# Ion Pairing of Magnesium Sulfate in Seawater: Determined by Ultrasonic Absorption

Abstract. Data from ultrasonic absorption in synthetic and natural seawater can be used to calculate pairing of magnesium and sulfate ions in seawater. Calculation under the assumption that data from ion pairing in single salt solution can be applied to seawater solution results in a value of 9.2 percent for the amount of magnesium paired with sulfate and 17.5 percent for sulfate paired with magnesium.

Pytkowicz, Duedall, and Connors (1) discussed the extent to which the Mg<sup>++</sup> ion is paired with the  $SO_4^{--}$ ion in seawater and concluded that between 39 and 53 percent of the total amount of the magnesium ions are paired with sulfate ions. This value is much higher than the figure of 11 percent calculated by Garrels and Thompson (2) and that of 3 percent calculated by Platford (3). Acoustic data show that 9.2 percent of the  $Mg^{++}$  is paired with  $SO_4 = -$ .

Calculations of MgSO<sub>4</sub> ion pairing in seawater to date have not made use of ultrasonic-absorption measurements (4, 5) in natural and synthetic seawater. In view of the fact that ultrasonic absorption in MgSO<sub>4</sub> solutions is proportional to the concentration of the associated or paired ions (6) (determined by conductivity measurements) and since neither MgCl<sub>2</sub>, Na<sub>2</sub>SO<sub>4</sub>, nor NaCl demonstrates significant ultrasonic absorption in pure water or seawater (4, 5), my calculations of the extent of MgSO<sub>4</sub> ion pairing in seawater were based on acoustic data.

Kurtze and Tamm (4) and Wilson and Leonard (5) found sound absorption in synthetic seawater equivalent to that observed in a pure-water solution of MgSO<sub>4</sub> at a concentration of 0.014 mole per liter. These two separate measurements agree within 10 percent. The measurements by Kurtze and Tamm (4) at 20°C were done with synthetic seawater containing (mole/ liter): Na+, 0.454; K+, 0.01; Mg++, 0.052; Ca++, 0.010; Cl-, 0.530; Br-, 0.001;  $SO_4^{--}$ , 0.0275; and  $CO_3^{--}$ 0.0025.

When we say that ultrasonic absorption in a solution of aqueous MgSO<sub>4</sub> (0.014 mole per liter) is equivalent to that observed in seawater, we mean that only 34 percent of this concentration (or 0.0048 mole per liter) is effective, because this is the extent to

18 AUGUST 1967

which MgSO<sub>4</sub> is paired in aqueous solution according to Fisher (7). Therefore, the extent of ion pairing of  $Mg^{++}$  to  $SO_4^{--}$  in seawater is 9.2 percent (0.0048/0.052), and that of  $SO_4^{--}$  to  $Mg^{++}$  is 17.5 percent (0.0048/0.0275). The values agree closely with 11 and 21.5 percent, respectively, obtained by Garrels and Thompson (2).

These calculations apply only to atmospheric-pressure measurements. Any attempt to make calculations at elevated pressures would have to take into consideration the large decrease in acoustic absorption (8) (about 60 percent) and the rather small decrease in the total amount of ion pairing of  $MgSO_4$  (4) (about 10 percent) observed at 1000 atmospheres. Fisher (8) showed that these apparently contradictory effects are resolved within the Eigen and Tamm multistate dissociation model (9) in which three forms of ion pairs interact through two pressure-dependent chemical reactions.

Experiments with acoustic absorp-

tion are an independent source of data to be considered in defining one aspect of the chemistry of seawater, namely, the amount of  $Mg^{++}$  ions paired with  $SO_4^{--}$  ions. My initial calculation supports the results of Garrels and Thompson (2).

## F. H. FISHER

Marine Physical Laboratory of the Scripps Institution of Oceanography, University of California, San Diego

### **References and Notes**

- R. M. Pytkowicz, I. W. Duedall, D. N. Connors, Science 152, 640 (1966).
  R. M. Garrels and M. E. Thompson, Amer. J. Sci. 260, 57 (1962).
  R. F. Platford, J. Fish. Res. Board Can. 22, 113 (1965)
- (1965). 13
- 4. G. Kurtze and K. Tamm, Acoustica 3, 33 (1953).
   O. B. Wilson and R. W. Leonard, J. Acous.
- S. D. Witson and R. W. Leonard, J. Acous. Soc. Amer. 26, 223 (1954).
  D. A. Bies, J. Chem. Phys. 23, 428 (1955).
  F. H. Fisher, J. Phys. Chem. 66, 1607 (1962).
  J. Acoust. Soc. Amer. 38, 2595 (1965). (1965).
- M. Eigen and K. Tamm. Z. Elektrochem. 66, 93 (1962); F. H. Fisher, J. Phys. Chem. 69, 695 (1965). 9.
- 10. I thank Dr. P. Rudnick for his helpful suggestions. Research sponsored by ONR and NSF.

19 April 1967

# Valyl-Transfer RNA: Role in Repression of the **Isoleucine-Valine Enzymes in Escherichia coli**

Abstract.  $\alpha$ -Aminobutyric acid is activated but not transferred to valine-specific transfer RNA and is unable to repress the isoleucine-valine enzymes in Escherichia coli strain W.  $\alpha$ -Amino- $\beta$ -chlorobutyric acid is activated and transferred to valinespecific transfer RNA and completely replaces valine in repression.

There is evidence that certain amino acids must be activated in order to repress their own biosynthetic enzymes (1). The importance of activation for repression was shown by the effect of either the inhibition or the alteration (by mutation) of an aminoacyl-tRNA synthetase (2). Since these enzymes catalyze both the activation of the amino acid as well as the attachment of the amino acid to tRNA, the relevant reaction required for repression is not apparent. Thus, either the formation of the aminoacyl-synthetase complex, the amino acid-adenylate synthetase complex, or aminoacyl tRNA could be the key step for the participation of amino acids in repression. In one study, amino acid attachment to tRNA appears to be the important reaction in that strains of Salmonella typhimurium containing small amounts of histidine-specific tRNA were derepressed for the histidine biosynthetic enzymes (3).

I now report evidence for the par-

ticipation of valyl-tRNA in the repression of the isoleucine-valine enzymes in Escherichia coli strain W. In these experiments two valine analogs, DL- $\alpha$ -aminobutyric acid (ABA) and DL-threo- $\alpha$ -amino- $\beta$ -chlorobutyric aciđ (ACBA) were used (4). Both compounds have been shown, by the amino acid-dependent exchange of ATP and PPi<sup>32</sup>, to be activated by E. coli valyltRNA synthetase (5).

The effect of ABA and of ACBA

Table 1. Supplements to the minimal medium. ABA was added at a concentration of 500  $\mu$ g/ml and ACBA was added at a concentration of 75  $\mu$ g/ml.

Supplement	Medium ( $\mu g/ml$ )		
	Com- plete	Valine limiting	Iso- leucine limiting
L-Isoleucine	50	50	12
L-Valine	40	0	50
L-Leucine	50	50	50
Glycyl-L-valine	25	25	0
Pantothenic acid	10	10	10

823