Aromatics Extraction from Naphtas
with Tetraethylene Glycol

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Abstract

Liquid-liquid extraction is one of the most commonly used unit operation, beside distillation, for the separation of certain components from complex mixtures in refineries and petrochemicals plants. This paper reports on laboratory tests results of liquid-liquid equilibrium using for the naphta-tetraethylene glycol system. Experimental results compared favourably with those published in literature.

Key words: *liquid-liquid extraction, tetraethylene glycol, naphtas, solvent ratio, rafinate, extract.*

Introduction

Aromatized naphtas obtained by reforming and pyrolisys processes represent the main source of raw materials the manufacturing low molecular weight aromatics. The separation of aromatics from naphtas is usually accomplished by liquid-liquid extraction or extractive distillation.

The liquid-liquid extraction has economical advantages over its competitive separation processes and is applied in most industrial cases where naphtas have a low aromatics content.

The extraction of aromatics (benzene, toluene, and xylene–BTX-) from naphta reformates has been commercially available for the last few decades, and several commercial processes are available.

For the extraction of aromatics from naphtas in the petroleum processing industry solvents as diethylene glycol (DEG), tetraethylene glycol (TETRA), sulfolane, N-methyl -2-pyrolidone, dimethylsulf oxide (DMSO), N-formylmorpholine, sulfur dioxide (SO2) are used [1-9].

High solvent-to-feed ratios in the extraction of naphtas with DEG led to the substitution of this solvent with poliglycols. The literature reports few data of the liquid-liquid equilibrium in the extraction of aromatics from naphtas with poliglycols.

This study presents liquid-liquid equilibrium data measured for the naphtas- tetraethylene glycol system. The extraction runs have been carried out at different temperatures, solvent compositions, and solvent-to-feed ratios.

Experimental Part

An experimental study was performed in a laboratory unit depicted in figure 1, which is located in the laboratory of the Faculty of Petroleum Technology and Petrochemistry, Petroleum – Gas University from Ploiesti, Romania.

In this laboratory set-up, the naphtas-solvent mixture was stirred with a magnetic system that allowed operation at 10 bar pressure, without any loss of hydrocarbons. The naphtas submitted to extraction consisted of surrogate mixtures obtained from mixing a rafinate product containing a low concentration of aromatics content and an aromatic concentrate consisting of benzene, toluene, and xylenes (BTX).
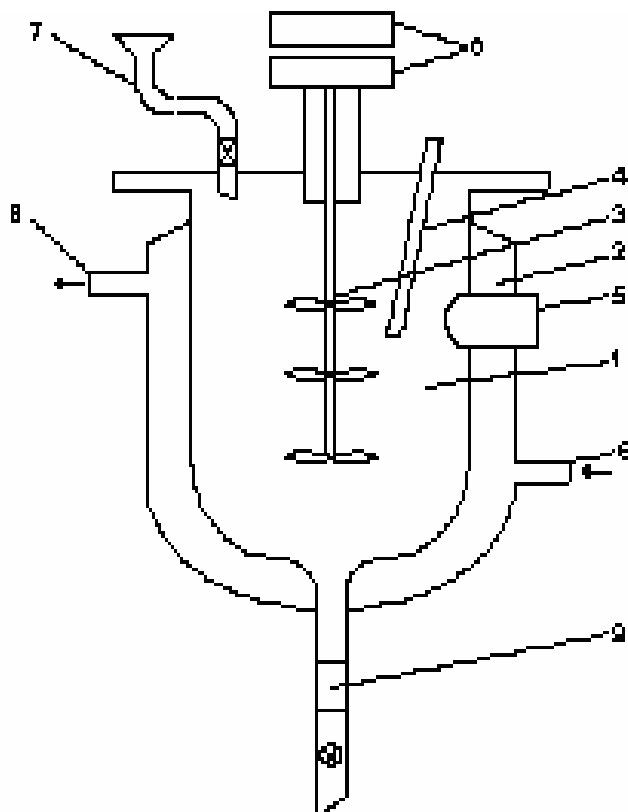
Fig. 1. Laboratory plant scheme for the extraction of aromatics
from naphtas with Tetraethylene Glycol:
1. extractor; 2. heating shell; 3. stirrer; 4. thermometer; 5. window; 6. magnetic stirring system;
7. feeding device; 8. inlet / outlet heating agent; 9. level indicator.

The liquid-liquid extraction was carried out at constant temperature. The solvent was separated from the rafinate solution by washing with water, and from extract solution by distillation of the hydrocarbon mixture.

The composition of hydrocarbons mixture was performed using a Perkin Elmer gas chromatograph, model F 11, equipped with flame ionisation detector, with a chromatographic column of 7.6 m, and Chromosorb -W 60/80 mesh support in 10 weight percent concentration. The oven temperature was varied in two ranges. The first range of oven temperature was 318-393 K with a temperature rise of 8 K/min. The initial time was 5 min, and the final time was 15 min. The second range of oven temperature was 393-533 K with a temperature rise of 15 K/min. The initial time was 15 min, and the final time was 17 min.

The characteristics of the rafinate used for the synthesis of the surrogate naphtas used in the extraction are given in Table 1, and the characteristics of the solvent are showed in the Table 2. The liquid-liquid extraction experiments are carried out at 70°C and 100 °C.

Table 1. Rafinate characteristics.

Characteristics	Values
Density, d_4^{20}	0,7431
Refraction index	1,4245
Distillation limits, °C	64 - 114
Aromatics concentration, weight %	11,89

Table 2. TETRA characteristics.

Characteristics	Values
Density, d_4^{20}	1,123
Refraction index	1,4580
TETRA content, weight %	97,4
Boiling point (at 300 torr, °C)	292

Results and Discussions

The results obtained following experiments at two extraction temperatures are presented in Tables 3 and 4.

Table 3. Experimental results at extraction temperature 70°C.

Extraction code	1	2	3
Aromatics in feed, weight %	20	40	60
Solvent ratio	2	2	1
Rafinate			
Aromatics in rafinate product, weight %	13,73	30,75	54,03
Aromatics in extract product, weight %	61,14	78,35	87,20
Solvent in rafinate, weight %	1,10	1,91	4,75
Solvent in extract, weight %	95,20	93,35	84,07

Table 4. Experimental results at extraction temperature 100°C.

Extraction code	4	5	6
Aromatics in feed, weight %	20	40	60
Solvent ratio	2	2	1
Rafinate, weight %	88,0	80,5	75,6
Aromatics in rafinate product, weight %	15,16	31,81	55,63
Aromatics in extract product, weight %	55,44	73,80	86,71
Solvent in rafinate, weight %	1,64	2,42	5,77
Solvent in extract, weight %	94,30	91,03	86,86

Based on these results, the compositions of the equilibrium solutions, the selectivity β and the distribution constants for the aromatics are calculated, using the following equations:

$$X_{A,E} = \frac{x_{PE}(100 - X_{S,E})}{100} \tag{1}$$

$$X_{NA,E} = 100 - X_{A,E} - X_{S,E} \tag{2}$$

$$X_{A,R} = \frac{x_{PR}(100 - X_{S,R})}{100} \tag{3}$$

$$X_{NA,R} = 100 - X_{A,R} - X_{S,R} \tag{4}$$

$$\beta = \frac{X_{A,E} * X_{NA,R}}{X_{NA,E} * X_{A,R}} \tag{5}$$

$$K_A = \frac{X_{A,E}}{X_{A,R}} \tag{6}$$

where $X_{A,E}$, $X_{NA,E}$, $X_{S,E}$, $X_{A,R}$, $X_{NA,R}$, $X_{S,R}$ are the concentration of the aromatics, nonaromatics and solvent in extract and rafinate solutions, respectively,

x_{PE}, x_{PR} - the concentration of aromatics in extract and rafinate products,

β, K_A - the selectivity and distribution coefficient of the aromatics.

Selection of the optimum extraction temperature is a complex issue which exceeds the purpose of this study [10-12]. The extraction temperatures have been chosen in the range reported in the literature for the extraction of the aromatics from naphtas using glycols as solvents [13-14].

In all conditions, a stirring period of 30 min and a settling period of not less than 3 hrs were allowed. No sensible changes in the equilibrium compositions occurred at longer extraction or settling times.

The assessment of the dissolving characteristics of tetraethylene glycol was made by comparing our results with the data published in the literature on the extraction of aromatics from naphtas using diethilene glycol as solvent [13-14]. This comparison is presented in Tables 5 to 7.

Table 5. Equilibrium data for Naphta – TETRA + 5% water system, t=70 °C.

Aromatics in feed, %	Extract composition, %			Raffinate composition, %			Selecti-vity	Distribution aromatics constant
	Solvent	Aromatics	Nonaro-matics	Solvent	Aromatics	Nonaro-matics		
20	95,20	2,93	1,87	1,10	13,57	85,33	9,85	0,201
40	93,35	5,21	1,44	1,91	30,16	67,93	8,15	0,172
60	84,06	13,89	2,05	4,75	51,46	43,79	5,76	0,270

Table 6. Equilibrium data for Naphta – TETRA + 5% water system, t=100 °C.

Aromatics in feed, %	Extract composition, %			Raffinate composition, %			Selecti-vity	Distribution aromatics constant
	Solvent	Aromatics	Nonaro-matics	Solvent	Aromatics	Nonaro-matics		
20	94,30	3,16	2,54	1,64	14,91	83,45	6,96	0,212
40	91,03	6,62	2,35	2,42	31,04	66,54	6,04	0,213
60	86,86	11,39	1,75	5,77	52,42	41,81	5,19	0,217

Table 7. Equilibrium data for Naphta – DEG + 10% water system, t=150 °C.

Extract composition, %			Rafinate composition, %			Selecti-vity	Distribution aromatics constant
Solvent	Aromatics	Nonaro-matics	Solvent	Aromatics	Nonaro-matics		
96,20	2,70	1,10	1,80	24,50	73,70	7,32	0,111
93,40	5,60	1,00	2,50	48,00	49,50	5,88	0,117
90,50	8,80	0,70	4,20	70,00	25,80	4,61	0,125

Conclusions

The experimental results compared with the data published in the literature suggest the following conclusions:

o   In the past few years tetraethyleneglycol has been more and more employed as extractant to produce high-purity aromatics from catalytic reformates because of its higher capacity and capability to form two phases at reasonable conditions and its physical and chemical stability;

o   tetraethyleneglycol has an acceptable selectivity for extraction of aromatics from naphtas and allows obtaining acceptable purities in industrial extractors;

o   the dissolving power of tetraethyleneglycol is considerably higher than that of diethyleneglycol, thus requiring significantly reduced solvent ratios for extraction;

o   the higher boiling temperature of TETRA allows easier separation of hydrocarbons from mixtures with the solvent;

o   the process water resulting from condensation of the stripping steam and from washing the extraction products can be reused for solvent removal from rafinate and extract products, decreasing the operating costs of the extraction process;

o   in addition, the use of tetraethyleneglycol or triethyleneglycol for the dehydration of gases is also a common process.

o   tetraethylenglycol can be used for the extraction of medium distillates.

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Extracţia aromatelor din benzine utilizând tetra etilen glicol

Rezumat

Extracţia lichid-lichid reprezintă, pe lângă distilare, procedeul cel mai utilizat pentru separarea anumitor componenţi din amestecurile complexe de produse din rafinării şi combinate petrochimice. În acest articol se prezintă rezultatele experimentale în studiul echilibrului lichid-lichid pentru sistemul benzina nafta-tetra etilen glicol. Rezulatele experimentale sunt comparate cu cele publicate în literatură şi se constată o bună concordanţă.