

# Influence of *N*-Methylpyrrolidone on the Relative Volatility in the System Benzene—Cyclohexane

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Presented are equilibrium  $P$ — $x$  data of binary systems benzene—cyclohexane, benzene—*N*-methylpyrrolidone, cyclohexane—*N*-methylpyrrolidone and  $P$ — $x$  data of the ternary system benzene—cyclohexane—*N*-methylpyrrolidone at a temperature of 69.7°C. By treatment of these equilibrium data a basis was obtained for the quantitative evaluation of the influence of *N*-methylpyrrolidone on the relative volatility in the mixture of hydrocarbons—benzene and cyclohexane.

As it is generally known, the direct separation of benzene (b.p. = 80.1°C) from cyclohexane (b.p. = 80.7°C) by rectification is hindered, apart from very close boiling points, especially by the existence of an azeotropic mixture, which contains practically equimolar participation of components at atmospheric pressure. One of the possible methods of separation of an azeotropic mixture is the extractive distillation with a suitable polar solvent, which is able by its properties so much influence the behaviour of the original mixture that the azeotrope will disappear. At the same time the values of relative volatility are being adequately altered. The results obtained by the treatment of measured vapour—liquid equilibrium data will show whether these effects are caused by *N*-methylpyrrolidone and under which conditions.

## EXPERIMENTAL

Benzene (component 1) was obtained from technical grade benzene without thiophene in a rectification column with a separation efficiency equivalent to 70 theoretical plates and twofold freezing.

Cyclohexane (component 2) was a product purified by rectification and employed for chromatographic purposes.

*N*-Methylpyrrolidone (component 3) was prepared from technical solvent by twofold vacuum rectification at a pressure of 4 kPa.

Physicochemical properties of materials prepared are listed in Table 1.

Isothermal  $P$ — $x$  equilibrium data were determined by a static method reported by *Renon* [1] and modified by *Surový* [2]. The pressure was measured with an accuracy of  $\pm 25$  Pa, the temperature was maintained with an accuracy of  $\pm 0.05$ °C. In Tables 2—5

Table 1. Physical Properties of Materials Prepared

Component	Refractive index at 20°C $n_D$	Density at 25°C g cm <sup>-3</sup>
Benzene	1.5010 1.5011 [3]	0.8736 0.8737 [3]
Cyclohexane	1.4262 1.4262 [3]	0.7785* 0.7786*[3]
<i>N</i> -Methylpyrrolidone	1.4686 1.4680 [3]	1.0284 1.0280 [3]

\*Measured at 20°C.

Table 2. Measured and Calculated Values of Vapour Pressure in the System Benzene—Cyclohexane at a Temperature of 69.7°C

$x_1$	$P_{exp}/\text{kPa}$	$P_{calc}/\text{kPa}$
0	72.17	—
0.0825	74.90	74.55
0.1594	76.22	76.30
0.2306	77.59	77.54
0.3110	78.41	78.57
0.3876	79.02	79.22
0.4604	79.41	79.57
0.5417	79.66	79.63
0.6213	79.87	79.39
0.6963	79.01	78.86
0.7584	78.01	78.18
0.8169	77.25	77.31
0.8785	76.03	76.14
1	72.86	—

Average deviation of pressure equals  $\pm 0.21$  %.

$x_1$  — mole fraction of benzene,  $P$  — vapour pressure above the solution.

**Table 3.** Measured and Calculated Values of Vapour Pressure in the System Benzene—*N*-methylpyrrolidone at a Temperature of 69.7°C according to [7]

$x_1$	$P_{\text{exp}}/\text{kPa}$	$P_{\text{calc}}/\text{kPa}$
0	0.73	—
0.1062	8.97	8.97
0.1931	15.83	15.73
0.2974	23.68	23.80
0.3886	30.72	30.76
0.4832	37.77	37.84
0.5525	42.82	42.89
0.6208	47.69	47.73
0.6927	52.93	52.66
0.7699	57.84	57.78
0.8216	61.14	61.10
0.8853	65.27	65.17
0.9445	68.94	68.99
0.9760	70.98	71.18
1	72.86	—

Average deviation of pressure equals  $\pm 0.22\%$ . $x_1$  — mole fraction of benzene,  $P$  — pressure above the solution.**Table 4.** Measured and Calculated Values of Vapour Pressure in the System Cyclohexane—*N*-Methylpyrrolidone at a Temperature of 69.7°C

$x_2$	$P_{\text{exp}}/\text{kPa}$	$P_{\text{calc}}/\text{kPa}$
0	0.73	—
0.0481	18.04	18.15
0.1023	31.50	31.69
0.1638	42.41	42.17
0.2407	50.90	50.56
0.2987	55.53	54.84
0.3621	58.66	58.17
0.4031	59.74	59.80
0.4663	61.47	61.74
0.5606	63.23	63.78
0.6456	64.66	65.07
0.7335	65.59	66.15
0.8284	67.25	67.35
0.9107	69.22	68.82
1	72.17	—

Average deviation of pressure equals  $\pm 0.64\%$ . $x_2$  — mole fraction of cyclohexane,  $P$  — vapour pressure above the solution.

are given vapour pressures measured above solutions of known composition.

The volatility of the component 1 referred to the component 2 is defined by the following relation

$$\alpha_{12} = \frac{y_1 x_2}{y_2 x_1} \quad (1)$$

In considering a system with an ideal vapour phase, the righthand side of eqn (1) can be modified by an equilibrium relation. Thus, eqn (1) takes the following

**Table 5.** Measured and Calculated Values of Vapour Pressure in the System Benzene—Cyclohexane—*N*-Methylpyrrolidone at a Temperature of 69.7°C

$x_1$	$x_2$	$P_{\text{exp}}/\text{kPa}$	$P_{\text{calc}}/\text{kPa}$
0.0395	0.1593	43.18	42.57
0.0783	0.3157	57.57	57.42
0.1205	0.4855	64.13	64.74
0.1574	0.6342	68.71	68.93
0.0796	0.1194	39.20	37.78
0.1613	0.2418	55.54	54.60
0.2428	0.3641	64.07	63.77
0.3170	0.4753	70.18	69.77
0.1159	0.0793	31.97	31.70
0.2375	0.1624	50.29	49.61
0.3528	0.2413	60.68	60.56
0.4755	0.3252	69.41	69.38
0.1574	0.0382	24.60	24.29
0.3202	0.0778	42.97	41.77
0.4859	0.1181	56.00	55.46
0.6410	0.1558	66.50	66.01

Average deviation of pressure equals  $\pm 1.09\%$ . $x_1, x_2$  — mole fractions of benzene and cyclohexane,  $P$  — vapour pressure above the solution.

form

$$\alpha_{12} = \frac{P_1^0 \gamma_1}{P_2^0 \gamma_2} \quad (2)$$

where  $P_1^0$  and  $P_2^0$  are saturated vapour pressures of pure components at the temperature of solution,  $\gamma_1$  and  $\gamma_2$  are activity coefficients of components in the liquid solution.Activity coefficients of components at  $T = \text{const}$  practically depend only on the composition of the liquid solution. For their calculation we can use the Wilson equation [4]

$$\ln \gamma_1 = -\ln(x_1 + x_2 A_{12}) + x_2 \left( \frac{A_{12}}{x_1 + x_2 A_{12}} - \frac{A_{21}}{x_2 + x_1 A_{21}} \right) \quad (3a)$$

$$\ln \gamma_2 = -\ln(x_2 + x_1 A_{21}) + x_1 \left( \frac{A_{21}}{x_2 + x_1 A_{21}} - \frac{A_{12}}{x_1 + x_2 A_{12}} \right) \quad (3b)$$

In the cases that  $\alpha_{12} = 1$  (azeotropic mixture) and the relative volatility differs from one only slightly, the separation of components by direct rectification is impossible. However, in the presence of a polar solvent, which will form more intensive interaction forces only with molecules of one component, in our case with molecules of the component 1, a change of activity coefficients of components in the solvent occurs. Consequently, according to eqn (2) also an alteration of relative volatility takes place. As it is known, on this principle is based the extractive distillation. The volatility of the component 1 relative to the component 2 in the presence of a polar solvent 3 will be

denoted as  $(\alpha_{12})_3$  and for its calculation according to eqn (2) one should know the values of activity coefficients  $\gamma_1$  and  $\gamma_2$  in ternary solutions. These were calculated by means of the Wilson equation, which was for a multicomponent system (generally for a system containing  $n$  components) modified by *Orye* and *Prausnitz* [5] into the following form

$$\ln \gamma_i = 1 - \ln \left( \sum_{j=1}^n x_j \Lambda_{ij} \right) - \sum_{k=1}^n \left( \frac{x_k \Lambda_{ki}}{\sum_{j=1}^n x_j \Lambda_{kj}} \right) \quad (4)$$

In eqn (4) parameters  $\Lambda_{ii}$  take the value of one. Parameters  $\Lambda_{ij}$  have a binary character and for their calculation one may employ binary  $P$ — $x$  data measured.

## RESULTS AND DISCUSSION

The pressure of saturated vapours above the binary and ternary solutions was calculated using the relationship

$$P = \sum_i P_i^0 x_i \gamma_i / \phi_i \quad (5)$$

in which the correction coefficient for the real behaviour of the vapour phase  $\phi_i$  was considered for low values of the pressure in the system to be dependent solely on the properties of pure components at the given temperature and pressure. Relations for its calculation were taken from paper [6].

The Gauss—Newton method was applied to the determination of the parameters of the Wilson equation which are sought in the minimum of the objective function

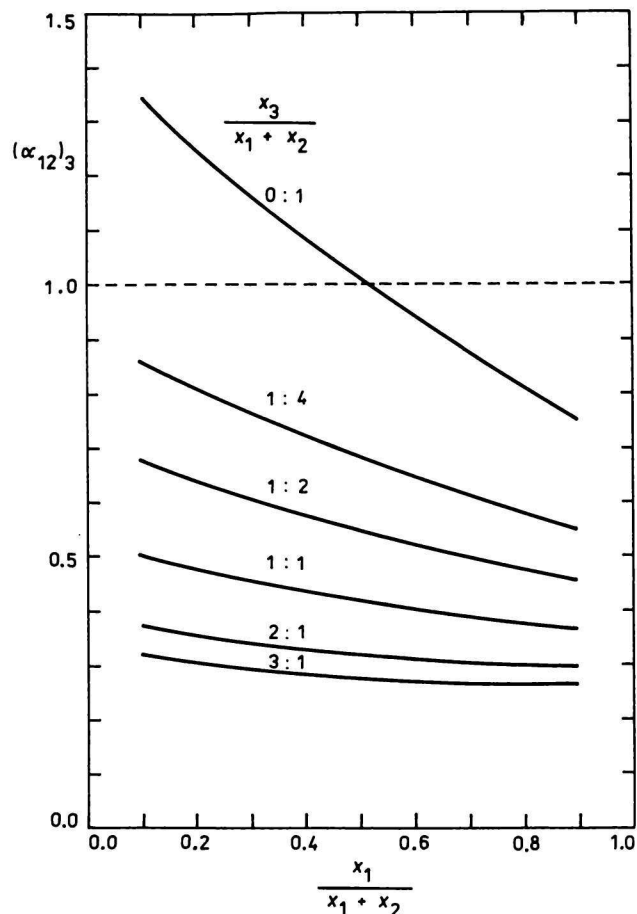
$$F = \sum_h \left( \frac{P_{\text{exp}} - P_{\text{calc}}}{P_{\text{exp}}} \right)_h^2 \quad (6)$$

where  $P_{\text{exp}}$  is the experimental value of the total pressure and  $P_{\text{calc}}$  is the calculated value of the  $h$ -th measurement.

Calculated values of Wilson parameters for three binary systems are given in Table 6. Values of calculated pressures according to eqn (5) are always given in the last column of Tables 2—5. At the bottom of these tables is given the relative deviation of the pressure.

**Table 6.** Calculated Values of the Wilson Equation Parameters  $\Lambda_{ij}$  and  $\Lambda_{ji}$  from Binary  $P$ — $x$  Data at a Temperature of 69.7°C

System $i$ — $j$	$\Lambda_{ij}$	$\Lambda_{ji}$
1—2	0.8780	0.7768
1—3	1.8657	0.2783
2—3	0.3939	0.1088



**Fig. 1.** Dependence of the relative volatility of the system benzene—cyclohexane on the composition of the hydrocarbon mixture for various ratios of the amounts of *N*-methylpyrrolidone to the hydrocarbon mixture.

In Fig. 1 are graphically represented the dependences of calculated values of the relative volatility of the component 1 referred to the component 2 in the solution with the component 3 on the composition of the hydrocarbon mixture. The parameter of the curves in Fig. 1 is the value of the ratio of the amounts of solvent to the hydrocarbon mixture given as  $x_3 / (x_1 + x_2)$  at constant temperature of 69.7°C.

The plot relative volatility *vs.* composition in the absence of a selective solvent (NMP) in the solution is represented by the upper curve in Fig. 1. The binary system benzene—cyclohexane exhibits an azeotropic point for which  $x_1 = 0.52$  and  $\alpha_{12} = 1.0$ . The appearance of this azeotropic point does not allow the separation of the aforementioned components by rectification.

Already a small amount of *N*-methylpyrrolidone added to a mixture of benzene—cyclohexane causes a significant alteration of the relative volatility and disappearance of the azeotropic point. Since *N*-methylpyrrolidone acts selectively on benzene, cyclohexane, though a component with a higher boiling

point becomes more volatile and thus easier separable from benzene. This is manifested by a decrease of the relative volatility of the benzene referred to the cyclohexane below the value 1.0.

Curves depicted in Fig. 1 confirm that the alterations of the relative volatilities are the greater the higher is the ratio of the amount of *N*-methylpyrrolidone to the mixture of hydrocarbons.

If we take into account the economical aspect of the separation process, *i.e.* acceptable are considered such working ratios of the amounts of solvent to the separated hydrocarbon mixture, for which the relative volatility takes values minimally by 20 % different from one, then the ratio of the amounts of *N*-methylpyrrolidone to the hydrocarbon mixture  $x_3/(x_1 + x_2)$  equal to 1:2 satisfies the values  $(\alpha_{12})_3 < 0.8$ .

### SYMBOLS

$F$	objective function
$P_i^0$	saturated pressure of pure component
$P$	pressure of saturated vapours above the solution
$P_{\text{exp}}$	measured pressure of saturated vapours above the solution
$P_{\text{calc}}$	calculated pressure of saturated vapours above the solution
$x_i$	mole fraction of component in the liquid phase
$y_i$	mole fraction of component in the vapour phase
$\alpha_{12}$	relative volatility of the component 1 referred to the component 2 in the binary mixture

$(\alpha_{12})_3$	relative volatility of the component 1 referred to the component 2 in the presence of the component 3
$\gamma_i$	activity coefficient of component in the solution at temperature and pressure of the system
$\Lambda_{ij}, \Lambda_{ji}$	parameters of the Wilson equation
$\phi_i$	correction coefficient for the real behaviour of component in the vapour phase

### Subscripts

$i$	arbitrary component
1, 2, 3	component of the system (1 – with lower boiling point, 2 – with higher boiling point, 3 – polar solvent)

### REFERENCES

1. Renon, H. and Prausnitz, J. M., *Ind. Eng. Chem., Process Des. Dev.* 7, 221 (1968).
2. Surový, J. and Dojčanský, J., *Chem. Zvesti* 28, 313 (1974).
3. Riddick, J. A. and Bunger, W. B., *Organic Solvents*. 3rd Edition. Wiley—Interscience, New York, 1970.
4. Wilson, G. M., *J. Am. Chem. Soc.* 86, 127 (1964).
5. Orye, R. V. and Prausnitz, J. M., *Ind. Eng. Chem.* 57, 18 (1965).
6. O'Connell, J. P. and Prausnitz, J. M., *Ind. Eng. Chem., Process Des. Dev.* 6, 245 (1967).
7. Dojčanský, J., Revús, M., Surový, J., and Mareček, V., *Ropa Uhlie* 22, 236 (1980).

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