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PREDICTION OF OPTIMUM COMPOSITION OF THE MIXED SOLVENT N-METHYLPYRROLIDONE/ETHYLENE GLYCOL FOR THE EXTRACTION OF AROMATICS

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ABSTRACT

The optimum composition of mixed solvent which is usually determined experimentally is predicted by a method in which the minimum total energy required for extraction and subsequent solvent recovery by distillation is calculated. The method is demonstrated using N-methylpyrrolidone (NMP) and monoethylene glycol (EG) as mixed solvent for the extraction of benzene from a hexane/benzene mixture. UNIFAC method was used to predict liquid phase equilibria in extraction and liquid-vapor equilibria in distillation. To demonstrate the method flexibility, ethylene glycol was replaced by water as another alternative solvent, and the optimum composition of the new mixed solvent of NMP/water was predicted. However this particular mixed solvent required much higher energy than NMP/EG case.

INTRODUCTION

In liquid-liquid extraction the selection of the appropriate solvent is the first step. The primary consideration is that selectivity, capacity and ease of recovery of the solvent should be favourable. Selectivity is a measure of product quality and capacity is a measure of quantity extracted. In solvent ranking there are usually solvents with high capacity and low selectivity, while other solvents are vice versa. However, a good solvent must have both high capacity and high selectivity (1). From this point of view the idea of solvent combination rises.

In the light of the great number of possible solvent combinations it is of great interest to find methods to optimize mixed solvent composition. However only some of solvents properties can be improved without affecting other properties at the same time. The most used method of solvent combination is based on the trade-off between capacity and selectivity. By mixing high capacity solvent with high selectivity solvent the capacity and selectivity of the mixture can be adjusted to optimum. The choice of solvents to make a mixture must include a narrow boiling range, otherwise heat consumption in solvent recovery will be greater than using one solvent.

One of the most important industrial solvent combinations used in aromatics extraction is N-methylpyrrolidone (NMP) and monoethylene glycol (EG) which is commercialized by Lurgi under "Arosolvan Process" (2). This method has a number of advantages. Glycol is the least expensive solvent and its boiling point of 198°C is rather attractive and only 6°C below that of NMP.

In this work a computational method is developed for the selection of the optimum ratio of NMP/EG mixture for the extraction of aromatics from hydrocarbon using UNIFAC. On the other hand the optimum composition is also determined experimentally using % yield calculations and compared with the predictive method.

PREDICTION OF OPTIMUM COMPOSITION OF NMP/EG

The separation of benzene from hexane process consists of extraction of benzene using NMP/EG as a solvent followed by solvent recovery by distillation as shown in Fig. 1. A feed of 25% hexane, 25% benzene and 50% solvent, as weighted percent was first introduced to a single stage extraction at 60°C, using different NMP/EG ratios.

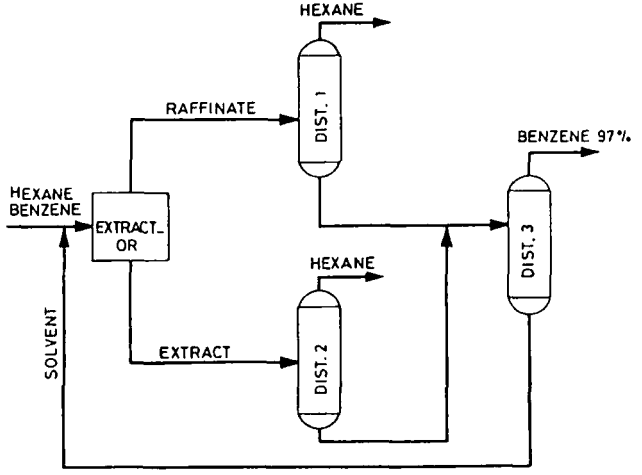

Fig.1 Typical Extraction/Distillation Flow Sheet

For the above feed composition and temperature, liquid-liquid equilibrium phase compositions were computed. An iterative procedure based on Newton-Raphson search technique was used. As a result, the mole fraction in raffinate X_i^r and that in extract X_i^e along with the corresponding activity coefficients γ_i^r, γ_i^e were predicted using UNIFAC method (3), where liquid-liquid equilibrium iteraction parameters were used from Fredenslund, et al. (4). A brief description of UNIFAC model equation is given in the appendix.

Solvent capacity and solvent selectivity are defined as follows:

$$\text{Capacity} = X_2^e/X_2^r \tag{1}$$

$$\text{Selectivity} = (X_2^e/X_2^r)/(X_1^e/X_1^r) \tag{2}$$

where X_2 is the mole fraction of benzene and X_1 is the mole fraction of hexane. The output compositions and activity coefficients of the overhead and bottoms of the distillation were calculated using a standard computer program (5).

ENERGY COMPUTATIONS

Energy was calculated using feed and output composition of each stage. The minimum rate of work is calculated from the relation (6):

$$W_{min} = RT\{\sum_{out} n_k \left[\sum_i X_{i,k} \ln(\gamma_{i,k} X_{i,k})\right] - \sum_{in} n_j \left[\sum_i X_{i,j} \ln(\gamma_{i,j} X_{i,j})\right]\} \tag{3}$$

where i stands for component, k for output streams and j for input streams, while n is number of moles, X is mole fraction and γ is activity coefficient. The above equation can be applied for both extraction and distillation.

The summation of work in extraction and distillation stages will give us the total energy needed to separate benzene as a product of 97% purity for all solvent ratios studied.

In order to use the UNIFAC model for determination of phase equilibrium and solvent recovery calculations, the interaction parameters between all the functional groups present in the feed must be known. In literature there is no data on NMP/EG interaction parameters. So, experiments had to be carried out to obtain liquid-liquid equilibrium data between NMP/EG. These data were used to estimate $a_{NMP,EG}$ and $a_{EG,NMP}$ for UNIFAC.

EXPERIMENTAL SECTION

Materials

N-Hexane, n-heptane and benzene were dried over 5A^{o} molecular sieves. N-methylpyrrolidone and ethylene glycol were distilled under vacuum in a high efficiency column to remove water traces. Chromatographic tests showed purities greater than 99% for all the components.

Procedure

The experimental work was carried out using a thermostated glass cell similar to that described by Soares (1972) (7). Temperature was measured within accuracy of 0.1%. Runs for determination of interaction parameters were carried out using the hexane-NMP-EG system and the heptane-NMP-EG system at two temperatures of 25^{o}C and 50^{o}C.

To compare between the predicted optimum ratio of NMP/EG and the experimental optimum ratio, hexane-benzene-NMP-EG system was used at 60^{o}C. The feed composition of hexane/benzene was 50/50. The solvent composition of NMP/EG was changed to obtain different ratios. The experiments were carried out using the same cell mentioned above.

The analysis was done using gas-liquid chromatograph (Varian-Vista-6000) equipped with a flame ionization detector and connected to a (Varian-Vista-402) data system. A 2m x 1/8" column packed with 10% OV-101 80/100 chromasorb QII was used. The flow rate of helium carrier gas was 30 ml/min. The flow rates were 300 ml/min for air and 30 ml/min for hydrogen.

The experimental liquid-liquid equilibrium data were used to calculate capacity, selectivity and % yield. The optimum experimental ratio was determined from the highest % yield value.

RESULTS AND DISCUSSION

1. Interaction Parameters

The experimental data obtained for mixtures of hexane-NMP-EG and heptane-NMP-EG at 25 and 50^{o}C and at two different feed ratios are presented in table 1. These experimental data were used as an input to a computer program for prediction of $a_{NMP,EG}$ and $a_{EG,NMP}$ for UNIFAC model. An initial guess of these interaction parameters was first used to calculate activity coefficients. The following liquid-liquid equilibrium criteria was then tested.

$$(X_i\gamma_i)^r = (X_i\gamma_i)^e \qquad (4)$$

If eq. (4) is not satisfied, another values of the interaction parameters are assumed. The new determined UNIFAC interaction parameters are presented in table 2 along with all the interaction parameters used in this work. The program calculates the liquid liquid equilibrium using these interaction parameters. The maximum percent deviation in extract phase reaches 10%, but it is much smaller in raffinate phase.

Table 1. Experimental Liquid-Liquid Equilibrium Composition (mole%)

Temperature (°C)	Phase I		Phase II	
	Mole % of (1)	Mole % of (2)	Mole % of (1)	Mole % of (2)
Ternary system Hexane (1) + NMP (2) + Glycol (3)				
25	72.96 82.34	14.98 16.54	0.588 0.230	43.90 45.47
50	75.77 55.26	22.97 41.97	0.103 0.140	44.00 46.17
Ternary system Heptane (1) + NMP (2) + Glycol (2)				
25	93.90 87.74	5.27 5.34	1.820 0.640	55.05 33.99
50	83.78 80.74	6.63 6.13	0.810 1.230	33.92 36.15

Table 2. UNIFAC Interaction Parameters as a Function of Temperature $a_{n,m} = A + B\,(T-273.15)$

$a_{n,m}$	A	B	Reference
$a_{NMP,glycol}$	-177.0	-1.2390	This work
$a_{glycol,NMP}$	-180.3	-1.3460	This work
$a_{CH_3,ACN}$	-11.978	0.1988	(10)
a_{ACN,CH_2}	- 0.014	-0.0242	(10)
$a_{CH_2,ACCH_2}$	-92.720	- 0.8490	(10)
a_{ACCH_2,CH_2}	336.560	2.3410	(10)
$a_{CH_2,NMP}$	379.400	- 0.7001	(10)
a_{NMP,CH_2}	-73.400	0.0670	(10)
$a_{CH_2,glycol}$	527.500	0.0	(4)
a_{glycol,CH_2}	108.500	0.0	(4)
$a_{CH_2,water}$	1300.000	0.0	(4)
a_{water,CH_2}	342.400	0.0	(4)
$a_{ACN,NMP}$	207.600	2.3080	(10)
$a_{NMP,ACN}$	-197.600	0.5815	(10)
$a_{ACN,glycol}$	358.900	0.0	(4)
$a_{glycol,ACN}$	247.300	0.0	(4)
$a_{ACN,ACCH_2}$	-34.690	-1.2776	(10)
$a_{ACCH_2,ACN}$	114.930	7.3700	(10)
$a_{ACCH_2,NMP}$	57.190	-6.7410	(10)
$a_{NMP,ACCH_2}$	32.910	-9.0	(10)
$a_{ACCH_2,glycol}$	337.700	0.0	(4)
$a_{glycol,ACCH_2}$	453.400	0.0	(4)
$a_{ACCH_2,water}$	5695.000	0.0	(4)
$a_{water,ACCH_2}$	203.700	0.0	(4)
$a_{NMP,water}$	-464.960	0.0	(9)
$a_{water,NMP}$	1022.960	0.0	(9)

2. Prediction of Optimum Solvent Composition

Energy requirements were calculated for extraction and distillation. All data needed for such calculations are derived from the UNIFAC model, which means that our prediction of solvent composition will be completely theoretical. As shown in Fig. 1 it is obvious that Dist 1 and Dist 2 are two extractive distillation columns, while Dist 3 is a distillation column. The quality of product benzene is 97% from Dist 3 and no further purification was carried out. In extractive distillation columns, about 3% of benzene or less is lost with hexane as an overhead products. All solvent was recovered and recycled back to the extraction stage. Each distillation column contains about 20 stages. The total energy required for the entire system, calculated for the production of one mole of benzene using different solvent ratios (NMP/EG) is shown in table 3 along with capacity and selectivity for each solvent mixture. A plot of total energy requirements versus solvent composition indicates that minimum energy requirements occurs at solvent composition around the 70:30 NMP/EG ratio as shown in Fig. 2.

Table 3. Calculated Total Energy for Hexane-Benzene-NMP-Glycol System with Capacity and Selectivity.

NMP: Glycol	Capacity	Selectivity	Total Energy kJ/mole of benzene
100:0	1.4870	2.380	43.64
90:10	1.6700	3.500	38.26
85:15	1.6180	3.997	37.50
80:20	1.4700	4.390	35.50
70:30	1.0560	4.730	34.78
65:35	0.8767	4.700	35.10
62:38	0.7000	4.500	34.60
60:40	0.7370	4.550	38.40
50:60	0.4500	3.750	42.20
40:60	0.4500	3.750	42.85
30:70	0.3610	3.430	44.10
20:80	0.2990	3.110	44.94
10:90	0.1600	2.550	45.55
0:100	0.0540	1.570	47.02

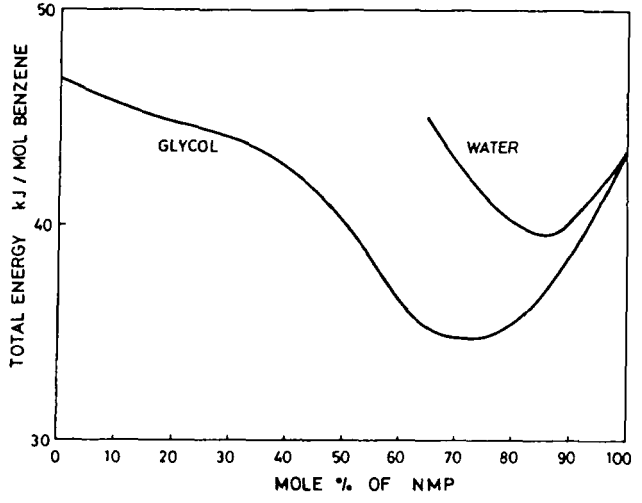

Fig. 2 Total Energy (kJ/mol Benzene) vs. Mole% of NMP for NMP/EG and NMP/Water Systems.

In the Arosolvan process a typical value for the temperature in the extractor is 60°C and a solvent composition corresponding to an NMP:EG weight ratio of 62:38 is normally adopted (1). However the feed to this process is actually naphtha reformate and not just simple benzene/hexane mixture.

3. Experimental Determination of Optimum Solvent Composition

The equilibrium experimental composition obtained for hexane-benzene-NMP-EG system are shown in table 4 along with predicted compositions and % yield for each feed ratio. The difference between predicted and experimental compositions was higher in the extract phase than in the raffinate phase because of the presence of the solvent in the extract phase. In addition, the solvent to feed ratios in the final equilibrium phases are listed in table 5, which is an indication of solvent splitting and increasing selectivity as NMP % increase.

Table (4)
Experimental Liquid-Liquid Equilibrium Compositions (mole fraction) at 60°C

% NMP	Raffinate						Extract Phase						% Yield
	Hexane		Benzne		NMP		Hexane		Benzene		NMP		
	exp.	calc.	exp.	calc.	exp	calc.	exp.	calc.	exp.	calc.	exp.	Calc.	
70	0.4126	0.4787	0.2571	0.2416	0.19599	0.2507	0.0822	0.1069	0.2335	0.2552	0.3741	0.4120	88.4
65	0.4105	0.5098	0.2731	0.2710	0.10330	0.1840	0.0491	0.0953	0.2524	0.2376	0.3365	0.4089	77.7
60	0.5775	0.5310	0.2716	0.2997	0.1175	0.1271	0.0872	0.0860	0.23612	0.2210	0.3258	0.4010	69.85
50	0.5910	0.5435	0.3960	0.3470	0.0994	0.0548	0.0720	0.0716	0.19450	0.1910	0.2685	0.3680	48.95
40	0.5833	0.5425	0.4051	0.3788	0.0641	0.0244	0.0172	0.0586	0.1305	0.1657	0.2011	0.3150	36.96

Table 5. Hydrocarbon to Solvent Ratios in Extract and Raffinate Phases Based on Experimental Data (Feed to Solvent Ratio Initially is 1:1)

% NMP	Extract Phase	Raffinate Phase
70	1:2.160	1:0.4930
65	1:2.017	1:0.4630
60	1:2.093	1:0.1780
50	1:2.750	1:0.0130
40	1:5.770	1:0.0117

A plot of mole % benzene in extract phase versus the composition of the mixed solvent NMP/EG is shown in Fig. 3. This plot indicates that the highest quality of benzene in extract phase occurs at 65% NMP. This ratio is comparable to that obtained from minimum energy calculations.

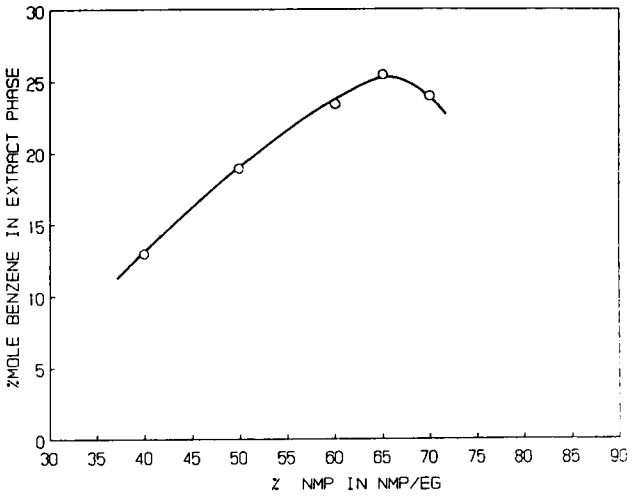

Fig. 3 Experimental mole % of Benzene in Extract Phase vs. % NMP for NMP/EG system

NMP/Water System:

The primary requirement demanded for mixing anti-solvent to NMP is that it must have a high polarity. An anti-solvent is another solvent, such as ethyleneglycol or water, which will decrease the miscibility of the aromatics in the mixed solvent. As a result of extensive comparisons it was decided in favour of water and monoethylene-glycol as the two alternatives, showing that price and availability play a major role in the choice.

There are identical mixtures in terms of capacity and selectivity for NMP/water and NMP/EG mixtures. A plot of capacity vs selectivity for different solvent ratios is shown in Fig. 4. It is obvious that 60:40 NMP:glycol system is approximately identical to 88:12 NMP:water system and 50:50 NMP:EG system corresponds to 80:20 NMP:Water system. The same conclusion was found earlier in literature by experiment.

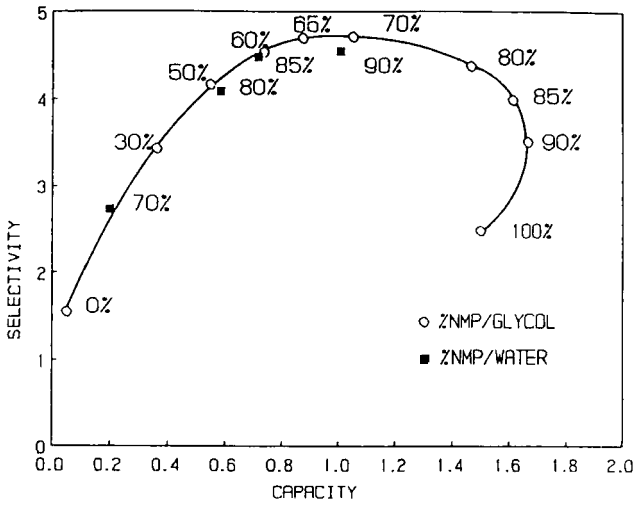

Fig. 4 Calculated Selectivity vs. Capacity for NMP/EG and NMP/Water Solvents.

The same procedure which was applied to NMP/EG mixtures was repeated on NMP/water system. NMP/water interaction parameters are listed in the literature (9). The total energy required for the entire system, calculated per mole of benzene using different

solvent ratios NMP/water is shown in table 6 at 30°C. Fig. 2 shows that the minimum energy in kJ/mole of benzene occurs at 85:15 NMP:water ratio. Energy in the NMP/water system is larger than that for NMP/EG system because water must be evaporated in solvent recovery stages. Water comes as overhead in the extractive distillation column. Only NMP is recovered and recycled. So water will be added with feed to compensate for the lost amount in distillation.

Table 6. Calculated Total Energy for Hexane-Benzene-NMP-Water System with Capacity and Selectivity.

NMP:Water	Capacity	Selectivity	Total Energy kJ/mole of benzene
90:10	1.01	4.56	40.50
88.12	0.72	4.50	39.10
85.15	0.65	4.40	39.85
80:20	0.58	4.10	41.20
70:30	0.20	2.75	43.10

CONCLUSIONS

The optimum mixed solvent composition was found by calculating the minimum energy requirements for separation of two components by extraction and distillation (Fig. 2). These results were confirmed when highest % yield was obtained at the same predicted solvent composition using UNIFAC. The flexibility of the method was further demonstrated by replacing ethylene glycol by water. The calculated predictions were checked favourably with experimental results.

NOMENCLATURE

$a_{n,m}$ = UNIFAC interaction parameter between group n and m

Q_k = UNIFAC group surface area for group k

R_k = UNIFAC group volume for group k

T = Temperature, K

W_{min} = Minimum work, kJ/mole benzene in feed

X_i^e = Mole fraction of component i in extract phase

X_i^r = Mole fraction of component i in raffinate phase

γ_i = Activity coefficient of component i

γ_i^c = Activity coefficient of component i for combinatorial part

γ_i^R = Activity coefficient of component i for residual part

APPENDIX

The UNIFAC Models Equations giving the activity coefficients as functions of composition and temperature are here stated very briefly. The model has a combinatorial contribution to the activity coefficients, due to difference in size and shape of molecules, and a residual contribution due to energetic interactions.

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R$$

I. Combinatorial Part

$$\ln \gamma_i^c = \ln \frac{\phi_i}{X_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{X_i} \sum_j X_j l_j$$

$$l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1)$$

$$Z = 10$$

$$\theta_i = \frac{q_i X_i}{\sum_j q_j X_j} \; ; \quad \phi_i = \frac{r_i X_i}{\sum_j r_j X_j}$$

where

$$r_i = \sum_k v_k R_k$$

$$q_i = \sum_k v_k Q_k$$

Where v_k is the number of groups of type k in molecule i.

II. Residual Part

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)}\right]$$

Γ_k is the group residual activity coefficient, and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution.

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \psi_{mk}\right) - \sum_m \left(\theta_m \psi_{km} / \sum_n \theta_n \psi_{nm}\right)\right]$$

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \; ; \; X_m = \frac{\sum_i v_m^{(i)} x_i}{\sum_i \sum_k v_k^{(i)} x_i}$$

X_m is the fraction of group m in the mixture

$$\psi_{nm} = \exp\left|-(a_{nm}/T)\right|$$

Parameter a_{nm} characteristizes the interaction between groups n and m.

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