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PURIFICATION OF DI(2-ETHYLHEXYL)-PHOSPHORIC ACID

J. M. Schmitt
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CONTENTS

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ABSTRACT

A procedure is described for the purification of di(2-ethylhexyl)phosphoric acid. Essential steps include acid hydrolysis, conversion to the sodium salt, extraction of the neutral impurities with petroleum ether, reconversion to the acid form, and extraction of the monoalkylphosphoric acids with ethylene glycol. Product, in batches of approximately 1200 g, has been obtained in greater than 99.8% purity, nearly free from monoalkylphosphoric acids, trialkylphosphates, alcohols, and complexed metals. The equipment size and reagent quantities may be scaled up or down conveniently. Di(2-ethylhexyl)phosphoric acid is available commercially as the acid itself or as a water solution of its sodium salt. Both forms may be treated successfully by this method. The procedure should be applicable to purification of other similar dialkylphosphoric acids.

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1. INTRODUCTION

Di(2-ethylhexyl)phosphoric acid (D2EHPA) is a widely studied solvent extraction reagent. Its use is cited 127 times in the review article by Coleman, Blake, and Brown.[1] Many of these studies, especially those of a systematic nature,[2-8] require reagents of high purity because many impurities can perturb both chemical and physical properties during solvent extraction operations. Such impurities may include alcohols, trialkylphosphates, monoalkylphosphorus acids, polyphosphorus or pyrophosphorus compounds, and metal contaminants. Some or all of these are sometimes present in commercial preparations of D2EHPA (and other dialkylphosphoric acids).

The following procedure was used successfully at Oak Ridge National Laboratory for the purification of D2EHPA. The essential features of the purification include: (1) treatment with hydrochloric acid to hydrolyze polymeric materials, (2) extraction of neutral impurities such as alcohols and trialkylphosphates away from the sodium salt of D2EHPA with petroleum ether, and (3) liquid-liquid partition of the mono- and dialkylphosphoric acids between ethylene glycol and petroleum ether following the general procedure reported by Stewart and Crandall.[9] A detailed description of the procedure is given below. A description of the method for analyzing the purified product by titration is also presented. Finally, a discussion is included which considers various parts of the procedure with relation to the chemistry of the impurities.

2. PROCEDURE

The following twelve-step procedure is for 1200 ml of di(2-ethylhexyl)-phosphoric acid to be handled in the continuous extractor described in Sec. 4. (Larger and smaller amounts have been prepared by appropriate adjustments in both reagent quantities and equipment size.)

1. Boil the di(2-ethylhexyl)phosphoric acid with an equal volume of 2 M HCl for 2 hr in a flask fitted with a water cooled condenser to give total reflux. This will be a two-phase system, and the temperature will be that of the 2 M HCl. The boiling of the 2 M HCl should be sufficient to mix the two phases.

2. Place the refluxed mixture in a separatory funnel, separate and discard the 2 M HCl. It is possible to remove iron here, if present, by diluting the di(2-ethylhexyl)phosphoric acid with at least twice its volume of low boiling (30 to 60°C) petroleum ether, and by washing this phase with 2 M to 4 M HCl or H_3PO_4 to strip out the iron. A "shakeout" of an organic-phase sample with aqueous NaOH will reveal the presence of iron by precipitating $Fe(OH)_3$ and will serve as a method for determining its subsequent removal. If iron is not removed here, it can be removed as the $Fe(OH)_3$ precipitate from the sodium salt of di(2-ethylhexyl)phosphoric acid in step 6.

3. Evaporate the petroleum ether if used in step 2, measure the volume of the remaining D2EHPA, and titrate a sample of this material

with NaOH as described in Sec. 3. Compute the amount of NaOH equivalent to the total volume of D2EHPA. Add this quantity of NaOH as a 3.5% (weight/volume) solution. (This concentration was chosen to ensure that the final concentration of sodium di(2-ethylhexyl)phosphate is in the range 20 to 23%.) The final solution should be alkaline (pH higher than 8). IMPORTANT: Only a slight excess of NaOH is allowed (less than 0.5 g/liter). The total volume here will be about 5.5 liters of viscous sodium di(2-ethylhexyl)phosphate.

4. Add petroleum ether with stirring to the viscous sodium di(2-ethylhexyl)phosphate. A second clear petroleum ether phase will separate above the sodium di(2-ethylhexyl)phosphate phase after it becomes saturated. The amount of petroleum ether needed to saturate the sodium salt phase will depend upon the inert materials present, such as 2-ethylhexanol and tri(2-ethylhexyl)phosphate. The volume here will be about 6.5 to 7 liters. The sodium di(2-ethylhexyl)phosphate will be much less viscous and easily pourable after saturation with petroleum ether.

5. Place the sodium di(2-ethylhexyl)phosphate in the continuous extractor (Fig. 4.1). Add petroleum ether until the level reaches the overflow arm. Place about a liter of petroleum ether in the boiler and begin reflux. Under reflux, the petroleum ether will disperse throughout the sodium di(2-ethylhexyl)phosphate, extract the inert materials, and collect them in the boiler. The petroleum ether in the boiler should be changed about three or four times during the extraction. The extraction should be continued for 24 hr. Samples may be taken periodically, and each may be treated as in steps 6 through 12, titrated, and tested for purity to ascertain when the extraction is complete.

6. Separate the sodium di(2-ethylhexyl)phosphate (bottom phase) from the petroleum ether and discard the petroleum ether (top phase). If iron has not been removed in step 2, it will be precipitated as $Fe(OH)_3$ and can be removed by filtration of the sodium-salt phase through a fine-fritted-glass filter.

7. Acidify the sodium-salt phase with an excess of concentrated HCl. The petroleum ether that has dissolved in the sodium-salt phase will separate here and will contain the di(2-ethylhexyl)phosphoric acid. (The reaction is exothermic and some of the petroleum ether may boil away.)

8. Discard the HCl and dilute the petroleum ether-di(2-ethylhexyl)-phosphoric acid phase with additional petroleum ether to a total volume of 3 liters. Wash this phase five times with 500 g (each time) of ethylene glycol. Before discarding the last glycol wash, test it by titration (see below) to see if it contains mono-2-ethylhexyl-phosphoric acid. If it does, continue washing until there is no mono-2-ethylhexyl-phosphoric acid in the last glycol wash.

9. Wash the petroleum ether, which contains the di(2-ethylhexyl)-phosphoric acid (about 3 liters), three times with 500-ml volumes (each time) of 6 $\underline{M}$ HCl and then once with a liter of water.

10. Shake the petroleum ether, containing the di(2-ethylhexyl)phosphoric acid, with activated carbon (about 2 g/liter) and anhydrous sodium sulfate (100 g/liter). The activated carbon will remove colored hydrocarbon impurities, and the anhydrous sodium sulfate will absorb water from the solution.

11. Filter the petroleum ether solution through a fine sintered-glass funnel with suction. The filtered solution should be water white.

12. Evaporate the petroleum ether under vacuum with a stream of dry air passing through the solution at room temperature. Continue evaporation until the concentration of di(2-ethylhexyl)phosphoric acid is constant.

3. ANALYSIS

Titration curves (pH plotted vs the number of milliliters of base) for mono- and dialkylphosphoric acids (free of pyro- and polyphosphorus impurities) show sharp well-defined inflections. The inflection for the single hydrogen ion of D2EHPA is similar to that for the stronger of the two hydrogen ions of the corresponding monoalkylphosphoric acid (M2EHPA), so that titration to successive end points for the stronger and weaker hydrogen provides a differential analysis for mono- and dialkylphosphoric acid in mixtures that contain no other acids. A more detailed discussion for the detection of small amounts of monoalkylphosphoric acid in the presence of a large amount of dialkylphosphoric acid is presented in Appendix D of ref 10.

Example: Titration of a commercial "as-received" D2EHPA is shown in Fig. 3.1. The titration indicates 86.7% D2EHPA, 2.5% M2EHPA, and 10.8% inert material (by difference). Figure 3.2 shows the titration of the same D2EHPA after purification by the present method. The titration indicates purification to 99.55% D2EHPA.

Original Material: 0.513 g

First end point (D2EHPA + 1/2 M2EHPA) = 14.4 ml

Second end point (D2EHPA + M2EHPA) = 15.0 ml

M2EHPA = 2(15.0-14.4)0.100 = 0.12 milliequivalents

D2EHPA = (14.4-0.6)0.100 = 1.38 milliequivalents

Milliequivalent weight D2EHPA = 0.32242

Milliequivalent weight M2EHPA = 0.10511

$$\% \text{ M2EHPA} = \frac{(0.12)(0.10511)}{(0.513)} \times 100 = 2.5$$

$$\% \text{ D2EHPA} = \frac{(1.38)(0.32242)}{(0.513)} \times 100 = 86.7$$

% inert material (by difference) = 10.8

Final Product: 0.502 g

First end point = 15.5 ml

Second end point = not observed

$$\% \text{ D2EHPA} = \frac{(15.5)(0.100)(0.32242)}{(0.502)} \times 100 = 99.55$$

4. CONTINUOUS EXTRACTOR

The extractor (Fig. 4.1) will handle 1000 to 1400 ml of di(2-ethylhexyl)phosphoric acid. The main container was made from a 2.5-gal Pyrex bottle, altered to provide a side arm and longer neck (see below). The disperser is a 10-mm-OD tube, sealed off and formed into a ring at its lower end. The ring is perforated with about 20 small holes. The diameter of the ring must be smaller than the opening in the neck of the bottle. The upper end of the tube is connected to a small funnel that can engage the drip tip of the condenser.

The condenser is of the drip-tip type which will discharge into the funnel of the disperser. Clearance must be left between the condenser tip and funnel so that petroleum ether vapors from the boiler may pass

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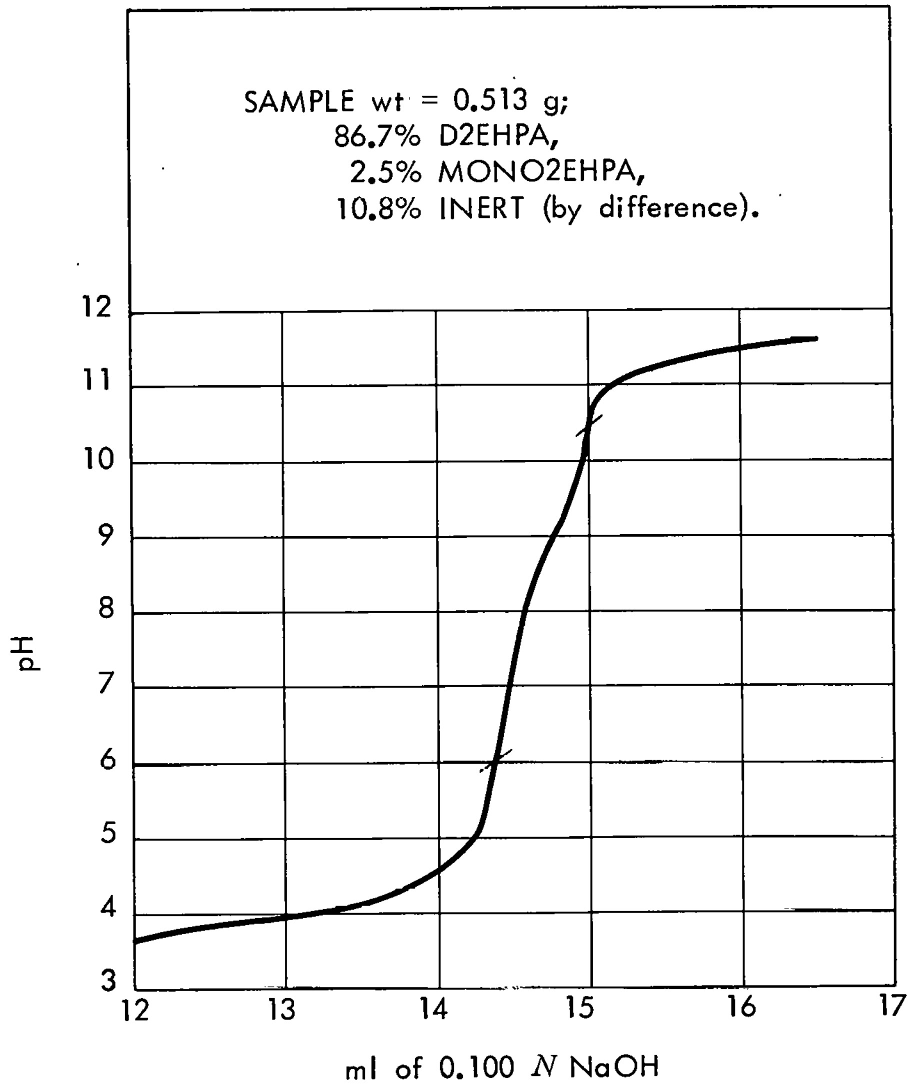

Fig. 3.1. Commercial Di(2-ethylhexyl)phosphoric Acid "As Received."

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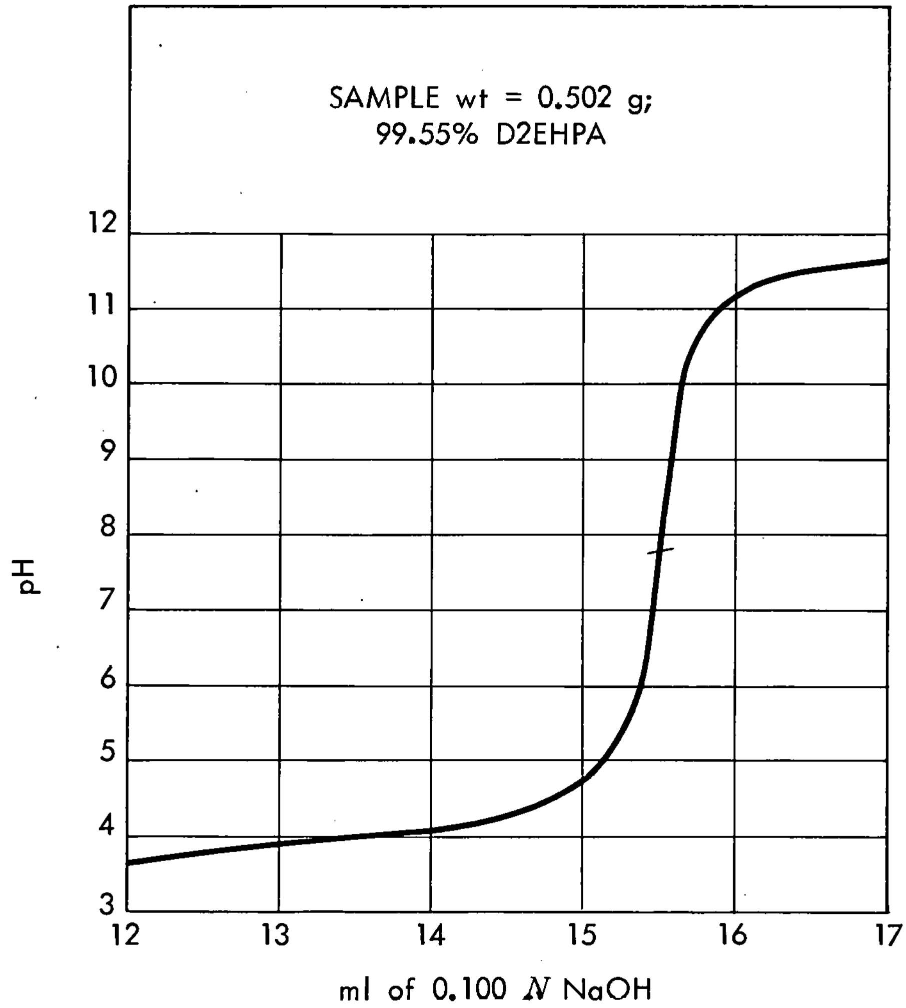

Fig. 3.2. Commercial Di(2-ethylhexyl)phosphoric Acid After Purification.

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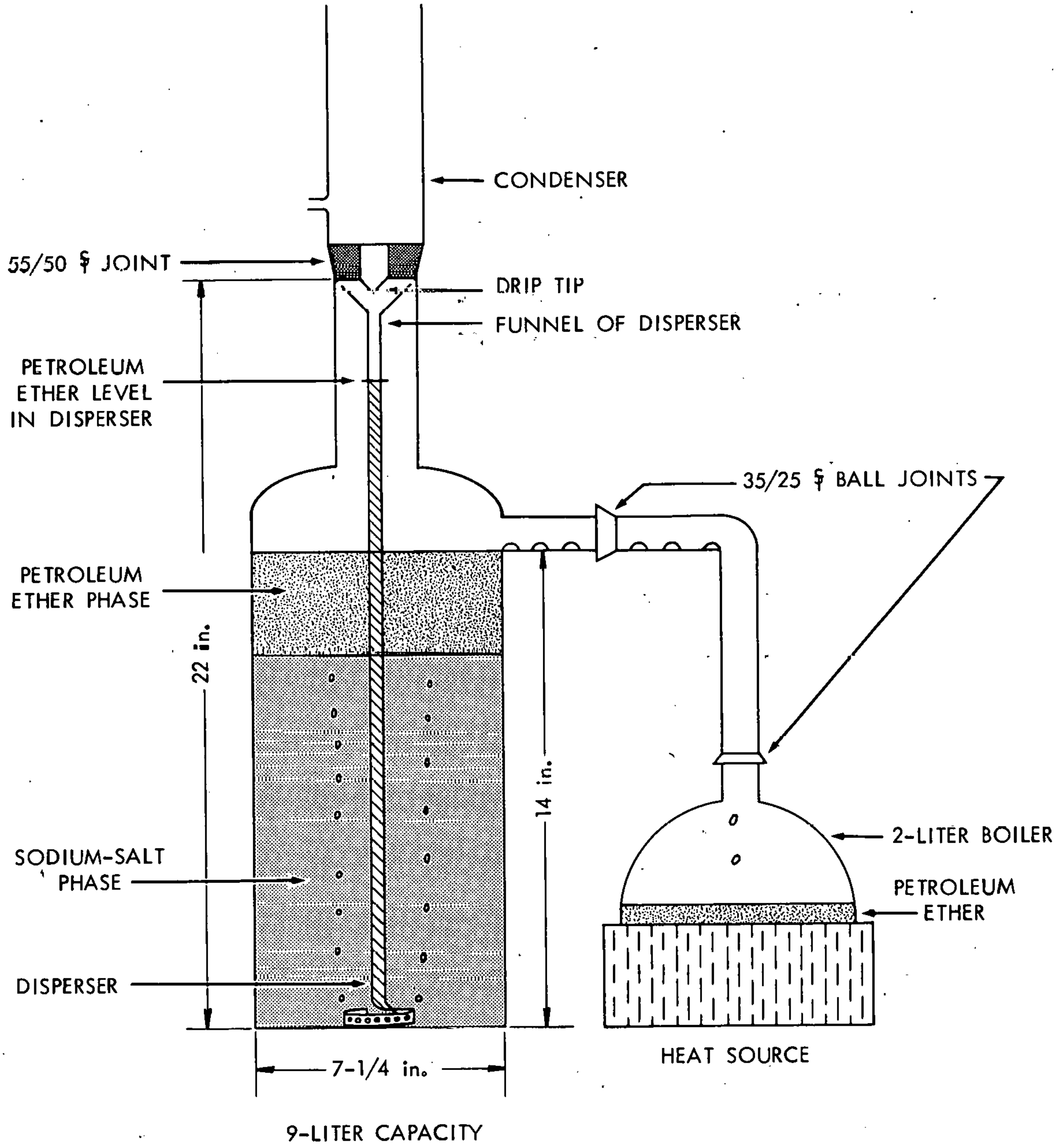

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Fig. 4.1. Continuous Extractor.

around the edges of the funnel and enter the condenser. The boiler is a 2-liter flask which can be heated with a heating mantle, steam, or hot water — NOT BY OPEN FLAME.

The petroleum ether, vaporized in the boiler, enters the condenser, condenses, drips into the disperser, flows out the small holes in the disperser ring, extracts materials preferentially soluble in petroleum ether while percolating through the sodium-salt phase, separates from the sodium-salt phase and overflows into the boiler. The extracted material collects in the boiler.

The specific gravity of the sodium-salt phase is such as to require a head of petroleum ether in the disperser tube which is 5 to 7 inches higher than the top of the petroleum ether layer to ensure dispersal of the petroleum ether. This space must be provided in the apparatus. To aid dispersal, the sodium-salt phase may be stirred with a paddle moving slow enough that interface mixing does not occur.

5. NOTES ON THE IMPURITIES AND METHODS OF REMOVAL

5.1 Alkylpoly-and Pyrophosphates

These compounds occur frequently in commercial preparations of dialkylphosphoric acids and are often strong extractants. Boiling with HCl hydrolyzes these compounds to their component mono- and dialkylphosphoric acids. They also undergo alkaline hydrolysis, and this can occur during titration with NaOH. "Drifting" of the pH at high levels frequently indicates their presence in the product being analyzed.

5.2 Inert Materials: Hydrocarbons, Trialkyl Phosphates and Alcohols

Trialkylphosphates in combination with D2EHPA give synergistic extraction of uranium and depress the extraction of many metals.[6] Alcohols, for example, 2-ethylhexanol, will depress the extraction of metals by D2EHPA. In this purification, D2EHPA is converted to its sodium salt [$NaOH + (RO)_2P\text{-}OH \rightarrow (RO)_2P\text{-}ONa$], and the inert materials are extracted away from this sodium dialkylphosphate phase by low-boiling petroleum ether. Sodium di(2-ethylhexyl)phosphate is soluble in water or very dilute base. The solubility of sodium di(2-ethylhexyl)phosphate in water at room temperature is about 25%. At a concentration above this, or upon cooling, another phase will separate out. The sodium di(2-ethylhexyl)-phosphate is not soluble in strong base (stronger than 2% NaOH). In the presence of strong base, another phase containing the sodium di(2-ethylhexyl)phosphate, tri(2-ethylhexyl)phosphate, 2-ethylhexanol, water, and some petroleum ether will separate above the strongly alkaline aqueous phase. Consequently, it is possible to have three phases in the extractor at one time. The addition of water to such a system will solubilize the bottom two phases.

5.3 Monoalkylphosphoric Acid

Mono(2-ethylhexyl)phosphoric acid is present in preparations of D2EHPA and, as mentioned above, may result from the hydrolysis of poly- and pyrophosphates. Mono(2-ethylhexyl)phosphoric acid has high extraction coefficients for many metals; also, its appreciable aqueous solubility frequently causes troubles in phase separations. Separations of the mono- and dialkyl acids are accomplished by providing two immiscible solvents, ethylene glycol in which the monoalkyl acid is preferentially soluble, and petroleum ether in which the dialkyl acid is preferentially soluble. Diethylene glycol and propylene glycol have also been used successfully in place of the ethylene glycol.

5.4 Metal Contaminants

Iron or other metal contaminants may be tightly complexed by D2EHPA and may resist stripping by dilute acids. Concentrated acids are generally effective stripping agents, especially from dilute dialkylphosphoric acid solutions, and alkaline reagents are almost always suitable.

5.5 Purification of Other Dialkylphosphoric Acids

Some phosphoric acids with straight-chain alkyl groups (or chains with branching near the end of the carbon chain) form solid sodium salts which are not water soluble. The addition of ethanol will usually make them soluble in the aqueous phase and thus amenable to the purification procedure described above.

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