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ION EXCHANGE PURIFICATION OF BIS(2-ETHYLHEXYL) PHOSPHATE ACID

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ION EXCHANGE PURIFICATION OF BIS(2-ETHYLHEXYL)PHOSPHORIC ACID

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ABSTRACT

Bis(2-ethylhexyl)phosphoric acid may be purified by absorption on a macroreticular, strong base anion exchange resin. Properties of ion exchange purified HDEHP are in excellent agreement with literature values.

INTRODUCTION

Bis-(2-ethylhexyl)phosphoric acid (HDEHP) is extensively used both in plant-scale applications and in systematic studies of solvent extraction phenomena. More than 200 references to HDEHP appear in the 8th Collective Index of *Chemical Abstracts*. Commercially available, technical grade HDEHP contains various impurities, including mono(2-ethylhexyl)phosphoric acid (H_2MEHP), neutral compounds, such as the triester and 2-ethyl-1-hexanol, pyro and polymeric phosphates, and iron. The impurities may alter the extractive abilities of HDEHP drastically. Therefore, a number of methods for producing purified HDEHP have been reported[1-5]. These ordinarily involve partitioning between immiscible solvents (e.g. Schmitt and Blake[2]) or isolation of the pure material via an insoluble salt (Partridge and Jensen[4]).

The present study involves purification via absorption of the HDEHP on a strong base macroreticular, anion exchange resin. The purification procedure is simple and produces a high purity product in excellent yield.

EXPERIMENTAL

Materials

Amberlyst A-26 strong base, anion exchange resin (20-50 mesh size) was obtained in the moist, chloride

form from the Rohm and Haas Company. It is a macroreticular resin developed for removal of mercaptans, acids, phenolics, color bodies, and other trace impurities from non-aqueous solution[6]. The resin bed (500 ml) was supported by a stainless steel screen in a 5.85 cm (i.d.) by 22.4 cm jacketed column.

The resin was converted to the hydroxide form by passing 1*M* NaOH through it at a rate of ten bed volumes per hour until the effluent gave no chloride test. The conversion required approximately 40 bed volumes of hydroxide solution. The bed was then washed with water to remove excess base. Although the manufacturer's literature recommends that washing be continued until no more than two drops of 0.1*M* HNO_3 is needed to neutralize 100 ml of effluent, this was found to require several thousand bed volumes of water. As a matter of practicality, water usually was pumped through the column overnight and washing with as little as 20 to 60 bed volumes of water was generally sufficient. The water wash was followed by passage of several bed volumes of isopropyl alcohol and then several bed volumes of isopropyl ether to remove any soluble organic substances. All liquids were pumped downflow unless otherwise noted. After washing, the resin was classified by a slow upflow of water through the column.

Batches of crude HDEHP from three different sources were purified by the ion exchange procedure. The various starting materials were Union Carbide technical grade, Eastman Practical grade material which had been irradiated (^{60}Co) to an exposure of about 2×10^8 rads, and a sample of unknown history, possibly obtained from Victor Chemical Company. Pertinent properties of these three starting materials are given in Table I.

All other materials were analytical reagent grade.

Purification Procedure

Removal of Iron and H_2MEHP. Isopropyl ether solutions (0.5*M* HDEHP) of the crude materials were washed twice with equal volume portions of 1.0*M* NaOH-0.1*M* sodium tartrate solutions and then with equal volumes of 3*M* HCl and water to remove iron and H_2MEHP. To provide H_2MEHP needed for other studies in this laboratory, the irradiated HDEHP was washed once with ethylene glycol, according to the method of Schmitt and Blake[2], prior to dilution with isopropyle ether and subsequent washing with the alkaline tartrate solution.

Precipitation of NaDEHP occured when isopropyl ether solutions containing more than about 0.5*M* HDEHP were washed with the alkaline tartrate solution. In some iron removal tests the ether HDEHP solution was washed with

Table 1. Starting Crude HDEHP Solutions

Source	Color	Weight Percent HDEHP	Weight Percent H_2MEHP	Fe ppm
Union Carbide Co.	Pale yellow	93.32	2.015	61.6
Eastman Kodak Co.[a]	Reddish-brown	84.19	12.81	120
Unknown[b]	Amber	95.64	2.047	1890

[a] Irradiated (^{60}Co) to $\sim 10^8$ rads.

[b] Possibly Victor Chemical Co.

0.1*M* NaOH solution to precipitate iron hydroxide. This iron removal procedure was not as effective as washing with alkaline tartrate solution. Separation of the iron hydroxide precipitate was also cumbersome.

Resin Bed Operations. The washed ethereal HDEHP solution was loaded onto the resin bed at a flow rate of approximately one bed volume per hour. During the loading and subsequent washing steps, the resin column was maintained at 40°C. Although no kinetics studies were done, some previous work with the A-26 resin indicated that the acid might load slowly at room temperature. HDEHP was not detected in the effluent as long as the amount of acid in the feed did not exceed approximately 0.7 meq per ml of bed volume. Loading of the HDEHP could be followed visually since the loaded resin was preceptibly lighter in color than the remainder of the bed. The loaded resin was washed with additional isopropyl ether, isopropyl alcohol, and water.

The loaded, washed resin was transferred to a beaker and 6*M* Hcl was added to elute the HDEHP. The eluted HDEHP was separated from the aqueous phase and washed with water. An alternate method of unloading the resin bed was to pump 6*M* HCl upflow, sweeping eluted HDEHP out of the column and collecting it in isopropyl ether. This

method was abandoned because of the tendency of the eluted HDEHP to become trapped in interstices of the resin bed. This resulted in yields significantly lower than the other procedure (49 percent as compared with 75-80 percent).

Final Purification. Dissolved water was removed by heating the product to 70° C at 20 torr for several hours in a rotary evaporator. The product, at this point, was pale yellow and contained visible, suspended particles of resin. Filtration through an 0.45 μm millipore filter removed the yellow color as well as the suspended resin particles.

Characterization Methods

Titrations were made with a Beckman model 1063 automatic buret coupled with a 1065 pH recording module. The solvent was 75 percent aqueous acetone.

Iron analyses were by atomic absorption.

Index of refraction measurements were made with a Bausch and Lomb Abbe refractometer thermostated at 26° C.

Viscosities were determined with a Wells-Brookfield model LVT Micro Viscometer at 20° C.

Specific gravities were determined with a pycnometer.

RESULTS AND DISCUSSION

Some physical properties of the ion exchange purified HDEHP obtained from the various starting crude materials

are listed in Table 2. All the purified HDEHP batches were free from H_2MEHP as indicated by a single end point when they were titrated with standard NaOH. As noted in Table 2, properties of HDEHP purified by the ion exchange procedure are in excellent agreement with those measured by Partridge and Jensen[4] for material purified by their precipitation scheme. The irradiated crude HDEHP as well as that of unknown history were initially so highly colored that the final purified products had a faint yellow color even after treatment with decolorizing carbon.

Yields in the ion exchange purification range from about 70 to 80 percent. In a typical run with a 500-ml resin bed 86 grams of purified HDEHP were obtained from 110 grams of crude starting material. The Amberlyst A-26 resin does not appear to be degraded in the purification process. One resin bed may be used for many purification cycles without either decreased yield or product purity.

The headend alkaline tartrate washing step is essential to preparation of highly purified HDEHP. When this step was omitted with crude Union Carbide Co. HDEHP the final ion exchange product still contained about one weight percent H_2MEHP and 26 ppm iron.

As a solvent for HDEHP for the ion exchange purification process, isopropyl ether has several advantages over other candidate diluents (e.g., chloroform, ethyl

Table 2. Some Physical Properties of Purified HDEHP

Purification Procedure	Crude HDEHP Source[a]	Purified HDEHP: Weight Percent HDEHP	Fe Content ppm	Color	Specific Gravity	Viscosity at 20°C, CP	Index of Refraction
This paper	1	99.87	3.85	Colorless	0.9712 (22°C)	39.53	1.4420 (26°C)
	2	97.81	4.05	Pale yellow	0.9778 (20°C)	[b]	[b]
	3	99.04	8.08	Pale yellow	0.9701 (22°C)	39.94	1.4420 (26°C)
Partridge-Jensen[4]	1	99.90	10.9[c]	Colorless	0.9727 (20°C)	39.8 ± 0.1	1.4418 (25°C)
Peppard *et al.*[1]	4	>99			0.975 (20°C)	42.2	1.4469 (25°C)

[a] 1 - Union Carbide Co.; 2 - Eastman Kodak Co., Irradiated (10^8 rad); 3 - Unknown (possibly Victor Chemical Co.); 4 - Victor Chemical Co.

[b] Not determined.

[c] Not reported by Partridge and Jensen, but run on a sample prepared in these laboratories by their procedure.

ether, dodecane, etc.). It is immiscible with water and dissolves up to 0.5*M* NaDEHP which makes iron removal by alkaline tartrate washing straightforward. Isopropyl ether solutions of HDEHP have a specific gravity less than one thus simplifying mechanical operations in both the headend washing step and in resin loading and elution.

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