Korean J. Chem. Eng., **27**(1), 214-217 (2010)
DOI: 10.1007/s11814-009-0328-y

Extraction of benzene from a narrow cut of naphtha via liquid-liquid extraction using pure-sulfolane and 2-propanol-sulfolane-mixed solvents

Jafar Mahmoudi and Mohammad Nader Lotfollahi†

School of Chemical, Gas and Petroleum Engineering, Semnan University, Semnan, Iran

(*Received 16 December 2008 • accepted 9 July 2009*)

Abstract−The extraction of benzene from a narrow cut of naphtha produced by the Iranian petrochemical company has been studied at the operating temperatures of 40, 45 and 50 °C, and four solvent-to-feed ratios (S/F) varied over the range of 1-4. Two extraction solvents, sulfolane as a pure-solvent and (sulfolane containing 7 wt% 2-propanol) as a mixed-solvent have been investigated for selective removal of benzene from the naphtha cut. The experimental results demonstrated that the mixed-solvent at 40 °C is a suitable solvent to replace sulfolane for an industrial extraction process for the separation of benzene from the naphtha cut because of its lower price and energy savings.

Key words: Liquid-liquid Extraction, Naphtha Cut, Benzene, Mixed Solvent

INTRODUCTION

Food grade n-hexane is used as a solvent for oil extraction from seeds. The main source of n-hexane is naphtha cut produced in the refinery and the petrochemical processes. However, this cut contains aromatic hydrocarbons, especially benzene. For example, the naphtha cuts from the Iranian crude oils contain about 2.5 to 5% by weight of benzene. Because benzene is carcinogenic, separation of benzene from the naphtha cut to reach the food grade specification is necessary [1].

In principle, the liquid-liquid extraction with solvents can be employed to extract the aromatics from the naphtha cut. Solvents used for liquid extraction require high selectivity for aromatics, high capacity, capability to form two phase at reasonable temperatures, capability of rapid phase separation, easy regeneration, good thermal stability and to be non-corrosive and non reactive [2].

Many investigators [3-10] have studied the liquid-liquid equilibrium (LLE) of ternary systems containing solvent, aromatic and aliphatic hydrocarbons. Krishna et al. [11] separated aromatics from 63-69 °C naphtha fraction using sulfolane and NMP (n-methyl pyrrolidone) as the solvents on a laboratory packed extraction column. Ali et al. [12] carried out the extraction of aromatics from the naphtha reformate with propylene carbonate as a solvent. Chen Dong Cho et al. [13] measured the liquid-liquid equilibrium of ternary systems (heptane+NFM+aromatic hydrocarbon (benzene, toluene, and xylene)) over the temperature range of (298 to 353) K. Rappel et al. [14] reported liquid-liquid equilibrium data for the ternary systems (sulfolane+p-xylene+cyclohexane), (sulfolane+p-xylene+n-hexane) and (sulfolane+toluene+n-hexane) at 308.15 and 323.15 K. Galie et al. [15] presented the optimal conditions of extraction of C6-C8 aromatic hydrocarbon from the reformate by triethylene glycol-sulfolane mixtures. Ko et al. [16] simulated the NFM (N-formylmorpholine) extractive distillation process for the purpose of recovering aromatics from hydrocarbon mixtures using the NRTL equation as the thermodynamic model.

In this work, benzene was extracted from naphtha cut produced by the Iranian petrochemical company by using sulfolane and a mixture of sulfolane and 2-propanol as solvents. Based on the Bandar Imam Petrochemical Complex (BIPC) report, the narrow cut of naphtha used in this work contained 2-methyl-pantane, 3-methyl-pantane, n-hexane, methyl-cyclo-pantane, benzene, cyclo-hexane, isopantane, n-pantane, cyclo-pantane, 2-methyl-hexane and 2,3-dimethyl-pantane.

EXPERIMENTAL

1. Materials

Sulfolane, propanol, ethanol were obtained from Merck Company (Germany), all with purity greater than 99.0%. All chemicals were used without further purification. The narrow cut of naphtha was from the Bandar Imam Petrochemical Complex (BIPC).

2. Procedure

The benzene from naphtha cut was extracted by using the sulfolane as a pure-solvent and a mixed-solvent of sulfolaneco-solvent at temperatures 40, 45 and 50 °C and at solvent-to-feed ratios of 1, 2, 3 and 4 by weight. Experiments were carried out in equilibrium 250 ml glass cells. The cell temperature was regulated by a thermostatic bath (Grant instruments (Cambridge) ltd. (type SE 15, England)), accurate to ±0.2 °C. The mixture was prepared directly inside the cell, and the components were weighted on an analytical balance (A & D Company, GF-600, Japan) accurate to 0.001 g. The mixture was agitated with a magnetic stirrer (Stuart scientific SM 27, UK) for 1 h and then left for 8 h. Then the system split in two liquid phases that became clear and transparent at equilibrium, with a well defined interface. After decanting, samples from the two phases were taken for analysis. The samples were diluted in pure ethanol and analyzed by a gas chromatograph equipped with a helium ionization detector (HID). The analysis was repeated at least three times. The average of these readings was taken for the component compositions. A good separation of the components was attained using a TRB-WAX capillary column (60 m×0.32 mm) with a poly eth-

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†To whom correspondence should be addressed.
E-mail: mnlotfollahi@semnan.ac.ir

Table 1. Percentage of benzene in the raffinate for different solvents

Solvents	Benzene in raffinate%
Pure sulfolane	1.547
Sulfolane containing 10 wt% 2-propanol	1.243
Sulfolane containing 10 wt% ethylenglycol	2.303
Sulfolane containing 10 wt% water	1.513

ylene glycol of 0.5 μm film. The temperature of the injector and the detector was maintained at 513.15 K. The column temperature was controlled by programming temperature; after 10 min of holding at 373.15 K, the column temperature was raised to the final temperature of 493.15 K at the rate of 15 K min-1. Helium was used as the carrier gas at the rate of 1 ml min-1. Software supplied by Chrompack (detailed hydrocarbon analyzer) was used to handle the data generated by GC. The gas chromatograph was calibrated by the external standard calibration method. Calibration mixtures were prepared by weighing different ratios of the pure components. Measurements were carried out in triplicate in order to exclude exceptions in the measurements that could lead to wrong conclusions. The average deviation of the compositions for calibration was about 0.85%.

3. Selection of a Suitable Co-solvent

To select a suitable mixed solvent, sulfolane containing 10 wt% 2-propanol, sulfolane containing 10 wt% ethylene-glycol and sulfolane containing 10 wt% water were considered as the mixed solvents to separate benzene from the naphtha cut. Table 1 shows the percentage of benzene in the raffinate for the pure sulfolane and the three mixed solvents at T=40 °C.

The results indicate that the mixture of sulfolane containing 10 wt% 2-propanol exhibits the best separation in comparison with the other mixed solvents. To find a suitable composition of 2-propanol in the mixed solvent, a variety of mixed solvents were used. These compositions were 40, 30, 20, 14, 10 and 7 wt% 2-propanol in the mixed solvent. Among the mixed solvents studied, sulfolane containing 7 wt% 2-propanol was found to be the best solvent in comparison with the other solvents.

RESULTS AND DISCUSSION

The extraction of benzene from the narrow cut of naphtha was performed by using sulfolane as a pure-solvent and (sulfolane containing 7 wt% 2-propanol) as a mixed-solvent at 40, 45 and 50 °C and at the solvent-to-feed ratios (S/F) of 1, 2, 3 and 4 by weight. A sample of the cut was analyzed by a gas chromatograph to specify the composition of n-hexane and benzene in the sample. The result shows that the narrow cut of naphtha contains 88.18% by weight of n-hexane and about 2.7% by weight of benzene.

To consider the reproducibility of the experimental results, the experiments at 40 °C were repeated three times. The average deviation of the measured composition of benzene in the raffinate phase was about 3.6%. The effects of solvent-to-feed ratio and operating temperature on the percentage of benzene in the raffinate are shown in Figs. 1 to 7.

The effect of solvent-to-feed ratio on the percentage of benzene in the raffinate is shown in Figs. 1 to 3. As shown, the percentage of benzene in raffinate decreased with increasing of the solvent-to-

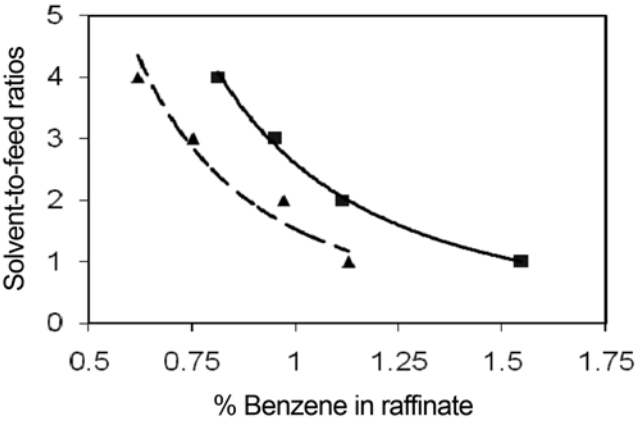

Fig. 1. Effect of solvent-to-feed ratio on the percentage of benzene in the raffinate at T=40 °C, using sulfolane as a pure-solvent (—■—) and (sulfolane 7 wt% 2-propanol) as a mixed-solvent (--▲--).

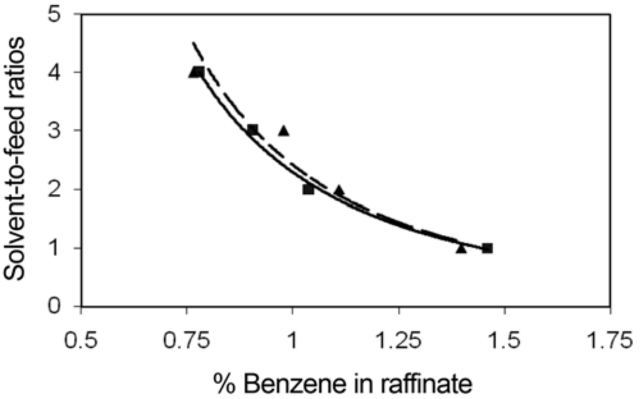

Fig. 2. Effect of solvent-to-feed ratio on the percentage of benzene in the raffinate at T=45 °C, using sulfolane as a pure-solvent (—■—) and (sulfolane 7 wt% 2-propanol) as a mixed-solvent (--▲--).

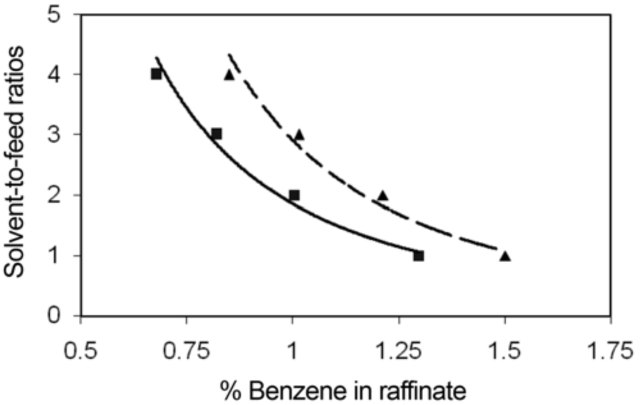

Fig. 3. Effect of solvent-to-feed ratio on the percentage of benzene in the raffinate at T=50 °C, using sulfolane as a pure-solvent (—■—) and (sulfolane 7 wt% 2-propanol) as a mixed-solvent (--▲--).

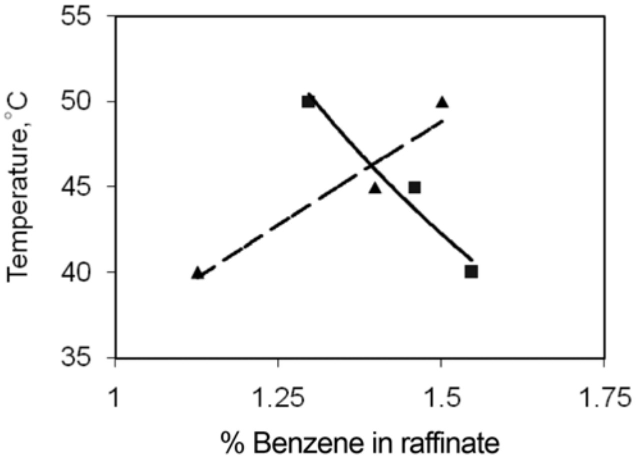

Fig. 4. Effect of operating temperature on the percentage of benzene in the raffinate at S/F=1, using sulfolane as a pure-solvent (—■—) and (sulfolane 7 wt% 2-propanol) as a mixed-solvent (--▲--).

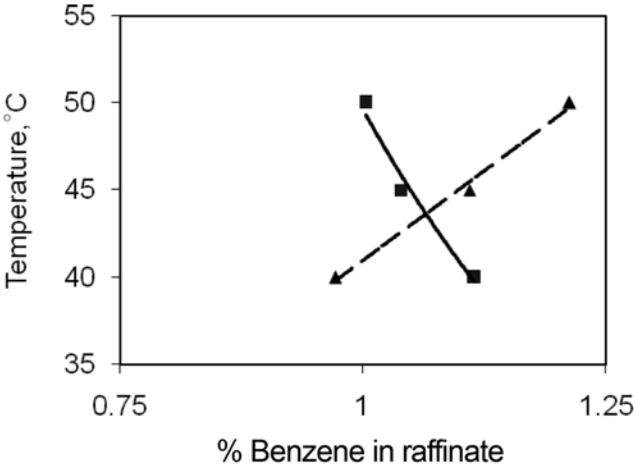

Fig. 5. Effect of operating temperature on the percentage of benzene in the raffinate at S/F=2, using sulfolane as a pure-solvent (—■—) and (sulfolane 7 wt% 2-propanol) as a mixed-solvent (--▲--).

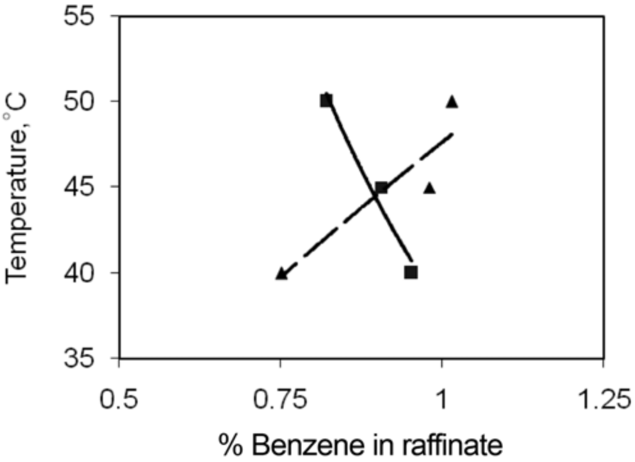

Fig. 6. Effect of operating temperature on the percentage of benzene in the raffinate at S/F=3, using sulfolane as a pure-solvent (—■—) and (sulfolane 7 wt% 2-propanol) as a mixed-solvent (--▲--).

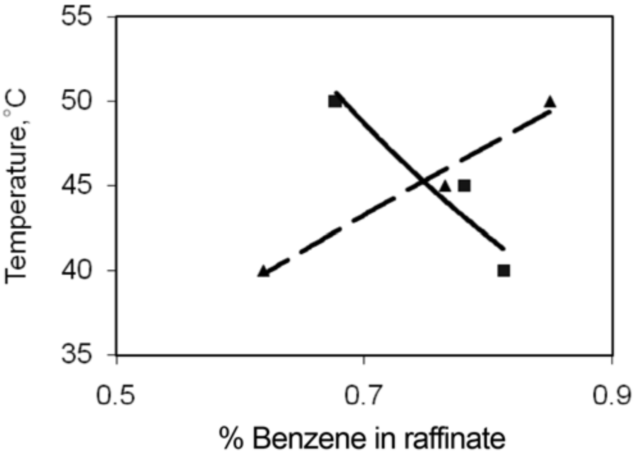

Fig. 7. Effect of operating temperature on the percentage of benzene in the raffinate at S/F=4, using sulfolane as a pure-solvent (—■ —) and (sulfolane 7 wt% 2-propanol) as a mixed-solvent (--▲--).

feed ratio. Fig. 1 shows that the percentage of benzene in the raffinate using the sulfolane solvent was decreased from 1.547 to 0.812 when the solvent-to-feed ratio increased from 1 to 4. Therefore, the extraction by the sulfolane solvent reduced about 70% of the benzene content of raffinate at solvent-to-feed ratio 4. The benzene content of raffinate was reduced about 77.1% by the mixed solvent (sulfolane containing 7 wt% 2-propanol) for the same condition (Fig. 1). At 45 °C (Fig. 2) for sulfolane, the benzene content of raffinate at solvent-to-feed ratio 4 was reduced about 71.1%. At the same condition, the mixed-solvent reduced 71.7% of the benzene content in the raffinate. At 50 °C the sulfolane and the mixed solvents separated 75% and 68.5% of the benzene content, respectively. These figures show that the mixed solvent at higher solvent-to-feed ratio works better than the pure solvent.

The effects of temperature on the percentage of benzene in the raffinate are shown in Figs. 4 to 7.

For sulfolane, when the temperature increased from 40 °C to 50 °C, at solvent-to-feed ratio of 1, the percentage of benzene in the raffinate was decreased about 16.1%. The values for the solvent-to-feed ratios of 2, 3 and 4 were 10%, 13.95% and 16.6%, respectively. These figures demonstrate that for the mixed solvent (sulfolane containing 7 wt% 2-propanol) the concentration of benzene in the raffinate increased with increasing the temperature. Therefore, a lower temperature is desirable for separating benzene from the narrow cut of naphtha using the mixed solvent. As the ultimate result, the extraction using the mixed solvent (sulfolane containing 7 wt% 2-propanol) at lower temperature (40 °C) is recommended because of its lower price and energy savings. The values of experimental data for the sulfolane as a pure-solvent and (sulfolane containing 7 wt% 2-propanol) as a mixed-solvent are shown in Tables 2 and 3, respectively.

CONCLUSION

This study includes the extraction of benzene from a narrow cut

Table 2. The percentage of benzene in the raffinate using the sulfolane solvent

Temperature (°C)	S/F=1	S/F=2	S/F=3	S/F=4
40	1.547	1.115	0.953	0.812
45	1.459	1.039	0.905	0.780
50	1.297	1.003	0.820	0.677

Table 3. The percentage of benzene in the raffinate using the (sulfolane+7% 2-propanol) solvent

Temperature (°C)	S/F=1	S/F=2	S/F=3	S/F=4
40	1.127	0.972	0.751	0.618
45	1.398	1.110	0.979	0.765
50	1.502	1.213	1.014	0.849

of naphtha using two solvents at different temperatures and various solvent-to-feed ratios. Two extraction solvents, sulfolane as a pure-solvent and (sulfolane containing 7 wt% 2-propanol) as a mixed-solvent have been investigated for selective removal of benzene from a narrow cut of naphtha. The operating temperature range was from 40 °C to 50 °C, and the solvent-to-feed ratio was varied over the range of 1-4. The experimental results demonstrated that the mixed-solvent at 40 °C and the solvent-to-feed ratio of 4 is recommended for the extraction of benzene from the naphtha cut.

REFERENCES

1. I. Uemaus, and S. Kushiyama, *Fuel Process. Technol.*, **85**, 1519 (2004).
2. T. A. Al-Sahhaf and E. Kapetanovic, *Fluid Phase Equilibria*, **118**, 271 (1996).
3. G. W. Meindersma, *Fuel Process. Technol.*, **87**, 59 (2005).
4. G. M. Radwan, S. A. A1-Muhtaseb and M. A. Fahim, *Fluid Phase Equilibria*, **129**, 175 (1997).
5. U. Domañska, *Fluid Phase Equilibria*, **259**, 173 (2007).
6. S. Lee and H. Kim, *J. Chem. Eng. Data*, **40**, 499 (1995).
7. M. Krummen and J. Gmehling, *Fluid Phase Equilibria*, **215**, 283 (2004).
8. P. Morawski, T. M. Letcher and P. K. Naicker, *J. Chem. Eng. Data*, **47**, 1453 (2002).
9. W. Wang and Z. Gou, *J. Chem. Eng. Data*, **43**, 81 (1998).
10. M. Mohsen-Nia, H. Modarress, F. Doulabi and H. Bagheri, *J. Chem. Thermodynamics*, **37**, 1111 (2005).
11. R. Krishna, A. N. Goswani, S. M. Nanoti, B. S. Rawat, M. K. Khanna and J. Dobhal, *Indian Journal of Technology*, **25**, 602 (1987).
12. S. H. Ali, H. M. S. Lababidi, S. Q. Merchant and M. A. Fahim, *Fluid Phase Equilibria*, **214**, 25 (2003).
13. C. D. Chu, Y. H. Qi and W. Hao, *J. Chem. Thermodynamics*, **39**, 1182 (2007).
14. R. Rappel, Luiz Mário Nelson de Góis and S. Mattedi, *Fluid Phase Equilibria*, **202**, 263 (2002).
15. A. A. Gaile, G. D. Zalishchevskii, A. S. Erzhenkov, E. A. Kayfadzhyan and L. L. Koldobskaya, *Russian J. Appl. Chem.*, **80**(4), 591 (2007).
16. M. S. Ko, S. Na, J. Cho and H. Kim, *Korean J. Chem. Eng.*, **19**, 996 (2002).