mated by disappearance of radioactivity from medium) presumably as the resultant of an exchange reaction with potassium at certain sites of the external surface. Typical results obtained after 16–24 hours of rotary shaking at 22–25° (at which time Rb uptake is near maximal) are shown in Table I. In the absence of a competing ion orthoclase prefers Rb to Na by a factor of about 4:1. However, Rb uptake is not significantly diminished by the presence of 10 times more Na (or Li) than Rb; similar Rb uptake values are obtained with Na:Rb mixtures at 30:1, but K in equimolar amounts inhibits Rb uptake. Na^{22} uptake cannot be detected in the presence of Rb.

TABLE I

2 g. orthoclase (20–80 mesh) incubated for 24 hr. with 2 ml. medium.

Medium	Concen., uM./ml.	Rb^{86} uptake uM. per 2 g.	Na^{22} uptake uM. per 2 g.
$Rb^{86}Cl$	2	2.06	
$Na^{22}Cl$	2		0.44
$Rb^{86}Cl$	2		
+ NaCl	20	2.00	
$Na^{22}Cl$	2		
+ RbCl	20		<0.1

Another feldspar, Microcline ($KAlSi_3O_8$), 20–80 mesh, exhibits ion selectivity properties similar to orthoclase, but Rb uptake is only about one-fifth that obtained with orthoclase; leucite (20–80 mesh) a feldspathoid, whose structure may be slightly more open than the feldspars,[3] does *not* exhibit a preference for Rb as against Na.

The selective cation uptake by orthoclase emphasizes the importance of steric relationships for "fitting" cations into sites at the surface of this crystal lattice. Highly hydrated cations (Li and Na) may have difficulty in approaching and replacing potassium at these sites relative to K and Rb, which have fewer molecules of associated water.

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RECEIVED MAY 22, 1959

SOLVENT CHARACTERISTICS OF TETRAMETHYLENE SULFONE

Sir:

Since sulfones should have moderately large dielectric constants and very small autoprotolysis constants, we have commenced a study of their characteristics as solvents for acid–base reactions. Tetramethylene sulfone (sulfolane)[1] was chosen because its melting point, reported to be 28.86°,[2] permits cryoscopy as a control upon other measurements. Some solvent characteristics, determined preliminary to a study of the acid–base aspects, are of unusual interest, particularly the very large cryoscopic constant (Table I). Sulfolane should find application in molecular weight determinations.

TABLE I

PHYSICAL PROPERTIES OF SULFOLANE

Dielectric constant (30°)	44
Density (30°)	1.2615 g./cc.
Viscosity (30°)	0.0987 poise
Heat of fusion (cryoscopic, 26°)	2.73 ± 0.03 cal./g.
Molal f.p. depression	66.2 ± 0.6 deg./mole

Plots of freezing point *vs.* concentration exhibit a sharp inflection at 15° indicative of a new solid phase. Below 15°, slopes correspond to a heat of fusion of 10.6 cal./g. Calorimetric measurements are consistent with these values.[3]

Ideal monomer depressions were taken as those given by acetanilide and benzothiophene sulfone. Acetic acid behaves as a monomer and water as a dimer over the concentration range 0.01 to 0.1 molal. Methanol shows some association. Tetraethylammonium iodide is extensively dissociated.

Using a cell with bright platinum electrodes, conductivities of five salts were determined in the concentration range 3×10^{-4} to 5×10^{-3} *M*. The specific conductance of the solvent was less than 2×10^{-8} ohm^{-1} cm.$^{-1}$ and always less than 1% of the conductivities of the solutions. As shown in Fig. 1, plots of Λ *vs.* $\sqrt{c}$ were linear. Tetraphenylarsonium chloride and phenyltrimeth-

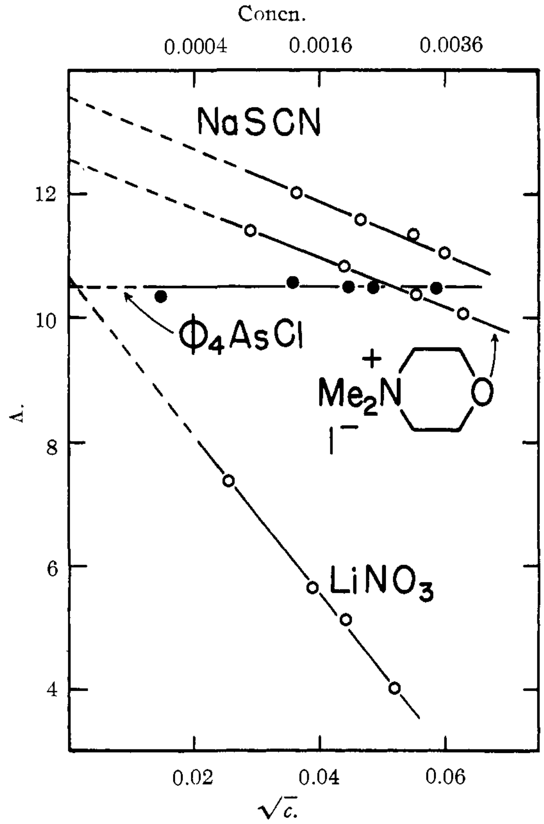

Fig. 1.—Equivalent conductances of several salts in sulfolane, at 30°.

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(1) We are indebted to the Shell Development Company for our sample of sulfolane. It could be purified adequately by vacuum distillation from powdered sodium hydroxide.

(2) A. R. Birch and J. MacAllen, *J. Chem. Soc.*, 2556 (1951).

(3) We are indebted to Mr. R. M. Hammaker and Professor M. Dole for a heat capacity study from −20 to 35° on the adiabatic calorimeter described by A. E. Worthington, P. C. Marx and M. Dole, *Rev. Sci. Instr.*, **26**, 698 (1955).

ylammonium iodide appear to be completely dissociated and their equivalent conductivities are independent of concentration to within 1%. However, the equivalent conductivity of the latter compound declines from 10.0 to 9.3 between 5×10^{-3} and 1.25×10^{-2} M as measured in a cell with platinized platinum electrodes. This decline may be largely a viscosity effect since the viscosity increase of the solution is of this order of magnitude. Accommodation of the conductance anomalies by introduction of finite ion size parameters would require unreasonably large values, several hundred Å.

Negative deviations from the Onsager slope were exhibited by sodium thiocyanate, dimethylmorpholinium iodide and lithium nitrate. The Davies[4] treatment gives ion pair dissociation constants of 0.021, 0.013 and 0.0011, respectively. At higher concentrations, as determined cryoscopically, lithium nitrate is largely undissociated.

(4) C. W. Davies, *Trans. Faraday Soc.*, **23**, 351 (1927).

(5) Monsanto Fellow, 1957–1958. National Science Foundation Predoctoral Fellow, 1958–1959.

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RECEIVED APRIL 20, 1959

THE BIOSYNTHESIS OF THIAMINE AND THIAMINE PHOSPHATES BY EXTRACTS OF BAKERS' YEAST[1]

Sir:

Preliminary reports from two different laboratories have established the ability of enzymes present in bakers' yeast to synthesize thiamine from the pyrimidine and thiazole moieties of the vitamin.[2,3] Recent experiments carried out in this laboratory have shown that the biosynthesis of thiamine and thiamine-PP[4] proceed in cell-free extracts of bakers' yeast according to the series of reactions

$$\text{Pyrimidine} + \text{ATP} \xrightarrow{\text{Mg}^{++}} \left[\begin{array}{c}\text{pyrimidine-P}\\ \text{Mg}^{++}\Big\downarrow\text{ATP}\\ \text{pyrimidine-PP}\end{array}\right] + \text{ADP}^5 \text{ or AMP}^5 \quad (1)$$

$$\text{Thiazole} + \text{ATP} \xrightarrow{\text{Mg}^{++}} \text{thiazole-P} + \text{ADP}^5 \quad (2)$$

$$\text{Pyrimidine-PP} + \text{thiazole-P} \xrightarrow{\text{Mg}^{++}} \text{thiamine-P} + \text{PP}^5 \quad (3)$$

$$\text{Thiamine-P} \longrightarrow \text{thiamine} + \text{P}^5 \quad (4)$$

$$\text{Thiamine} + \text{ATP} \longrightarrow \text{thiamine-PP} + \text{AMP}^5 \quad (5)$$

The two compounds shown as products of reaction 1 both have been isolated from enzymatic reaction mixtures. One compound was identified as pyrimidine-P by analyses which showed one mole of phosphorus per mole of pyrimidine. Pyrimidine was measured spectrophotometrically as well as by microbiological assay with a mutant of *Salmonella typhimurium* which requires this specific pyrimidine or thiamine for growth. Since the compound which is thought to be pyrimidine-PP is quite labile, it has not been possible to isolate it in large enough quantities for accurate phosphorus analyses. Indirect evidence which indicates that it is pyrimidine-PP includes (a) an elution pattern from Dowex-1 columns which is similar to that of cytidine diphosphate, (b) its relative lability to acid hydrolysis (when compared to pyrimidine-P) to yield both the free pyrimidine and pyrimidine-P, (c) the inhibition of the formation of thiamine-P (reaction 3) by PP (which presumably is a product of reaction 3), (d) its conversion to pyrimidine-P and free pyrimidine by phosphatases, and (e) its formation enzymatically from pyrimidine-P in the presence of ATP. Whether or not pyrimidine-P is an obligate intermediate in the formation of pyrimidine-PP cannot be decided from the evidence currently available.

Thiazole-P was prepared by cleaving thiamine-P with sulfite and then chromatographing on Dowex-1 (formate) to separate the compound from the other components of the reaction mixture. The isolated compound, which contained by analysis one mole of phosphorus to one of thiazole, was shown by paper chromatography to be identical with the compound formed enzymatically from thiazole and ATP (reaction 2). The isolated thiazole-P also was able to serve as substrate along with pyrimidine-PP for the synthesis of thiamine-P.

The products of reactions 3, 4 and 5 have been identified by comparing their mobilities on paper chromatograms, in a variety of systems, with the mobilities of the corresponding known compounds. Thiamine cannot be used as a substrate in place of thiazole for reaction 2. Free thiazole cannot be used as substrate for reaction 3 and thiamine-P cannot be used as substrate for reaction 5. Thus thiazole-P, thiamine-P, and thiamine are all necessary intermediates in the biosynthesis of thiamine-PP from pyrimidine-PP and thiazole.

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(1) This work was supported by a grant from the National Science Foundation.

(2) D. L. Harris and J. Yavit, *Fed. Proc.*, **16**, 192 (1957).

(3) I. G. Leder, *Fed. Proc.*, **18**, 270 (1959).

(4) Abbreviations used are: pyrimidine, pyrimidine-P, and pyrimidine-PP for 2-methyl-4-amino-5-hydroxymethylpyrimidine, the orthophosphoric acid ester and the pyrophosphoric acid ester of this compound, respectively; thiazole and thiazole-P for 4-methyl-5-β-hydroxyethylthiazole and the orthophosphoric acid ester of this compound, respectively; thiamine-P and thiamine-PP for thiamine mono- and diphosphate; AMP, ADP, and ATP for adenosine mono-, di-, and triphosphate; and P and PP for inorganic ortho- and pyrophosphate.

(5) These compounds are assumed to be the products of the reactions shown even though they have not yet been well characterized as such.

(6) Karl T. Compton Fellow of the Nutrition Foundation (1956–1959).

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RECEIVED JUNE 1, 1959

TRIMERIC DIMETHYLAMINOBORINE

Sir:

The first of the "saturated" boron-nitrogen six membered ring compounds to be reported was the trimer of N-methylaminoborine,[1] which was prepared by heating methylamine-borine. In con-

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(1) T. C. Bissot and R. W. Parry, THIS JOURNAL, **77**, 3481 (1955).