

Application of Zwanzig Theory for Different Ions in Pure Solvents at 30°C

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Summary: The Zwanzig theory of dielectric friction was applied to s- acetylthiocholine halides and perchlorate in different pure solvents at 30°C. The resulting points for the given ions in different solvents were found to be scattered around the straight lines. The scattered values may be attributed to the uncertainty in the values of the relaxation time (τ). The values of the radius from slope (hydrated radius) and intercept (hydrodynamic radius) were increase with increasing the size of ions, while the values of the slope greater than the values of the intercept may be due to the solvation of the ions. Such differences were investigated and discussed on the basis of the assumptions of Zwanzig theory.

Keywords: Zwanzig theory, hydrated radius, hydrodynamic radius, Conductance, s-acetylthiocholine halides and perchlorates.

Introduction

Ionic conductance of Br^- , I^- and ClO_4^- in water [1], methanol [2] and acetonitrile [3] has been reported at 30°C.

Fuoss [4] has given a relationship between the ionic conductivity of an ion in different solvents with solvent properties. Boyd [5] and Zwanzig [6] have improved it and expressed λ_i^o as

$$\lambda_i^o = \frac{F^2}{N[6\pi\eta_o\gamma_i + (2e^2\tau/3r_i^3)/(\epsilon_0 - \epsilon_\infty)/\epsilon_0^2]} \quad (1)$$

It was considered interesting to examine the applicability of Fuoss-Boyd-Zwanzig (F.B.Z) theory to present data. Equation (1) can be used most conveniently in the linear form suggested by Atkinson and Mori [7], 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 \AA^0 , we obtain

$$(F^2/\eta_o\lambda_i^o) = 6\pi r_i + (2e^2/3r_i^3) \left[\frac{\tau}{\eta_o} (\epsilon_0 - \epsilon_\infty) / \epsilon_0^2 \right]$$

Or

$$(15.5/\eta_o\lambda_i^o) = 188r_i + (15.3 \times 10^{12}/r_i^3) \left[\frac{\tau}{\eta_o} (\epsilon_0 - \epsilon_\infty) / \epsilon_0^2 \right] \quad (2)$$

For convenience in plotting, this can be written as

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

where $L^* = \frac{15.5}{\eta_o\lambda_i^o}$ and $R^* = \left[\frac{\tau}{\eta_o} (\epsilon_0 - \epsilon_\infty) / \epsilon_0^2 \right]$

So that a plot of L^* vs. R^* should be linear and r_i can be obtained from both intercept and slope.

The aim of the present work, is applying the Zwanzig theory to investigate the values of the slope and the intercept for different ions in pure solvents at 30°C. The obtained new data were interpreted.

Results and Discussion

Table-1 summarizes the ionic conductances of various ions in some pure solvents, water, methanol and acetonitrile, while Table-2 shows the solvent parameters needed for the F.B.Z calculations. Tables 3-5 have depicted the parameters obtained from F.B.Z calculations. Fig. 1 represents a plot L^* vs. R^* (10^{11}), where the least square method was used to calculate the values.

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Table-1: Ionic equivalent conductances of different ions in pure solvents at 30°C.

Solvent	Water[1]	Methanol[2]	Acetonitrile [3]
$\lambda^{0-} \text{ Bromide}^-$	86.00	59.7	106.74
$\lambda^{0-} \text{ iodide}^-$	84.5	65.5	108.18
$\lambda^{0-} \text{ perchlorate}^-$	73.5	75.0	109.14

Table-2: Pure solvent parameters at 30°C.

Solvent	[1-3] ϵ_0	ϵ_∞ [8]	[1-3,8] $10^2 \eta_0$ (poise)
water	76.60	4.2	0.798
methanol	30.68	6	0.505
acetonitrile	35.97	2	0.327

ϵ_0 : Static (low frequency) dielectric constant of pure solvent at 30°C.

ϵ_∞ : Optical (infinite frequency) dielectric constant of pure solvent at 30°C.

τ : Dielectric relaxation time of pure solvent at 30°C.

η_0 : Bulk viscosity of pure solvent at 30°C.

Table-3: Application of Zwanzig equation for bromide in different solvents at 30°C.

Solvent	Water	methanol	acetonitrile
$\lambda^0 Br^-$	86	59.7	106.74
$10^2 \eta_0$	0.7977	0.503	0.327
$\lambda^0 * \eta_0$	0.686	0.300	0.349
$[15.5 / \lambda^0 Br^- * \eta_0] = L^*$	22.594	51.617	44.408
$10^{11} \tau$	7.2	47	3.6
$10^{10} \tau / \eta_0$	90.259	934.394	110.092
ϵ_0	76.6	30.68	35.97
ϵ_∞	4.2	6	2
$\epsilon_0 - \epsilon_\infty$	72.4	24.68	33.97
$10^{-2} \epsilon^2$	58.676	9.413	12.938
$R^* = \left[10^{10} \frac{\tau}{\eta_0} (\epsilon_0 - \epsilon_\infty) / \epsilon_0^2 \right]$	1.114	24.500	2.890
$10^{11} R^*$	11.137	244.999	28.905

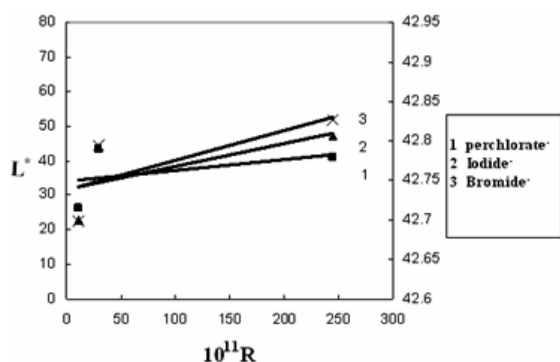
Fig. 1: A plot of eqn. (3) for the Br^- , I^- and ClO_4^- in water, methanol and acetonitrile at 30°C.

Table-4: Application of Zwanzig equation for iodide in different solvents at 30°C.

Solvent	water	methanol	acetonitrile
$\lambda^0 Br^-$	84.5	65.5	108.18
$10^2 \eta_0$	0.7977	0.503	0.327
$\lambda^0 * \eta_0$	0.674	0.329	0.354
$[15.5 / \lambda^0 Br^- * \eta_0] = L^*$	22.995	47.046	43.816
$10^{11} \tau$	7.2	47	3.6
$10^{10} \tau / \eta_0$	90.259	934.394	110.092
ϵ_0	76.6	30.68	35.97
ϵ_∞	4.2	6	2
$\epsilon_0 - \epsilon_\infty$	72.4	24.68	33.97
$10^{-2} \epsilon^2$	58.676	9.413	12.938
$R^* = \left[10^{10} \frac{\tau}{\eta_0} (\epsilon_0 - \epsilon_\infty) / \epsilon_0^2 \right]$	1.114	24.500	2.890
$10^{11} R^*$	11.137	244.999	28.905

Table-5: Application of Zwanzig equation for perchlorate in different solvents at 30°C.

Solvent	water	methanol	acetonitrile
$\lambda^0 Br^-$	73.5	75	109.14
$10^2 \eta_0$	0.7977	0.503	0.327
$\lambda^0 * \eta_0$	0.586	0.377	0.357
$[15.5 / \lambda^0 Br^- * \eta_0] = L^*$	26.437	41.087	43.431
$10^{11} \tau$	7.2	47	3.6
$10^{10} \tau / \eta_0$	90.259	934.394	110.092
ϵ_0	76.6	30.68	35.97
ϵ_∞	4.2	6	2
$\epsilon_0 - \epsilon_\infty$	72.4	24.68	33.97
$10^{-2} \epsilon^2$	58.676	9.413	12.938
$R^* = \left[10^{10} \frac{\tau}{\eta_0} (\epsilon_0 - \epsilon_\infty) / \epsilon_0^2 \right]$	1.114	24.500	2.890
$10^{11} R^*$	11.137	244.999	28.905

The points for the given ions were found to be scattered around the straight lines. The scattered values may be attributed to the uncertainty in the values of (τ) the relaxation time. Table-6 includes values of radii (r_1) calculated from the intercepts and slopes of the straight line graph according to equation (3) as shown in Fig. 1. A quantitative test for equation (3) is to compare the values of (r_1) obtained from the slope and intercept of the straight lines of each ion. It is noticed that the two values are different; both are increasing with the increase of the size of the anions in different solvents. The increase in the value of hydrated radii (r_1 slope) for Br^- , I^- and ClO_4^- with increase in ion size may be attributed to the ion solvent interaction.

Table-6: Hydrodynamic radii from intercept and also hydration radii from slope of F.B.Z equation

Ion	$r_1 \Delta^\circ$ (intercept)	$r_1 \Delta^\circ$ (Slope)
Bromide ⁻	1.67	112.12177
iodide ⁻	1.69	13.24815
perchlorate ⁻	1.81	16.89964

Nightingale [9] and kay *et al.* [10], have calculated the hydrated radii and hydrodynamic radii for tetra-alkyl ammonium ions. They found that the hydrated radius increases with increasing ion size. The intercept value reflects factor closely related to the ion solvent interaction for a particular ion. Evan and Gardam [11] applied F.B.Z equation for tetra-alkylammonium salts in MeOH, EtOH, n-PrOH and n-BuOH at 25°C. They attributed the scattering of the points and difference between the (r_1 intercept) and (r_1 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 mobility. El-Hammamy *et al.*[12], calculated the hydrated radii and hydrodynamic radii for acetylcholine ion and Cl^- , Br^- , I^- and ClO_4^- and s-alkylisothiuronium ions (s-Meis⁺, s-n-Buis⁺, s-n-Amis⁺ and s-n-Heptis⁺) in H₂O, MeOH, n-PrOH and CH₃CN at 25°C. They found that the radii from the slope increase with increase in size for both cation and anions. The increase in the value of hydrodynamic radii (r_1 intercept) for s-Meis⁺, s-n-Buis⁺, s-n-Amis⁺ and s-n-Heptis⁺ with increase in ion size may also be attributed to ion solvation interaction.

Experiment

Purification of s-acetylthiocholine halides and perchlorate was reported in the literature [1]. Purification of water, methanol and acetonitrile was reported in literatures [1-3]. Ionic equivalent conductance at infinite dilution of different ions in water, methanol and acetonitrile were taken from previous investigations [1-3]. The dielectric constant (ϵ_∞) for pure solvents at 30°C was also reported in the literatures [1-3]. The values of Optical dielectric constant (ϵ_∞), relaxation time (τ) and Bulk viscosity (η_∞) for pure solvents at 30°C were taken from previous investigations (1-3,8).

Conclusion

The application of Zwanzig equation to bromide, iodide and perchlorate in pure solvents at 30°C was investigated. It was found that the straight lines graph according to equation (3). A quantitative analysis for equation (3) was done, by comparing the values of (r_1) obtained from slope and intercept of the straight lines of each ion. Although the two values were different, both increasing with increase of the size of the anions. The increase in ion size may be attributed to ion solvent interaction. The scattering of the points and difference between the (r_1) values is attributed to certain specific factors such as solvation which are ignored in the continuum model and these play an important role in determining ionic mobility.

References

1. A. I. Kawana, *Alexandria Journal of Pharmaceutical Sciences*, **16**, 128 (2002).
2. N. H. El-Hammamy, A. I. Kawana, M. N. El-Hammamy and H. M. Moharem, *International Journal of Chemical Sciences (Der Chemica Sinica)*, **2**, 51 (2011).
3. N. H. El-Hammamy, A. I. Kawana, M.N. El-Hammamy and H. M. Moharem, *International Journal of Chemical Sciences (Der Chemica Sinica)*, **2**, 292 (2011).
4. R. M.Fuoss, *Proceeding of National Academic Science*, **45**,807 (1959).
5. R. M.Boyd, *Journal of Chemical Physics*, **35**, 1281 (1961).
6. R. Zwanzig, *Journal of Chemical Physics*, **38**, 1603 (1963).
7. G. Atkinson and Y. Mori, *Journal of Physical Chemistry*, **71**, 3523 (1967).
8. M. Nakara and K. Emi, *Journal of Chemical Physics*, **99**, 5418 (1993).
9. E. R.Nightingale, *Journal of Physical Chemistry*, **63**, 1381 (1959).
10. R. L. Kay, G. P. Cunningham and D. F. Evans, "Hydrogen-Bonded Solvent Systems", Ed. By A. K. Covington and P. Jones, P, 250, Taylor and Francis LTD, London (1968).
11. D. F. Evans and P. Gardam, *Journal of Physical Chemistry*, **73**, 158 (1969).
12. N. H. El-Hammamy, A. I. Kawana and F. M. Abd El- Halim, *Journal of Electrochemical Society of India*, **36**, 255 (1987).