## COMMUNICATIONS TO THE EDITOR

## ANION EXCHANGE STUDIES. XVI. ADSORPTION FROM LITHIUM CHLORIDE SOLUTIONS<sup>1,2</sup>

Sir: A study was undertaken of the adsorbability of a number of metal ions from LiCl solutions by a quaternary amine polystyrene-divinylbenzene anion exchange resin to compare with earlier similar studies of the adsorbability of these elements from HCl solutions on the same batch of resin (Dowex-1). Since the activity coefficients of LiCl and HCl in aqueous solutions do not differ greatly,<sup>8</sup> it was anticipated that most metals would adsorb similarly from these two media. It was found, however, quite unexpectedly, that for all metals studied, adsorption from LiCl solutions was very much greater than from HCl solutions of the same concentration. A typical case is Mn(II). In 12 M solutions the distribution coefficient D (amount per kg. dry resin/amount per liter solution) of Mn(II) is approximately 550 from LiCl solutions,<sup>4</sup> while D is only ca. 4 from HCl solutions.<sup>5a</sup> The effect is still pronounced in 6 M HCl solutions, although the ratio of the distribution coefficients for the two media is less. Similar effects have been so far observed for

Sc(III), Fe(III), Co(II), Zn(II), Ga(III) and Au-(III). In general the distribution coefficients in 12 M LiCl solutions were more than a factor of 100 greater than in 12 M HCl solutions. This is particularly striking since the adsorbabilities of these elements vary widely (in 12 M HCl solutions the distribution coefficients are: ca. 2 (Sc(III)),<sup>6</sup> ca. 4 (Mn(II)),<sup>5a</sup> ca. 80 (Co(II), Zn(II)),<sup>5a</sup> ca. 6000  $(Au(III))^7$  and ca. 50,000 (Fe(III),<sup>5b</sup> Ga(III)<sup>6</sup>). Even Be(II) shows considerable adsorption from concentrated LiCl solutions (D = ca. 8 in 13 M LiCl) while it had essentially negligible adsorption from concentrated HCl.<sup>6</sup> This adsorbability of Be(II) in concentrated LiCl is sufficient to permit anion exchange separation from non-adsorbable elements (e.g., alkali metals, Mg(II), etc.) and in general the use of LiCl-low acidity media may permit anion exchange separations which are only marginal or ineffective with HCl solutions.

At the present time the reason for this pronounced effect is not clear. Qualitatively the results might be explained by assuming that the negatively charged chloride complexes of these elements form essentially non-adsorbable undissociated acids at very high acidities. However, this

(1) This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Previous communication: K. A. Kraus and G. E. Moore, THIS JOURNAL, 77, 1383 (1955).

(3) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publishing Corp., New York, N. Y., 1950, pp. 577, 601.

(4) All lithium chloride solutions contained a small amount (0.1 M) of HCl to avoid complications from possible hydrolytic reactions.

(5) K. A. Kraus and G. E. Moore, THIS JOURNAL, (a) 75, 1460 (1953); (b) 72, 5792 (1950); and unpublished results.

(6) K. A. Kraus, F. Nelson and G. W. Smith, J. Phys. Chem., 58, 11 (1954).

(7) K. A. Kraus and F. Nelson, J. Am. Chem. Soc., 76, 984 (1954).

appears to be an unlikely explanation since the effect is so general.<sup>8</sup> More probably it is due to differences in the activity coefficients in the resin phase when the resin is immersed in these two media.

(8) A similar, though less pronounced, effect had earlier been found for  $HNO_2$  and  $NH_4NO_2$  solutions, F. Nelson and K. A. Kraus. THIS JOURNAL, **76**, 5916 (1954).

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## BIOSYNTHESIS OF PENTOSE PHOSPHATE FROM ERYTHRULOSE 1-PHOSPHATE AND FORMALDE-HYDE<sup>1</sup> Sir:

A soluble enzyme system from the liver, kidney or muscle of the rat catalyzes the anaerobic utilization of formaldehyde in the presence of erythrulose 1-phosphate. Although some formaldehyde is utilized by the system, the addition of erythrulose phosphate stimulates increased utilization of formaldehyde 10–15-fold. The enzyme can be obtained in a soluble state from a homogenate of liver in isotonic potassium chloride, by centrifugation at 38,000 r.p.m. for one hour on the Spinco Ultracentrifuge using rotor no. 40. The clear supernatant fluid contained all the activity. Using erythrulose 1-phosphate-4-C<sup>14</sup> (specific activity 13,300 c.p.m. per micromole) and unlabeled formaldehyde the products of this reaction were identified by paper chromatography of the phosphatefree sugars according to published methods.<sup>2</sup> Ribose was identified as the major radioactive product by chromatography in three different solvent systems.<sup>2</sup> Upon spraying with aniline oxalate the characteristic cherry-pink spot for aldopentoses was obtained. Elution of the spot from large scale chromatograms yielded a compound which in the orcinol test gave a spectrum characteristic for ribose. The specific activity of the eluted pentose was 9300 c.p.m. per micromole and the total radioactivity incorporated ranged from 3 to 6% in eight different experiments. Smaller amounts of radioactivity were detected in the areas corresponding to xylulose or arabinose. Using both  $\dot{C}^{14}$ -erythrulose phosphate and  $C^{14}$ -formaldehyde (specific activities 13,300 and 30,000 c.p.m. per micromole, respectively) the specific activity of the isolated pentose was 34,760 c.p.m. per micromole. In these experiments the specific activities of the recovered erythrulose phosphate and formaldehyde at the end of the experiment did not vary significantly from the initial values of these compounds. Incubation of either substrate alone yielded no labeled pentose (Table I). The specific

<sup>(1)</sup> Supported by grant No. C-2228 from the United States Public Health Service.

<sup>(2)</sup> F. C. Charalampous and G. C. Mueller, J. Biol. Chem., 201, 161 (1953).