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AROMATIC EXTRACTION PROCESS WITH DIGLYCOLAMINE SOLVENT

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U.S. Cl. 208—331 11 Claims

ABSTRACT OF THE DISCLOSURE

Diglycolamine for extracting aromatic compounds from hydrocarbon liquids.

INTRODUCTION

In many processes conducted by the petroleum and petrochemical industries, it is desirable that certain hydrocarbon liquids which contain aromatic compounds be treated to remove such aromatic compounds therefrom. Many processes have been used for effectuating such separations. One commonly used technique is solvent extraction. While solvent extraction has proved helpful in separating aromatics from non-aromatic hydrocarbon liquids, it is not entirely satisfactory. In certain cases the degree of extraction does not reduce the aromatic content to a sufficiently low level. In other cases the extracting solvent is difficult to separate from the extracted aromatic compounds.

Illustrative of processes where it is desirable to remove aromatics from hydrocarbon liquids are the following:

Extraction of aromatics from reformed naphtha and subsequent purification into benzene, toluene, and xylene.

Extraction of aromatics from jet fuel and kerosene to improve the burning quality. Improves smoke point, heat of combustion, aniline point, and other physical properties.

Extraction of aromatics from diesel to improve octane number, diesel index, and general burning quality.

Extraction of aromatics from light catalytic cycle oil to upgrade it to diesel fuel.

Extraction of aromatics from solvents so that they will comply with pollution regulations pertaining to allowable aromatic content.

It is obvious that an improved solvent extraction process for removing aromatics from hydrocarbon liquids would be of great benefit to the art. Therefore, the following become the objects of the invention.

OBJECTS OF THE INVENTION

An improved solvent extraction process for removing aromatics from hydrocarbon liquids.

An improved solvent extraction process for removing aromatic liquids from petroleum hydrocarbon liquids.

Other objects will appear hereinafter.

THE INVENTION

In accordance with the invention, it has been found that aromatics may be extracted from hydrocarbon liquids and, in particular, petroleum hydrocarbon liquids by using as an aromatic extraction solvent, diglycolamine. Diglycolamine is also known chemically as 2-(2-aminoethoxy) ethanol and has the structural formula:

$$NH_2CH_2CH_2OCH_2CH_2OH$$

In practicing the invention, it is desirable that the amount of diglycolamine used in relation to the aromatic compound containing hydrocarbon liquid to be such that the ratio of diglycolamine to hydrocarbon liquid is at least 1:1. Good results are obtained when the ratio of diglycolamine to hydrocarbon liquid is within the range of 3:1 to 10:1. Excellent results are achieved in the case of petroleum hydrocarbon liquids containing aromatics when the ratio is at about 5:1.

The process is conducted by contacting the aromatic compound containing hydrocarbon liquid with the diglycolamine under conditions to produce intimate admixture of the two components. Mixing and agitation should be mild. Countercurrent extraction techniques may be employed to good advantage.

In a specific embodiment of the subject invention, the aromatic compound can be contacted with the diglycolamine in an extractive distillation process.

One of the surprising features of the invention is that the extraction may be conducted over a wide variety of temperatures with good results being obtained in all cases. As will be shown by the later presented examples, the temperatures may be within the range of 75–400° F. and, more preferably, 75–200° F. with good extraction of aromatics being accomplished. It is understood that the temperature range should not exceed the boiling point of the liquids treated or of the diglycolamine.

One of the surprising discoveries of the invention is that the diglycolamine is an effective material for extracting aromatics when the diglycolamine contains as much as 10% by volume of water. This means that the material can be used in repeated multistage extraction processes without continuous water removal being necessary. When the water content of the diglycolamine exceeds about 10% by volume, then it is desirable that the diglycolamine be separated from the water since aromatic extraction efficiency tends to be diminished.

To illustrate the efficacy of diglycolamine for aromatic extraction, the following are presented by way of examples:

Examples

Small scale laboratory tests were run to determine the efficacy of diglycolamine as an aromatic extractant for hydrocarbon liquids contaminated with aromatic components. Equilibrium extraction experiments were performed on an aromatic contaminated platformate stock and on a naphtha-type solvent which contained 13% by volume of aromatic components. The characteristics of these liquids are set forth in Tables I and II.

TABLE I

Physical properties of naphtha-type solvent

Specific gravity—0.7665
Aromatic content—13.0 volume percent (by FIA)
Distillation data:

	° F.
I.B.P.	312
5%	329
10%	333
20%	337
30%	341
40%	344
50%	348
60%	351
70%	355
80%	361
90%	371
95%	384
F.B.P.	395

The characteristics of the platformate are set forth in Table II.

TABLE II

Physical properties of platformate

Specific gravity—0.7732
Aromatic content—43.8 volume percent (by FIA)

Distillation data:	° F.
I.B.P.	101
5%	142
10%	164
20%	190
30%	210
40%	228
50%	247
60%	267
70%	290
80%	316
90%	360
F.B.P.	417

All of the experiments presented hereinafter were conducted using mild agitation in the form of either tumbling or mixing with the time period being within the range of 20 minutes to one hour. In certain of the experiments, two stages of extraction were used to indicate how the diglycolamine could be maximized commercially. The results of these experiments are presented in Tables II and IV.

TABLE III.—EQUILIBRIUM AROMATIC EXTRACTION FROM THE NAPHTHA—TABLE I

DGA:[1] naphtha (Table I) (volume:volume)	Temperature, (° F.)	Fraction extracted (percent)	D[2]
One stage extraction:			
10:1	75	56	0.12
7:1	75	51	0.14
5:1	75	45	0.15
3:1	75	31	0.14
5:1[3]	84	51	0.20
5:1	102	52	0.20
5:1	148	58	0.24
5:1	200	60	0.27
Second stage extraction: 5:1	75	36	0.073

[1] Diglycolamine.
[2] $D = \frac{\text{Molar aromatic concentration in heavy phase}}{\text{Molar aromatic concentration in light phase}}$
[3] Product from this run used as feed in the second stage extraction.

TABLE IV.—EQUILIBRIUM AROMATIC EXTRACTION FROM THE PLATFORMATE—TABLE II

DGA:[1] platformate (volume:volume)	Temperature, ° F.	Fraction extracted (percent)	D[2]
One stage extraction:			
10:1	75	65	0.13
7:1	75	65	0.19
5:1[3]	75	53	0.17
3:1	75	20	0.15
Second stage extraction, 5:1	75	44	0.14

[1] Diglycolamine.
[2] See Table III for definition of D.
[3] Product from this run used as feed to the second stage extraction.

It was of interest to examine the extent to which the aromatics would be extracted in a multiple extraction experiment. A DGA (diglycolamine) sample of Table II platformate was extracted in four stages at room temperature. The initial ratio of diglycolamine to platformate was 5:1; and, in the subsequent stages, the ratio of 5:1 diglycolamine to raffinate from the previous extraction was maintained. The results are summarized in Table V.

TABLE V.—FOUR-STAGE, SEQUENTIAL EQUILIBRIUM AROMATIC EXTRACTION FROM TABLE II PLATFORMATE

Stage	Temperature, ° F.	Final aromatics content: Volume percent, FIA	Final aromatics content: Mole/liter, UV	Fraction extracted: Per stage percent	Fraction extracted: Cumulative, percent	D[1]	(DGA[1,2])
Untreated	75	41.0	3.65				
First	75	31.0	1.56	51 (35)	51 (35)	0.16	0.033
Second	75	15.1	0.66	66 (68)	83 (79)	0.30	0.045
Third	75	5.4	0.25	66 (60)	94 (92)	0.35	0.025
Fourth	75	4.2	0.20	21 (24)	95 (94)	0.05	0.052

[1] See Table III for definition of D.
[2] DGA=Diglycolamine.

To illustrate the amount of diglycolamine present in the reaffinate, a series of tests were run with the data being set forth in Table VI.

TABLE VI.—EQUILIBRIUM AROMATIC EXTRACTION FROM NAPHTHA—TABLE I

DGA:[1] naphtha (volume: volume)	Temperature, ° F.	Aromatics (mole/liter)	Fraction extracted (percent)	D[2]	(DGA)[3] (mole/liter)
10:1	75	0.65	56	0.12	0.039
7:1	75	0.69	51	0.14	0.022
5:1	75	0.69	45	0.15	0.028
3:1	75	0.69	31	0.14	0.026
5:1	200	0.69	60	0.27	0.026
5:1	75	0.78	45	0.19	
5:1	75	1.00	45	0.19	
5:1	75	1.23	39	0.14	

[1] DGA=Diglycolamine.
[2] See Table III for definitions of D.
[3] DGA in raffinate.

It can be seen that the diglycolamine concentration ranges between 0.02 and 0.06 mole/liter. Increasing the temperature from 75 to 200° F. does not product a substantial change. Most of the experiments were done at a diglycolamine:hydrocarbon ratio of 5:1; hence, the carryover amounts to less than 0.04 to 0.12 percent of the total diglycolamine. This can be further reduced by water washing the raffinate. For example, a raffinate from a platformate extraction containing 0.0390 mole/liter of diglycolamine was washed with an equal volume of water. The wash water contained 0.0376 mole/liter and the treated raffinate 0.0015 mole/liter of diglycolamine. Similar results have been obtained with other raffinate samples.

In another series of experiments the effect of water on the diglycolamine was determined. These results are presented in Table VII.

TABLE VII.—EQUILIBRIUM AROMATIC EXTRACTION FROM PLATFORMATE—TABLE II
[Effect of H_2O in DGA[1]]

DGA[1]: platformate (volume: volume)	Water (volume percent in DGA)	Temperature, ° F.	Fraction extracted percent	D[2]	(DGA) (mole/liter)
5:1	0.0	75	51–53	0.17	0.040
5:1	1.0	75	58	0.20	0.057
5:1	3.0	75	54	0.17	0.058
5:1	5.0	75	53	0.16	0.062
5:1	10.0	75	35	0.09	0.052

[1] DGA=Diglycolamine.
[2] See Table III for definition of D.

Table VII summarizes the effects of up to 10% (by volume) of water in the diglycolamine in the extraction of the Table II platformate. It can be seen that 1–5% water does not exert pernicious effects on the extraction efficiency of diglycolamine. In fact, the results suggest a beneficial effect of a small amount (1%) of water. The presence of 10% water in the diglycolamine reduces the extraction efficiency. The diglycolamine concentration in the raffinate is not strongly influenced by the introduction of water into the system.

In all of the above tables the aromatic content was determined by both ultra-violet and F.I.A.[1].

[1] Fluorescent indicator analysis.

Additional extraction tests were done on the platformate of Table II using a countercurrent extraction process. In repeated tests 90%, or a greater portion of the aromatics were extracted at room temperature and a diglycolamine to platformate ratio of 5:1. Extractive distillation tests give comparable results.

From the above it is seen that diglycolamine is an excellent solvent for aromatics from hydrocarbons and provides the art with a new improved solvent extraction material. The diglycolamine is very effective when used to extract low molecular weight single ring aromatics such as benzene, toluene, and xylene.

The diglycolamine is also effective when used to extract aromatics boiling in higher temperature regions, such as naphtha, kerosene and diesel oil. As an illustration of this fact, diglycolamine was compared with the well-known solvents sulfolane and diethyleneglycol. The solvent system was a benzene-heptane mixture and the comparisons were made based on the data supplied in E. Mueller and G. Hoehfeld, 7th World Petroleum Congress Proceedings, 4, 13 (1967). The results are formulated below in Table VIII.

TABLE VIII.—COMPARISON OF SOLVENT PROPERTIES

	Capacity	Selectivity	Specific gravity	Boiling point (° F.)
Diglycolamine	0.44	90	1.05	430
Sulfolane	0.50	72	1.23	555
Diethyleneglycol	0.32	45	1.12	472

The aromatics which have been extracted from hydrocarbon liquids by means of the diglycolamine are completely recovered from the diglycolamine by means of a distillation process. The aromatic can also be recovered with an efficiency which is almost as high, as when the distillation process is used, by subjecting the diglycolamine to a solvent displacement process with a suitable solvent, such as water.

We claim:

1. A process for extracting aromatic compounds from a hydrocarbon liquid containing aromatic compounds comprising contacting said hydrocarbon liquid with an aqueous mixture of diglycolamine containing from about 1% to about 5% water, by volume, for a time sufficient to extract substantial quantities of aromatic compounds from said hydrocarbon liquid.

2. A process as described in claim **1** wherein the resulting hydrocarbon liquid from which substantial quantities of aromatic compounds have been extracted and the aqueous mixture of diglycolamine are thereafter separated.

3. A process as described in claim **1** wherein the ratio of the aqueous mixture of diglycolamine to hydrocarbon liquid is at least 1:1, by volume.

4. A process as described in claim **1** wherein the hydrocarbon liquid is naphtha, kerosene or diesel oil.

5. A process as described in claim **1** wherein the aromatic compounds are substantially benzene, toluene, xylene or mixtures thereof.

6. A process as described in claim **1** wherein the ratio of the aqueous mixture of diglycolamine to hydrocarbon liquid does not exceed 10:1, by volume.

7. A process as described in claim **1** wherein the ratio of the aqueous mixture of diglycolamine to hydrocarbon liquid is between about 3:1 and 10:1, by volume.

8. A process as described in claim **1** wherein the hydrocarbon liquid is naphtha, kerosene or diesel oil; the aromatic compounds are substantially benzene, toluene, xylene or mixtures thereof; the ratio of the aqueous mixture of diglycolamine to hydrocarbon liquid is between about 3:1 and 10:1, by volume; and the resulting hydrocarbon liquid from which substantial quantities of aromatic compounds have been extracted and the aqueous mixture of diglycolamine are thereafter separated.

9. A process as described in claim **8** wherein aqueous mixture of diglycolamine contains from about 1% to about 3% water, by volume.

10. A process as described in claim **8** wherein the aqueous mixture of diglycolamine contains from about 3% to about 5% water, by volume.

11. A process as described in claim **8** wherein the aqueous mixture of diglycolamine contains from about 2% to about 4% water, by volume.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 40, "Tables II and IV" should read
--Tables III and IV--.

Signed and sealed this 4th day of January 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents