

## Calculation of the Size and Energy Parameters of N-Methylpyrrolidone

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The activity coefficient of N-methylpyrrolidone (NMP) in the mixture with lube-oil cut is essential for phase equilibrium calculations and for design purposes in the lube-oil extraction units. UNIFAC is an applied effective method for activity coefficient calculations. However, the size and energy parameters for NMP are required for applying the UNIFAC model. In this work, the size parameters for NMP have been calculated by the method of Bondi and the energy parameters between NMP and other functional groups have been obtained. Then, the activity coefficient and phase equilibria calculations have been performed by the UNIFAC model. The results of the calculations have been compared with the experimental data and good agreement has been observed.

### INTRODUCTION

For many years, a great deal of attention has been paid to selective solvents for extracting aromatic compounds from hydrocarbon mixtures and petroleum fluids. One of these solvents, which has been used extensively for this purpose, is furfural [1]. Due to problems reported regarding the lube-oil extraction processes in which furfural is used as the solvent, attempts have been made to replace it with other solvents such as NMP [2]. The most important advantages of NMP over furfural are as follows:

- Lower energy consumption in the utilities section of the lube-oil extraction units,
- Lower solvent to oil ratio in the lube-oil extraction units,
- Lower toxicity,
- Lower fouling of rotating disk contactors used as extracting equipment.

For design purposes, the activity coefficient of NMP is needed, which can be calculated from thermodynamic models such as UNIFAC. In applying the UNIFAC

model, van der Waals surface and volume size parameters as well as the interaction parameters between different functional groups are required. In this work these parameters have been calculated.

### CALCULATIONS AND RESULTS

In the first step of this work, Bondi method [3] of functional groups is used for calculating van der Waals surface and volume size parameters for NMP. Then, by considering NMP as a functional group, the interaction parameters with the other functional groups involved in heptane and benzene have been calculated. The idea of taking NMP as a functional group for obtaining the interaction parameters is based on similar works by Mukhopadhyay and Dongaonkar [4] and Rahman et al. [5]. These researchers considered sulfolane and dimethylformamide solvents as functional groups. To obtain the interaction parameters, the system of *n*-heptane-benzene-NMP was considered. This system is separated into two liquid phases in equilibrium, which are named the benzene-rich phase (extract phase) and the benzene-lean phase (raffinate phase). Experimental data of this system have been reported in Table 1 [6]. The equilibrium condition for these phases is as follows:

$$x_i^{(I)} \gamma_i^{(I)} = x_i^{(II)} \gamma_i^{(II)}, \quad (1)$$

where the superscripts (I) and (II) refer to the raffinate and extract phases, respectively, and the symbols  $x_i$  and  $\gamma_i$  represent the mole fraction and activity coefficient of component *i* in the mixture.

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**Table 1.** Liquid-liquid equilibrium data for the system *n*-heptane (1) / benzene (2) / NMP (3) at 25°C [6].

| $x_1^I$ | $x_2^I$ | $x_3^I$ | $x_1^{II}$ | $x_2^{II}$ | $x_3^{II}$ |
|---------|---------|---------|------------|------------|------------|
| 0.796   | 0.060   | 0.144   | 0.166      | 0.079      | 0.755      |
| 0.745   | 0.091   | 0.164   | 0.190      | 0.113      | 0.697      |
| 0.615   | 0.148   | 0.237   | 0.268      | 0.169      | 0.563      |
| 0.592   | 0.152   | 0.256   | 0.283      | 0.172      | 0.545      |
| 0.577   | 0.160   | 0.263   | 0.306      | 0.175      | 0.519      |

In the UNIFAC model, the activity coefficient is represented as having two parts, i.e., combinatorial (C) and residual (R) activity coefficients:

$$\ln \gamma_i = \ln \gamma_i^{(C)} + \ln \gamma_i^{(R)}. \quad (2)$$

The combinatorial part is given by the following equation:

$$\ln \gamma_i^{(C)} = (\ln \phi_i / x_i + 1 - \phi_i / x_i) - (zq_i/2)[\ln \phi_i / \theta_i + 1 - \phi_i / \theta_i], \quad (3)$$

where,

$$\phi_i = \frac{x_i r_i}{\sum_{j=1}^M x_j r_j}, \quad (4)$$

$$\theta_i = \frac{x_i q_i}{\sum_{j=1}^M x_j q_j}, \quad (5)$$

$$r_i = \sum_{k=1}^N \nu_k^{(i)} \nu_k^{(i)} R_k, \quad (6)$$

and:

$$q_i = \sum_{k=1}^N \nu_k^{(i)} Q_k, \quad (7)$$

in which  $R_k$  is the volume parameter,  $Q_k$  is the surface area parameter of group  $k$  and  $\nu_k$  is the number of  $k$  groups in the  $i$ th molecule in the mixture. Moreover,  $M$  is the number of components,  $N$  is the number of functional groups in the mixture and  $z$  is the coordination number.

The residual part of the activity coefficient is given as:

$$\ln \gamma_i^{(R)} = \sum_{k=1}^N \nu_k^{(i)} (\ln \Gamma_k - \ln \Gamma_k^{(i)}), \quad (8)$$

where  $\Gamma_k$  is the activity coefficient of group  $k$  defined as follows:

$$\ln \Gamma_k = Q_k \left[ 1 - \ln \left( \sum_{m=1}^N \theta_m \psi_{mk} \right) - \sum_{m=1}^N \left( \frac{\theta_m \psi_{km}}{\sum_{p=1}^N \theta_p \psi_{pm}} \right) \right], \quad (9)$$

where the parameters used in the above equation are defined as follows:

$$\psi_{mn} = \exp(-a_{mn}/T), \quad (10)$$

$$\theta_m = Q_m X_m / \sum_{n=1}^N Q_n X_n, \quad (11)$$

and:

$$X_m = \frac{\sum_{j=1}^M \nu_m^{(j)} x_j}{\sum_{j=1}^M \sum_{n=1}^N \nu_n^{(j)} x_j}, \quad (12)$$

$a_{mn}$  is the interaction parameter between functional groups  $m$  and  $n$ .

It can be seen from Equation 3 that for calculating the combinatorial part of the activity coefficient, it is necessary to have  $R_k$  and  $Q_k$  for different functional groups in the mixture. Since these parameters are not reported in [7], Bondi method has been applied to calculate the desired parameters and the results are given in Table 2.

The mixture has three components. Therefore, three equations can be obtained using Equation 1. Considering the experimental data of Table 1 and the parameters of Table 2 along with Equations 1 to 12, the interaction parameters have been calculated using standard routines for solving non-linear system of equations for which the results have been presented in Table 3.

To verify the accuracy of calculated parameters, the liquid-liquid equilibrium data of the ternary system *n*-heptane (1) / benzene (2) / NMP (3) have been compared at 25°C (which are given in Table 1 [6]) with the predicted composition of the extract phase using these parameters. The results have been illustrated in Table 4.

**Table 2.** Van der Waals surface area and volume size parameters.

| Group<br>k      | Surface Parameter<br>$Q_k$ | Volume Parameter<br>$R_k$ |
|-----------------|----------------------------|---------------------------|
| CH <sub>2</sub> | 0.5400                     | 0.6744                    |
| CH <sub>3</sub> | 0.8480                     | 0.9011                    |
| ACH             | 0.4000                     | 0.5313                    |
| NMP             | 3.2000                     | 3.981                     |

**Table 3.** The UNIFAC interaction parameters between functional groups.

| Group           | CH <sub>2</sub> | CH <sub>3</sub> | ACH     | NMP    |
|-----------------|-----------------|-----------------|---------|--------|
| CH <sub>2</sub> | 0               | 0               | 61.13   | 4833   |
| CH <sub>3</sub> | 0               | 0               | 61.13   | 4833   |
| ACH             | -11.12          | -11.12          | 0       | 1262.5 |
| NMP             | -123.19         | -123.19         | -567.98 | 0      |

**Table 4.** Experimental data and the calculated results using the parameters obtained in this work.

|         |         |         | Experimental |            |            | Calculated |            |            |
|---------|---------|---------|--------------|------------|------------|------------|------------|------------|
| $x_1^I$ | $x_2^I$ | $x_3^I$ | $x_1^{II}$   | $x_2^{II}$ | $x_3^{II}$ | $x_1^{II}$ | $x_2^{II}$ | $x_3^{II}$ |
| 0.796   | 0.060   | 0.144   | 0.166        | 0.079      | 0.755      | 0.156      | 0.084      | 0.805      |
| 0.745   | 0.091   | 0.164   | 0.190        | 0.113      | 0.697      | 0.182      | 0.117      | 0.701      |
| 0.615   | 0.148   | 0.237   | 0.268        | 0.169      | 0.563      | 0.261      | 0.172      | 0.567      |
| 0.592   | 0.152   | 0.256   | 0.283        | 0.172      | 0.545      | 0.277      | 0.176      | 0.547      |
| 0.577   | 0.160   | 0.263   | 0.306        | 0.175      | 0.519      | 0.300      | 0.178      | 0.522      |

As can be seen from Table 4, the calculated composition of the extract phase is in good agreement with the experimental data.

## NOMENCLATURE

|          |   |
|----------|---|
| $a_{mn}$ | interaction energy parameter between $m$ and $n$ groups |
| $q$      | parameter defined in Equation 7                         |
| $Q$      | van der Waals surface area parameter                    |
| $r$      | parameter defined in Equation 6                         |
| $R$      | van der Waals volume size parameter                     |
| $T$      | absolute temperature                                    |
| $x$      | mole fraction   |
| $z$      | coordination number                                     |

## Greek Letters

|          |                                  |
|----------|----------------------------------|
| $\phi$   | parameter defined in Equation 4  |
| $\theta$ | parameter defined in Equation 5  |
| $\gamma$ | activity coefficient             |
| $\Gamma$ | group activity coefficient       |
| $\nu$    | number of functional groups      |
| $\psi$   | parameter defined in Equation 10 |

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