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ORNL-TM-183 *W.J.*

COPY NO. - *31*

DATE - March 30, 1962

Syntheses of Some Alkali-metal p-Ethylbenzenesulfonates

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ABSTRACT

Methods were developed for the syntheses of alkali-metal p-ethylbenzenesulfonates. First, p-ethylbenzenesulfonic acid is isolated and is purified as barium p-ethylbenzenesulfonate. This salt is converted to the sodium, potassium or cesium p-ethylbenzenesulfonate by means of a slight excess of the corresponding alkali-metal carbonate. Lithium sulfate is used to form the lithium p-ethylbenzenesulfonate.

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Syntheses of Some Alkali-metal *p*-Ethylbenzenesulfonates

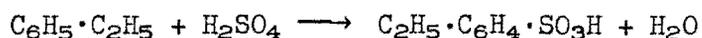
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It is impossible to determine directly the activity coefficients of strongly cross-linked cation-exchange resins. It is therefore necessary in equilibrium studies (i.e., in the determination of osmotic and activity coefficients) of cation-exchange resins to use instead of the resins certain sulfonic acids having the monomeric structure representing these resins.

Bonner, Easterling, West, and Holland⁽¹⁾ have plotted the activity coefficients of *p*-toluenesulfonic acid and its lithium, sodium, and potassium salts as a function of water activity. They have suggested that the *p*-ethylbenzenesulfonates could be more favorably compared with ion-exchange resins because their structures are more similar to those of the resins than are the structures of the *p*-toluenesulfonates. Consequently, a request was made for the preparation of the sodium, potassium, lithium, and cesium salts of *p*-ethylbenzenesulfonic acid in order to determine the significance of their activity coefficients in the interpretation of ion-exchange equilibria. Methods are described herein for preparing *p*-ethylbenzenesulfonic acid, the intermediate barium *p*-ethylbenzenesulfonate, and the alkali-metal *p*-ethylbenzenesulfonates.

Preparation of *p*-Ethylbenzenesulfonic Acid

Two methods were used to prepare *p*-ethylbenzenesulfonic acid in the crystalline state. According to the method of Wiley and Davis,⁽²⁾ the sulfonic acid was prepared by heating excess ethylbenzene (9.4 moles) with concentrated sulfuric acid (5 moles)

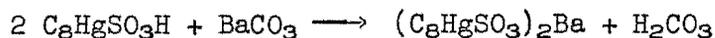


under conditions that permitted mechanical removal of the water, formed during the reaction, as the ethylbenzene-water azeotrope. The reaction was continued until the theoretical amount of water had been collected.

The method of Sempotowski⁽³⁾ consists in heating ethylbenzene to the boiling point and then adding to it, while hot, an equal volume of concentrated sulfuric acid, with vigorous agitation. The mixture was allowed to reflux for 10 minutes. On being cooled to room temperature, the mixture turned a wine-yellow color. Crushed ice was added cautiously and produced a slurry of colorless crystals. The adhering liquor was filtered off leaving the crystalline, very hygroscopic p-ethylbenzenesulfonic acid. According to Sempotowski,⁽³⁾ these conditions give only the para form of the sulfonic acid; therefore no separation of isomers was necessary.

Preparation of Barium p-Ethylbenzenesulfonate

The second stage of the syntheses consisted in isolating the p-ethylbenzenesulfonic acid as the barium salt according to the reaction



One-kilogram batches of the p-ethylbenzenesulfonic acid were dissolved in 2 liters of distilled water and, with warming and constant stirring, the solutions were neutralized with barium carbonate. Excess sulfate was precipitated as barium sulfate, which was removed by successive filtrations through coarse-, medium-, and fine-fritted funnels. The volume of the filtrate was reduced by one half on a hot plate, and the liquid was refiltered. Excess water was then removed from the concentrated filtrate by the freeze-dry method as follows. A 500-ml flask was one-fourth filled with the filtrate, which was frozen in liquid air while the flask was rotated at an angle. Vacuum was applied to the flask while the temperature

of the flask was allowed to increase slowly. The rate of evaporation of water decreased as the surface area of the subliming ice decreased. The barium p-ethylbenzenesulfonate was obtained as small granular crystals, which were purified further by recrystallization from aqueous solution. They were again dried by means of the freeze-dry technique and then oven-dried at 130°C for 2 to 4 hours.

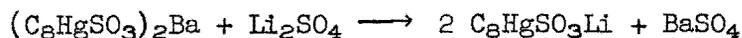
Since the emphasis in this work was on purity rather than quantity of product, the yields were not calculated. Some portions of product were discarded if any doubt about their purity existed. For example, the mother liquor was discarded because Paquette, Lingafelter, and Tartar⁽⁴⁾ found that 30% of the product at this stage was in a much more soluble form than the para isomer from which it could be completely separated, was different in physical appearance, and was evidently the barium o-ethylbenzenesulfonate.

Preparation of Alkali-metal p-Ethylbenzenesulfonates

The purified barium p-ethylbenzenesulfonate was converted to the sodium, potassium, or cesium salt by means of a slight excess of the corresponding alkali-metal carbonate. The reaction for the separation of the potassium salt is



Lithium p-ethylbenzenesulfonate was formed by use of lithium sulfate instead of lithium carbonate because of the insolubility of lithium carbonate in water



These reactions proceeded without difficulty when barium p-ethylbenzenesulfonate was dissolved in warm water and the alkali-metal carbonate (or sulfate) was slowly added with stirring. The mixture was stirred for 10 minutes at 50 to 60°C and was then filtered through a fine-fritted funnel. The filtrate was evaporated until it became supersaturated; then crystallization was allowed to occur overnight. The mother liquor was decanted, and the white crystalline solid was dried by means of the freeze-dry process.

The alkali-metal p-ethylbenzenesulfonates were purified by two recrystallizations from a minimum of methanol and by further freeze-drying.

In order to confirm the formation of an aromatic sulfonic acid, arylamine derivatives of the p-ethylbenzenesulfonates were formed with o-toluidine and p-toluidine according to the method of Dermer and Dermer.⁽⁵⁾ Each derivative was prepared as follows. Two grams of the p-ethylbenzenesulfonate was dissolved in 30 ml of boiling water. Ten milliliters of the amine solution (25 g of amine, 30 ml of HCl, and 50 ml of water) was added to the solution of the salt. The solution was cooled to room temperature, the mixture was filtered, the precipitate was washed with cold water and was then recrystallized two times from a 1% aqueous solution of acetic acid. The experimentally determined melting points, shown in Table 1, agreed essentially with those given in the literature; thus, the formation of an aromatic sulfonic acid was indicated.

Table 1. Melting Points of Arylamine Derivatives of Some Alkali-metal p-Ethylbenzenesulfonates

<u>Alkali-metal p-Ethylbenzenesulfonate</u>	<u>Melting Point of Derivative, °C</u>	
	<u>o-Toluidine^a</u>	<u>p-Toluidine^b</u>
Cs	190—192	206—208
Li	190—192	207—209
K	191—193	208—210
Na	190—192	206—208

^a Melting point from literature, 192—193°C.

^b Melting point from literature, 208—209°C.

The neutral equivalent for p-ethylbenzenesulfonic acid was determined by the following procedure. An accurately weighed portion (0.1 to 0.3 g) of the barium or alkali-metal p-ethylbenzenesulfonate was dissolved in 20 to 30 ml of distilled water, the solution was rinsed into a 3 cm x 15 cm ion-exchange column half-filled with fresh Dowex 50W-2X (50 to 100 mesh) cation-exchange resin. The solution containing the sample was allowed to pass through the column of a rate of 2 to 3 drops per second. The column was washed with eight to ten 20-ml portions of distilled water or until the effluent coming from the column was no longer acid to litmus. The total effluent was then titrated with a standard solution of sodium hydroxide to a phenolphthalein end point. Calculations of neutral equivalents and molecular weights for the alkali-metal p-ethylbenzenesulfonates were based on the equations.

Neutral Equivalent, % = $100 \frac{eNV}{WF}$ and

Gram Molecular Weight = $1000 \frac{W}{VN}$

Where

N = normality of standard sodium hydroxide solution = 0.0768,

e = milliequivalent weight of p-ethylbenzenesulfonic acid,

g = 0.18622,

V = volume of standard sodium hydroxide required to neutralize
effluent, ml,

W = weight of sample, g, and

F = theoretical amount of acid equivalent in the alkali-metal
p-ethylbenzenesulfonates, weight fractions

= 0.5822 for Cs salt

= 0.8257 for K salt

= 0.8896 for Na salt

= 0.9639 for Li salt

The results of the elemental analysis of the compounds synthesized,
as well as the molecular weights found for test compounds, are shown in
Table 2.

Table 2. Compositions and Molecular Weights of
Alkali-metal p-Ethylbenzenesulfonates

<u>Salt</u>	<u>Component</u>	<u>Composition</u>		<u>Molecular Weight</u>	
		<u>Theoretical</u>	<u>Found</u>	<u>Theoretical</u>	<u>Found</u>
C ₈ HgSO ₃ Li	Carbon	50.0	49.1	192	192
	Hydrogen	4.7	4.7		
	Lithium	3.6	3.5		
C ₈ HgSO ₃ Na	Carbon	46.2	45.7	208	207
	Hydrogen	4.4	4.4		
	Sodium	11.0	10.9		
C ₈ HgSO ₃ K	Carbon	42.8	42.1	224	226
	Hydrogen	4.0	4.1		
	Potassium	17.4	17.5		
C ₈ HgSO ₃ Cs	Carbon	30.2	29.7	318	317
	Hydrogen	2.9	2.9		
	Cesium	41.8	41.8		

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