

## ION ASSOCIATION OF SIMPLE ELECTROLYTES IN WATER SATURATED 1-BUTANOL

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**ABSTRACT** The electrical conductances of solutions of physiologically important simple electrolytes in water saturated 1-butanol have been measured at 25°C as functions of salt concentration. Values for both  $\lambda_o$ , the conductance at infinite dilution, and  $K$ , the dissociation constant, have been derived by subjecting the data to the procedures given by Shedlovsky and Fuoss.

### INTRODUCTION

Artificial membranes prepared from a number of polymeric materials have been used as models in a number of studies to gain insight into the possible physicochemical principles governing the behavior of biological membranes. Ion exchange membranes have proved their usefulness in the study of membrane potentials and other transport problems (Lakshminarayanaiah, 1965). Similarly, nonaqueous liquid membranes have been used by Schulman and his coworkers (1961 *a*, 1961 *b*, 1962, 1965) and others (Ting et al., 1966; Shean and Sollner, 1966; Rosano, 1967) to study ion and water fluxes. Shedlovsky and Uhlig (1934) studied the electrical conductivity of sodium and potassium guaiacولات in water saturated guaiacol (dielectric constant,  $\epsilon = 14.3$ ) to understand ion association in nonaqueous solvents. The state in which physiologically important simple ions, viz.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{++}$ , and  $\text{Mg}^{++}$ , exist in the cell membrane of low dielectric constant, although understandable qualitatively from the works of Bjerrum, Kraus, and Fuoss (Robinson and Stokes, 1959 *a*), has not been quantitatively established for a number of nonaqueous solvents of low dielectric constant except in the case of salts of sodium and potassium (Davies, 1962). Such data for solutions of some simple salts in water saturated 1-butanol are presented in this communication.

### EXPERIMENTAL

The solvent, 1-butanol, was a Fisher certified reagent (Fisher Scientific Co., King of Prussia, Pa.) which was used always after distillation. Distilled water redistilled in a two-stage quartz

still was used to saturate the solvent. The chemicals were of reagent grade. The dielectric constant of water saturated 1-butanol was measured in Prof. Schwan's laboratory, Moore School of Electrical Engineering, University of Pennsylvania, and found to be 29.0. The viscosity of the solvent was 0.0288 poise at 25°C.

Anhydrous salt or pure crystals of known weight were dissolved in water saturated 1-butanol to give 100 ml of 0.01 N stock solution. The exact normality was always checked spectrophotometrically after evaporation of an aliquot of salt solution in 1-butanol on a Rinco Flash Evaporator (Rinco Instrument Co., Inc., Greenville, Ill.) and extraction with deionized water.

The other dilute solutions were made up by the weight method. The volume concentration was calculated by taking the density of the very dilute solution to be that of the water saturated solvent (0.84 g/ml).

Resistance measurements of these standard electrolyte solutions were made in the usual way (Robinson and Stokes, 1959 *b*) using a Model 31 conductivity bridge obtained from the Yellow Springs Instrument Company (Yellow Springs, Ohio) set at 1000 cycles/sec. The bridge resistances were calibrated using standard resistors. The conductivity cell was constructed so that the platinum electrodes were about 1.5 mm apart. The electrodes were platinized and steamed. The cell constant was 0.11833. The resistance measurements which were accurate to  $\pm 0.5\%$  were obtained at 25°C in an oil bath held constant to  $\pm 0.01^\circ$ .

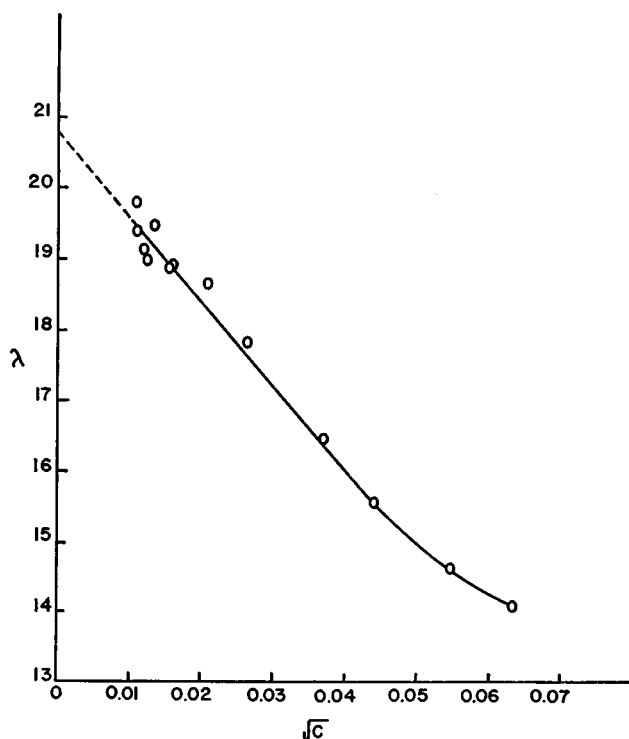


FIGURE 1 Kohlrausch plot of equivalent conductance  $\lambda$ , against  $\sqrt{C}$  for KCl solutions in water saturated 1-butanol.

## RESULTS AND DISCUSSION

The equivalent conductance,  $\lambda$ , of the different solutions was calculated using the equation

$$\lambda = \frac{1000 k}{C} (\text{cm}^2 \Omega^{-1} \text{eq}^{-1}) \quad (1)$$

where  $k (\Omega^{-1} \text{cm}^{-1})$  was the specific conductance and  $C (\text{eq/liter})$  the normality of the solution. In calculating  $k$ , the specific conductance value due to solvent alone (water saturated 1-butanol) was subtracted from that of the solution.

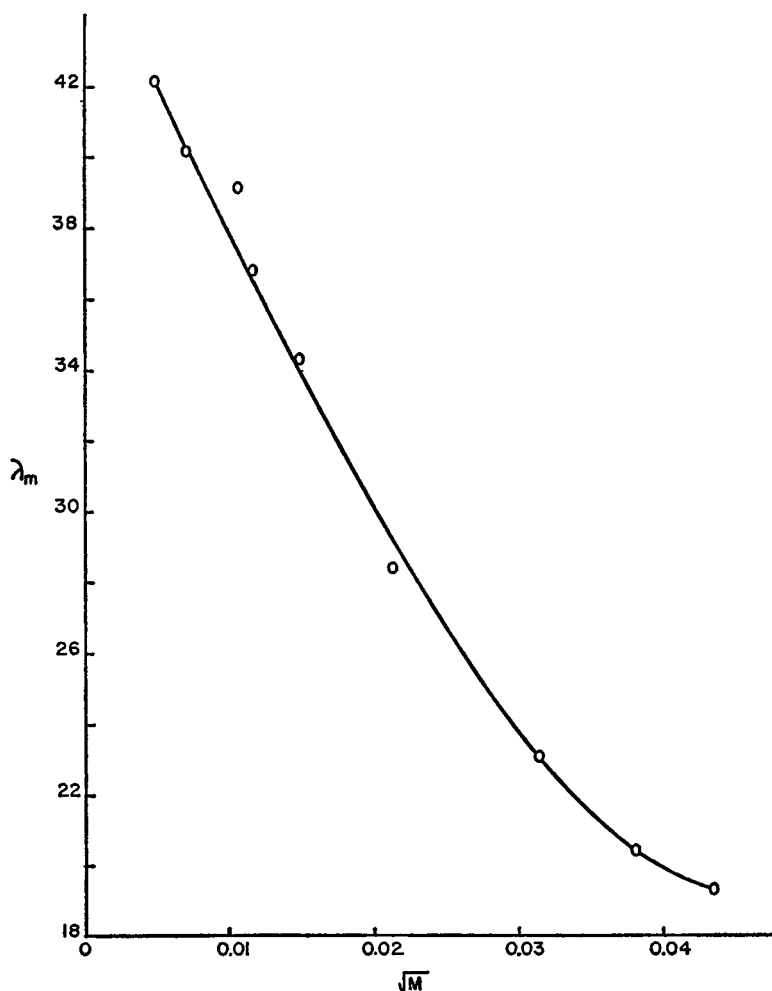


FIGURE 2 Kohlrausch plot of molar conductance  $\lambda_m$ , against  $\sqrt{\text{molarity}}$  for  $\text{CaCl}_2$  solutions in water saturated 1-butanol.

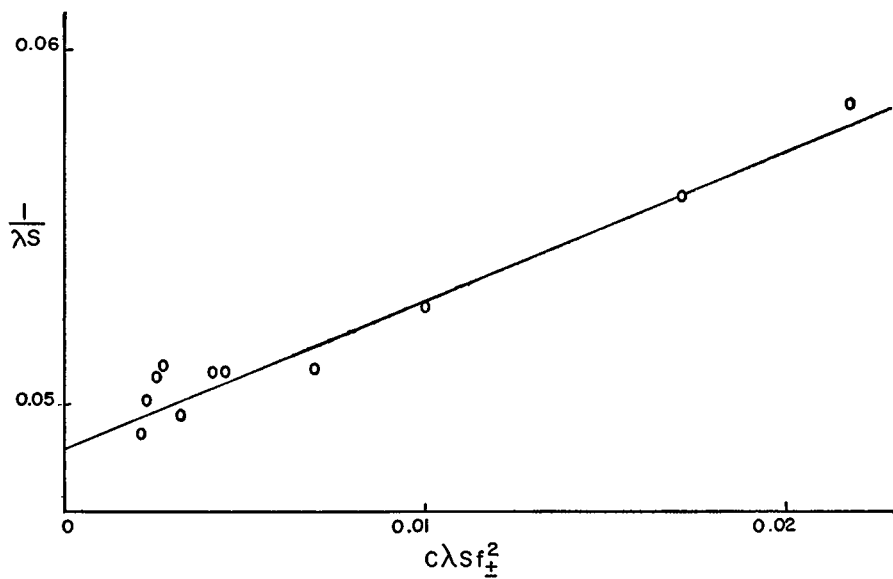


FIGURE 3 A plot of  $\frac{1}{\lambda S}$  against  $C\lambda S f_{\pm}^2$  for KCl solutions.

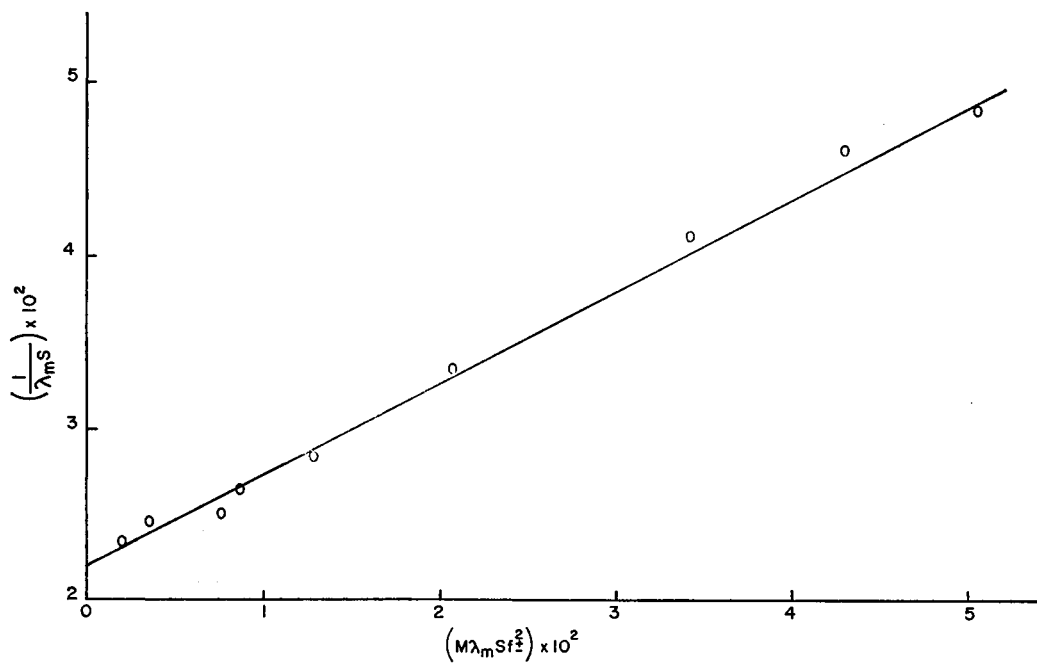


FIGURE 4 A plot of  $\lambda_m S$  against  $M\lambda_m S f_{\pm}^2$  for  $\text{CaCl}_2$  solutions.

In Fig. 1 a typical Kohlrausch plot of  $\lambda$  against  $\sqrt{C}$  is given for KCl solutions. Other (1-1) electrolytes gave similar plots. In the case of (2-1) or (1-2) electrolytes, they were treated as (1-1) electrolytes, and in Fig. 2 the Kohlrausch plot for  $\text{CaCl}_2$  solutions is given by plotting molar conductance  $\lambda_m$  against  $\sqrt{\text{molarity}}$ . Other (2-1) or (1-2) electrolytes gave similar plots.

In order to derive values for conductance at infinite dilution ( $\lambda_o$ ) and for the dissociation constant ( $K$ ), the data were subjected to the treatment given in the publications of Shedlovsky (1938) and Fuoss (1935, 1949). The equation from which  $\lambda_o$  and  $K$  are derived simultaneously is:

$$\frac{1}{\lambda S} = \frac{1}{\lambda_o} + \frac{C\lambda S f_{\pm}^2}{K\lambda_o^2} \quad (2)$$

where  $S$  is a complex function of Onsager slope,  $C$  and  $\lambda$ .  $f_{\pm}$  is the mean activity coefficient.

In Figs. 3 and 4 are given the typical linear plots of  $1/\lambda S$  against  $C\lambda S f_{\pm}^2$  for KCl and  $\text{CaCl}_2$  solutions. Similar linear plots were obtained for the other (1-1) electrolytes and others (2-1 or 1-2) treated as (1-1) electrolyte.

The intercept and slope, according to equation 2 are equal to  $1/\lambda_o$  and  $1/K\lambda_o^2$ , respectively. The values of  $\lambda_o$  and  $\text{pK}$  ( $\text{pK} = -\log K$ ) so derived are given in Table I. Also given in the same table are the observed values (as derived from Kohlrausch plot of  $\lambda$  vs.  $\sqrt{C}$ ) and theoretical values (as derived from theory [Robinson and Stokes, 1959 *c*]) for the Onsager slope. The values of the experimental slope deviate widely from the theoretical values. This deviation is an indication of the state in which the ions existed. The large deviation indicates a paucity of the current-carrying

TABLE I  
SUMMARY OF DATA FOR DIFFERENT ELECTROLYTE SOLUTIONS  
IN WATER SATURATED 1-BUTANOL AT 25°C

Salt	$\lambda_o$	Onsager slope		pK
		Theoretical $\alpha$	Actual	
LiCl	18.53	-49.8	-90.0	2.15
NaCl	19.60	-50.9	-89.6	2.06
KCl	20.42	-51.7	-117.4	2.24
RbCl	18.92	-50.2	-200.0	2.84
CsCl	19.60	-50.9	-164.7	2.77
$\text{NaNO}_3$	22.67	-54.2	-136.4	2.26
NaBr	21.42	-52.9	-103.4	2.15
NaI	22.55	-54.8	-125.0	1.93
NaCNS	22.17	-53.5	-66.6	1.68
$\text{Na}_2\text{SO}_4$	2.80	-33.8	-131.4	3.64
$\text{CaCl}_2$	45.40	-78.4	-835.2	3.05
$\text{MgCl}_2$	34.09	-67.0	-657.4	3.34
$\text{Ca}(\text{NO}_3)_2$	44.15	-80.3	-1028.6	3.28

ions; i.e. ion association exists. The extent of association is quantitatively indicated by the  $pK$  values given in Table I.

The following interesting features are obvious. The  $\lambda_o$  values are all low. The values of alkali metal chlorides follow the sequence  $Li < Na < K > Rb < Cs$ , in contrast to the sequence  $Li < Na < K < Rb < Cs$  observed in aqueous solutions.

The conductance sequence of the anions (Table I) exhibit variation from the sequence observed in aqueous solutions. The sequence in aqueous solutions is as  $Br^- > I^- > Cl^- > NO_3^- > CNS^-$ , whereas the sequence observed in this study is as  $NO_3^- > I^- > CNS^- > Br^- > Cl^-$ . The  $\lambda_o$  values for the sodium salts of these anions do not correlate with the sequence observed for their  $pK$  values. This lack of correlation between  $\lambda_o$  and  $pK$  values exists in the scant literature of conductances in nonaqueous solvents (Robinson and Stokes, 1959 *d*).

Although iodide ion is bigger and heavier than bromide or chloride, the association is smaller. So, it is possible that  $NaCl$ ,  $NaNO_3$ , and  $NaBr$  are more solvated than  $NaI$  or  $NaCNS$ , the latter being the least solvated salt.

Ion association is again increased when the charge on the anion or cation is increased. This follows from the values realized for  $pK$  in the case of  $Ca$  and  $Mg$  salts or of  $Na_2SO_4$ .

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## REFERENCES

- AGOSTINI, A. M., and J. H. SCHULMAN. 1965. In *Surface Activity and Microbial Cell*. S.C.I. Monograph No. 19. Society of Chemical Industry, London, England. 37.
- DAVIES, C. W. 1962. *Ion Association*. Butterworth Inc., Washington, D.C. 95.
- FUOSS, R. M. 1935. *J. Am. Chem. Soc.* **57**:488.
- FUOSS, R. M., and T. SHEDLOVSKY. 1949. *J. Am. Chem. Soc.* **71**:1496.
- LAKSHMINARAYANAIAH, N. 1965. *Chem. Rev.* **65**:491.
- ROBINSON, R. A., and R. H. STOKES. 1959 *a*. *Electrolyte Solutions*. Butterworth & Co., Ltd., London, England. 392.
- ROBINSON, R. A., and R. H. STOKES. 1959 *b*. *Electrolyte Solutions*. Butterworth & Co., Ltd., London, England. 87.
- ROBINSON, R. A., and R. H. STOKES. 1959 *c*. *Electrolyte Solutions*. Butterworth & Co., Ltd., London, England. 164.
- ROBINSON, R. A., and R. H. STOKES. 1959 *d*. *Electrolyte Solutions*. Butterworth & Co., Ltd., London, England. 550.
- ROSANO, H. L. 1967. *J. Colloid Sci.* **23**:73.
- ROSANO, H. L., P. DUBY, and J. H. SCHULMAN. 1961 *a*. *J. Phys. Chem.* **65**:1704.
- ROSANO, H. L., J. H. SCHULMAN, and J. B. WEISBUCH. 1961 *b*. *Ann. N.Y. Acad. Sci.* **92**:457.
- SCHULMAN, J. H., and H. L. ROSANO. 1962. In *Retardation of Evaporation by Monolayers*. V. K. LaMer, editor. Academic Press, Inc., New York. 97.
- SHEAN, G. M., and K. SOLLNER. 1966. *Ann. N.Y. Acad. Sci.* **137**:759.
- SHEDLOVSKY, T. 1938. *J. Franklin Inst.* **225**:739.
- SHEDLOVSKY, T., and H. H. UHLIG. 1934. *J. Gen. Physiol.* **17**:549.
- TING, H. P., G. L. BERTRAND, and D. F. SEARS. 1966. *Biophys. J.* **6**:813.