

EXTRACTION OF AROMATICS FROM HEAVY NAPHTHA USING DIFFERENT SOLVENTS

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Abstract

Aromatic hydrocarbons are very important to the petrochemical industry. Among these are benzene, toluene and xylene (BTX), which are basic raw materials for the production of a number of important petrochemicals. There are many processes used to separate aromatic from non aromatic such as fractionation, azeotropic distillation and liquid / liquid extraction, etc. Liquid - liquid extraction is unique, efficiently used for heat sensitive, close boiling components and for separation of components not possible by other unit operations and it could be done at ambient temperature makes it more energy efficient.

The choice of solvent depends on the properties and boiling range of the feedstock. Through the years, a lot of selective solvents has been proposed and selected for the physical separation of aromatics in liquid - liquid extraction. Among the selection criteria are the stability, chemical compatibility, availability, environmental hazards and price of the solvent. But the basic solvent properties that make it efficient are selectivity and capacity. Four different types of solvents which are: ethylene glycol,

diethylene glycol, dimethyl sulfoxide and dimethyl formamide are used to extract aromatics (BTX) from heavy naphtha.

The effects of degree of mixing, S/F ratio, temperature, time of mixing and time of settling on the extraction of aromatics (BTX) were studied. The highest percentage of aromatics (BTX) extracted from heavy naphtha is achieved by using dimethyl sulfoxide as a solvent and it was also found that the concentration of extracted aromatics (BTX) decreases by increasing the solvent / feed ratio due to dilution and the best S/F ratio is 5. The optimum degree of mixing was found to be 900 R.P.M. The highest concentration of BTX extracted takes place at 63 °C. By studying the effect of time of mixing, it was found that the extraction of aromatics (BTX) increases as the time of mixing increased until equilibrium and the best time of mixing is 40 minutes. Finally by increasing the time of settling, the extraction was increased and the best time of settling was increased and the best time of settling is 90 minutes.

Introduction

Aromatic hydrocarbons are very important to the petrochemical industry. Among these are benzene, toluene and xylene (BTX), which are basic raw materials for the production of a number of important petrochemicals. Aromatics extracted from naphtha are also used as thinner for certain types of paints.

Liquid – liquid extraction: is the most widely used method for the separation of aromatics and non - aromatics. A prerequisite for the application of the process is that the solvent and the mixture to be separated form two phases and that the solvent can be separated from the extract in a simple way. It is a process whereby the separation of the desired component from the liquid mixture is obtained by adding another immiscible liquid called solvent. The separation by extraction process takes into account the difference in

relative solubilities of the desired component in the liquid feed and solvent phases.

The solvent rich liquid phase is called "Extract" and solvent lean phase is called "Raffinate" [1-3]. Thus, a solvent, which preferentially dissolved aromatic compounds from a mixture of hydrocarbons, could be used to remove aromatics from kerosene and lubricating oils. In the former case, this treatment improves the clean burning properties of the fuel, while separating the aromatics from the isoparaffins and naphthenes in lubricating oil improves the viscosity – temperature relation. In both cases the end product is a high quality raffinate [4-5].

Field, S. [6] discussed the importance of aromatic benzene, toluene and xylene (BTX) as raw materials in the chemical industry. In solvent extraction, the C₆ – C₉ fractions from catalytic reforming and steam cracking are relatively high in aromatics concentrations. Some of the most popular solvents in major use today are sulfolane, N - methyl pyrrolidone and various glycols such as mono – di – tri and tetra – ethylene glycols.

Winward, A. [7] reviewed the published information on recent developments in the application of liquid / liquid extraction for petroleum products and petrochemical feedstocks. Most of the developments are referred to extraction processes, which depend on physically selective solvents. Liquid / liquid extraction became well suited for the petroleum industry because it meets the challenge so that petroleum is becoming the major source of naphthalene as well as of benzene, toluene and xylene.

Fenske, M. R. et al [8] made an article, which brings up to date the current status of this useful technique. The material is presented in the following sections: petrochemicals, naphthas, distillate fuels, catalytic

feedstocks, lubricating oils and extraction equipment. In petrochemical industries, many of the steps of isolating or converting petroleum hydrocarbons into chemicals, extraction in some form is used e.g., BTX and aromatics. These aromatics are extracted from hydrocarbon streams by diethylene glycol or sulfur dioxide.

Deal, G. H. et al [9] made a comparison between sulfolane and diethylene glycol in the extraction of aromatics (BTX). The comparison depended on the following properties: solvency – selectivity, water effect, volatility, stability and corrosivity and miscellaneous physical properties. They explained the advantages and disadvantages of each solvent.

Stewart, L. D. et al [10] described Udex process as one of the processes used to extract aromatic (BTX) from gasoline by using diethylene glycol as a solvent.

Choffe, B. et al [11] used dimethyl sulfoxide as a solvent for the extraction of the aromatic (BTX) from petroleum fraction. Also they studied the effect of dilution of solvent with water on the phase equilibrium in extraction method. They found that DMSO is a low cost solvent that offers economic extraction of aromatics at ambient temperature; minimum corrosion of carbon steel equipment, easy separation of solvent from product and its solvent stability is excellent. The solvent used to extract aromatics from gasoline and kerosene is promising.

Renon, H. et al [12] first they compared between the properties of industrial extraction solvents, especially selectivity, capacity, viscosity and density. The high selectivity of dimethyl sulfoxide makes possible to obtain

aromatic hydrocarbons of high purity in one extraction step without additional extractive distillation.

Khanna, M. K. and B. S. Rawat [13] studied extraction of aromatics from naphtha and kerosene using eight different solvents. The parameters studied were aromatic contents in the feed, temperature, solvent / feed ratio and water content in the solvent.

Hamid, S. H. and M. A. Ali [14] carried out an experimental investigation to evaluate the efficiencies of different selective solvents used for the extraction of aromatic hydrocarbons from naphtha distilled from Saudi Arabian light crude oil. The solvents used were 3 – methoxypropionitrile, ethylene glycol, dimethyl sulfoxide, sulfolane, phenol and nitrobenzene. They studied the effect of different parameters such as operating temperature (20 – 125 °C), solvent / oil ratio (1–3), selectivity and solvent capacity.

Experiments for the extraction of aromatic hydrocarbons

The objective of this experimental work is to deal with heavy naphtha to remove or extract the aromatic hydrocarbons such as benzene, toluene and xylene (BTX) for using the raffinate naphtha in different purposes and BTX in the petrochemicals industry.

The operating parameters controlling the performance of the experiments have been studied are:

- Solvent – to – feed ratio (S/F ratio)
- Degree of mixing, R.P.M.
- Temperature, °C

- Time of mixing, min
- Time of settling, min

Experimental Plan

The experimental work of the present paper is concerned with the extraction of aromatic hydrocarbons (BTX) from heavy naphtha (obtained from Assuit Oil Refining Company, Egypt) using different types of solvents.

Stream	Heavy naphtha
ASTM Dist. Range, °C.	122 – 166
Sp. Gr. 15 °C	0.7538
Aromatics	
Benzene, % wt.	0.01
Toluene, % wt.	0.46
Xylene, % wt.	7.30
Total	7.77

Four different types of solvents are used in the experimental work for reformate naphtha. These solvents are: ethylene glycol, diethylene glycol, dimethyl sulfoxide and dimethyl formamide and the operating parameters are:

- Solvent / feed ratio (1 – 6)
- Degree of mixing (100 – 1100 R.P.M.)
- Temperature (room temperature , 95 °C)
- Time of mixing (10 – 60 minutes)
- Time of settling (15 – 135 minutes)

Experimental Procedure

This procedure is used for each solvent as follows:

The extraction runs were carried out in a jacketed vessel fitted with tap at the bottom. The temperature was controlled by a water bath, which circulated hot water in the vessel jacket with the aid of a pump. After bringing the naphtha feed to extraction temperature, the hot solvent at the same temperature was added (according to the predetermined ratio). A rotating stainless steel shaft was used for mixing naphtha and solvent at a controlled degree of mixing determined previously.

The extraction was carried out for a predetermined mixing time and the mixture was left to separate into a raffinate phase at the top and an extract phase at the bottom for a predetermined settling time. Extract was then separated, the extinction was measured by spectrophotometer (model 1601) and the concentration of aromatics (BTX) were determined from the calibration curves.

Results and discussions

- Ethylene glycol

- **Effect of the degree of mixing and solvent / feed ratio**

The results from figure (1) indicate that the concentration of extracted aromatics (BTX) increases as degree of mixing increases till 1100 R.P.M. This may be due to the necessity of vigorous mixing of an extraction system and it is known that increase in mixing gives an initial rapid increase in interfacial area through reducing the average drop size. This will consequently produce an increase in mass transfer rate [15] in order to

establish equilibrium in a short time. On the other hand, excessive mixing higher than 1100 R.P.M. may have unfavorable effect of settling [16], and results in secondary haze formation [17]. Also the results indicate that the concentration of extracted aromatics (BTX) decreases by increasing the solvent / feed ratio due to dilution and a maximum concentration of 5.15 g/l is noticed at S/F ratio of 4.

- **Effect of the temperature and solvent / feed ratio**

The results from figure (2) indicate that the concentration of extracted aromatics (BTX) is continue to decrease until concentration reaches a constant value at S/F ratio of 4 and also it increases by increasing the temperature till 95 °C. This is because this solvent is of high critical solution temperature with non aromatic hydrocarbons [18] so, the best concentration of extracted aromatics (BTX) of 6.953 g/l is achieved.

- **Effect of the time of mixing**

The results from figure (3) indicate that the concentration of extracted aromatics (BTX) increases as the time of mixing is increased until equilibrium is reached at time of 40 minutes that results in 6.931 g/l of extracted aromatics (BTX).

- **Effect of the time of settling**

The results from figure (4) indicate that the concentration of extracted aromatics (BTX) increases as the time of settling is increased until equilibrium is reached after 120 minutes and this satisfied 7.13 g/l of extracted aromatics (BTX).

- **Diethylene glycol**

- **Effect of the degree of mixing and solvent / feed ratio**

The results from figure (5) indicate that the concentration of extracted aromatics (BTX) increases as the degree of mixing increases till it reaches a constant value at 900 R.P.M. Also the results indicate that the concentration of extracted aromatics (BTX) decreases by increasing the solvent / feed ratio due to dilution and a maximum concentration of 13.446 g/l is noticed at S/F ratio of 5.

- **Effect of the temperature and solvent / feed ratio**

The results from figure (6) indicate that the concentration of extracted aromatics (BTX) is decreases until it reaches a constant value at S/F ratio of 5 and also it increases with increasing the temperature till 95 °C. This is because this solvent is of high critical solution temperature with non aromatic hydrocarbons [18] so, the best concentration of extracted aromatics (BTX) of 14.77 g/l is achieved.

- **Effect of the time of mixing**

The results from figure (7) indicate that the concentration of extracted aromatics (BTX) increases as the time of mixing is increased until equilibrium is reached at time of 40 minutes that corresponds to 14.74 g/l of extracted aromatics (BTX).

- **Effect of the time of settling**

The results from figure (8) indicate that the concentration of extracted aromatics (BTX) increases as the time of settling is increased until

equilibrium is reached at 75 minutes that corresponds to 15.61 g/l of extracted aromatics (BTX).

- **Dimethyl sulfoxide**

- **Effect of the degree of mixing and solvent / feed ratio**

The results from figure (9) indicate that the concentration of extracted aromatics (BTX) increases as the degree of mixing increases till it reaches a constant value at 900 R.P.M. Also the results indicate that the concentration of extracted aromatics (BTX) decreases with increasing the solvent / feed ratio due to dilution and a maximum concentration of 51.61 g/l is noticed at S/F ratio of 5.

- **Effect of the temperature and solvent / feed ratio**

The results from figure (10) indicate that the concentration of extracted aromatics (BTX) decreases with decreasing S/F ratio until concentration is constant at S/F ratio of 5. It also increases with increasing the temperature till 80 °C. Extraction in the temperature range of 47 – 63 °C is better than 80 °C because at this range of temperature the selectivity and solvent power are in balance also the dimethyl sulfoxide is of lower critical solution temperature with non - aromatic hydrocarbons as a result of it has a methyl group [18] so, the best concentration of extracted aromatics (BTX) of 58.57 g/l is achieved at 63 °C.

- **Effect of the time of mixing**

The results from figure (11) indicate that the concentration of extracted aromatics (BTX) increases as the time of mixing is increased until equilibrium is reached at time of 40 minutes that satisfies 57.89 g/l of extracted aromatics (BTX).

- **Effect of the time of settling**

The results from figure (12) indicate that the concentration of extracted aromatics (BTX) increases as the time of settling is increased until equilibrium is reached at time of 90 minutes that satisfies 59.42 g/l of extracted aromatics (BTX).

• **Dimethyl formamide**

- **Effect of the degree of mixing and solvent / feed ratio**

The results from figure (13) indicate that the concentration of extracted aromatics (BTX) increases as the degree of mixing increases till it reaches a constant value at 900 R.P.M. Also the results indicate that the concentration of extracted aromatics (BTX) decreases by increasing the solvent / feed ratio due to dilution and the best concentration of 25.909 g/l is noticed at S/F ratio of 3.

- **Effect of the temperature and solvent / feed ratio**

The results from figure (14) indicate that the concentration of extracted aromatics (BTX) is decreases with increasing S/F ratio until concentration is reached a constant value at S/F ratio of 3. It increases by increasing the temperature till 80 °C. Extraction at 47 °C is better than 80 °C because at 47 °C the selectivity and solvent power are in balance also the dimethyl formamide is of lower critical solution temperature with non aromatic hydrocarbons as a result of it has a methyl [18]. The best concentration of extracted aromatics (BTX) of 28 g/l is achieved at 47 °C.

- **Effect of the time of mixing**

The results from figure (15) indicate that the concentration of extracted aromatics (BTX) increases as the time of mixing is increased until equilibrium is reached after 40 minutes. This corresponds to a concentration of 27.86 g/l of extracted aromatics (BTX).

- **Effect of the time of settling**

The results from figure (16) indicate that the concentration of extracted aromatics (BTX) increases as the time of settling is increased until equilibrium is reached at time of 90 minutes that satisfies 29.48 g/l of extracted aromatics (BTX).

Comparison between solvents

Figure (17) compares between different types of solvents with respect to their effect on the extraction of aromatics (BTX) from heavy naphtha and it was found that: the highest percentage of extraction of aromatics (BTX) from heavy naphtha of 90.194 was achieved by using dimethyl sulfoxide then 53.18 by dimethyl formamide then 23.652 % by diethylene glycol finally 9.1329 % by ethylene glycol

Conclusions

The effects of degree of mixing, solvent / feed ratio, temperature, time of mixing and time of settling on the extraction of aromatics (BTX) were studied.

The concentration of extracted aromatics (BTX) increases as the degree of mixing increases till 1100 R.P.M in order to establish equilibrium in a short time. On the other hand, excessive mixing higher than 1100 R.P.M may have unfavorable effect of settling and results in secondary haze formation.

The concentration of extracted aromatics (BTX) decreases by increasing the solvent / feed ratio due to dilution but the percentage of extraction will be increased.

Also, it is noticed that the concentration of extracted aromatics (BTX) increases by increasing the temperature and the best extraction temperature is set at the value when selectivity and solvent power are in balance.

By comparing the results of the experimental work it was found that the high concentration of extracted aromatics (BTX) is achieved by using dimethyl sulfoxide as a solvent and the best operating conditions is as follow:

by using dimethyl sulfoxide as a solvent that extract aromatics (BTX) from heavy naphtha it was found that a concentration of 59.42 g/l. is achieved at optimum degree of mixing of 900 R.P.M., S/F of 5, temperature of 63 °C , time of mixing of 40 minutes and time of settling of 90 minutes.

Comparing the different types of solvents as their effect on the extraction of aromatics (BTX) from heavy naphtha, it is shown that: the highest percentage of extraction of aromatics (BTX) from heavy naphtha of 90.194 was achieved by using dimethyl sulfoxide then 53.18 by dimethyl formamide then 23.652 % by diethylene glycol finally 9.1329 % by ethylene glycol.

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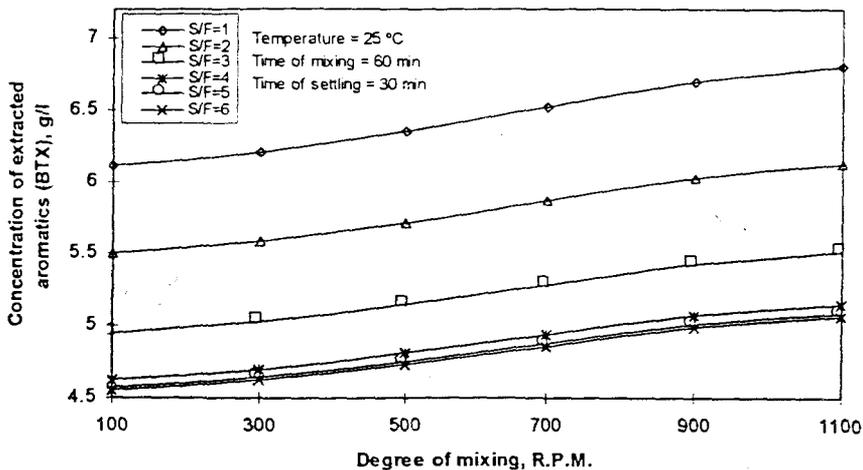


Figure (1): Effect of the degree of mixing on the extraction of aromatics (BTX) from heavy naphtha at different S/F ratios using ethylene glycol as a solvent

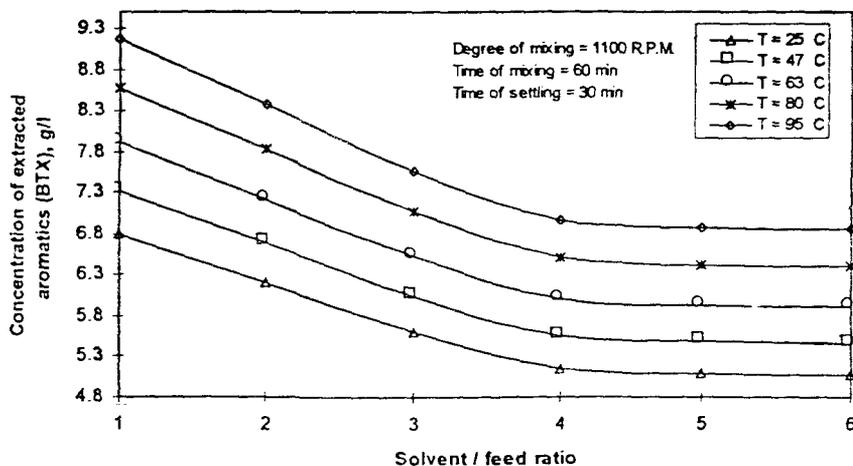


Figure (2): Effect of S/F ratio on the extraction of aromatics (BTX) from heavy naphtha at different temperatures using ethylene glycol as a solvent

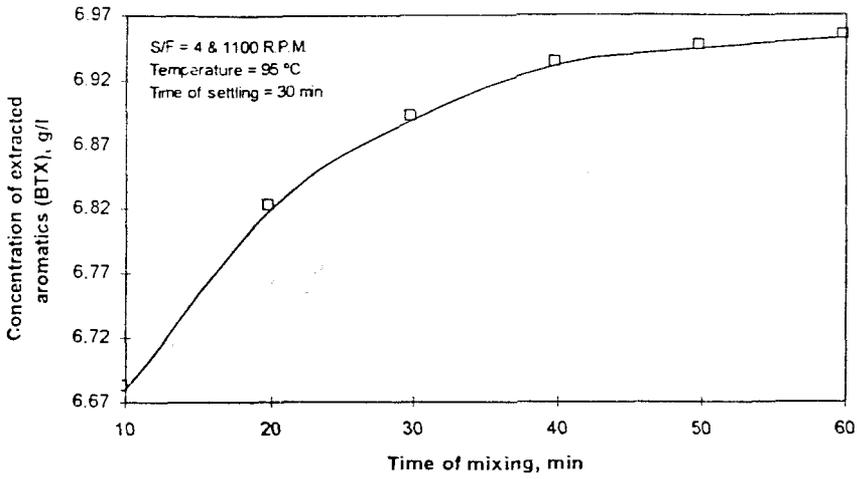


Figure (3): Effect of the time of mixing on the extraction of aromatics (BTX) from heavy naphtha using ethylene glycol as a solvent

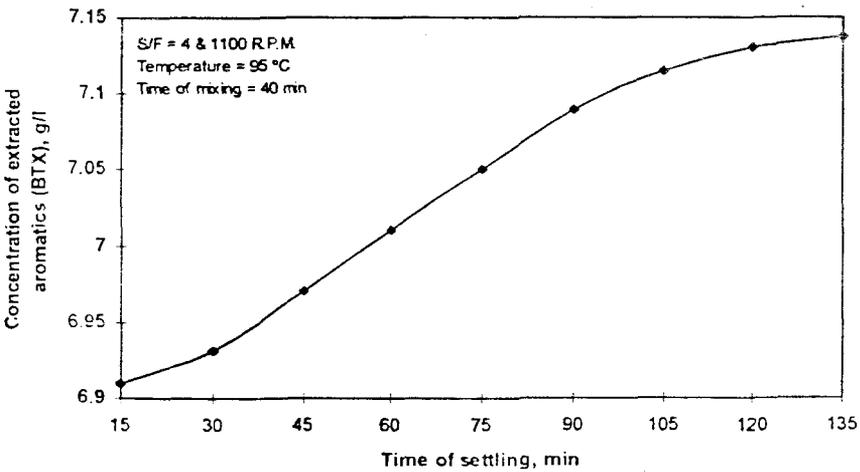


Figure (4): Effect of the time of settling on the extraction of aromatics (BTX) from heavy naphtha using ethylene glycol as a solvent

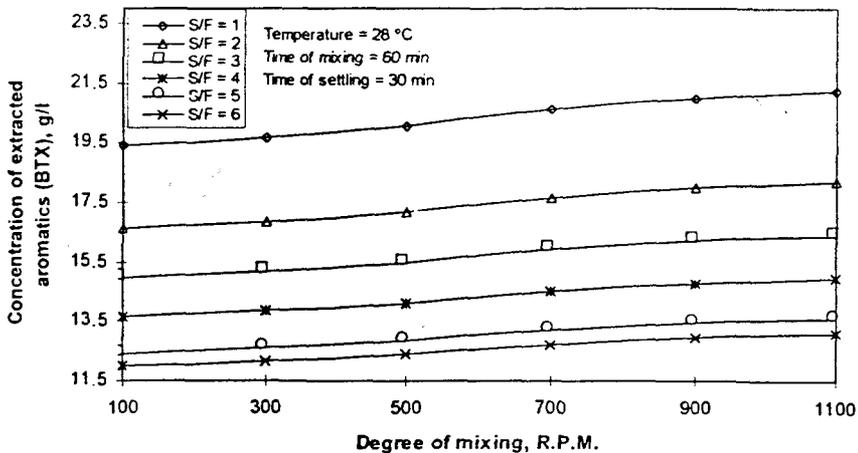


Figure (5): Effect of the degree of mixing on the extraction of aromatics (BTX) from heavy naphtha at different S/F ratios using diethylene glycol as a solvent

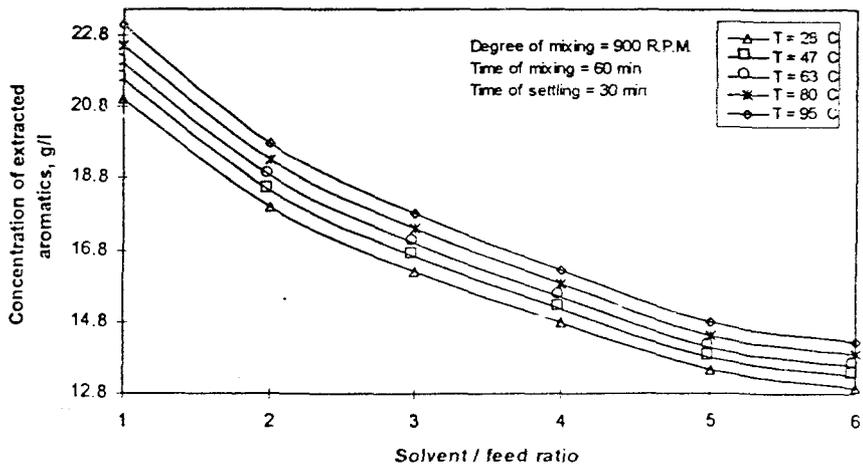


Figure (6): Effect of S/F ratio on the extraction of aromatics from heavy naphtha at different temperatures using diethylene glycol as a solvent

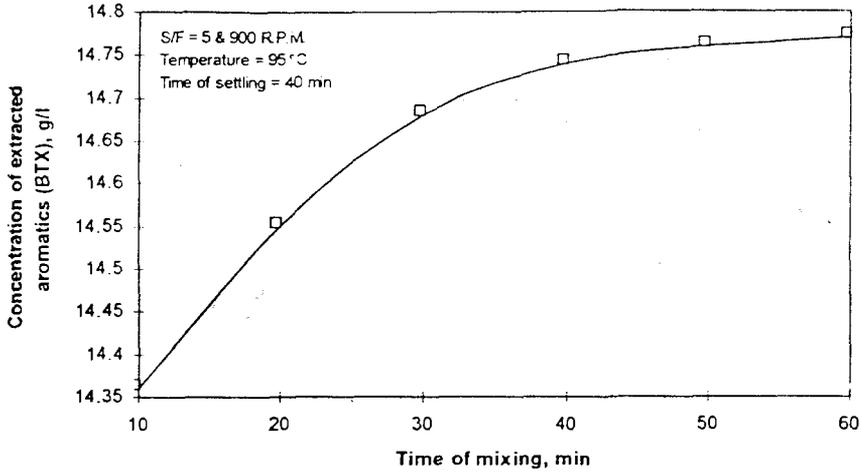


Figure (7): Effect of the time of mixing on the extraction of aromatics (BTX) from heavy naphtha using diethylene glycol as a solvent

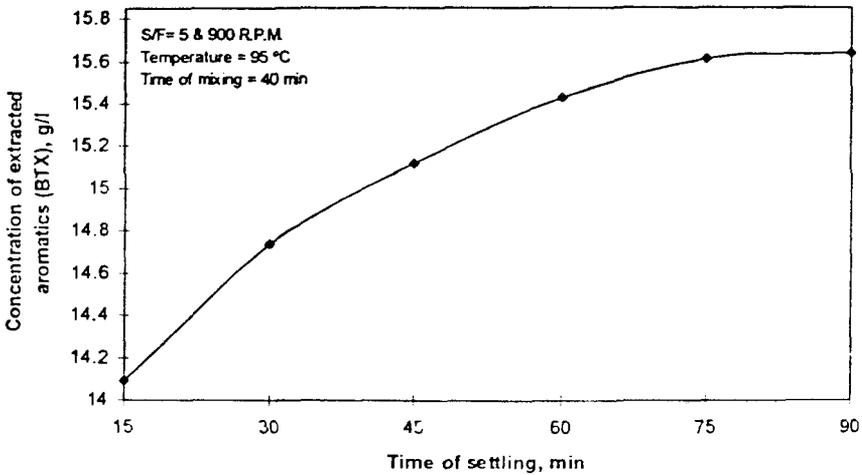


Figure (8): Effect of the time of settling on the extraction of aromatics (BTX) from heavy naphtha using diethylene glycol as a solvent

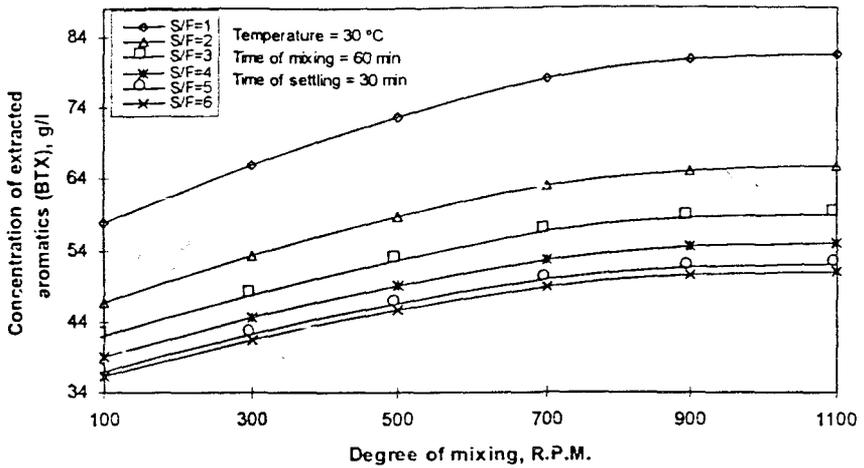


Figure (9): Effect of the degree of mixing on the extraction of aromatics (BTX) from heavy naphtha at different S/F ratios using dimethyl sulfoxide as a solvent

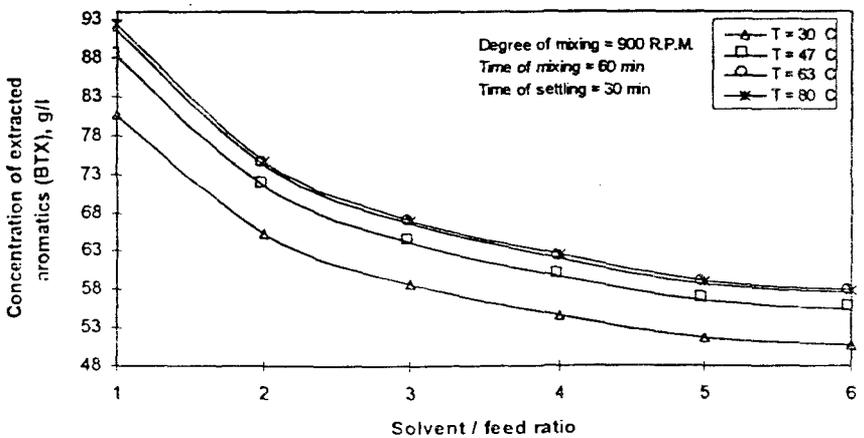


Figure (10): Effect of S/F ratio on the extraction of aromatics (BTX) from heavy naphtha at different temperatures using dimethyl sulfoxide as a solvent

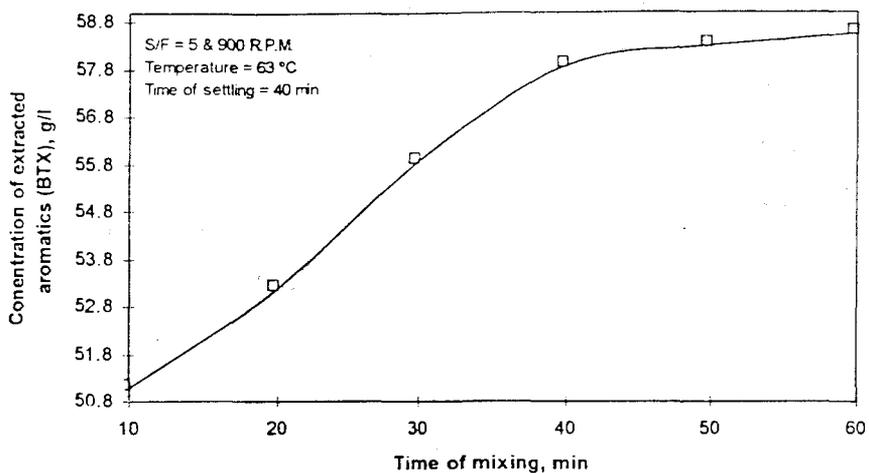


Figure (11): Effect of the time of mixing on the extraction of aromatics (BTX) from heavy naphtha using dimethyl sulfoxide as a solvent

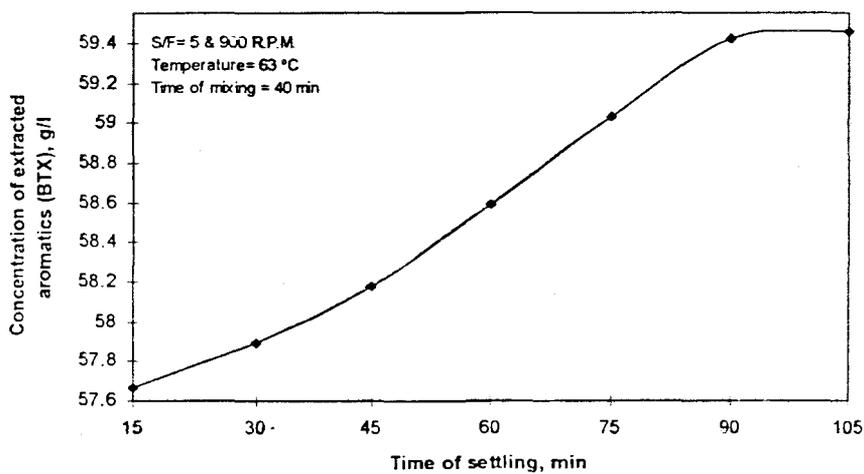


Figure (12): Effect of the time of settling on the extraction of aromatics (BTX) from heavy naphtha using dimethyl sulfoxide as a solvent

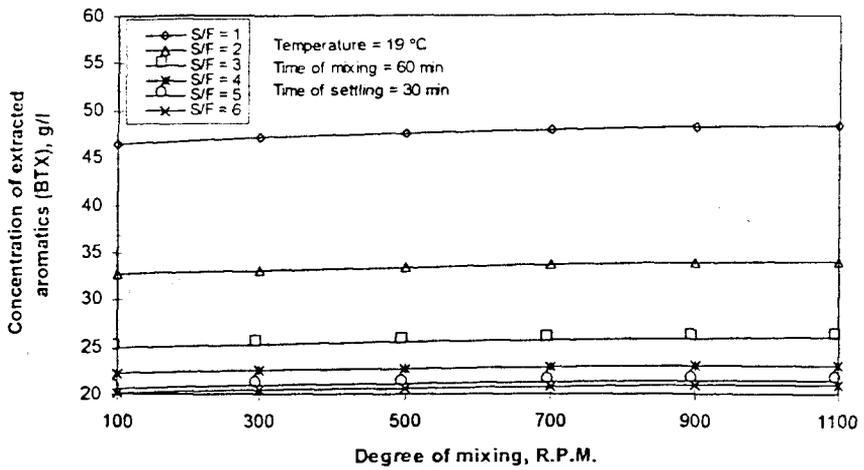


Figure (13): Effect of the degree of mixing on the extraction of aromatics (BTX) from heavy naphtha at different S/F ratios using dimethyl formamide as a solvent

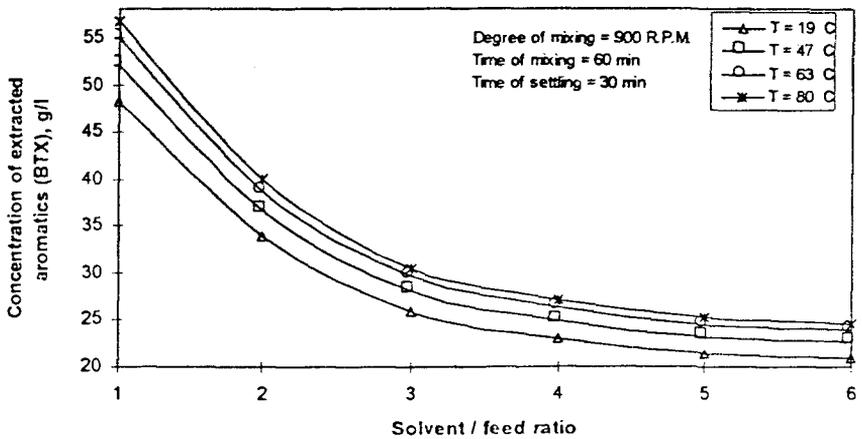


Figure (14): Effect of S/F ratio on the extraction of aromatics (BTX) from heavy naphtha at different temperatures using dimethyl formamide as a solvent

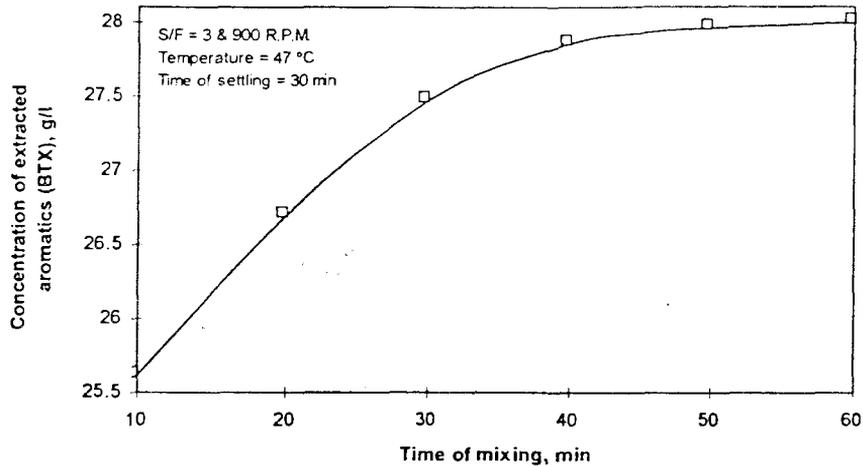


Figure (15): Effect of the time of mixing on the extraction of aromatics (BTX) from heavy naphtha using dimethyl formamide as a solvent

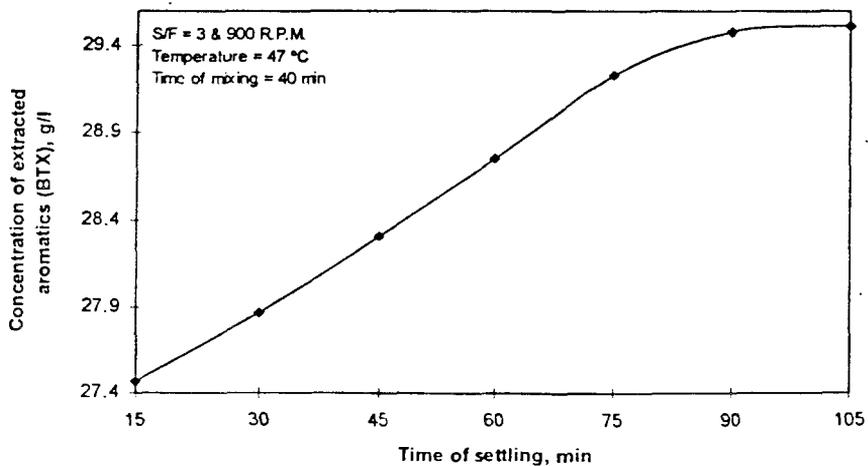


Figure (16): Effect of the time of settling on the extraction of aromatics (BTX) from heavy naphtha using dimethyl formamide as a solvent

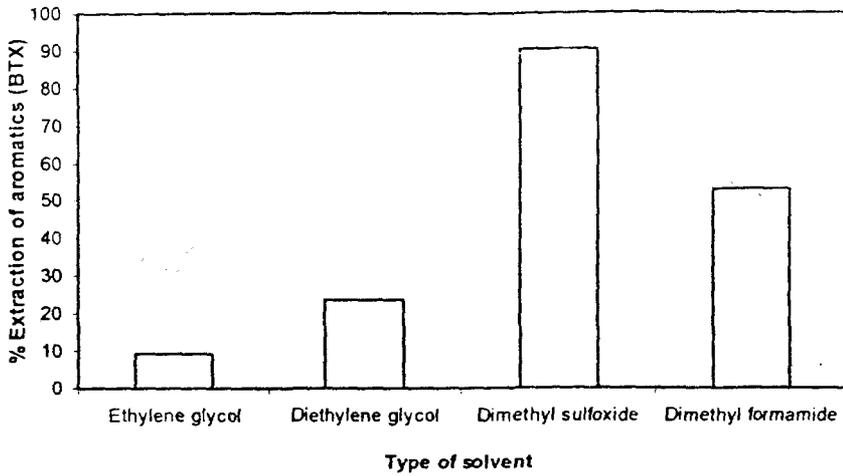


Figure (17): Comparison between solvents for their effect on the extraction of aromatics (BTX) from heavy naphtha