



Utilization of Binary Mixtures of Different Solvents for Aromatics Extraction from a Petroleum Wax Distillate Feedstock

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MOST of petroleum fractions contain detectable contents of aromatic structures that include different categories. Aromatics in general and condensed aromatics particularly are of strong hazardous impact due to their toxic and carcinogenic nature. Therefore, the disposal of such compounds from the various petroleum products is powerfully advised. This research work introduces the use of various binary solvents mixtures for removal of aromatics from a petroleum wax distillate fraction. N-methyl pyrrolidone (NMP) was individually used at the first place as a main extracting agent. Significant reduction of aromatics content was noticed however not limited to the condensed aromatic structures. Binary mixtures made of NMP and different percentages of water, ethylene glycol or ethanol amine (as anti-solvent) were then utilized to improve the selectivity of removal toward condensed aromatics. Noticeable variations in the contents of di- and poly aromatics with corresponding increases in the mono-aromatic content through the use of the different binary mixtures could be attained. Optimization of the most suitable composition for each of the binary mixtures was then determined, based on the characteristics of the gained products from the extraction processes.

Keywords: Aromatic removal, Physical separation, Solvent composition, Petroleum wax distillate.

Introduction

Lubricants are introduced between two moving metal surfaces to reduce friction and wear. In some cases, improving the efficiency of relative movement of two bearing surfaces is only possible if the lubricant is present [1,2]. Therefore, the manufactured lubricating base oil should have good quality and free of undesirable components such as sulfur and condensed aromatic compounds [3]. To obtain such specifications, the utilized feedstock in production of lube base-stocks; distillate or de-asphalted oil, is preceded through various processes. These processes include solvent extraction (aromatic removal stage) followed by dewaxing and finishing processes [4].

Removal of aromatic hydrocarbon compounds in general and carcinogenic; multiple-ring structures, in particular is considered one of the most important stages in lubricating oils production. One of the techniques that are used for the disposal of such aromatic compounds from lube feedstocks is solvent extraction [6,7]. The extraction of aromatics by solvents is a physical separation process. The selectivity of the solvent toward aromatics is an important parameter in its choice as a proper extracting media. In addition, the solvents of expanded selectivity towards polycyclic aromatics, that contain two or more aromatic rings, have attracted greater attentions [8].

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Experimental

In this study, a middle wax distillate fraction (b.r.400-450°C) conducted from EL-Ameria Petroleum Refining Company was used as a feedstock. NMP was introduced as the main solvent to execute the process of aromatics removal. Subsequently, the use of its binary mixtures with H₂O, Ethylene glycol and Ethanol (anti-solvents) for the aromatics removal was also studied. The extraction processes was performed via using a jacketed batch mixer-settler apparatus equipped with a mechanical stirrer. This apparatus is connected with water circulator in order to adjust the extraction temperature.

Solvent Extraction Process

The middle wax distillate fraction was subjected to the bench scale extraction using either NMP alone or its mixtures with the above stated anti-solvents. The extraction processes were carried out at fixed temperature and solvent feed ratio (S/F) of 70°C and 2 respectively. Additionally, the impact of following solvent compositions on aromatics removal was studied

- a- NMP + H₂O mixture (the percentage of H₂O from 0–5 wt%),
- b- NMP + EG mixture (the percentage of EG from 0–20 wt%)
- c- NMP + EA mixture (the percentage of EG from 0–20 wt%).

Characterization

The feedstock and all the acquired raffinates after each extraction process were subjected to the determination of their structural and compositional characteristics. Following techniques and methods were utilized to obtain such properties :

- I- ASTM standard methods [9]: to determine the physico-chemical characteristics,
- II- Liquid solid column chromatography technique [10]: obtaining hydrocarbon component analysis,
- III- n-d-m method [11]: structural group analysis.

Results and Discussion

At the beginning of aromatics removal investigation, the full characteristics of the feedstock (using the stated methods in section 2.2) were determined. Then, the aromatics extraction process using pure NMP was executed at the pre-determined conditions in section 2.1. The full characteristics of both the feedstock and collected raffinate after the extraction process are presented in Table 1. It can be obviously noticed

that the implementation of solvent extraction stage could reduce the aromatics content of raffinate, compared to feedstock. Specifically, about 22% of the aromatics content was reduced in the produced raffinate. However, the detected removal had included all the existing aromatics categories in the feedstock, with no strong orientation towards condensed aromatic structures. Thus, the addition of other solvents to the NMP, in order to improve its selectivity to di- and poly-aromatics, was necessary. Generally, the change in aromatic content was accompanied with observable changes in the features of the gained raffinate. Exactly, the reduction if aromatics was joined by reductions also in values of sulfur compounds, viscosity, density and viscosity gravity constant (VGC). Also decrease in aromatic carbon percentage (%C_A) as well as the total ring content R_T of raffinate could be displayed. These reductions were compromised by the increase of paraffinic nature of raffinate; hence its viscosity index and mean molecular weight were enhanced.

Raffinate I is the product of extraction process at temperature of 70 °C and solvent oil ratio of 2/1 these conditions has been chosen because of using in industry scale.

Effect of Solvent Composition

In the current stage, three binary mixtures made of mixing NMP solvent with water, ethylene glycol and ethanolamine respectively, as anti-solvents, were used for the process of solvent extraction. The use of these anti-solvents was meant to control the solvency power of NMP and enhance its selectivity toward the extraction of condensed/ poly aromatic structures. The critical solution temperature (CST) for each of the binary mixtures was firstly measured at a solvent feed ratio of 2/1. Figure 1 illustrates the CST values of feed-solvent system at different concentrations of water, ethylene glycol (EG) and ethanolamine (EA). It can be clearly noticed that increasing the concentration of H₂O, EG and EA in NMP elevates the CST of the system. This may consequently refer to the decrease in solvent power of NMP with a simultaneous increase in its selectivity. It can also be seen that the lowest CST value for the mixtures could be detected around 100 °C. Therefore, the utilization of 70°C as the operational temperature, at this stage of extraction, could be then validated.

After determining the CST values, the different binary mixtures were forwarded for the aromatics removal process. The physical features, component analysis, carbon distribution and ring content of the obtained raffinates are exhibited in

TABLE 1. Physical Characteristics, Hydrocarbon Component Analysis and Structural Group Analysis of the Feedstock (400-450°C) and raffinate I.

Characteristics	Feed	Raffinate I
Yield, wt.%	---	63.03
Refractive index, 70°C	1.4875	1.4650
Density, gm/cc, 70°C	0.8782	0.8434
Mean molecular weight	391	415
Pour point, °C	39	42
Sulfur content, wt%	2.41	1.16
Kinematic viscosity, 40°C, cSt	39.28	26
Kinematic viscosity, 100°C, cSt	5.68	4.98
Viscosity index	76	118
Viscosity-gravity constant (VGC)	0.8694	0.8341
Component analysis:		
Total saturates, wt%	50.03	61.16
Total aromatics, wt%	49.97	38.84
Mono aromatics, wt%	14.51	12.53
Di aromatics, wt%	25.46	19.55
Poly aromatics, wt%	10.00	6.76
Structural group analysis:		
Carbon distribution		
%C _A	18.27	6.88
%C _N	20.39	27.60
%C _R	38.66	34.47
%C _P	61.34	65.53
Ring content analysis		
R _A	0.89	0.34
R _T	2.06	2.00
R _N	1.17	1.66

C_A = Aromatic carbon; C_N = Naphthenic carbon; C_R = C_p + C_A; C_p = Paraffinic carbon; R_A = Aromatic ring; R_N = Naphthenic ring; R_T = R_A + R_N.

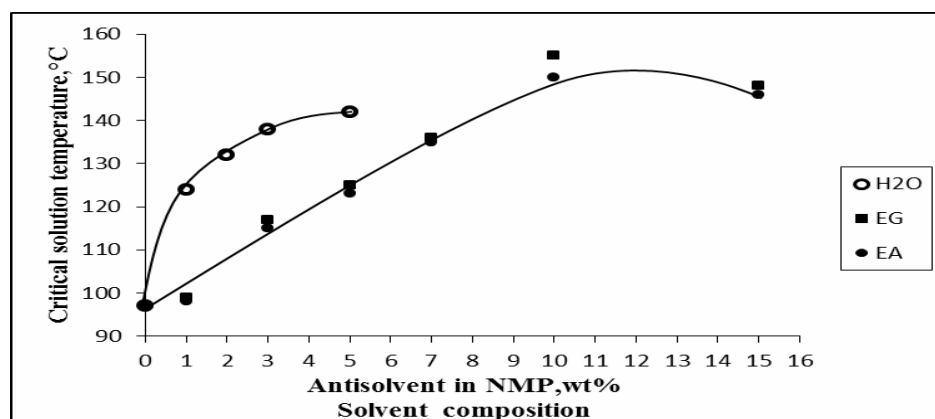
**Fig. 1. Effect of Solvent Composition on the Critical Solution Temperature of the Feed-Solvent Systems.**

Fig. 2-7.

It can be observed that the increase of H₂O, EG and EA concentrations in the solvent mixtures

could increase the yield of obtained raffinates (Fig. 2a, 4a & 6a). This increase in yield percentages of raffinates was accompanied with improvement in

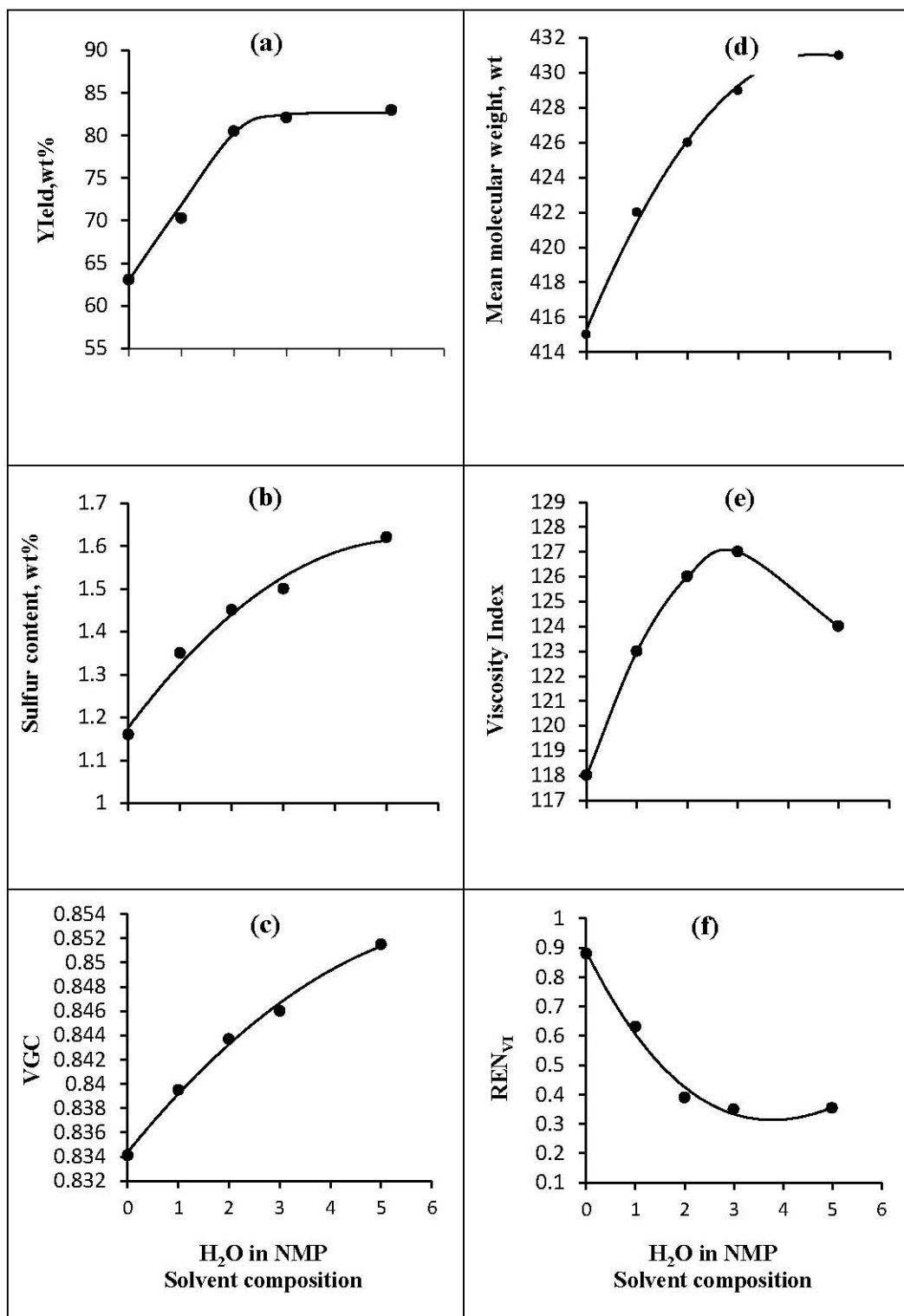


Fig. 2. Effect of Solvent Composition (NMP+H₂O) on the Yield and Physical Characteristics of the Raffinates.

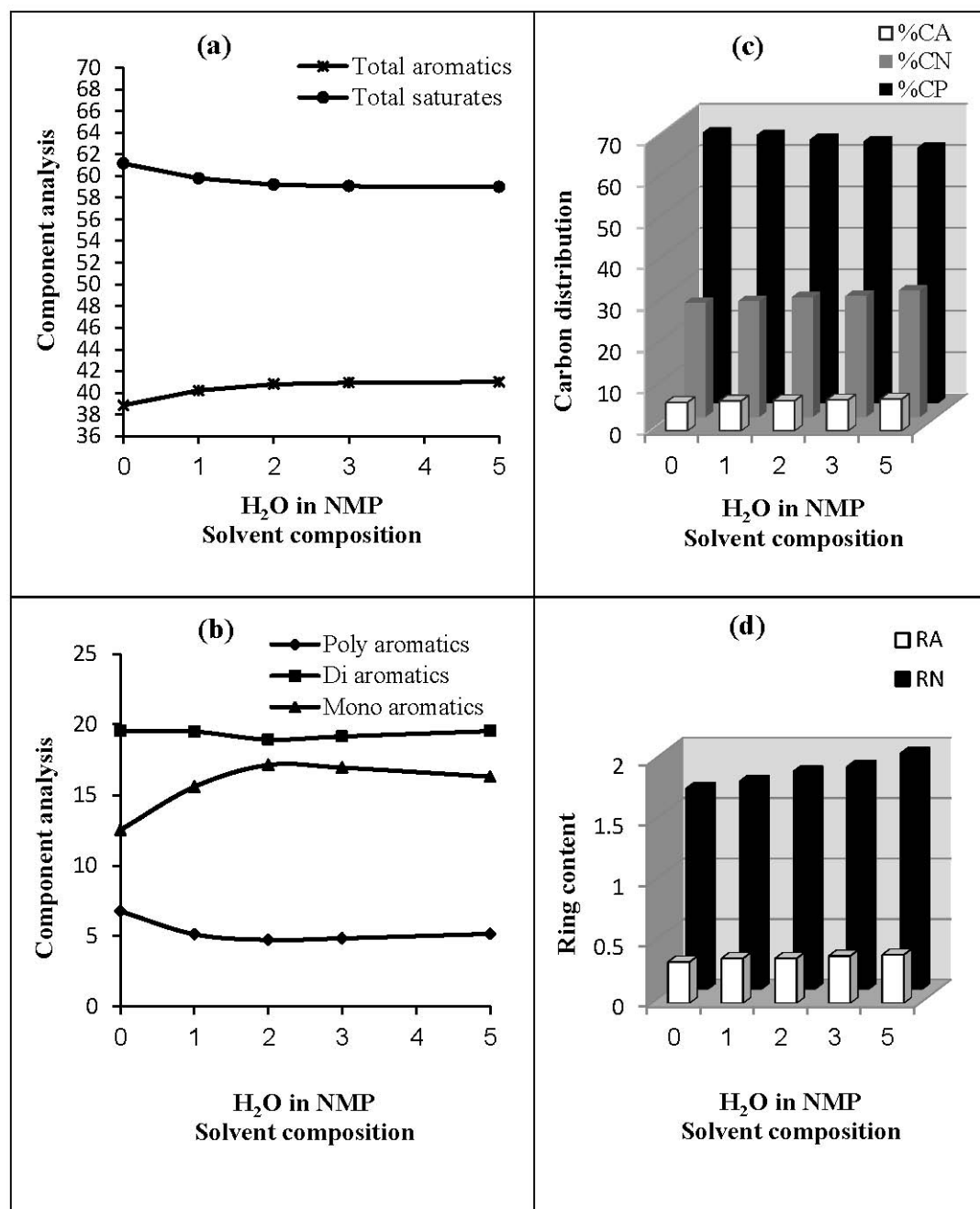


Fig. 3. Effect of Solvent Composition (NMP+ H₂O) on Component Analysis, Carbon Distribution and Ring Content of the Raffinates.

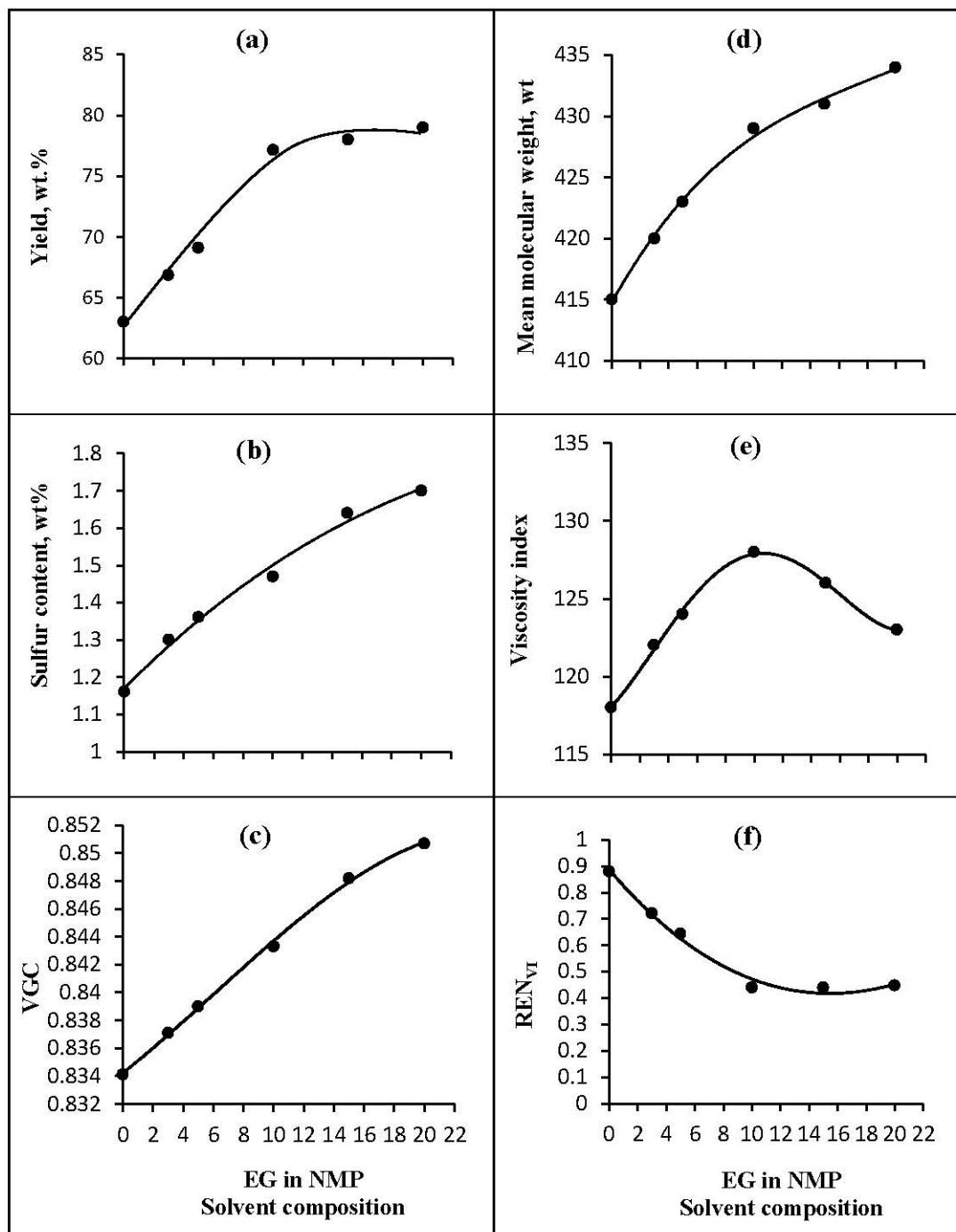


Fig. 4. Effect of Solvent Composition (NMP+EG) on the Yield and Physical Characteristics of the Raffinates.

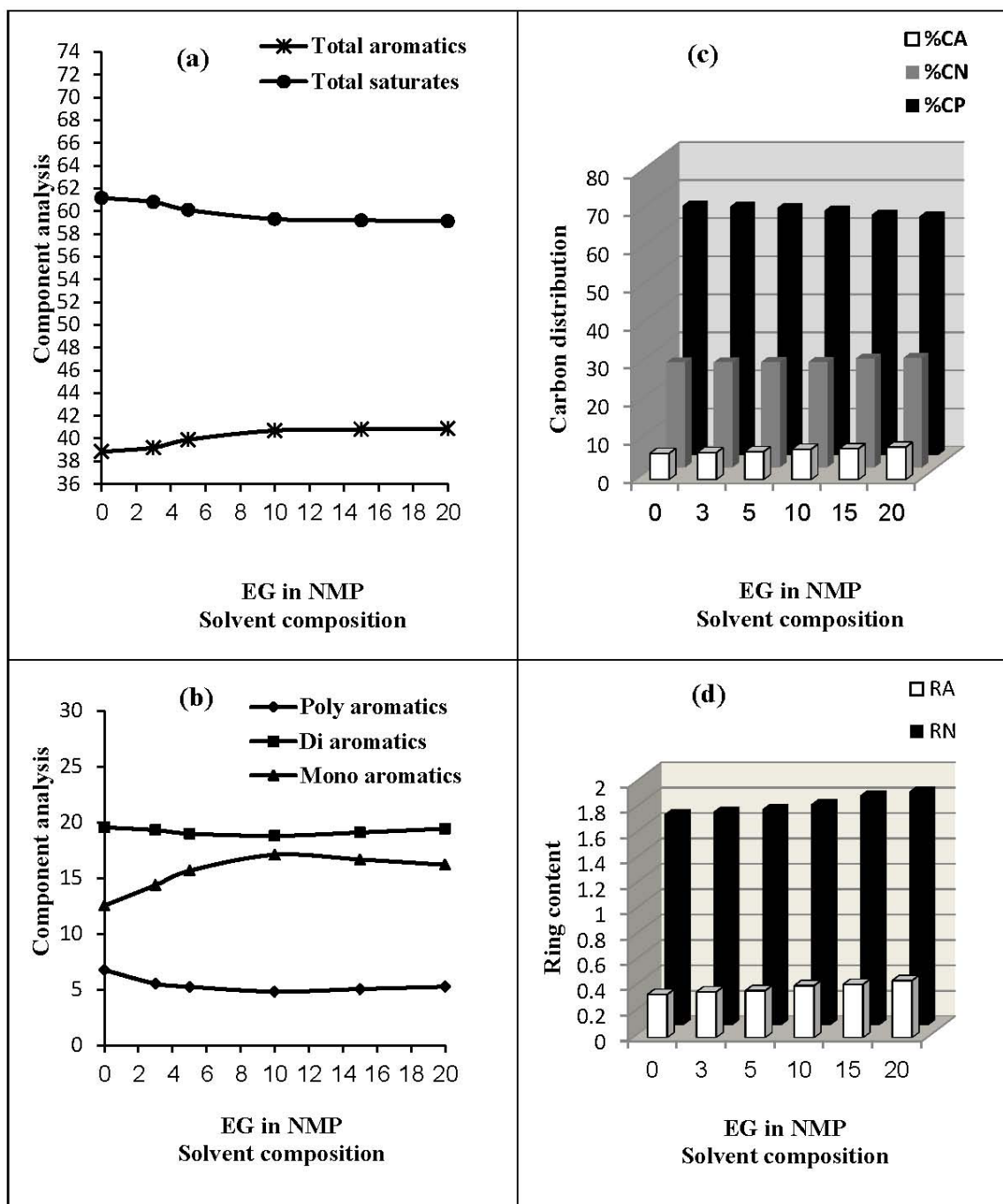


Fig. 5. Effect of Solvent Composition (NMP+EG) on Component Analysis, Carbon Distribution and Ring Content of the Raffinates.

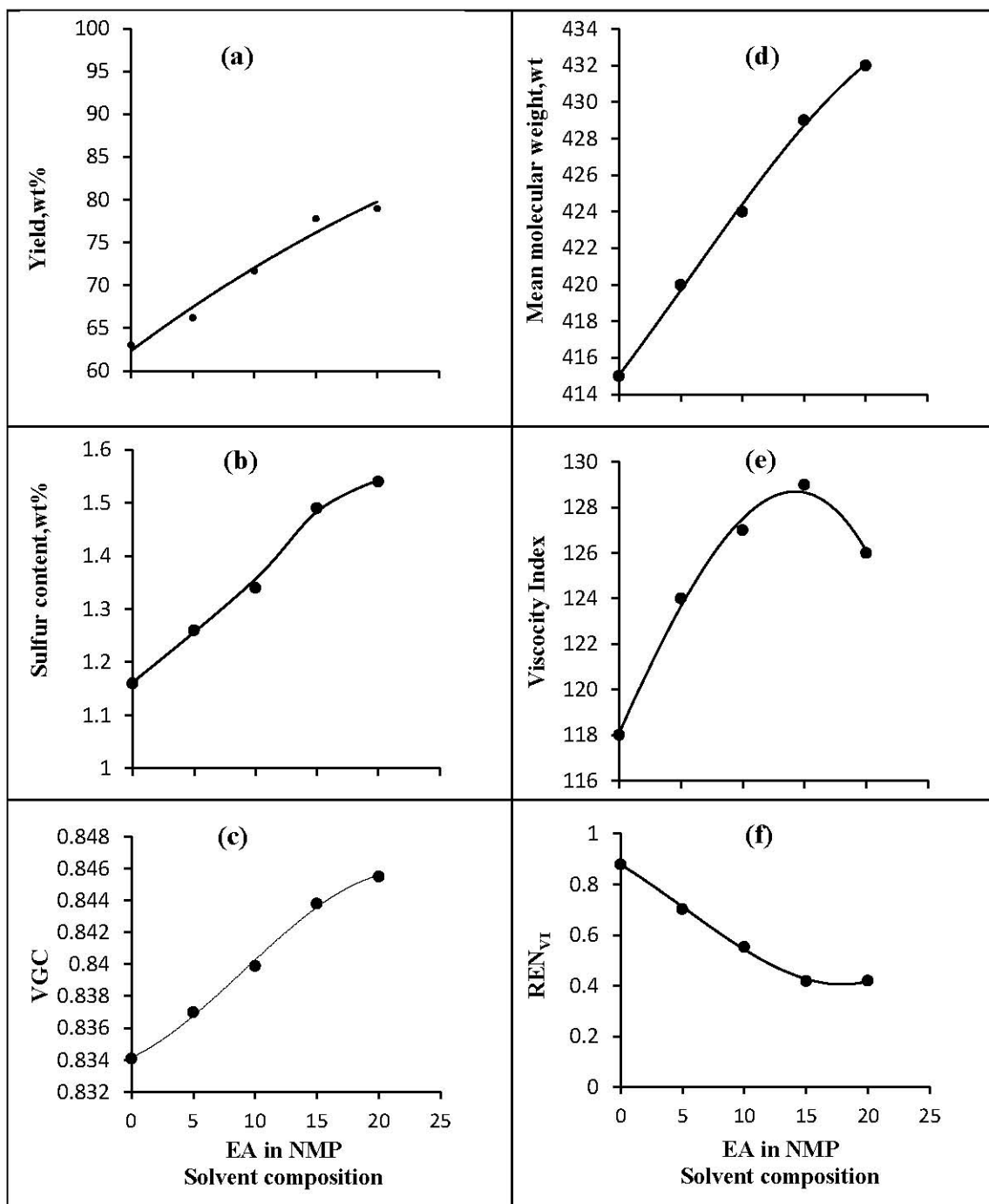


Fig. 6. Effect of Solvent Composition (NMP+EA) on the Yield and Physical Characteristics of the Raffinates.

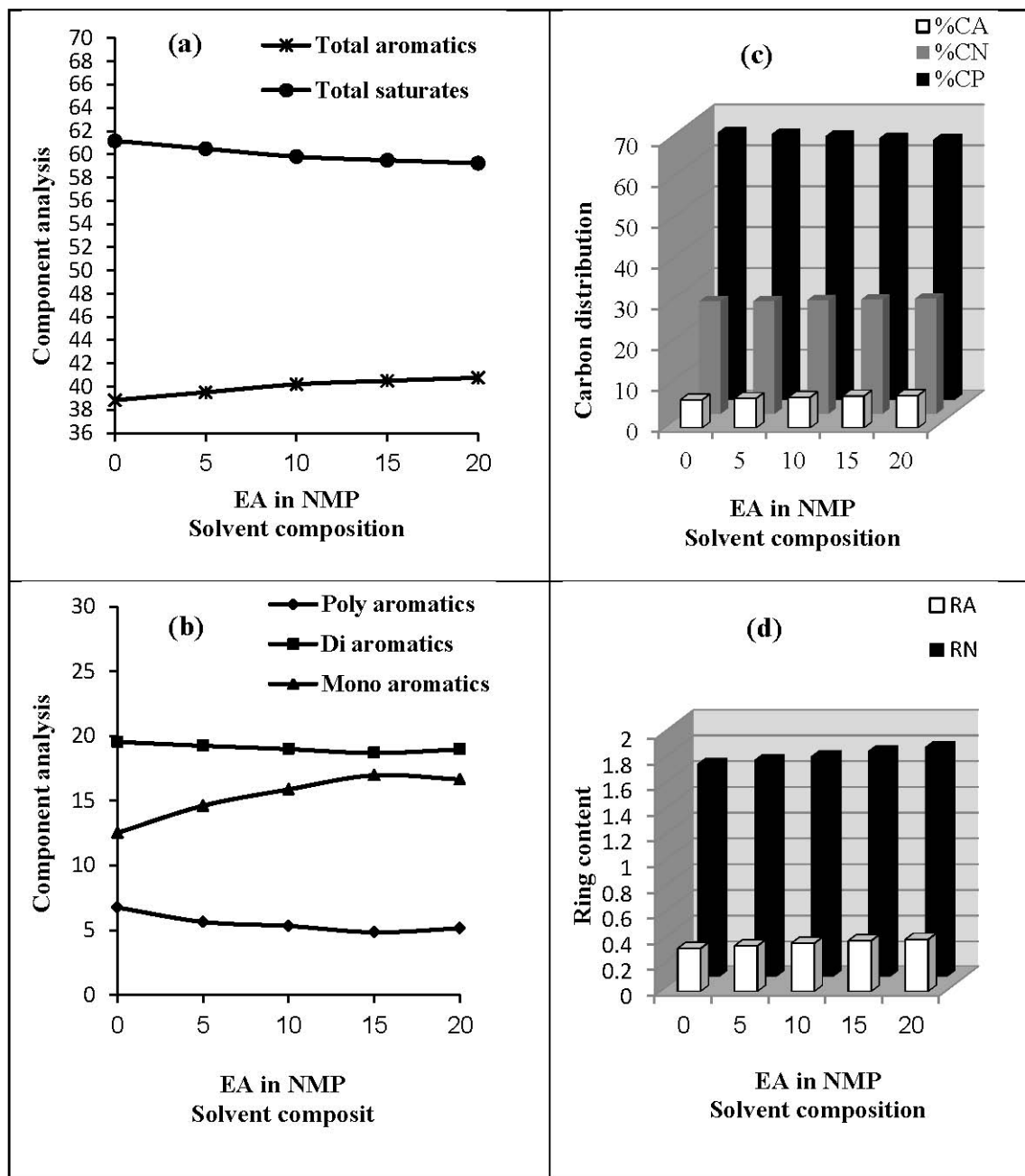


Fig. 7. Effect of Solvent Composition (NMP+EA) on Component Analysis, Carbon Distribution and Ring Content of the Raffinates.

their qualities in terms of elevating the values of mean molecular weight and viscosity index (Fig. 2d, 2e, 4d, 4e, 6d & 6e).

Correlating data of component analysis, carbon distribution and ring content with those of viscosity index and mean molecular weight of the raffinates, it can be noticed that the percentages of both di- and poly-aromatics of raffinates had decreased by increasing the amount of anti-solvents (Fig. 3b, 5b & 7b). These declines were accompanied by corresponding increases in the mono-aromatics contents and subsequently the percentages of aromatic and naphthenic carbons (% C_A & % C_N) and aromatic and naphthenic rings (R_A & R_N) per molecule (Fig. 3, 5 & 7). This findings could explain the increase of mean molecular weight and viscosity indices since such aromatic structure may contain long paraffinic side chain and/or of naphthenic structure attached to its ring. This attitude had continued until the concentration of anti-solvents reached 3,10 and 15% for H₂O, EG and EA respectively. Above these percentages of anti-solvents in the extracting mixture, the behavior had been reversed. This can be explained by increasing the selectivity of extracting mixtures toward di- and poly-aromatic structures (most polar compounds) by the increase of anti-solvent concentrations to prior-stated percentages. Above these concentrations, selectivities of these mixtures were partly lost and their solvent power could consequently increase.

Conclusion

Removal of different aromatic structures from a petroleum wax distillate fraction was performed using the solvent extraction technique. Individual extracting agent (NMP) as well as its sub-driven binary mixtures were utilized during the elimination of aromatics. The collected results of this study reveal that the addition of anti-solvents (H₂O, ethylene glycol and ethanol amine) to NMP could improve its efficiency in reducing the polycyclic aromatics content. The most suitable combinations of these mixtures were found to be those containing 3 % H₂O, 10 % ethylene glycol and 15 % ethanol amine in NMP.

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إستخدام الخلائط الثنائية من المذيبات المختلفة لإستخلاص المركبات الأروماتية من خام المقطر الشمعى البترولوى

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تحتوي معظم المقطرات البترولية على مركبات أروماتية و التي تشمل فئات مختلفة. المركبات الاروماتية بشكل عام و العديدة الحلقات بشكل خاص لها تأثير خطير قوي بسبب طبيعتها السامة والمسرطنة. لذلك ، ينصح بشدة التخلص من هذه المركبات من المنتجات البترولية المختلفة. يقدم هذا العمل البحثي استخدام مخاليط المذيبات الثنائية المختلفة لإزالة المركبات الاروماتية من المقطر الشمعى البترولوى. تم استخدام ميثيل بيروليدون بشكل فردي في المقام الأول كعامل استخراج رئيسي. ولوحظ انخفاض كبير في محتوى المركبات الاروماتيه ولكن لا يقتصر على المركبات لاروماتية عديدة الحلقات. ثم استخدمت الخلائط الثنائية المصنوعة من الميثيل بيروليدون والنسب المئوية المختلفة من الماء ، جلايكول الإيثيلين أو أمين الإيثانول (كمضاد للمذيبات) لتحسين انتقائية الإزالة نحو المركبات الاروماتية عديدة الحلقات. يمكن تحقيق اختلافات ملحوظة في محتويات المركبات الاروماتية الثنائية والعديدة الحلقات مع زيادة مقابلة في محتوى المركبات أحادية الحلقات من خلال استخدام الخلائط الثنائية المختلفة. ثم تم تحديد أمثلية التركيب الأنسب لكل من المخاليط الثنائية ، بناءً على خصائص المنتجات المكتسبة من عمليات الاستخراج.