# Comments on Dielectric Relaxation in Solutions and Moisture Sorption in Cellulose Acetate

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## Synopsis

The model of Fuoss and Boyd which interprets the Stokes' radius $r_s$ of an ion in solution as a sum $(r + s/\epsilon)$ of the ionic radius $r$ and a dielectric interaction term $s/\epsilon$ is shown to be at least semiquantitatively applicable to alkali halides in aqueous solutions. Possible applications of the model to amorphous hydrophilic polymers are suggested. This note also contains several corrections to a previous paper.

This paper has a twofold purpose: (1) to correct some errors which occurred in a previous paper[1] in this journal; and (2) to suggest that an extension by Fuoss[2] and Boyd[3] of Stokes' law (for ionic conduction) to include the effect of dielectric relaxation appears to be in reasonable order of magnitude agreement with the values given by Nightingale[4] for aqueous salt solutions.

In ref. 1, page 1936, it was stated that the saturation solubility [$\Delta m/m_0 \approx 9.5\%$ of the dry weight of cellulose 2.5 acetate (C 2.5 A)] corresponds to 1.5 $H_2O$ molecules per cellulose unit. At best this statement is ambiguous. In C 2.5 A five of every six of the —OH groups in cellulose have been replaced by acetyl groups —O—CO—CH$_3$, so that the average molecular weight per residual OH group is 534 g./mole. Since 9.5% of 534 is 50.5 g. $H_2O$ per mole of OH groups, it may be seen that there are $50.5/18 \approx 2.8$ $H_2O$ molecules/residual OH group.

On page 1938 of ref. 1, the figure captions should read "40% acetyl" rather than "40% acetylated." And on page 1940, the relation following eq. (10) should be

$$r_{ion}^* \approx 1130 \ [\text{A.-sec.}^{-1/4}\text{-poise}^{1/4}] \ (\tau/\eta\epsilon)^{1/4} \tag{1}$$

Finally, the synopsis, line 7, should read "about 600 acetyl groups per polymer molecule = 40% acetyl" instead of "100."

Fuoss[2] has made the important suggestion that dielectric relaxation in polar solvents gives rise to part of the resistance encountered by a moving ion within the solvent. Boyd[3] has placed the hypothesis on a firmer basis by deriving from macroscopic electric field theory the same modified form of Stokes' law that Fuoss arrived at by a semiempirical approach. Converting to ion mobility, $\mu$(cm.$^2$/v. sec.) their relation is

$$300\mu = e/6\pi\eta(r + s/\epsilon) = \epsilon/6\pi\eta r_s, \tag{2}$$

where $e = 4.802 \times 10^{-10}$ statC., $\eta$ is the viscosity in poise, $\epsilon$ the dielectric constant, $r$ is the actual ionic radius, $r_s$ is the usual Stokes' radius, and $s$ is Fuoss' empirical parameter. From Boyd's derivation it is easy to show that

$$r_s = r + a\tau/(r^3\eta\epsilon) \tag{3}$$

where $a = 2e^2/27\pi \approx 0.544 \times 10^{-20}$ e.s.u.

Equation (1) gives $r^*$ the value of $r$ for which $r_s$ is a minimum. For dilute aqueous solutions at 25°C., $\eta \approx 10^{-2}$ poise and $\epsilon \approx 78$, so that $r^* \approx 1.20$ A., provided $\tau \approx 1$ psec. (which seems to be a reasonable value). Several other values of $\tau$ and $r^*$ are given in Table I.

<div align="center">TABLE I</div>

| —log $\tau$, sec. | $r^*$, A. |
|:---:|:---:|
| 14 | 0.38 |
| 13 | 0.68 |
| 12 | 1.20 |
| 11 | 2.12 |
| 10 | 3.78 |
| 9 | 6.80 |
| 8 | 12.0 |

From Table I of the paper by Nightingale,[4] it may be seen that $r_x^* \approx 1.58$ A. for the alkali ions and $r_y^* \approx 2.0$ A. for the halogen ions; thus if eq. (1) applies, $\tau_x \approx 2.9$ psec. and $\tau_y \approx 7.6$ psec.

In terms of the conductivity $\sigma$ (ohm.$^{-1}$ cm.$^{-1}$) the relaxation time of a homogeneous dielectric medium is[5]

$$\tau = \epsilon\epsilon_0/\sigma = 8.8542 \times 10^{-14} \epsilon/\sigma \tag{4}$$

so that eq. (3) becomes

$$r_s \approx r + 4.82 \times 10^{-34}/(\sigma r^3\eta) \tag{5}$$

with $r$ in centimeters. For example, if $r \approx 1$ A., $\sigma \approx 10^{-12}$ ohm$^{-1}$ cm.$^{-1}$, and $\eta \approx 10^{10}$ poise, then $r_s \approx 5.82$ A. and $\tau \approx 8.85\epsilon \times 10^{-2}$ sec. The magnitudes suggest that the Fuoss-Boyd relations may have applications for ionic conduction in amorphous hydrophylic polymers.[6,7]

### References

1. Thomas, C. R., and R. E. Barker, Jr., *J. Appl. Polymer Sci.*, **7**, 1933 (1963).
2. Fuoss, R. M., *Proc. Natl. Acad. Sci. U. S.*, **45**, 807 (1959).
3. Boyd, R. H., *J. Chem. Phys.*, **35**, 1281 (1961).
4. Nightingale, E. R., *J. Phys. Chem.*, **63**, 1381 (1959).
5. Panofsky, W. K. H., and M. Phillips, *Classical Electricity and Magnetism*, Addison-Wesley, Cambridge, Mass., 1955, p. 111.
6. Barker, R. E., Jr., and C. R. Thomas, *J. Appl. Phys.*, **37**, 87 (1964).
7. Barker, R. E., Jr., and C. R. Thomas, *J. Appl. Phys.*, to be published.

## Résumé

On montre que le modèle de Fuoss et Boyd, qui interprète le rayon de Stokes $r_s$ d'un ion en solution comme étant une somme $(r + s/\epsilon)$ du rayon ionique $r$ et d'un terme d'interaction diélectrique $s/\epsilon$, est applicable du moins semi-quatitativement aux halogénures alcalins en solutions aqueuses. On suggère des applications possibles de ce modèle aux polymères hydrophiles amorphes. Cette note contient également plusieurs corrections relatives à un article précédent.

## Zusammenfassung

Das Modell von Fuoss und Boyd, welches den Stokes-Radius $r_s$ eines Ions in Lösung als Summe $(r + s/\epsilon)$ des Ionenradius $r$ und eines dielektrischen Wechselwirkungsterms $s/\epsilon$ interpretiert, ist zumindest halbquantitativ auf Alkalihalogenide in wässriger Lösung anwendbar. Es wird die Möglichkeit einer Anwendung des Modells auf amorphe hydrophile Polymere vorgeschlagen. Die vorliegende Arbeit enthält auch einige Verbesserungen einer früheren Arbeit.