Aza-steroid (X)

λ_{max} 225, 284 mμ (log ε = 4·528, 3·938)
λ_{min} 250 mμ (log ε = 3·534)

Aza-steroid (XI)

λ_{max} 255, 393 mμ (log ε = 4·041, 4·2492)
λ_{min} 235, 290 mμ (log ε = 3·996, 3·218)

Infra-red absorption bands:—3300, 2930, 1630, 1530, 1455, 1360, 1295, 1190 cm^{-1}.

Starting from compound(V) and *m*-methoxyphenylhydrazine, a synthesis of the desired 3-oxy-derivative of compound (X) appears possible although problems in isomer separation will then arise. Although the above synthesis leads to several reaction products, it is nevertheless of interest in view of the fact that a complex steroidal skeleton is built up in one step starting from readily accessible intermediates.

It is hoped that a detailed account of the work will be published in *Tetrahedron* in the near future.

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The hydration heat of the benzenesulphonate ion

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One mole of a solid salt MX may be directly dissolved in excess of water to form hydrated ions, when the enthalpy change is equal to the total heat of solution S; alternatively it may first be split up into gaseous ions, with enthalpy change U equal to the lattice energy, and the ions then hydrated, with enthalpy change H. It follows that

$$S = U + H, \tag{1}$$

and the hydration heat of the pair of gaseous ions M^+ and X^- may be derived if values of U and S are known. Although only hydration heats of pairs of ions may be determined experimentally, it is possible to split up the hydration heats of a pair into the separate contributions of cation, W_{M^+}, and anion, W_{X^-}:

$$H = -(W_{M^+} + W_{X^-}) \tag{2}$$

This problem has been studied by a number of investigators, who have produced consistent values for a number of monatomic ions. Individual ion hydration heats due to Latimer *et al.*[1] and due to Verwey[2] are shown in Table 1.

Table 1. Hydration heats of ions, kcal/g ion

Ion	Li^+	Na^+	K^+	Rb^+	Cs^+	F^-	Cl^-	Br^-	I^-
Latimer *et al.*[1]	121·2	94·6	75·8	69·2	62·0	122·6	88·7	81·4	72·1
Verwey[2]	120	94·5	75	69	61	122	89·5	83	73·5

In the case of an unsymmetrical polyatomic anion such as benzenesulphonate, the hydration heat W_{X^-} cannot be derived from equations (1) and (2), since the lattice energy of a crystalline

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[2] E. J. W. Verwey, *Rec. Trav. Chim. Pays-Bas* **61**, 127 (1942).

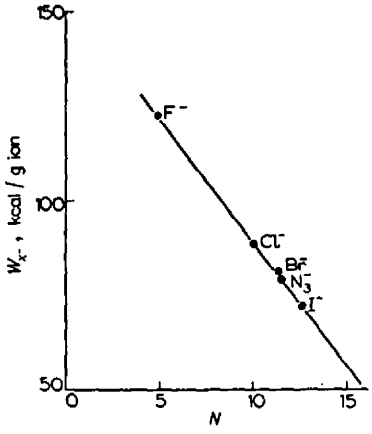

FIG. 1. Relationship between hydration heat of anions and lyotropic numbers.

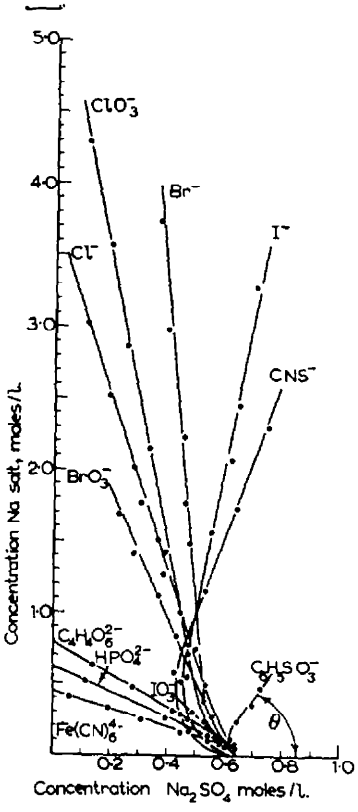

FIG. 2. Concentrations of different sodium salts plotted against concentrations of sodium sulphate, mixtures of which are necessary to bring about flocculation of gelatin sols (Buchner and Postma[9]).

compound such as an alkali benzenesulphonate cannot be computed accurately (for example, it would be necessary to know the Madelung constant for the crystal structure, and the charge distribution of the polyatomic anion).

However, an empirical correlation between anion hydration heat and lyotropic number has been observed and substantiated.[3-5] The lyotropic number, developed by Buchner *et al.*[6-8] is a quantitative expression of the position of an anion in the lyotropic (Hofmeister) series. When known hydration heats of anions are plotted against the corresponding lyotropic numbers, a linear relationship is observed (Fig. 1). If the lyotropic number of the benzenesulphonate ion can be obtained therefore, the hydration heat of the ion may be determined by interpolation.

The lyotropic number of the benzenesulphonate ion can be derived from the graph due to Buchner and Postma[9] on the flocculation of gelatin sols (Fig. 2). If θ is the angle between the line for $C_6H_5SO_3^-$ and the abscissa, then

$$N - 4{\cdot}78 \cot \theta + 11{\cdot}55 \qquad (3)$$

From the measurement of θ it can be calculated that $N = 14{\cdot}95$, and by interpolation in Fig. 1 it follows that the heat of hydration of the benzenesulphonate ion $W_{\bar{X}} = 56{\cdot}4$ kcal/g ion (298°K).

The procedure illustrated here appears to be the only possible one available at present for the accurate derivation of the hydration heats of various unsymmetrical polyatomic anions.

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Synthesis of methyl 2-acetamido-2-deoxy-β-D-glucofuranoside

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DESPITE the wide distribution of glucosamine in natural products, the ring form and mode of linkage is known only in a few cases and in these, only the pyranose modification has so far been found.[1-3]

The stability which many polysaccharides containing glucosamine show towards acidic hydrolysis is consistent with the behaviour of known pyranosides of glucosamine under identical conditions[4,5] and this is often taken as evidence of the predominance of pyranose form of the amino-sugar in polysaccharide chains.

It is now of interest to examine the stability of furanoside derivatives of glucosamine with a view to assessing the contribution that this form of the amino-sugar may make in polysaccharide structures, particularly as potential sites of acid-labile linkages.

The failure of glucosamine to form glycosides with methanolic hydrogen chloride has led to the investigation of an alternative synthesis via the neutral scission of the sugar mercaptal. Wolfrom *et al.*[6] synthesised a methyl β-thioglycoside of glucosamine and by an analogous route we have now obtained in a crystalline form methyl 2-acetamido-2-deoxy-β-D-glucofuranoside from N-acetyl

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