

## ON GUAIACOL SOLUTIONS

### I. THE ELECTRICAL CONDUCTIVITY OF SODIUM AND POTASSIUM GUAIACOLATES IN GUAIACOL

By THEODORE SHEDLOVSKY AND HERBERT H. UHLIG

(From the Laboratories of The Rockefeller Institute for Medical Research)

(Accepted for publication, December 1, 1933)

#### INTRODUCTION

Chemists need information about the behavior of electrolytes in non-aqueous solutions. Biologists likewise need this information since there is considerable evidence that the protoplasmic surface consists of such substances and they have been employed in models designed to imitate the action of the living cell.

A quantitative relationship between the equivalent electrical conductance and the concentration of dilute electrolytic solutions in which the solute is considered to be entirely in the form of free ions has been derived theoretically by Onsager,<sup>1</sup> following the work of Debye and Hückel.<sup>2</sup> In this treatment the decrease in equivalent conductance with increasing concentration is attributed to a decrease in the ionic mobilities arising from the influence of interionic electrostatic forces. For strong electrolytes in water, calculations based on Onsager's equations are in good agreement with measurements on dilute solutions.<sup>2,3</sup>

However, similar calculations, based on the assumption of complete ionization, do not adequately represent the facts for electrolytes in most non-aqueous solvents which, in general, have dielectric constants appreciably lower than that of water. In such solvents all electrolytes appear to be "weak," and measurements on these solutions seem to indicate that a considerable portion of the solute is not in the form of "free" ions.

<sup>1</sup> Onsager, L., *Phys. Z.*, 1927, **28**, 277.

<sup>2</sup> Debye, P., and Hückel, E., *Phys. Z.*, 1923, **24**, 305.

<sup>3</sup> Shedlovsky, T., *J. Am. Chem. Soc.*, 1932, **54**, 1411; MacInnes, D. A., Shedlovsky, T., and Longworth, L. G., *Chem. Rev.*, 1933, **13**, 29.

It will be shown in this paper that the electrical conductivity of solutions of sodium and potassium guaiacolate in guaiacol can be accounted for satisfactorily by assuming an ionic equilibrium in addition to the interionic attraction effects on the mobilities of the ions.

Mass action constants for sodium guaiacolate and potassium guaiacolate can thus be calculated from conductivity measurements. It is desirable, however, to obtain these constants if possible from another type of measurement. Such an independent method is available in the determination of the partition coefficients of the electrolyte between guaiacol and water,<sup>4</sup> the two liquids forming non-miscible phases. Since, however, the nature of distribution experiments is such as to render the two non-miscible liquids saturated with each other, a fair comparison between the two methods for determining the ionization constants can be made only if the conductivity measurements also refer to solutions in guaiacol saturated with water. Consequently, the conductivity measurements reported in this paper, from which the ionization constants are computed, were made on solutions containing guaiacol from the same source and with practically the same water content as in the case of the subsequent distribution experiments.

In computing the results from the conductivity data it is necessary to know the dielectric constant, viscosity, and density of the "wet" guaiacol solvent. These values were measured and are reported in this paper, since they are not available in the literature. For completeness the corresponding values for dry guaiacol are also given. The same computations which give the ionization constants of the alkali guaiacolate in wet guaiacol from conductivity determinations, also give the limiting equivalent conductance values ( $\Lambda_0$ ), corresponding to the sum of the positive and negative ion mobilities at zero concentration. These ( $\Lambda_0$ ) values have been combined with corresponding transference numbers, yielding values for the limiting mobilities of potassium, sodium, and guaiacolate ions in wet guaiacol.

#### THEORETICAL

In discussing weak electrolytic solutions we shall assume that only a portion of the solute is in the form of free ions able to carry current,

<sup>4</sup> The distribution of sodium and potassium guaiacolate between water and guaiacol is the subject of the following paper.

while the rest can be considered "undissociated," and that a corresponding ionic equilibrium exists in accordance with a mass action equation. However, it is not necessary to assume that the undissociated solute consists of stable molecules bound by chemical or quantized forces. We prefer to consider them to be ion pairs as suggested by Bjerrum.<sup>5</sup>

The electrostatic force between a pair of ions of opposite charge which have approached to "contact" tends to hold them together as a stable pair. The mutual potential energy of this ion pair, in accordance with Coulomb's law, depends on the charges, the dielectric constant of the medium, and the distance between the charge centers (the sum of the ionic radii, if we consider the ions to be spherical). Now, if the average kinetic energy of the solvent molecules is greater than this potential energy, the ion pair cannot exist for any appreciable time. This is the case for strong uni-univalent electrolytes in water. However, if the average kinetic energy of the solvent molecules is less than the mutual potential energy of the ion pair, it will exist until it is struck by a solvent molecule having sufficient kinetic energy to break it up.

This viewpoint predicts that there should be relatively more ion pairs (undissociated solute) when the dielectric constant is low, when the ions are small, when the charges are large, and when the temperature is low. Calculations of ionization constants as a function of ion size, dielectric constant, etc., based on this view were made by Bjerrum<sup>5</sup> for electrolytes in solvents of relatively high dielectric constant, and more recently by Fuoss and Krauss<sup>6</sup> for tetraisoamylammonium nitrate in dioxane-water mixtures, and for silver nitrate in benzonitrile, acetonitrile, and ammonia.

Our problem is to interpret the electrical conductivity of weak electrolytic solutions; namely, of sodium guaiacolate and potassium guaiacolate in guaiacol. The mass action equation for the ionic equilibrium we have assumed is

$$K = \frac{(A_{M^+})(A_{G^-})}{(A_{M^+G^-})} = \frac{(C\theta\gamma)^2}{C(1-\theta)} \quad (1)$$

<sup>5</sup> Bjerrum, N., *K. Danske Vidensk. Selsk.*, 1926, **7**, No. 9.

<sup>6</sup> Fuoss, R. M., and Kraus, C. A., *J. Am. Chem. Soc.*, 1933, **55**, 1019.

in which  $A_{M^+}$  is the activity of the positive (metal) ions,  $A_{G^-}$  is the activity of the negative (guaiacolate) ions, and  $A_{M^+G^-}$  is the activity of the undissociated ions, or paired ions.  $C$  is the concentration,  $\theta$  the "degree of dissociation," and  $\gamma$  the mean ionic activity coefficient. We assume that the undissociated portion behaves as a normal solute, and consequently has an activity equal to its concentration.

The mean ionic activity coefficient will be computed from the Debye-Hückel equation

$$-\log_{10} \gamma = \frac{a \sqrt{C\theta}}{1 + b \sqrt{C\theta}} \quad (2)$$

in which

$$a = \frac{0.4343 e^2}{(DkT)^{3/2}} \sqrt{\frac{2 \pi N}{1000}}$$

and

$$b = \sqrt{\frac{8 \pi N e^2 r^2}{1000 DkT}}$$

$e$  = electronic charge,  $N$  = Avogadro's number,  $k$  = Boltzmann's constant,  $D$  = dielectric constant,  $T$  = absolute temperature,  $r$  = distance of closest approach between ions. For water-saturated guaiacol at 25°C.  $a = 6.52$ , and for sodium and potassium guaiaculates in this solvent we have used an approximate value of 7 Å. for  $r$  (estimated from crystal structure data), which gives a value of  $b = 5.36$ . Actually, of course,  $r$  is not the same for the two salts, but nearly enough so for the present purpose, since the term  $b\sqrt{C\theta}$  enters as a correction. We shall assume that the Onsager equation adequately represents the relationship between the equivalent conductance and the concentration for the dissociated (free) ions. For a completely dissociated electrolyte this is  $\Lambda_e = \Lambda_0 - A\sqrt{C_i}$ , in which  $\Lambda_e$  is the equivalent conductance,  $\Lambda_0$  the limiting value of equivalent conductance at zero concentration,  $C_i$  is the ionic concentration,

$$A = \alpha \Lambda_0 + \beta = \frac{8.18 \times 10^{-8}}{(DT)^{3/2}} \Lambda_0 + \frac{82}{\eta (DT)^{1/2}}$$

$\eta$  being the viscosity, and  $D$  and  $T$  having the same meaning as above. For water-saturated guaiacol  $A = 2.93 \Lambda_0 + 19.36$ . The equivalent

conductance,  $\Lambda$ , is defined as  $\Lambda = \frac{100 \bar{L}}{C}$ ,  $\bar{L}$  being the specific conductance; thus  $\Lambda_\epsilon = \frac{1000 \bar{L}}{C_i}$ .

Since  $C_i = C\theta$ , the Onsager equation gives us

$$\Lambda/\theta = \Lambda_0 - (\alpha \Lambda_0 + \beta)\sqrt{C}\theta$$

or

$$\theta = \frac{\Lambda}{\Lambda_0 - (\alpha \Lambda_0 + \beta)\sqrt{C}\theta} \quad (3)$$

Fuoss and Kraus<sup>7</sup> have discussed the mathematical treatment of these equations and have indicated a convenient method of solution. It consists of assuming a provisional value of  $\Lambda_0$  and then computing values of  $\theta$  for the series of measurements, from equation (3) which is conveniently solved by successive approximations. Corresponding values of  $\gamma$  are then obtained from equation (2), and values of  $\gamma\sqrt{C}$  are plotted against  $\frac{\sqrt{1-\theta}}{\theta}$ . Since equation (1) can be easily transformed to  $\frac{\sqrt{K}\sqrt{1-\theta}}{\theta} \gamma\sqrt{C}$ , such a plot should give a straight line passing through the origin, with a slope of  $\sqrt{K}$ , if the correct value of  $\Lambda_0$  has been chosen. Successive values of  $\Lambda_0$  are assumed until this is found to be the case.

With the values of  $\Lambda_0$  and of  $K$  thus determined from a series of conductance measurements, a theoretical conductance curve corresponding to these constants can be computed by reversing the calculations described above. A direct graphical comparison between the measured and computed conductance values is thus afforded.

#### EXPERIMENTAL

1. *Guaiacol*.—Synthetic guaiacol (Kahlbaum's c.p. crystalline guaiacol) was redistilled under reduced pressure in a slow stream of nitrogen, using an all glass (Pyrex) distilling apparatus with a fractionating column. The distillate was protected from atmospheric moisture. Colorless fractions, having melting points from 28.0—28.36°C., were collected.<sup>8</sup>

<sup>7</sup> Fuoss, R. M., and Kraus, C. A., *J. Am. Chem. Soc.*, 1933, **55**, 476.

<sup>8</sup> The freezing point of guaiacol is quite sensitive to traces of impurities because of its high cryoscopic constant. We determined the molal freezing point lowering ( $\Delta T$ /mole of solute in 1 liter of solution) with water, toluene, and carbon tetrachloride. The values were 5.4°, 6.1°, and 6.4° respectively.

Although the melting point of guaiacol is several degrees above the temperature at which our conductivity measurements were made, namely 25°C., no difficulties from crystallization were encountered due to the readiness with which this substance supercools.

The solubility of water in guaiacol was determined from density measurements on a series of solutions containing known quantities of water in the solvent guaiacol. A plot of density against water content, extrapolated to the density of guaiacol saturated with water, was used for this purpose. The density measurements were made with a Sprengel pyknometer. Physical properties of dry and water-saturated guaiacol at 25°C. are listed in Table I.

TABLE I  
*Physical Properties of Dry and Water-Saturated Guaiacol at 25°C.*

|   | Anhydrous guaiacol | Water-saturated guaiacol |
|---|--------------------|--------------------------|
| Density.....  | 1.1289             | 1.1275                   |
| Dielectric constant*.....   | 11.8               | 14.3                     |
| Relative viscosity†.....  | 6.10               | 7.23                     |
| Specific conductance.....   | $1 \times 10^{-8}$ | $3-5 \times 10^{-8}$     |
| Solubility of water in guaiacol = 4.60 gm. water/100 gm. solution |                    |                          |

\* We are indebted to Dr. S. O. Morgan of the Bell Telephone Laboratories for the dielectric constant measurements.

† The viscosities (relative to water at 25°C.) were measured in an Ostwald viscosimeter. The relative viscosity values for various water contents in the guaiacol were

|                         |      |      |      |                 |
|-------------------------|------|------|------|-----------------|
| Per cent water.....     | 0    | 0.9  | 2.3  | 4.6 (saturated) |
| Relative viscosity..... | 6.10 | 6.44 | 6.81 | 7.23            |

2. *Sodium and Potassium Guaiaculates.*—The alkali guaiaculates were prepared by the reaction of the ethylates with guaiacol in a medium of anhydrous ethyl alcohol, from which the salts were subsequently crystallized. Freshly made alkali metal wire was introduced directly into anhydrous alcohol through a sodium press. After the metal had dissolved, an equivalent quantity of guaiacol was introduced. The crystallized salt was washed several times with anhydrous ether and then dried in an Abderhalden (vacuum) drier. The purity of the product was checked by titrating weighed samples with standard hydrochloric acid, and computing the alkali metal content.

The solubilities of the salts in anhydrous and water-saturated guaiacol at 25°C. were determined also by titration with standard acid. The results, expressed in moles of salt per thousand grams of solvent, were:

|                            | Anhydrous guaiacol | Water-saturated guaiacol |
|----------------------------|--------------------|--------------------------|
| Potassium guaiacolate..... | 0.0071             | 0.0763                   |
| Sodium guaiacolate.....    | 0.0063             | 0.154                    |

3. *Conductivity Measurements.*—The conductivity measurements were made in a "flask cell" of the type described by one of us,<sup>9</sup> having a cell constant of 0.0832. An alternating current conductivity bridge and an oil thermostat at 25.000°C. were used.<sup>10</sup> A known quantity of guaiacol (about 500 cc.) which had been almost, but not quite, saturated with conductivity water<sup>11</sup> was introduced into the cell and its conductance was measured. Then, successive weighed increments of a relatively concentrated stock solution of known guaiacolate content were added, and corresponding conductance determinations were made. Thus it was possible to measure the conductance of a whole series of concentrations in the same solvent. The solution in the cell was protected from atmospheric impurities at all times with purified nitrogen.<sup>9</sup>

It was interesting to know the effect of the water content of the solvent guaiacol on the conductance. This was determined by making a series of measurements, starting with a solution of guaiacolate in anhydrous guaiacol and successively increasing the water content.

#### RESULTS

The results of the conductivity measurements on solutions of sodium guaiacolate and potassium guaiacolate in wet guaiacol are summarized in Tables II and III respectively. The listed values of equivalent conductance have not had a solvent correction applied to them. We have assumed that the conductance of the solvent is due to ions arising from guaiacol, and this dissociation is practically repressed by the very much greater number of guaiacolate ions supplied by the salts.

The fact that the molal freezing point lowering of guaiacol with water was found to be no greater than with toluene or carbon tetrachloride, is definite evidence against the possibility of ions arising from the water in the solvent. For these reasons, and because the solutions were protected against foreign impurities throughout the course of the measurements, we believe that the solvent corrections should be neglected.

The effect of water content on the conductivity of sodium guaiacolate in guaiacol ( $C = 0.0009$  molal) is shown in Fig. 1, in which the

<sup>9</sup> Shedlovsky, T., *J. Am. Chem. Soc.*, 1932, **54**, 1415.

<sup>10</sup> Shedlovsky, T., *J. Am. Chem. Soc.*, 1930, **52**, 1793.

<sup>11</sup> This was done to make sure that no water would separate out in the subsequent additions of solute. The dielectric constant and viscosity of the nearly saturated guaiacol can be safely assumed to be the same as that of the completely saturated solvent for our purposes.

ratio of the equivalent conductance ( $\Lambda$ ) to the equivalent conductance in anhydrous guaiacol ( $\lambda^\circ$ ) is plotted against the water content, expressed as per cent of (water) saturation. The curve rises from a value of 1 at zero water content to 34.5 at 100 per cent (water) saturation.

TABLE II  
*Conductance of Sodium Guaiacolate in Wet Guaiacol at 25°C.*  
 Water content = 99 per cent saturated  
 Specific conductivity =  $5.18 \times 10^{-8}$

| Concentration mole/liter | $\Lambda = \frac{\text{Specific conductivity}}{\text{Concentration}} \times 10^8$ |            |
|--------------------------|---|------------|
|                          | Observed  | Calculated |
| 0                        | —   | 7.50       |
| 0.000206                 | 2.893   | 2.835      |
| 0.000771                 | 1.707   | 1.717      |
| 0.00224                  | 1.097   | 1.100      |
| 0.00454                  | 0.809   | 0.813      |
| 0.00901                  | 0.601   | 0.602      |
| 0.01666                  | 0.460   | 0.461      |

TABLE III  
*Conductance of Potassium Guaiacolate in Wet Guaiacol at 25°C.*  
 Water content = 98 per cent saturated  
 Specific conductivity =  $2.84 \times 10^{-8}$

| Concentration mole/liter | $\Lambda = \frac{\text{Specific conductivity}}{\text{Concentration}} \times 10^8$ |            |
|--------------------------|---|------------|
|                          | Observed  | Calculated |
| 0                        | —   | 8.00       |
| 0.000442                 | 2.461   | 2.463      |
| 0.000959                 | 1.808   | 1.819      |
| 0.002151                 | 1.300   | 1.301      |
| 0.003719                 | 1.037   | 1.032      |
| 0.005765                 | 0.862   | 0.857      |

The relatively great increase in conductance (over thirtyfold), cannot be satisfactorily explained on the basis of difference in the dielectric constants of anhydrous guaiacol ( $D = 11.8$ ) and wet guaiacol ( $D = 14.3$ ). It is rather due to the fact that the water molecules



(whose mole fraction is about  $\frac{1}{4}$  in water-saturated guaiacol) are definitely more polar than guaiacol molecules, and tend to orient themselves with some stability around the salt ions in the solution. This polarization of water dipoles in the strong electric fields around the ions may be regarded as an hydration which has the effect of increasing the size of the ions.

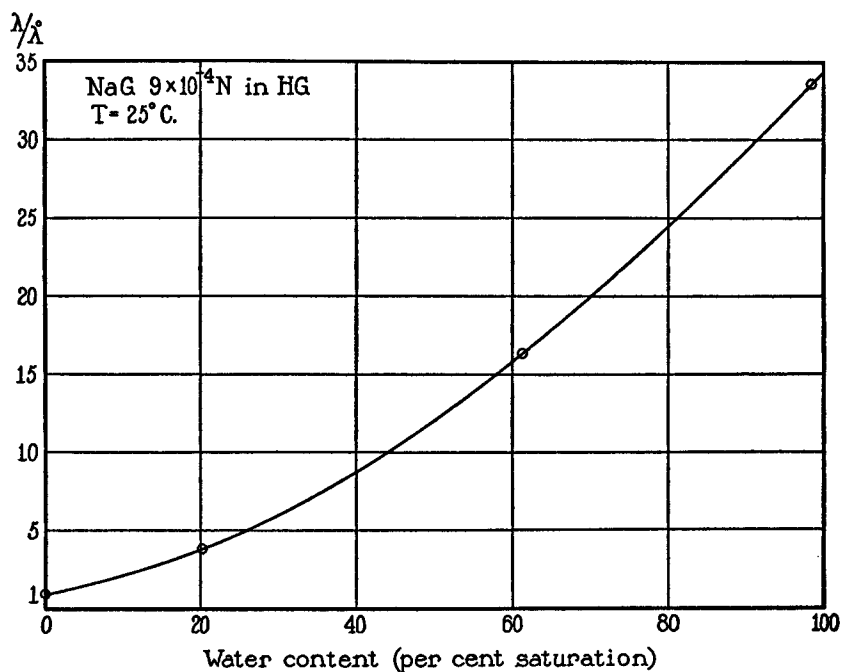


FIG. 1. Effect of water content on the conductance of sodium guaiacolate in guaiacol, expressed as the ratio of the observed conductance ( $\lambda$ ) to the conductance in anhydrous guaiacol ( $\lambda^\circ$ ).

It has been pointed out in the theoretical portion of this paper that, other things being equal, an increase in the size of ions tends to increase the "strength" of an electrolyte. On this basis, we may attribute the conductance increase with increasing water content to a greater number of free ions, capable of carrying current as the average size of the ions is increased.

From the results shown in Tables II and III values of the dissocia-

tion constants and the limiting conductances of sodium and potassium guaiacolate were computed in the manner previously discussed, using the equations

$$K = \frac{C\theta r^2}{1-\theta} \quad (1)$$

$$-\log_{10} \gamma = \frac{6.52 \sqrt{C\theta}}{1 + 5.36 \sqrt{C\theta}} \quad (2)$$

$$\theta = \frac{\Lambda}{\Lambda_0 - (2.93 \Lambda_0 + 19.36) \sqrt{C\theta}} \quad (3)$$

The results of the computations are tabulated in Tables IV and V.

TABLE IV  
*Sodium Guaiacolate.*  $\Lambda_0 = 7.50$

| $C$<br>(mole/liter) | $\theta$<br>(degree of dissociation) | $\gamma$<br>(mean ionic activity coefficient) | $K \times 10^6$               |
|---------------------|--------------------------------------|---|-------------------------------|
| 0.000206            | 0.406                                | 0.877   | 4.38                          |
| 0.000771            | 0.2463                               | 0.825   | 4.22                          |
| 0.00224             | 0.1635                               | 0.771   | 4.25                          |
| 0.00454             | 0.1241                               | 0.727   | 4.22                          |
| 0.00901             | 0.0956                               | 0.683   | 4.25                          |
| 0.01666             | 0.0764                               | 0.638   | 4.28                          |
|                     |                                      |   | Average $4.27 \times 10^{-5}$ |

TABLE V  
*Potassium Guaiacolate.*  $\Lambda_0 = 8.00$

| $C$<br>(mole/liter) | $\theta$<br>(degree of dissociation) | $\gamma$<br>(mean ionic activity coefficient) | $K \times 10^6$               |
|---------------------|--------------------------------------|---|-------------------------------|
| 0.000442            | 0.3288                               | 0.844   | 5.07                          |
| 0.000959            | 0.2462                               | 0.808   | 5.02                          |
| 0.002151            | 0.1818                               | 0.765   | 5.07                          |
| 0.003719            | 0.1484                               | 0.731   | 5.13                          |
| 0.005765            | 0.1258                               | 0.701   | 5.13                          |
|                     |                                      |   | Average $5.08 \times 10^{-5}$ |

In Fig. 2 are shown plots of  $\frac{\sqrt{1-\theta}}{\theta}$  against  $\gamma\sqrt{C}$ . From equation (1) we obtain  $\frac{\sqrt{1-\theta}}{\theta} = \frac{1}{\sqrt{K}} \gamma\sqrt{C}$ , so that if the correct values of

$\Lambda_0$  have been chosen, these plots should be straight lines, passing through the origin, as is the case. The slope of these lines is  $1/\sqrt{K}$ .

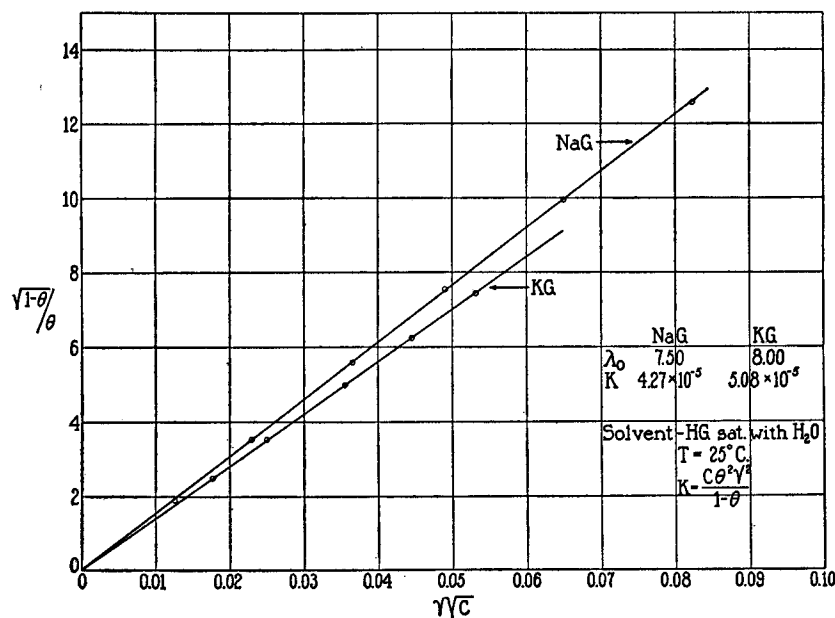


FIG. 2. Plots of  $\sqrt{\frac{1-\theta}{\theta}}$  against  $\gamma\sqrt{C}$  for sodium and potassium guaiacolate in water-saturated guaiacol.

TABLE VI

Solvent: Guaiacol Saturated with Water.  $T = 25^\circ\text{C}$ .

|                            | $\Lambda_0$ | $T_+$ | $l_0(G^-)$ | $l_0(+)$                |
|----------------------------|-------------|-------|------------|-------------------------|
| Sodium guaiacolate.....    | 7.50        | 0.54  | 3.45       | 4.05 (Na <sup>+</sup> ) |
| Potassium guaiacolate..... | 8.00        | 0.57  | 3.44*      | 4.56 (K <sup>+</sup> )  |

\* The viscosity of wet guaiacol, being 7.2 times that of water, we can estimate the magnitude of the limiting conductance of the guaiacolate ion to be about 25 in water, assuming the validity of Stokes' law; that is,  $l_0(G^-)$  in water =  $7.2(3.45) = 25$ . This is an entirely reasonable value. However, a similar computation gives 29 for the sodium ion and 33 for the potassium ion, whereas these values should be about 50 and 76 respectively. The discrepancy is probably due to the fact that, although Stokes' law seems to hold for large ions, such as the guaiacolate ion (6 Å.), it fails for the smaller ions.

We are indebted to Dr. L. G. Longworth of The Rockefeller Institute for supplying us with values for the transference numbers ( $T_+$ ) for

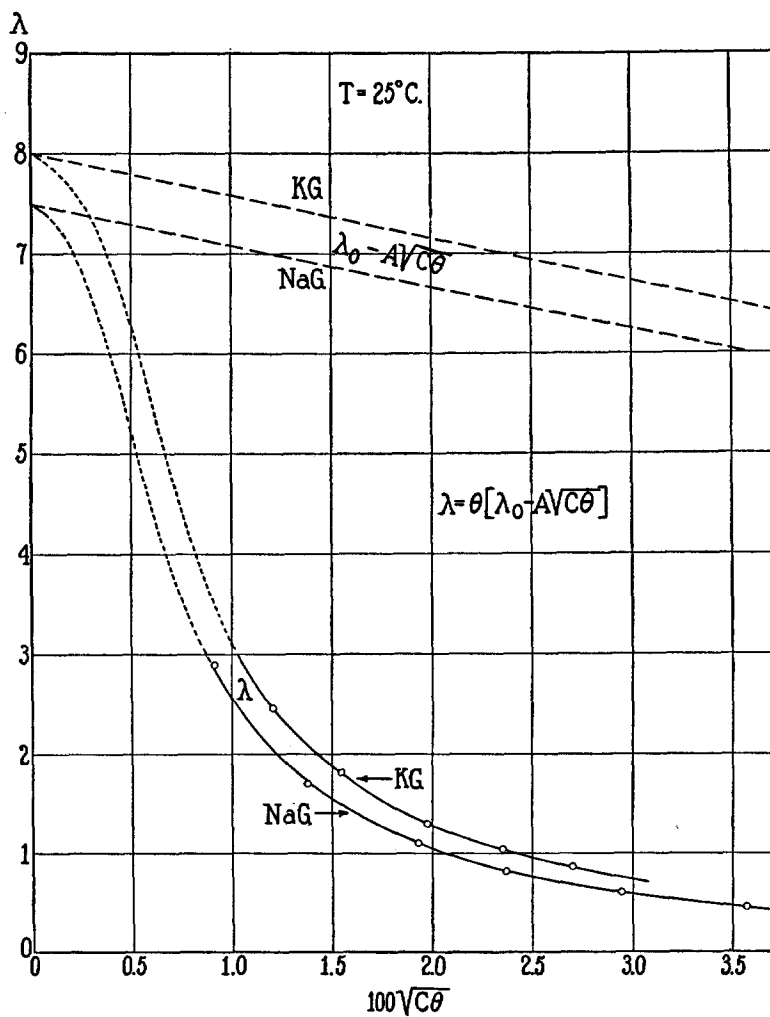


FIG. 3. The conductance of sodium and potassium guaiacolate in water-saturated guaiacol.

sodium and potassium guaiacolate in wet guaiacol, obtained by the moving boundary method. By combining them with our limiting

conductance values ( $\Lambda_0$ ) we are able to obtain the limiting conductances ( $l_0$ ) of sodium, potassium, and guaiacolate ions. In Table VI these quantities are listed.

Using the values  $\Lambda_0 = 7.50$ ,  $K = 4.27 \times 10^{-5}$  for sodium guaiacolate, and  $\Lambda_0 = 8.00$ ,  $K = 5.08 \times 10^{-5}$  for potassium guaiacolate, calculated values for the equivalent conductance,  $\Lambda$ , of these salts at the concentrations measured were obtained. These are shown in the last column of Tables II and III, and agree reasonably well with the values actually observed.

We may therefore conclude that the conductivity of the alkali guaiacolates in water-saturated guaiacol can be satisfactorily accounted for on a basis of an ionic equilibrium, assuming that the "associated" portion of the salt behaves as an "ideal" solute, and correcting for the effects of interionic attractions on the mobilities and activities of the free ions present. From this point of view these salts were found to be weak electrolytes, not unlike acetic acid in water.

#### SUMMARY

1. Measurements on the densities, viscosities, dielectric constants, and specific conductances of pure anhydrous and water-saturated guaiacol at 25°C. are reported.

2. The solubility of water in guaiacol at 25°C., and its effect on the electrical conductivity of a sodium guaiacolate solution is given.

3. Electrical conductivity measurements are reported on solutions of sodium and potassium guaiacolates in water-saturated guaiacol at 25°C.

4. The decrease of electrical conductivity with increasing concentration for these salts is explained on the basis of an ionic equilibrium combined with the interionic attraction theory of Debye and Hückel.

5. The limiting equivalent conductances of sodium and potassium guaiacolates in water-saturated guaiacol at 25°C., the corresponding limiting ionic mobilities, and the dissociation constants are computed from the conductivity measurements. The salts are found to be weak electrolytes with dissociation constants of the order of  $5 \times 10^{-5}$ .