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THE INTERIONIC ATTRACTION THEORY OF ELECTROLYTES

By Dr. D. A. MacINNES

THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH

IN 1883 Arrhenius advanced the theory that in solutions of salts, acids and bases the molecules are, partly at least, split up into positively and negatively charged *ions*. Thus, for example, an aqueous solution of sodium chloride was conceived to consist in large part of positively charged sodium ions and negatively charged chloride ions, which may be represented by Na^+ and Cl^- . The theory encountered vigorous opposition, based mostly on the apparently quite reasonable objections that sodium, for instance, which is well known to be a soft inflammable metal, could hardly be present in water, and also, that if positive and negative ions are as close together as they must be in a solution they would certainly be expected to attract each other and recombine. In spite of these objections and others, the theory gained adherents rapidly since it accounted more or less adequately for the main facts about solutions of what we now term electrolytes. The most im-

portant facts about such solutions are that, in the first place, they are conductors of electricity and, in addition, that they exhibit abnormal thermodynamic properties, by which we mean that, for example, they produce exceptionally large depressions of the freezing points and vapor pressures of the solvents in which they are dissolved.

The mental picture with which Arrhenius worked was somewhat as shown in Fig. 1. The symbols + and - represent the positive and negative ions, respectively. A part of the ions are considered to be free, and another portion of the ions are in contact with each other, forming neutral molecules. The former were considered to conduct electricity and the latter to have no influence on the conductance of a solution. The positions of the ions and neutral molecules would, of course, be rapidly shifting, due to thermal vibrations. Neutral molecules were thought to be constantly break-

considerable doubt concerning its classification at that time. The authors are indebted to B. L. Robinson, of the Gray Herbarium, and H. Harms and O. E. Schulz, of the Botanisches Museum, Berlin, for having identified this sweet clover since as an annual flowering form of the typically biennial *Melilotus dentata* (W. K.) Pers. Schulz describes the species as occurring sparingly from central Europe eastward to central Asia, usually on salty soils. It does not appear to have become naturalized in America.

The non-bitter condition of this one stock of *M. dentata* led us to assemble an extensive collection of the species for further study. We are indebted mainly to several European correspondents for seed. Examination of 28 different lots (27 of which were biennials) mostly from central Europe, but a few from Russia and one from Mongolia, has shown that all are free of the characteristic bitter taste of the common sweet clovers, *M. alba* and *M. officinalis*. Apparently *M. dentata* as a species is typically non-bitter. Suvorov's³ report on the Russian species of sweet clover bears out this conclusion.

As the bitterness of the common sweet clovers is due mainly, if not entirely, to coumarin and closely related substances, it was anticipated that *M. dentata* would differ in its content of these compounds. The analytical findings show clearly that this is the case. Roberts and Link have recently developed a micro-method, to be described elsewhere, for estimating coumarin, melilotic acid and coumaric acid, which not only permits the determination of these substances separately but to an accuracy of about 0.001 per cent. on the dry basis. The earlier methods of Obermayer,⁴ Kanewskaja and Fedorowa,⁵ Duncan and Dustman⁶ and Clayton and Larmour⁷ severally encounter various analytical difficulties, such as failure to separate the three constituents, inclusion of other phenolic substances in the coumarin fraction and interference by plant pigments. These disadvantages are largely overcome by the procedure used in the present investigation.

Using the highly refined method of Roberts and Link no coumarin, melilotic acid or coumaric acid were detected in the vegetative tissues of *M. dentata* at the flowering stage. Seven different races were tested as follows: F.P.I. 90753, Botanic Garden, Peiping, China; Botanic Garden, Copenhagen, Denmark; Thüringen and Saxony, Germany; Moravia, Czechoslovakia; Saratov and West Siberia, U.S.S.R.; Altai Mountains, Mongolia. All these stocks, except those

from the botanical gardens and possibly that from Saratov, represent the forms indigenous to these respective regions, according to the information supplied by the correspondents to whom we are indebted for the seed. It is probable, therefore, that if these substances are present at all in the leaves and stems of *M. dentata*, the amounts are less than 0.001 per cent.

A sample of common yellow sweet clover, *M. officinalis*, analyzed at the same stage of development, was found to contain 0.65 per cent. coumarin, 0.25 per cent. melilotic acid and 0.036 per cent. coumaric acid. The corresponding values for a commercial strain of common white sweet clover, *M. alba*, were found to be 0.36 per cent., 0.27 per cent. and 0.048 per cent. The common sweet clovers vary rather widely in composition from strain to strain and at different stages of development so that the above results are not necessarily representative of the respective species.

A small amount of coumarin is present in the seed of *M. dentata*. Analysis of three of the above-mentioned stocks (Peiping, Copenhagen and Moravia) showed 0.021 per cent., 0.074 per cent. and 0.040 per cent., respectively, on the dry basis. A sample of *M. officinalis* seed run concurrently was found to contain 0.63 per cent. coumarin and an *M. alba* lot, 0.46 per cent. It will be noted that these values are roughly ten times as high as those for *M. dentata*. That the material determined as coumarin in the analysis of the seed is actually that substance was shown by the isolation of 25 mg of pure coumarin from 31 g of *M. dentata* (Copenhagen strain) seed. The melting point of the isolated material and the mixed melting point with pure coumarin were 71.0–71.5° C., the same as that for pure coumarin. The iodine-potassium iodide test and certain coupling tests were positive, and the chemical characteristics exhibited during the isolation were identical with those of coumarin. The regular method of analysis indicates that if any melilotic acid and coumaric acid occur in the seed of *M. dentata* the amounts are extremely small.

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BOOKS RECEIVED

- BLACKWOOD, O. H. *An Outline of Atomic Physics*. Second edition, revised. Pp. ix+414. 29 figures. Wiley. \$3.75.
- BORING, EDWIN G. and others. *A Manual of Psychological Experiments*. Pp. ix+198. Illustrated. Wiley. \$1.75.
- JONES, ARTHUR T. *Sound*. Pp. xii+450. 141 figures. Van Nostrand. \$3.75.
- OSGOOD, WILLIAM F. *Mechanics*. Pp. xv+495. Illustrated. Macmillan. \$5.00.
- PORTEUS, S. D. *Primitive Intelligence and Environment*. Pp. viii+325. Macmillan. \$3.00.
- SPINNEY, L. B. *A Textbook of Physics*. Fifth edition. Pp. xii+721. 481 figures. Macmillan. \$3.75.
- ³ Semenovodstvo, No. 2 (quoted from Herb. Abstr. 5: 153).
- ⁴ *Zeits. Anal. Chem.*, 52: 172–191.
- ⁵ *Ibid.*, 93: 176–180.
- ⁶ *Jour. Ind. Eng. Chem.*, 6: 210–213.
- ⁷ *Can. Jour. Res. (C)* 13: 89–100.

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The report that constitutes the chapters of this volume was prepared by a special committee appointed by the American Association of University Professors . . . with the onset of the depression it became quickly apparent that conditions were developing, both on the campus and off of it, that would unquestionably react adversely upon the teaching profession. It was the recognition of this that led to the appointment of Committee Y . . .

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Secondly, the Committee has ventured interpretations of the data it has collected . . . in accord with the third purpose of the Committee: to prepare a report that will stimulate thinking and engender discussion among those engaged in college work and among laymen as well.

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