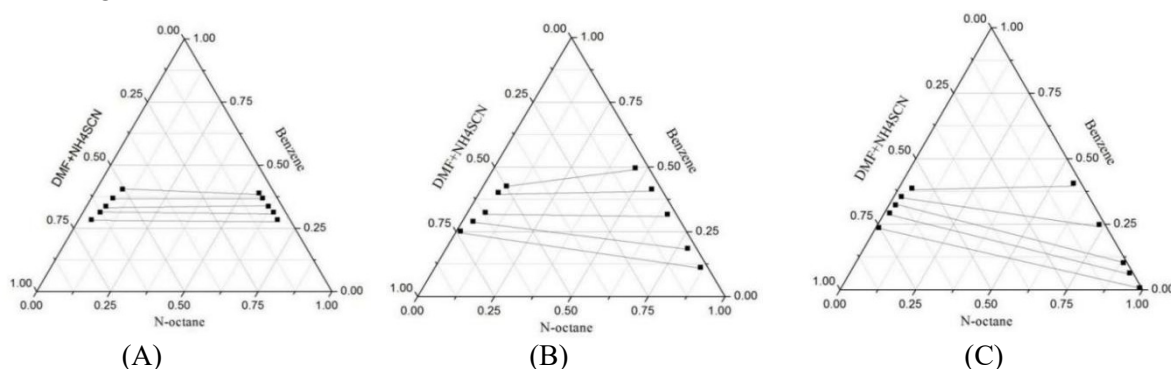
Figure 10. Extraction efficiencies obtained with varying salt concentrations in the solvent

Figure 11. K1, K2 and β as functions of the solvent salt content

From these data, we can conclude that NH_4SCN concentrations in the solvent of 3% to 10% gave higher mole fractions of benzene and n-octane in the extraction phase. With increases in the salt content, the mole fraction of n-octane decreased while that of benzene increased. At salt contents of 13% to 20%, there were no obvious changes in the mole percentages. Figure 11 demonstrates that the benzene distribution coefficient fluctuated while the distribution coefficient of n-octane did not change. The selectivity coefficient of the composite solvent increased as the salt content was raised to 13%. These data again confirm that the optimal salt content is 20%.

3.4.3 Analysis of the liquid-liquid equilibrium phase diagram

Using the experimental data in Tables 1 to 3, the liquid-liquid equilibrium three element phase diagrams shown in Figure 12 was constructed, at 25 °C and 101.325 kPa.

Figure 12. Liquid-liquid equilibrium phase diagrams for benzene/n-octane/DMF/ NH_4SCN with NH_4SCN concentrations of (A) 10%, (B) 15% and (C) 20%.

Within these diagrams, it is evident that the lines decrease in length in the order of (C) > (B) > (A). This result demonstrates that employing 20% NH_4SCN gives a post-extraction phase that comes closest to being composed of a single substance. With increases in the NH_4SCN concentration in the extractant, the area of the biphasic region also increases, indicating that raising the salt content improves the phase separation, confirming the trend seen in Figure 11. These data show that the addition of the thiocyanate salt in the extraction process reduces the mutual solubility of the mixed solution and increases the two-phase region, which in turn promotes the phase separation, due to the salting out effect.

4. Conclusions

The extraction and separation of benzene/n-octane mixtures was examined and the selectivity coefficient of a mixed DMF/ NH_4SCN solvent was found to be significantly higher than that of pure DMF, with a coefficient greater than 120. This solvent system also showed superior selectivity compared with DMF/KSCN and DMF/NaSCN. Increasing the NH_4SCN concentration in the extraction solvent was

also found to increase the two-phase area region in the phase diagram, indicating that raising the salt content improves the phase separation.

Acknowledgements

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