VAPOR-LIQUID EQUILIBRIA OF MINUTE AMOUNTS OF N-METHYLSUCCINIMIDE AND WATER IN N-METHYL-2-PYRROLIDONE

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Introduction

N-Methyl-2-pyrrolidone (NMP) is produced from maleic anhydride by partial oxidation. In the process of NMP production, NMSI is also produced as a by-product. These reactions are expressed by Eqs. (1) and (2).

Table 1 shows the physical properties of NMP and NMSI. NMP contains a nitrogen atom and has strong polarity. Most organic solvents and inorganic compounds dissolve in NMP. For example, water completely dissolves in NMP. Generally, the boiling point, inflammation point, and chemical and thermal stability of NMP are higher than those of other common solvents. The freezing point and corrosiveness of NMP are lower than those of common solvents. A minor amount of NMSI in NMP is formed from NMP by oxidation. Distillation has been employed to remove water and NMSI from NMP. The distillation condition, however, is not optimized due to lack of equilibrium data of water and NMSI in NMP.

1. Experimental

Vapor-liquid equilibria were measured at 25.33 kPa. A schematic diagram of an Othmer type still with a vacuum system used is shown in **Figure 1**. The pressure was reduced by an aspirator. Commercial NMP used contained about 400 ppm of NMSI and about 800 ppm of water. NMSI and water in NMP were removed by mole-

cular sieve 5A if necessary. 400 g of NMP solution containing desired amounts of NMSI and water was charged in the still. The apparatus was operated for 7 hours at 25.33 kPa. After the heaters and stirrers were stopped, pure nitrogen was introduced through the upper stopcock to prevent the contents from deteriorating through contact with moisture and oxygen in the atmosphere. Liquid samples were taken from the still and the condensed liquid reservoir for analysis. The concentrations of NMP and NMSI were measured by a gas chromatograph. The concentration of water was measured by a Karl Fischer type moisture meter (MITSUBISHI KASEI CA-02)

2. Calculation of Equilibrium Ratio

ASOG (Correa *et al.*, 1989, Tochigi *et al.*, 1990), one of the group contribution methods, was used to calculate vapor-liquid equilibria.

2.1 Water equilibrium ratio in NMP

Recently, the group interaction parameters of NMP were reported (Tochigi *et al.*, 1990). NMP-water equilibrium ratio was calculated using NMP-water group interaction parameters.

2.2 NMSI equilibrium ratio in NMP

The NMSI equilibrium ratio was calculated using CH₂, C=O, -N-, and CyCH (cyclic methylene) interaction parameters. The NMP-NMSI equilibrium ratio in NMP-NMSI-water system was calculated using CH₂, C=O, -N-, and H₂O interaction parameters. The interaction parameter of CH₂ and H₂O was used in this study because the interaction parameter of H₂O and CyCH has not been reported.

3. Results and Discussion

3.1 Water equilibrium ratio in NMP

Figure 2 shows the equilibrium ratio of water in NMP. The experimental data of water equilibrium ratios exhibit values around 10 at concentrations of H₂O lower than 0.01 in mole fraction, and this shows that water can be removed easily from NMP. The concentration dependency of the experimental equilibrium ratio is reproduced

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Table 1. Properties of NMP and NMSI

	NMP	NMSI
molecular weight	99.14	113.12
boiling point [K]	477.15	507-508
melting point [K]	250.18	334-343
specific gravity [kg/m ³]	1023	—
vapor pressure		
NMP		
$\log(P)=9.708 - 2030.8/(t - 45.289)$		
NMSI		
$\lg(P)=9.7216 - 2050.42/(t - 79.0482)$		
	P [Pa] t [K]

Fig. 1 Schematic diagram of apparatus for vapor liquid equilibrium measurements

by ASOG, though the calculated values are slightly smaller than the experimental ones.

3.2 NMSI equilibrium ratio in NMP

Figure 3 shows the equilibrium ratios of NMSI in the NMSI-NMP-water system. The observed NMSI equilibrium ratios show almost constant values of about 0.4 at low water concentrations ranging from 2,000 to 5,000 ppm, and decrease with increasing water contents. The calculated NMSI equilibrium ratios from ASOG show slightly smaller values than the observed.

Conclusions

The vapor-liquid equilibria of minute amounts of water and NMSI in NMP were investigated to obtain a quantitative basis for purification of NMP by distillation. The equilibrium ratios of minor water and NMSI in NMP observed were about 10 for water and about 0.4 for

Fig. 2 H₂O equilibrium ratio in NMP solution. The solid line shows the calculated from ASOG using NMP-H₂O group interaction parameters **Fig. 3** NMSI equilibrium ratio in NMP solution. The solid line shows the calculated from ASOG using CH₂, C=O, -N-, H₂O and CyCH group interaction parameters

NMSI, which showed little concentration dependencies. The result reveals that water and NMSI can be easily removed from NMP by distillation. The calculation from ASOG shows about 20 % lower equilibrium ratios for both minute components.

Literature Cited

- Correa, A., J. Tojo, M. Correa. and A. Blanco; "New Analytical Solution of Groups Method Parameters for the Prediction of vapor-Liquid Equilibrium," *Ind. Eng. Chem. Res.*, **28**, 609-611 (1989)
- Tochigi, K., D. Tiegs, J. Gmehling and K. Kojima; "Determination of New ASOG Parameters," *J. Chem. Eng. Japan.*, **23**, 453-462 (1990)