A Study on the Liquid-Liquid Equilibrium of DMSO - Heavy Aromatics - Octane System

Qiang Wang, Lilian Xu, Weiyang Fei, and Jiading Wang

Department of Chemical Engineering in Tsinghua University,
Beijing 100084, P.R. China

ABSTRACT The multi-component liquid-liquid equilibrium of heavy aromatics extraction by DMSO (dimethylsulfoxide) were studied systematically in this paper. Distribution ratios of n-butyl benzene, naphthalene, 2-methyl naphthalene, fluorene, phenanthrene, and pyrene between DMSO and n-octane were measured. The impacts of the aromatics structure, temperature, and water content in solvent on distribution ratios of aromatics were also studied.

1. Introduction

Aromatics Extraction is an important process in petrochemical industry. DMSO is widely used for this process because it has large solvency and high selectivity. It is suitable for operation at ambient temperature and recycle by stripping[1]. However, most liquid-liquid equilibrium data published for aromatics extraction by DMSO are about light aromatics such as benzene, toluene, etc. Heavy aromatics extraction by DMSO, especially polycyclic aromatics, is seldom studied[2]. Therefore, the multi-component liquid-liquid equilibrium of heavy aromatics extraction by DMSO were studied in this paper.

2. Liquid-Liquid Equilibrium Experiments

The solution of mixed heavy aromatics (n-butyl benzene, naphthalene, 2-methyl naphthalene, fluorene, phenanthrene, and pyrene) at certain concentration in n-octane was taken as modeling raw material, and the solution of DMSO mixed with certain water was taken as solvent. Liquid-liquid equilibrium experiments were conducted in a shaker with constant water temperature (25±0.1℃ or 70±0.1℃). After the mixture of raw material and solvent being vibrated for more than 50 minutes, the mass transfer of aromatics solutes between oil (light) and solvent (heavy) phases can reach thermodynamic equilibrium. Then being settled for more than 90 minutes, the two phases can be separated perfectly. Sample the two phases quickly.

A capillary gas chromatograph - mass selective detector (GC/MSD) was used to determine mass concentration of aromatics in each phase. The operating conditions of capillary gas chromatograph were:

Type of Column: HP-1 12m×0.2mm×0.33μm
Inlet Temperature: 350℃
Gas Flowrate: Helium 1 ml/min
Sample Amount: 0.1~0.2 μl
Oven Temperature: Initial Temperature: 80℃ Initial Time: 2 min
Rate: 10℃/min
Final Temperature: 250℃ Final Time: 20 min

The operating condition of mass selective detector were:
Filament Voltage: -70V
Scan/sec: 1.9
Mass Range: 33~300

In order to eliminate the disturbance of impurities in the samples and to carry out qualitative analysis simultaneously, the mass chromatography was used to perform quantitative analysis. Internal standard method was used, and biphenyl was selected as the internal standard substance. The distribution ratio K_i of certain aromatics i was calculated as the ratio of mass fractions of aromatics i in solvent phase y_{wi} to that in oil phase x_{wi}, i.e., $K_i=y_{wi}/x_{wi}$.

3. Results and discussion

The liquid-liquid equilibrium experiments were carried out at 25 and 70℃, and at different water content in solvent from 0%wt to 40%wt. The distribution ratios of heavy aromatics are shown in Fig. 1~3 and Table 1~2.

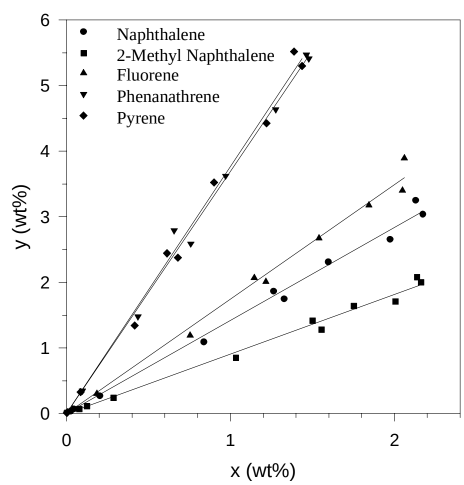

Fig. 1 Distribution Ratios of Aromatics between DMSO and n-Octane at 25℃

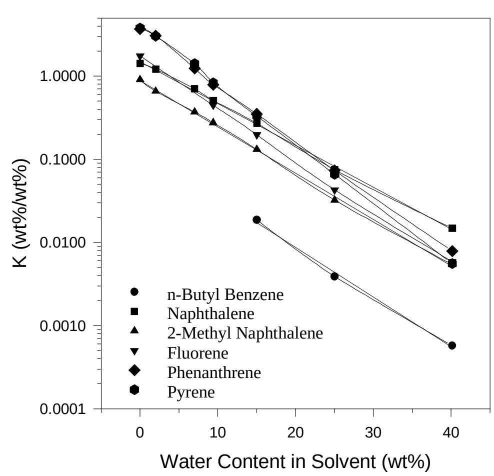

Fig. 2 Effect of the Water Content on Distribution Ratios of Aromatics at 25℃

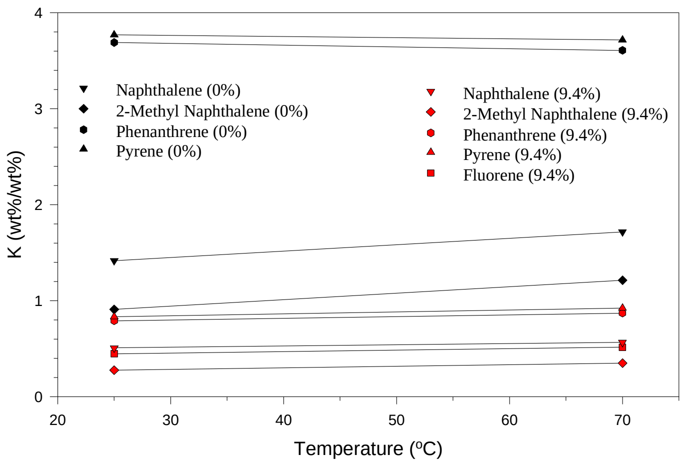

Fig. 3 Effect of Temperature on Distribution Ratios of Aromatics at Various Water Content

Table 1 Distribution Ratios of Heavy Aromatics between DMSO and n-Octane

Temperature ℃	Heavy Aromatics	Water Content in Solvent (wt%) 0	2	7	9.4
25	Naphthalene	1.418	1.212	0.703	0.508
	2-Methyl Naphthalene	0.908	0.660	0.372	0.275
	Fluorene	1.746			0.447
	Phenanthrene	3.690	3.067	1.241	0.790
	Pyrene	3.768	3.026	1.407	0.832
70	Naphthalene	1.715			0.564
	2-Methyl Naphthalene	1.211			0.349
	Fluorene				0.514
	Phenanthrene	3.607			0.870
	Pyrene	3.715			0.922

Table 2 Distribution Ratios of Heavy Aromatics between DMSO and n-Octane at 25℃

Water Content	n-Butyl Benzene	Naphthalene	2-Methyl Naphthalene	Fluorene	Phenanthrene	Pyrene
15.01 %wt	0.0187	0.270	0.131	0.197	0.351	0.331
25.02 %wt	0.00388	0.0750	0.0323	0.0429	0.0732	0.0660
40.14 %wt	0.000572	0.0148	0.00543	0.00589	0.00788	0.00559

The effects of some important factors on the distribution ratios of heavy aromatics are discussed as follows:

(1) Number of Aromatic Rings

It is shown from the results that within 0~20%wt of water content in DMSO the more the number of aromatic rings, the higher the distribution ratios of heavy aromatics. That is, DMSO has the privilege of extracting polycyclic aromatics.

(2) Length of Paraffinic Chain on Aromatic Ring

It is clear from the comparison of the distribution ratio between naphthalene and 2-Methyl naphthalene that the paraffinic chain on aromatic ring reduces the distribution ratio of aromatics.

(3) Water Content in Solvent

It can be seen from the figures that water content in solvent has large effect on the distribution ratios of aromatics. The distribution ratios reduce enormously as the water content increases. This means that heavy aromatics extracted into DMSO can be easily stripped by adding water into the extract. Moreover, the reduction becomes more slight when the water content is higher. For different heavy aromatics, the higher the distribution ratios at low water content, the larger the scale of the reduction.

(4) Temperature

The temperature of equilibrium system also has certain effect on the distribution ratio of heavy aromatics. But compared with the effect of the water content, its effect is relatively slight.

4. Conclusion

(1) DMSO is an excellent solvent for heavy aromatic extraction.
(2) DMSO has the privilege of extracting polycyclic aromatics.
(3) The distribution ratios of aromatics reduce greatly as the water content increases.
(4) The temperature has only a slight impact on the distribution ratios of heavy aromatics.

References

[1] B. Choffe, et al., Hydrocarbon Processing, 45(5), 188(1966)
[2] JiaXiong Ke, 1992, M.S. Thesis, Tsinghua University, China