

Fig. 2. Oscilloscopic record of stimulus movement (upper trace) and the corresponding tracking movement of the eye (lower trace). Velocity of stimulus movement constant at 21.5 deg/sec. Extent of movement, 8 deg, left to right. Horizontal sweep time, 200 msec/cm. Change in angular position of eye is linearly related to voltage change. Voltage scale, 5 volt/cm (vertical).

of the target, which consisted of a dark vertical hairline and which moved 8 deg from right to left at a constant velocity. The constant velocity is indicated by the linear sides of the envelope. Cessation of motion of the stimulus is indicated by the point where the sides of the envelope become parallel.

The eye-movement record (lower trace) in Fig. 2 shows a reaction time of approximately 160 msec and a pattern of an initial and final saccadic movement with a brief intermediate smooth pursuit movement of duration approximately 200 msec. A slight overshoot is evident for about 600 msec after cessation of the movement of the stimulus. When this record was made, the stimulus was visible in a fixed position both before and after movement. Eye fixations at these stages of the display are indicated by the horizontal components of the record at the beginning and the end of the eye-movement trace. The noise level in the record is a combination of electronic noise and physiological nystagmus.

From records such as that shown in Fig. 2, reaction time and rate characteristics of eye movement are determined easily, as well as lag-lead errors with respect to the stimulus at any point in time. Considering the flexibility of the stimulus-generating system described, it will now be possible to obtain systematic and extensive data on the eye as a tracking mechanism, and correlated with these data, the perceptual data for moving stimuli. Moreover, the principle of measurement used in conjunction with a miniaturized detector which can

be worn by the observer without external support will make possible for the first time eye-movement measurement with free head movement. The miniaturization of the detector and the use of the present principle of measurement in recording vertical motions of the eye are currently being developed.

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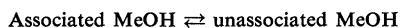
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1. G. Westheimer, *A.M.A. Arch. Ophthalmol.* **52**, 932 (1954).
2. Research on design and development of this technique for measuring eye movements has been supported by the National Science Foundation. We acknowledge the valuable assistance rendered by Theodore Marton of Princeton University.
3. RCA 931-A or RCA 1P-21. The latter is a "selected" tube; for a given noise level it has greater sensitivity than the former.
4. Dumont model 185-A, modified to provide electronic regulation of the anode voltage supply within the switch.
5. A headpiece for each observer is made from fast-setting plaster bandage. The detector is attached to the headpiece by screws and a metal base imbedded in the plaster.

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### Electrolyte-Solvent Interactions: Effect of Electrolytes on Vibrational Spectrum of Methanol

**Abstract.** The addition of quaternary ammonium halides to dilute solutions of methanol in benzene shifts the equilibrium



to the left. For several tetrabutylammonium salts, the order of increasing effectiveness in causing the shift is: picrate < nitrate < bromide < chloride. The results provide evidence for the solvation of electrolytes by polar molecules.

There has been considerable interest in spectral studies of electrolyte-solvent interactions in recent years. Most of these have involved metallic ions and a study of their ultraviolet or visible spectra in various solvents. The results of these studies have been interpreted in terms of charge-transfer complexes.

Another question is whether the extent of electrolyte association—for example, ion-pair formation—affects these spectra. Quite recently Popov and Humphrey (1) have shown that when anion-cation interaction is purely electrostatic, as in the quaternary ammonium salts, the extent of ion-pair formation has no effect on the ultraviolet and visible spectra.

No corresponding work has been done in the infrared. In this region of vibrational spectra it is conceivable that the interaction of electrolytes with polar molecules would modify the spectra of the latter—for example, by solvation.

We report here what is, as far as we know, the first observation of such an interaction—the influence of electrolytes on the equilibrium between associated and nonassociated methanol when both are dissolved in benzene.

It is well known that the O-H stretching vibration for methanol occurs at  $2.75 \mu$  and that the (self)-association peak occurs at  $3.0 \mu$  in pure liquid methanol (2). In a moderately dilute solution ( $>25 \times 10^{-3}M$ ) of methanol in a nonabsorbing, nonpolar solvent (benzene), both peaks are present, their intensity ratio depending on the total concentration. In a very dilute solution the associated peak is absent. A plot of absorbancy versus total concentration for both peaks is shown in Fig. 1. The addition of an electrolyte tends to enhance the associated peak at the expense of the nonassociated one. A plot of the concentration ratio of the two forms as a function of total concentration is shown for various concentrations (molar concentrations are used throughout this report) of the electrolyte—tetrabutylammonium bromide ( $\text{Bu}_4\text{NBr}$ ). The cationic charge is buried in a paraffin ball in this salt, and in the environment most of the electrolyte exists in the form of electrostatically associated ion pairs and quadrupoles, with the free-ion concentration rather low. However, in spite of what are probably rather weak electrostatic ion-dipole interactions, the effect of the salt in enhancing the associated methanol concentration is considerable, increases in the two concentrations being roughly equal to each other.

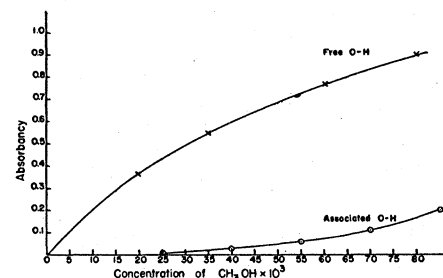


Fig. 1. Absorbancy of the free O-H ( $2.75 \mu$ ) and associated O-H ( $3.0 \mu$ ) peak as a function of total concentration in benzene.

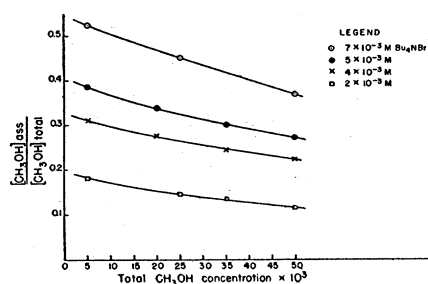


Fig. 2. Effect of various concentrations of tetrabutylammonium bromide on the equilibrium between free and associated methanol.

The effect of changing the anion is striking. Thus, for several tetrabutylammonium salts, the molar-extinction coefficient of associated methanol is as follows: for the picrate,  $\sim 0.0$ ; for nitrate, 6.5; for bromide, 11.0; and for chloride, 12.0. Evidently the effectiveness of the anion in producing association increases in the same order as the anion charge density. This suggests that association in these cases is not self-association but ion-dipole association—that is, solvation.

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### Occurrence of $\beta$ -Aminoisobutyric Acid in *Mytilus edulis*

**Abstract.**  $\beta$ -Aminoisobutyric acid was isolated from organ extracts of *Mytilus edulis*. Ion-exchange resins and large-scale paper chromatography were used to isolate minute quantities of the compound.  $\beta$ -Aminoisobutyric acid was identified by paper chromatography in several solvents and by conversion to DNP- $\beta$ -aminoisobutyric acid and subsequent chromatography of the derivative in several solvents.

$\beta$ -Aminoisobutyric acid was first found in human urine by Crumpler *et al.* (1). They observed that some individuals excrete large amounts of this amino acid and that the excretion is an individual characteristic determined genetically. Several papers dealing with genetic factors involved in the excretion of this amino acid (2) have appeared since the paper by Crumpler *et al.* was published. Fink *et al.* found that  $\beta$ -aminoisobutyric acid is formed in the rat from thymine (3). Awapara

and Shullenberger (4) observed that leukemic patients excrete large quantities of this acid only when given nitrogen mustard (methyl-bis[ $\beta$ -chloroethyl]amine hydrochloride) or thymine.

During an investigation of nitrogen metabolism in marine invertebrates, we observed that extracts of *Mytilus edulis* contain a compound with all the characteristics of  $\beta$ -aminoisobutyric acid as determined by paper chromatography. It was not an  $\alpha$ -carboxyl amino acid, as was shown by treatment with copper carbonate (5). Extracts of *M. edulis* contain a large number of amino acids in large quantities. Proper identification by paper chromatography became difficult. The quantity of the unknown was not very large, and to isolate it in sufficient quantities for chemical analysis would be something of a tour de force. We have, however, isolated minute amounts of this compound and shown it to be chromatographically identical with  $\beta$ -aminoisobutyric acid.

For isolation, 100 gm of pooled organs of *Mytilus* were extracted with 80 percent ethanol (6). The extract was treated first with Amberlite CG-50  $H^+$  to remove basic compounds, then with Dowex 50,  $H^+$ , to remove all amino acids except taurine and other strongly acidic substances. The amino acids were displaced from the column with 4N  $NH_4OH$ . The effluent was evaporated under a vacuum. The residue was dissolved in 4 ml of water and decolorized with activated charcoal. To isolate the unknown from all other ninhydrin-reactive compounds, the solution was chromatographed on several sheets of filter paper. Known  $\beta$ -aminoisobutyric acid was chromatographed on the same paper to serve as a guide. The area corresponding to  $\beta$ -aminoisobutyric acid was cut and eluted. The eluate was chromatographed three more times with different solvents until only one ninhydrin-reactive substance was obtained. The  $R_f$  values of the unknown and known  $\beta$ -aminoisobutyric acid were identical in several solvents, and when mixed they could not be separated chromatographically (Table 1). A DNP derivative was prepared by the method of Sanger (7). Chromatography of the DNP derivative and of DNP- $\beta$ -aminoisobutyric acid showed that they had identical  $R_f$  values in several solvents (Table 2). No separation occurred when they were mixed. From this evidence we concluded that the unknown was  $\beta$ -aminoisobutyric acid.

This compound is present in all parts of the animal. Analyses were carried out chromatographically, and the estimated concentrations are shown in Table 3. This compound appears to be present in other marine invertebrates,

Table 1.  $R_f$  values of unknown and  $\beta$ -aminoisobutyric acid.

Solvent	$R_f$
Lutidine, water (62:38)	0.34
Phenol, water (72:28)	0.58
<i>n</i> -Butanol, acetic acid, water (120:30:50)	0.43
<i>n</i> -Butanol, formic acid, water (75:15:10)	0.48

Table 2.  $R_f$  values of DNP- $\beta$ -aminoisobutyric acid and DNP-unknown.

Solvent	$R_f$
<i>n</i> -Butanol, ethanol, water (40:10:50)	0.71
<i>n</i> -Butanol, water (saturated)	0.53
<i>n</i> -Butanol, 0.1% $NH_3$ (saturated)	0.40
<i>m</i> -Cresol, 0.3% $NH_3$ (saturated)	0.74

Table 3. Concentration of  $\beta$ -aminoisobutyric acid in organs of *Mytilus edulis*.

Organ	Concentration ( $\mu$ mole/100 gm of fresh tissue)
Mantle	44
Gill	103
Viscera	62
Foot	93

but its identity needs to be established with certainty. It is interesting that mammals and invertebrates catabolize thymine by a similar mechanism.  $\beta$ -Alanine also seems to be present in *Mytilus* and in several species of marine invertebrates studied (8). If these two amino acids are found in more species, there will be little doubt that thymine and uracil are catabolized to give rise to  $\beta$ -aminoisobutyric acid and  $\beta$ -alanine, respectively (9).

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9. This work was supported by grants from the Robert A. Welch Foundation, Houston, Tex., and from the National Institutes of Health.

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