LIQUID-LIQUID EQUILIBRIA OF N-METHYLPYRROLIDONE AND HYDROCARBON

Akl M. Awwad*, Khalida A. Jaffer, and A. H. Sulymon
Chemical Engineering Department – College of Engineering – University of Baghdad – Iraq
* Al-Basil Research Center - Iraq

ABSTRACT

Liquid-liquid equilibria of binary systems of N-methylpyrrolidone with n-hexane, n-octane, benzene, toluene , and p-xylene were studied to verify the selectivity of N-methylpyrrolidone towards diferrent hydrocar-bon components. They were also useful to determine the optimum temperature at which the ternary systems could be carried out . The miscibility of aromatics in N-methylpyrrolidone was higher than that of non-aromatics.All aromatics were completely miscible in N- methylpyrrolidone at 298.15 K at a relatively wide range of concentration of N-methylpyrrolidone (34% and above) .

INTRODUCTION

The basic principles of the extraction process is the phase equilibria between two liquid phases contacted to each other. Equilibrium is a static condition in which no changes occur in the macroscopic properties of a system with time. When the phases are not in equilibrium, mass transfer occurs between the phases. The rate of transfer of each species depends on the departure of the system from equilibrium at a specific temperature and pressure. Therefore equilibrium data indicates the optimum operating conditions of any extraction unit and helps in the design.

Extraction of aromatic hydrocarbons from petroleum feed stocks can be held in two processes, either by liquid-liquid extraction, or by extractive distillation. The choice of the process depends mainly on whether the simultaneous recover of benzene, toluene, and xylenes or the recovery of one single aromatic component is required . Generally, in the oil industry, aromatics are recovered by liquid-liquid extraction using a selective, high polar, high dense, and high boiling solvent (Muller and Hoefeld, 1971). Extraction has the advantage that a cut with a wide boiling range from C_6 to C_9 aromatics can be processed in one single step and that the pure aromatics recovered merely have to be fractionated to individual components or separated by crystallization .

EXPERIMENTAL WORK

N-methylpyrrolidone (NMP), n-hexane (>99 mol%) from Riedel-De haen; toluene, benzene, and p-xylene (99 mol%) from Fluka. All solvents were used as received but kept over freshly activated molecular sieves type 4A before use.

The method of cloud point was used to obtain the solubility curves of the binary systems. The cloud point is the temperature at which haziness is first observed at the bottom of the test jar. The experimental measurements were carried out in a closed glass thermostated flask, with a capacity of up to a 100 cm^3 . Temperature was measured with an accuracy of 0.01°C.

Samples were heated up to 15°C above the expected cloud point with simple stirring. Then left for cooling to the cloud point. The cooling rate was 1°C /min each measurement was repeated for about four times. The heating source was water bath, and another water bath was used for cooling. The test flask was isolated from water bath by a glass jacket, fitted by a gasket made of rubber to prevent the test flask from touching the jacket.

RESULTS AND DISCUSSION

The experimental solubility data of the five binary systems are given in tables 1-5. These data are presented in figures 1-5. Data of Malanowski et al., 1994 for the systems NMP-n-hexane and NMP-n-octane are plotted in the same figures for comparision. The critical solution temperatures are listed in table 6. They were estimated by the method rectangular diameters (West, 1963).

From figures 1-5, it can be seen that the two-phase region of NMP mixtures with saturated hydrocarbons ranges between 0 to 0.9 of NMP composition. This leads to the conclusion that NMP has higher miscibility towards aromatics than paraffins. According Francis, 1944, selectivity of any solvent for aromatics with respect to paraffins can be measured by the difference between critical solution temperature (CST) values for the same solvent with appropriate pairs of hydrocarbons. Table 6 can serve this criteria. There is an obvious difference between CST of aromatics with NMP and CST of n-hexane and n-octane with NMP. Figure 6 represents the data of Table 6. The CST of NMP with aromatics are less than those with paraffins which is a fair indication to the high selectivity of NMP for the former compared to the latter.

From figures 3-5, it can be observed that at 298.15 K all the three aromatics are totally miscible with NMP at a reasonably wide range of NMP concentrations, > 0.34. While n-hexane and n-octane are immiscible at this temperature, figures 1 and 2. From these results we planned to study the ternary mixtures at 298.15 K.

REFERENCES

1. E.Muller, G.Hoefeld. 8th World Petroleum Congress, 4,213,(1971).
2. F.A.West. Liquid-Liquid Equilibria, Wiley, N.Y. (1963).
3. S.Malanowski; V.H.J.Bittrich; D.A. Lempe; K. Reinhardt; J.U.Wustling. Fluid Phase Equilibria 96, 185 (1994).
4. A.W.francis. Ind. Eng.Chem. 36,764(1944).

Table (1) Solubility data of NMP (1) –n- Hexane (2)

x_{NMP}	T/K	x_{NMP}	T/K
0.035	297.5	0.523	323.9
0.047	301.5	0.609	321.2
0.086	310.0	0.695	315.5
0.113	313.0	0.750	311.0
0.139	317.5	0.798	309.2
0.253	320.3	0.869	201.5
0.378	325.2	0.905	271.0
0.455	324.5		

Table (2) Solubility data of NMP (1) –n-Octane

x_{NMP}	T/K	x_{NMP}	T/K
0.025	310	0.462	328.5
0.546	317	0.532	326.6
0.125	324	0.701	320.0
0.194	327	0.750	312.7
0.245	328.5	0.789	308.5
0.289	329	0.823	304.5
0.352	329.5	0.879	302.0
0.392	330.2		

Table (3) Solubility Data of NMP (1)-Benzene (2)

x_{NMP}	T/K	x_{NMP}	T/K
0.029	297.0	0.223	301.1
0.044	300.5	0.265	295.5
0.065	301.4	0.301	282.0
0.085	302.5	0.325	279.0
0.096	304.5	0.350	278.0
0.152	310.5	0.364	275.0
0.198	307.5		

Table (4) Solubility Data of NMP (1)-Toluene (2)

x_{NMP}	T/K	x_{NMP}	T/K
0.028	293	0.347	299
0.055	295	0.352	297
0.116	304	0.366	296
0.156	304.5	0.375	291.5
0.209	305.5	0.409	283
0.295	306.5	0.425	280.5
0.342	300.5	0.447	277

Table (5). Solubility Data of NMP (1)-p-Xylene (2)

x_{NMP}	T/K	x_{NMP}	T/K
0.044	292	0.257	309.5
0.084	296.5	0.275	305.5
0.096	305.5	0.294	299
0.156	312.5	0.325	296.5
0.205	313.5	0.334	291.5
0.217	314	0.365	286.5
0.232	310.5	0.396	277.5

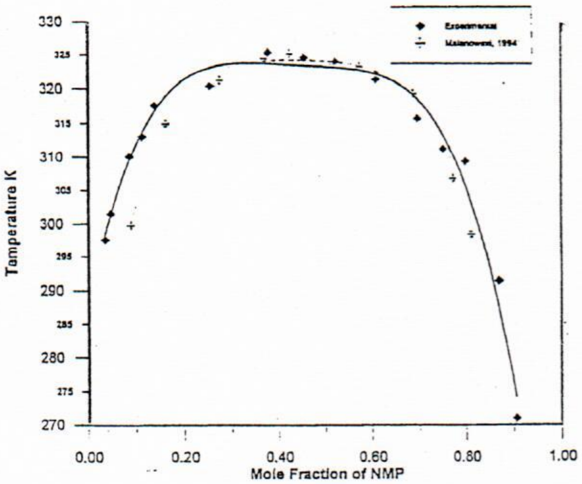

Fig. (1) Experimental solubility diagram for NMP-n-hexan

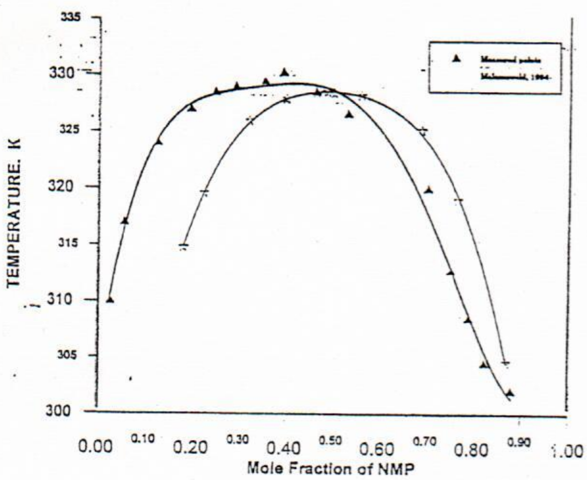

Fig. (2) Experimental solubility diagram for NMP-n-octane

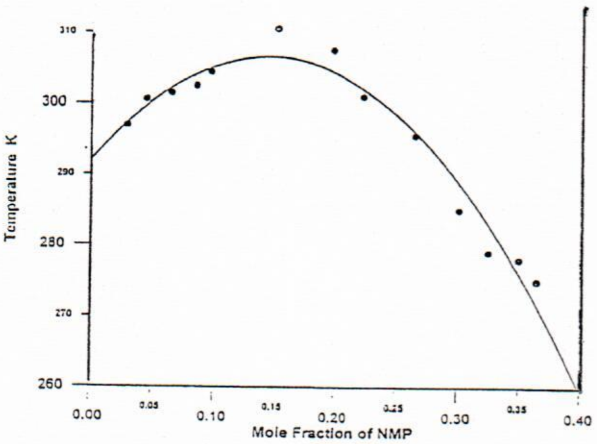

Fig. (3) Experimental solubility diagram for NMP-benzene

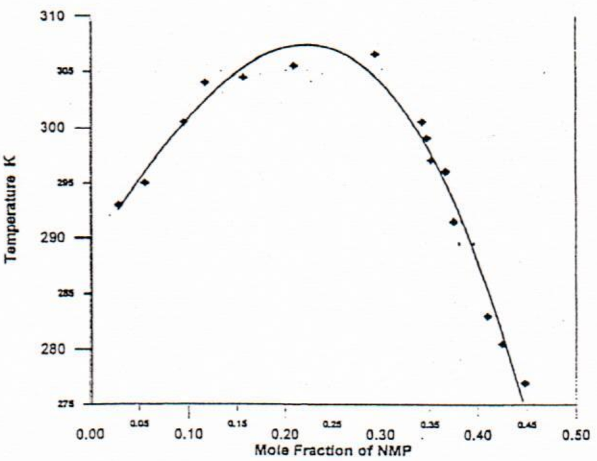

Fig. (4) Experimental solubility diagram for NMP-toluene

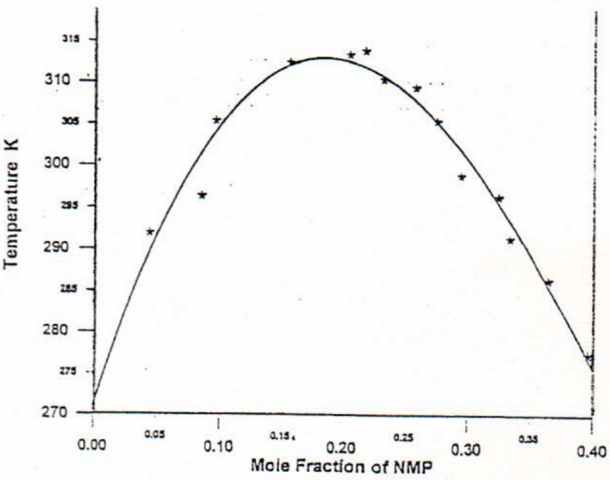

Fig. (5) Experimental solubility diagram for NMP-p-xylene

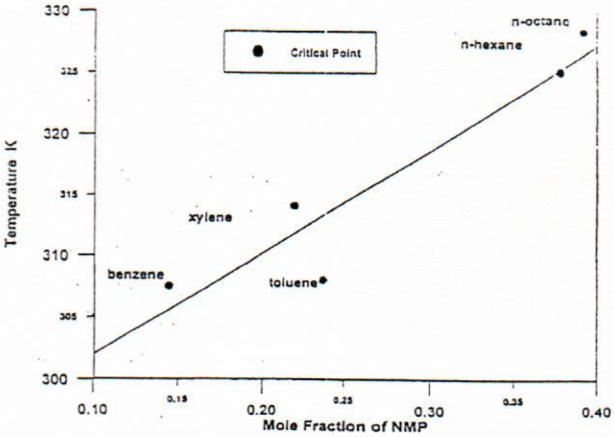

Fig. (6) Upper critical solution temperature for NMP with different hydrocarbons