CONDUCTANCE OF DIFFERENT IONS IN A VARIETY OF SOLVENTS AND APPLICATION OF ZWANZIG THEORY

N.H. El-Hammamy, A.I. Kawana, and F.M. Abd El-Halim

Department of Chemistry, Faculty of Science, Alexandria University, A.R.E, Egypt

The zwanzig theory of dielectric friction has been applied to acetyl choline$^+$, Cl^-, Br^-, I^-, ClO_4^-, S-methyl isothiouronium$^+$, S-n-butyl isothiouronium$^+$, S-n-amyl isothiouronium$^+$ and S-n-hephyl isothiouronium$^+$ ions in different solvents at 25°C. The values of the radius from slope (hydrated radius) and intercept (hydrodynamic radius) are examined and the cause for such difference discussed on the basis of the assumptions of zwanzig theory.

Ionic conductance of acetylcholine$^+$, Cl^-, Br^-, I^- and ClO_4^- in water [1], methanol [2], ethanol [3] and n-proponol [4] and that of S-methyl, S-n-butyl-, S-n-amyl- and S-n-heptyl isouranium ions in water [5], methanol [5] and acetonitrile [6] have been reported at 25°. Fuoss [7] has given a relationship between the ionic conductivity of an ion in different solvents with solvent properties. Boyd [8] and Zwanzig [9] have improved it and expressed λ_i° as

$$\lambda_i^\circ = \frac{F^2}{N[6\pi\eta r_i + (2e^2\tau/3r_i^3)(\varepsilon_\circ - \varepsilon_\infty)/\varepsilon_\circ^2]} \qquad (1)$$

It was considered interesting to examine the applicability of Fuoss-Boyd-Zwanzig theory to the present data.

Equation (1) can be used most conveniently in the linear form suggested by Alkinson and Mori [10], where results in a number of solvents are to be compared. When equation (1) is inverted and rearranged with insertion of the numerical constant and radii in A°, we obtain-

$$\frac{F^2}{N\eta\lambda_i^\circ} = 6\pi r_i + \frac{2e^2}{3r_i^3}\left[\frac{\tau}{\eta}\left(\frac{\varepsilon_\circ \varepsilon_\infty}{\varepsilon_\circ^2}\right)\right] \text{ or}$$

$$\frac{15.5}{\eta\lambda_i^\circ} = 18.8\, r_i + \frac{15.3 \times 10^{12}}{r_i^3}\left(\frac{\tau}{\eta}\,\frac{\varepsilon_\circ - \varepsilon_\infty}{\varepsilon_\circ^2}\right) \qquad (2)$$

For convenience in plotting, this can be written as

$$L^* = 18.8\, r_i + (15.3 \times 10^{12}\ /r_i^3)\, R^* \qquad (3)$$

where $L^* = 15.5/\lambda_i^\circ\eta$ and $R^* = [(\tau/\eta)(\varepsilon_\circ - \varepsilon_\infty)/\varepsilon_\circ^2)]$ so that a plot of L^* vs R^* should be linear and r_i can be obtained from both intercept and slope.

Table 1 summarizes the ionic conductances of the various ions in some pure solvents, while Table 2 gives the solvent parameters needed for the F-B-Z calculations.

Shown in Fig. (1) and (2) is a plot of L^* vs R^* using least square method for different ions. The points for the given ions are found to be scattered around straight lines. The extent of this scattering reflects the failure of equation (3), or to what extent it reflects the uncertainity in relaxation time (τ) and consequently in R^*.

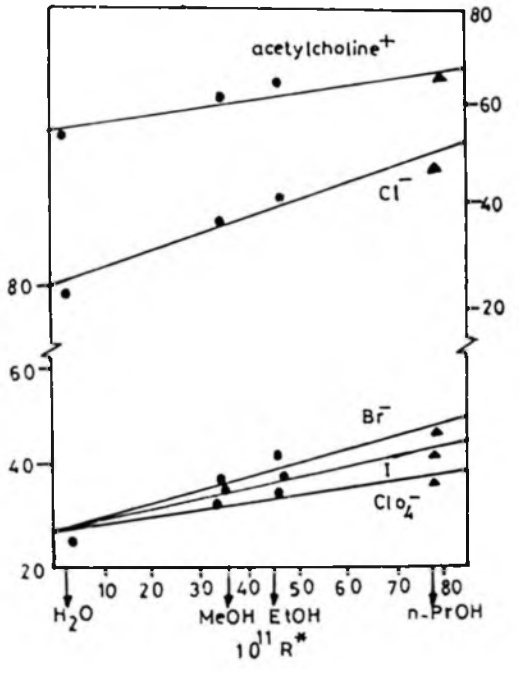


Fig. 1 A plot of Eqn. (3) for the Acetylcholine$^+$, Cl^-, Br^-, I^- and ClO_4^- ions in the pure solvents water, Methanol, Ethanol and n-Propanol at 25°C.

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TABLE 1

IONIC CONDUCTANCES OF DIFFERENT IONS IN PURE SOLVENTS AT 25° C

Solvent	H_2O [1,5]	MeOH [2,5]	EtOH [3]	n-PrOH [4]	MeCN [6]
Acetyl-choline$^+$	31.37	44.68	20.39	10.39	-
Cl^-	76.42	52.31	21.87	10.39	-
Br^-	78.65	56.26	24.23	12.07	-
I^-	76.28	62.30	26.75	13.39	-
ClO_4^-	67.10	70.35	31.65	16.51	-
S-Meis$^+$	39.45	47.63	-	-	98.35
S-n-Buis$^+$	29.97	40.94	-	-	90.90
S-n-Amis$^+$	27.42	40.10	-	-	79.37
S-n-Heptis$^+$	26.46	37.43	-	-	70.11

TABLE 2

PURE SOLVENT PARAMETERS AT 25 C. (10 AND 11)

Solvent	ε_o	ε_∞	$10^{11}\tau$ (sec)	$10^2\eta$ (Poise)
H_2O	78.54	5.5	0.83	0.8903
MeOH	32.63	5.3	6.9	0.5445
EtOH	24.33	4.5	14.4	1.084
n-PrOH	20.45	3.23	37.12	1.952
Me-CN	35.95	1.81	3.8	0.3415

ε_o :Static (low-frequancy) dielectric constant of solvent.

ε_∞ :Optical (infinite frequency) dielectric constant of the solvent

τ :Dielectric relaxation time of solvent

η :Bulk viscosity of the solvent

Table (3) gives values of radii (r_i) calculated from the slopes and intercepts of the straight line graphs in Fig. (1) and (2).

A quantitative test for equation 3 is to compare the values of r_i obtained from the slope and the intercept of the straight lines for each ion. It is noted that the two are far different. It can be seen that the radii from the slope increase with increase in size for both cations and anions. However the radius from the intercept for Cl^-, Br^- and I^- slightly decrease with increasing ion size. This may be attributed to decreased solvation as

TABLE 3

HYDRODYNAMIC RADII FROM INTERCEPT AND ALSO HYDRATED RADII FROM SLOPE OF FBZ EQUATION FOR DIFFERENT IONS

Ion	r_i (Å) (Intercept)	r_i (Å) (Slope)	r_i (Å) (Pauling)[13]
Cl^-	1.46	6.04	1.81
Br^-	1.45	6.47	1.95
I^-	1.42	6.86	2.16
ClO_4^-	1.53	8.11	2.88
S-MeiS$^+$	2.29	7.75	-
Acetylcholine$^+$	2.96	8.21	-
S-n-BuiS$^+$	3.03	11.31	-
S-n-AmiS$^+$	3.34	13.97	-
S-n-HeptiS$^+$	3.46	9.42	

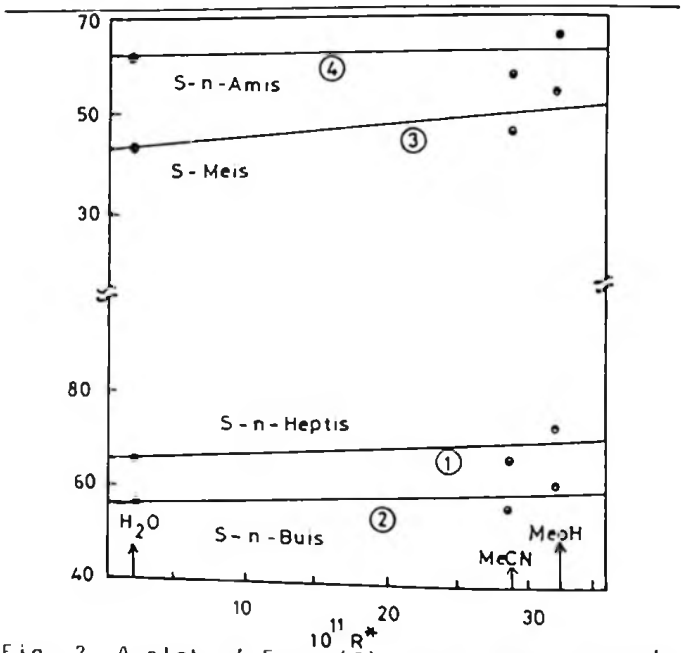


Fig. 2 A plot of Eqn. (3) for the S-Meis$^+$, S-n-Buis$^+$, S-n-Amis$^+$, S-n-Heptis$^+$ ions in the pure solvents water, acetonitril and methanol at 25° C

previously reported in a similar work [10,13,14]. The increase in the value of hydrodynamic radii (r_i from intercept) for S-Meis$^+$, acetylcholine$^+$, S-n-Buis$^+$, S-n-Amis$^+$ and S-n-Heptis$^+$ with increase in ion size may also be attributed to ion solvent interaction.

Nightingale [13], Kay et al [14] calculated the hydrated radii and hydrodynamic radii for tetraalkyl ammonium ions. They found that the hydrated radius increases with increasing ionic size. The intercept value reflects factors closely related to the ion solvent interaction for a particular ion.

Evans and Gardam [15] applied FRZ equation for tetraalkylammonium salts in methanol, ethanol, n-propanol, and n-butanol at 25° C. They attributed the scattering of the points and difference between the r_i (intercept) and r (slope) values to certain specific factors such as solvation which are ignored in the continuum model and these play an important role in determining ionic mobilities.

Application of FRZ equation for Br^- ion and s-alkylisothiouronium$^+$ions [16] in dioxane-water mixtures at 25°C showed that the obtained line still gave values of r_i from the slope which differ from those determined from the intercept. This was attributed to the use of the continuum model and bulk viscosity of the solvent as a basis in the derivation of FRZ equation.

It may be concluded that the Zwanzig equation has been shown to give correct overall trends in the effect of solvent dielectric relaxation on ion mobility. This is true both in pure solvents and also in solvent mixtures of different character. The difference between r_i (slope) and r_i (intercept) is not too disturbing. The intercept value still reflects factors closely related to the ion-solvent interaction for a particular ion. The slope value-the real concern of the Zwanzig theory-is identical for the Li^+, Na^+, K^+, and Cs^+ metal ions. This could be interpreted as a distance beyond which the solvent is no longer affected by the ion field. In short, the Zwanzig theory may be reminding us that the concept of an ion radius in a structured solvent is not an easily defined parameter. Furthermore, it has been pointed out that the "wetted" sphere of the Stokes law is to some extent inconsistent with the zwanzig treatment which ignores the existance of stream lines in the medium. It should be noted that zwanzig examined only the special case where the rate of dielectric relaxation is slower than the rate of solvent exchange. The relative constancy of solvent-exchange rate on simple monovalent ions probably helps us to obtain the relatively good qualitative agreement. However, a more general treatment must probably consider the relationship between solvent-exchange rates and ion mobility in a more detailed way.

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