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PROCESS OF EXTRACTION WITH 2-OXAZOLIDONE SOLVENTS

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16 Claims. (Cl. 196—14.27)

This invention relates to a process for the separation of mixtures of hydrocarbons into fractions of diverse structural type by selective solvent extraction with specified 5-membered ring compounds of the 2-oxazolidone series. In one particular aspect this invention is concerned with separation of aromatic hydrocarbons from mixtures thereof with aliphatic hydrocarbons. Such mixtures of hydrocarbons may be commercially produced as processed or unprocessed petroleum oils or mineral oils, coal tar oils, shale oils and the like. The production of highly aromatic extracts from such mixtures is commercially desirable to produce benzene, toluene, xylene, and mixtures thereof, or higher molecular weight aromatics for use as solvents, plasticizers, components of aviation gasoline and as stocks for sulfonation and manufacture into water-soluble detergents. Dearomatization of hydrocarbon mixtures may be desired in order to prepare hydrocarbon stocks for thermal or catalytic cracking, for hydrogenation operations, for use as heater oils or for other purposes.

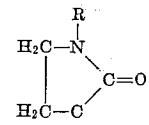
With the commercial development of new processes for producing aromatic hydrocarbons boiling within the gasoline boiling range by cyclization-dehydrogenation of paraffinic hydrocarbons and by the dehydrogenation of cycloalkanes, there has come an increased demand for processes to separate and concentrate the aromatic hydrocarbons thus produced. Thus with the commercial development of such processes as hydroforming, platinum catalyst reforming of naphthas, and the like, a tremendous potential has been created for the production of nitration-grade aromatics such as benzene, toluene and xylenes for use by both the petroleum and chemical industries.

The use of solvent extraction for the separation of mixtures of hydrocarbons has long been known. This method of purifying hydrocarbon mixtures takes advantage of the differences in solubility of various hydrocarbon types in solvents or mixtures of solvents. Such hydrocarbon types may be conveniently designated by the ratio of hydrogen to carbon atoms in the compound. Thus for hydrocarbons of approximately equal molecular weight, i. e. equal carbon content, the H/C ratio will vary from a high value for the paraffinic compounds to a low value for the aromatic hydrocarbon compounds. For example, the H/C ratio may be calculated for compounds containing 8 carbon atoms, and is found to vary from 2.25 for paraffinic hydrocarbons to 1.25 for unsubstituted aromatic hydrocarbons, with intermediate values of 1.50 for cyclic dienes, 1.75 for open-chain dienes and alicyclic mono-olefins and 2.00 for cycloparaffins and open-chain mono-olefins. The solubility of such hydrocarbon types is roughly related to the hydrogen-carbon ratio, and for polar solvents the solubility has been found to increase as the H/C ratio decreases.

Numerous solvents have been proposed to effect the separation of mixtures of such diverse hydrocarbon types having similar boiling points by extractive processes. For example, aromatic hydrocarbons can be separated from paraffinic hydrocarbons by extraction with a number of well known solvents. Saunders, Industrial and Engineering Chemistry, 43, 121, (1951) has reported his study of many such solvents and has recommended several nitriles such as beta,beta'-oxydipropionitrile for the separation of aromatics and non-aromatics. Wilkes, U. S. Patent No. 2,439,534 has proposed nine solvents of the some class, that is, nitriles.

It is an object of our invention to provide a process for the selective extraction of hydrocarbon mixtures with a solvent selected from the group comprising 2-oxazolidone and certain of its N-substituted derivatives as hereinafter described. A further object of our invention is to provide the art with certain novel solvents for the extraction of hydrocarbon mixtures. Another object is to provide a method for separating hydrocarbon mixtures into fractions of diverse structure type. A still further object of our invention is to provide a process for the concentration and purification of aromatic hydrocarbons by solvent extraction with 2-oxazolidone and certain of its N-substituted derivatives. Yet another object is to provide a process for the separation of close boiling or azeotropic mixtures of hydrocarbons. A further object is to provide a solvent extraction process for the separation of aromatic hydrocarbons from mixtures thereof with olefinic hydrocarbons. An additional object is to provide a process for refining hydrocarbon oils by extraction with a novel class of solvents as herein described. A further object is to provide a process for the separation of hydrocarbon mixtures by extractive distillation with liquid solvents comprising 2-oxazolidone or certain of its N-substituted derivatives. These and other objects of our invention will become apparent from the ensuing description thereof.

The novel solvents which are employed in the process of our invention comprise 5-membered ring compounds of the 2-oxazolidone series. These compounds have the general formula



in which R is selected from the group consisting of hydrogen, methyl and hydroxyethyl. The parent compound of the series, 2-oxazolidone, as well as the aforementioned N-substituted derivatives are water-soluble, high boiling substances which may be either liquids or low melting solids at ordinary temperatures and pressures. They are colorless, odorless and neutral compounds of substantial stability both to chemical reagents and to pyrolysis. They are readily prepared by the reaction of a beta-amino alcohol and an alkyl carbonate e. g. as described in U. S. Patent No. 2,399,118 of A. H. Homeyer. Although the aforementioned hydroxyethyl derivative may be either the N-(α-hydroxyethyl)-2-oxazolidone or the β-hydroxyethyl isomer, the latter was chosen to illustrate the process of our invention because of the ease of preparation thereof from the readily available diethanolamine.

The 2-oxazolidone selective solvents or our invention are useful for the separation of monocyclic aromatic hydrocarbons, such as benzene, toluene, xylenes or the like, from mixtures containing the same. The solvents may also be used for the separation of polycyclic aromatic hydrocarbons such as naphthalene, methylnaphthalene, tetralin and the like from mixtures containing the same. They are effective in separating an aromatic fraction from a mixture containing more than one aromatic compound, and their effectiveness is not limited by the concentration of aromatic hydrocarbons in the mixture treated. Such mixtures containing aromatics are obtained commercially in a variety of ways. Among them may be mentioned the alkylation of aromatics, the catalytic cracking of gaso-

line, the reforming of cracked gasoline, the hydrogenation of coal, the aromatization of selected petroleum hydrocarbon fraction and the like. In general such mixtures are in the gasoline boiling range, and consist of hydrocarbon mixtures having a molecular weight range of 72 to 200.

The 2-oxazolidone solvents of this invention may be employed in aqueous solution or in conjunction with various other diluents which will affect their solvent power for aromatics. Such diluents are partially or completely miscible with water, and generally contain hydroxy groups, although this is not a limitation. Such diluents may be effective in modifying the solvency, while avoiding the corrosivity characteristic of water. Among the diluents may be mentioned glycerol, ethylene glycol, diethylene glycol, pentaerythritol, formic acid, lactic acid, ethanolamines such as mono-, di-, and tri-ethanolamine and the like. Certain of these diluents may be more advantageous than water since long continued contact of water with the oxazolidone solvents can cause partial hydrolysis. For this reason formic acid and bases such as ethanolamines may be less efficient. Other examples of diluents which may be mentioned are liquid sulfur dioxide, the sulfolanes, dimethyl sulfoxide, dimethyl sulfone, methyl ethyl sulfone, various nitriles such as acetonitrile, bis-2-cyanoethyl ether and the like; ethers or glycol ethers, tetrahydrofuran and the like; beta- beta'-oxydipropionitrile, beta, beta'-thiadipropionitrile and the like; halogenated hydrocarbon solvents; esters of monocarboxylic acids and dicarboxylic acids; neutral organic nitrogen compounds such as dimethyl formamide, dimethyl hydantoin and the like; ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone and the like; aldehydes for example furfuraldehyde, crotonaldehyde and the like; compounds such as N-methylpyridone, gamma-butyrolactone, gamma-butyrolactam, ethylene carbonate, etc. When a diluent or co-solvent such as we have described is used, we prefer to use from about 0.1 to about 20% by volume thereof based on the volume of oxazolidone solvent employed.

In addition to the co-solvents or diluents described above, anti-solvents can also be used to aid in the extraction step. Suitable anti-solvents such as saturated hydrocarbons, perfluorocarbons, perfluoroamines, perfluoroethers and the like may be used in proportions of about 10 to about 100 volume percent of the feedstock treated, and may be added to the feedstock to be dearomatized or introduced directly into the extraction zone.

In conducting the extraction we prefer to use an amount of solvent sufficient to form a two phase system, and preferably from about 1 to about 20 volumes of solvent per volume of the hydrocarbon feed to be treated. In the practice of the invention either continuous, semi-continuous, or batch operation may be employed. Known types of solvent extraction or extractive distillation equipment can be used.

In accordance with our invention, we first contact the hydrocarbon feed mixture either as liquid or vapor with a suitable proportion of the liquid 2-oxazolidone or derivative thereof. A liquid extract phase is produced which contains the more aromatic portion of the feedstock as well as any polar impurities derived from the feedstock, for example, organic compounds of oxygen, nitrogen or sulfur. Separation of the resultant layers, for example by decantation, is followed by removal of the solvent from the separated layers by suitable means, as by dilution with water. It is thus possible to recover from the extract phase and from the raffinate phase hydrocarbons of similar boiling point, but of different physical characteristics and chemical composition as characterized, for example, by different H/C ratios.

In carrying out the process of our invention we can use temperatures in the range of about 0° C. or even less to about 200° C. Economic considerations indicate the use of temperatures of about 35° C. to about 80° C. whenever this temperature range is technically feasible. Sufficient pressure is maintained within the extraction zone to prevent substantial volatilization of the hydrocarbon charging stock or solvent under the liquid-liquid extraction conditions, and it is obvious that pressure and temperature are related variables in the extraction process. Usually pressures within the range of about 0 to about 100 p. s. i. g. are sufficient, it being appreciated that the particular pressure which is required in a given case can readily be determined by experiment.

This invention is illustrated by experimental extraction data obtained on a toluene-n-heptane feedstock by the use of 2-oxazolidone or its N-substituted derivatives, alone or with a diluent. All of these were single stage batch operations which were effected at the indicated temperatures. A feedstock of 50 volume percent n-heptane–50 volume percent toluene was contacted with an equal volume of solvent until equilibrium was established; the phases were then separated and the hydrocarbons were recovered from both phases by washing out the solvent with water. The β-value or separation factor in the table is the molar ratio of toluene to heptane in the extract divided by the ratio of these components in the raffinate, and corresponds to alpha, the separation factor calculated in fractional distillation processes.

TABLE I

EXTRACTION OF n-HEPTANE-TOLUENE MIXTURES

Example	Solvent	Temp., °C.	Mol Fraction Toluene			β Value	Extract Yield, Vol. percent	Vol. percent of Toluene Extracted
			Feed	Extract	Raffinate			
1	2-Oxazolidone	100	.580	.940	.511	15.0	13.0	26.0
2	N-Methyl-2-Oxazolidone	25	.580	.850	.353	10.4	24.5	42.6
3	N-Methyl-2-Oxazolidone, 10 vol. percent H_2O.	25	.580	.913	.570	13.0	14.7	25.9
4	N-(β-Hydroxy-ethyl)-2-Oxazolidone.	100	.580	.916	.476	12.0	8.1	15.0

The above data indicate the excellent selectivity and high total solvent capacity of 2-oxazolidone and its N-substituted derivatives. The addition of 10% of water to the N-methyl-2-oxazolidone solvent results in a decrease in the quantity of toluene extracted, but the solvent is extremely selective as will be noted from the high β-value and the high concentration of toluene obtained in the extract of Example 3.

The solvents of our invention are particularly useful for the separation of aromatic hydrocarbons from mixtures thereof with olefinic hydrocarbons. This effect is illustrated by the following example.

Example 5

A feed having the composition 50 volume percent toluene–50% octene-2 was subjected to single-batch extraction with an equal volume of 2-oxazolidone at 100° C. This operation yielded 22.2 volume percent, based

on feed, of extract hydrocarbons containing 82.7 volume percent toluene, corresponding to 36.7 volume percent toluene extraction from the feedstock. The selectivity factor, β, was 6.8.

Example 6

The following is an example of the use of an auxiliary solvent with 2-oxazolidone. The solvent consisted of 50 weight percent of 2-oxazolidone and 50 weight percent diethylene glycol. A feed having the composition 50 volume percent toluene–50 volume percent n-heptane was subjected to one stage batch extraction with an equal volume of the mixed solvent at 100° C. This operation yielded 10.6 volume percent, based on feed, of extract hydrocarbons containing 94.0 volume percent toluene corresponding to 20 volume percent toluene extraction from the feedstock. The selectivity factor, β, was 13.3. In general, diethylene glycol: 2-oxazolidone molar ratios of about 0.25 to about 4 may be employed in extraction.

While the process of the present invention has been illustrated by examples in which the hydrocarbon mixture and the selective solvent are employed as liquids, it should be understood that the solvent may be charged as a liquid and the feedstock may be charged to the process as vapor, as in extractive distillation. In extractive distillation of naphthas, the temperature should be between the dew point of the hydrocarbon mixtures and about 240° C. and contacting of the liquid solvent and feed vapors is usually countercurrent. In Table II, data are supplied to show the effect of 2-oxazolidone as an extractive distillation solvent. These data were obtained by boiling a system of known composition, namely 50 volume percent toluene–50 volume percent of n-heptane with the solvent in the proportions indicated in the table at total reflux until equilibrium was attained, and analysis of a small sample of condensed vapor by refractive index after removing the solvent by water washing. Also included in the table are data for phenol, a solvent which is widely used in commercial installations for extractive distillation processes in which aromatic concentrates are produced. In this table the selectivity factor, alpha, is defined as

$$\alpha=\left(\frac{\text{Mol Fraction Toluene}}{\text{Mol Fraction n-Heptane}}\right)_{\text{Distillate}}\left(\frac{\text{Mol Fraction n-Heptane}}{\text{Mol Fraction Toluene}}\right)_{\text{Residue}}$$

TABLE II

EXTRACTIVE DISTILLATION

Solvent	Solvent Conc., Wt. Percent	Mol Fraction Toluene		α
		Distillate	Residue	
2-Oxazolidone	88.0	0.255	0.580	4.04
Do	91.2	0.215	0.580	5.04
Phenol	87.3	0.281	0.580	3.53

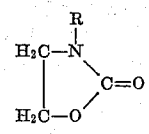
The data above show that 2-oxazolidone is highly effective in the separation of aromatics from paraffins by extractive distillation, as indicated by the high value of alpha obtained with this solvent. It may be further noted that at approximately equal solvent concentration, the 2-oxazolidone solvent is superior to the commercially used phenol solvent.

The present process may also be applied to the refining of various hydrocarbon oil fractions derived from petroleum coal, shale, etc. In the refining of such fractions the present refining agents serve not only to effect selective extraction of aromatic hydrocarbons but also to remove sulfur compounds, oxygen compounds and nitrogen compounds. It should be understood that the above specific examples of feedstocks which may be refined in accordance with the present invention are illustrative only and are not intended to delimit the field of applicability of the process of the present invention.

The present invention can be carried out in batch, continuous or semi-continuous operating cycles and in one or more actual or theoretical stages, employing contacting and separation of equipment such as has heretofore been employed in selective solvent refining of petroleum stocks. Various types of liquid-liquid extraction operations and suitable extraction equipment are well known in the art and it should be understood that the specific equipment employed forms no part of the present invention and that any equipment adaptable for the purposes of contacting the solvent with the hydrocarbon charging stock and thereafter separating an extract phase from the refined charging stock can be employed for the purposes of the invention.

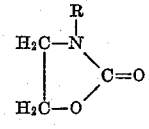
Having thus described our invention what we claim is:

1. A process for selectively separating a hydrocarbon from a mixture of hydrocarbons of diverse structural type which process comprises selectively extracting said mixture with a liquid 2-oxazolidone compound having the formula



wherein R is selected from the group consisting of hydrogen, methyl and hydroxyethyl.

2. A process for the selective extraction of an aromatic hydrocarbon from a mixture of aromatic and aliphatic hydrocarbons, which process comprises contacting said mixture with a liquid 2-oxazolidone compound having the formula



wherein R is selected from the group consisting of hydrogen, methyl and hydroxyethyl, and separating an extract phase comprising essentially said 2-oxazolidone compound and said aromatic hydrocarbon.

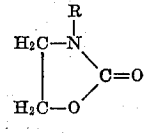
3. The process of claim 2 wherein said compound is 2-oxazolidone.

4. The process of claim 2 wherein said compound is N-methyl-2-oxazolidone.

5. The process of claim 2 wherein said compound is an N-hydroxyethyl-2-oxazolidone.

6. The process of claim 2 wherein said 2-oxazolidone compound contains from about 1 to about 20 percent by volume of water.

7. A process for the extraction of an aromatic hydrocarbon from a mixture containing aromatic and aliphatic hydrocarbons, which process comprises contacting each volume of said mixture in the liquid phase with from about 0.5 volumes to about 50 volumes of a liquid 2-oxazolidone compound having the formula



wherein R is selected from the group consisting of hydrogen, methyl and hydroxyethyl, effecting said contacting at a temperature of from about 0° C. to about 150° C. and at a pressure sufficient to maintain liquid phase extraction conditions, and separating a raffinate phase and

an extract phase comprising essentially said 2-oxazolidone compound and said aromatic hydrocarbon.

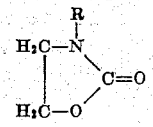
8. The process of claim 7 in which said mixture boils in the gasoline boiling range.

9. The process of claim 7 in which said aromatic hydrocarbon is benzene.

10. The process of claim 7 in which said aromatic hydrocarbon is toluene.

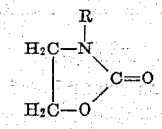
11. The process of claim 7 wherein said 2-oxazolidone compound contains from about 1 to about 20 percent by volume of water.

12. A process for the refining of hydrocarbon oils which comprises contacting said oils with a liquid 2-oxazolidone compound having the formula



wherein R is selected from the group consisting of hydrogen, methyl and hydroxyethyl, and separating liquid raffinate and extract phases.

13. A process for the extractive distillation of a naphtha containing aromatic hydrocarbons, which process comprises contacting the vapors of said naphtha at a temperature above its dew point but below about 240° C. with a liquid 2-oxazolidone compound having the formula



wherein R is selected from the group consisting of hydrogen, methyl and hydroxymethyl, and separating an extract phase comprising essentially said 2-oxazolidone compound and said aromatic hydrocarbons.

14. The process of claim 13 wherein said compound is 2-oxazolidone.

15. The process of claim 13 wherein said compound is N-methyl-2-oxazolidone.

16. The process of claim 13 wherein said compound is an N-hydroxyethyl-2-oxazolidone.

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