

Factors Affecting Diffusion Coefficient of the Hydroxide Ion in Aqueous Tetraalkylammonium Nitrate Solutions

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Abstract. The effect of OH^- concentration on its diffusion coefficient in aqueous Me_4NNO_3 and Bu_4NNO_3 solutions at total ionic strength of 0.50 mol dm^{-3} was studied. The diffusion coefficient was found to increase from a low value and reached a steady-state. The possibility of ion-pair formation is discussed. The mobility of the hydroxide ion is less in aqueous Bu_4NNO_3 than in the corresponding solutions of alkali metal nitrates. This was attributed to the hydrophobic hydration of Bu_4N^+ ion. In the concentration range of 0.10 to 0.50 mol dm^{-3} Bu_4NNO_3 , the rapid decrease of the diffusion coefficient of the hydroxide ion with increasing solute concentration was found to be mainly due to the obstruction effect of the cations aggregates. Bu_4N^+ ions tended to interact in the form of an assembly of three ions with their hydrophobic hydration spheres overlapping with each other. No structural effects on the water molecules were found to be necessary to explain this behaviour of the hydroxide ion.

Introduction

Ionic hydration depends on the nature and concentration of the dissolved ions. This property determines the structure of aqueous electrolyte solutions. The structure of water near these ions will differ from that of bulk water. If the mobility of water is decreased then the ion is classified as structure promoting (positive hydration), and if it is increased the ion is considered as structure breaking (negative hydration) [1].

The diffusion coefficient of the hydroxide ion (D_{OH^-}) provides important information about the effect of other ions on the water structure because this ion moves by a proton exchange mechanism through the hydrogen bonded network of the water molecules in addition to the hydrodynamic migration [2]. It has been established that the transport properties in the electrolyte solutions are affected by the type of hydration present in the solution [3;4].

The aim of the present work is to study the dependence of D_{OH^-} on the concentration of OH^- in tetramethylammonium nitrate (Me_4NNO_3) and tetrabutylammonium nitrate (Bu_4NNO_3) at a total ionic strength of 0.50 mol dm^{-3} and the dependence of D_{OH^-} on the concentration of lithium nitrate (LiNO_3) and of tetrabutylammonium nitrate by using electrochemical techniques.

Experimental

A nickel disc electrode 99.99% pure (Goodfellow metals Ltd.) was used as working electrode. The electrochemical measurements were made using an Applied Corrosion Monitoring (ACM Ltd) potentiostat and a sweep generator. A chart recorder was used to record the rotating disc electrode (RDE) voltammograms, whereas for chronoamperometric measurements a digital memory ammeter was used. De-aeration was carried by passing purified nitrogen gas through the test solution at $25.0 \pm 0.1 \text{ }^\circ\text{C}$. The electrochemical cell was provided with three electrodes, a saturated calomel electrode as reference electrode, a platinum gauze auxiliary electrode and the working electrode. The solutions were prepared from A.R. grade chemicals and double distilled water.

The diffusion coefficients were calculated from the limiting diffusion currents for the anodic oxygen evolution measured by RDE [5;6, pp. 53-58] as a function of angular velocity using the Levich equation as modified by Burckenstein [7]:

$$D = \nu [(J^{-1} - 0.122939)^{1/2} - 0.149]^{-3} \quad (1)$$

$$J = \frac{I_L}{0.62048 nF(\omega\nu)^{1/2}C} \quad (2)$$

where D is the diffusion coefficient, ω is the angular velocity and C is the concentration of OH^- ion. The other terms have their usual meaning.

Chronoamperometric OH^- diffusion coefficients were calculated from the diffusion current measured as a function of time using the Cottrell equation as modified by Soos and Lingane [8] following the procedure of Kakihana *et al* [9]:

$$it^{1/2} = \frac{nFAD^{1/2}}{\pi^{1/2}} \left[1 + b \left(\frac{Dt}{r^2} \right)^{1/2} \right] \quad (3)$$

where r is the radius of the electrode and b is an empirical constant having an approximate value of 2.

Results and Discussion

The effect of hydroxide ion concentration on D_{OH^-} in Bu_4NNO_3 was investigated with chronoamperometry, whereas for that in Me_4NNO_3 a rotating disc electrode was used. The effect of LiNO_3 and Bu_4NNO_3 on the diffusion of OH^- ion was investigated using rotating disc electrode and chronoamperometry. D_{OH^-} at 0.50 mol dm^{-3} of Bu_4NNO_3 was determined chronoamperometrically. Diffusion coefficients in aqueous solutions of LiNO_3 and Bu_4NNO_3 at different concentrations were carried out at a triplicate experiment.

D_{OH^-} in aqueous Bu_4NNO_3 and Me_4NNO_3 at $0.500 \text{ mol dm}^{-3}$

The effect of the hydroxide ion concentration on its diffusion coefficient in aqueous solutions of Bu_4NNO_3 and Me_4NNO_3 at $0.500 \text{ mol dm}^{-3}$ are shown in Fig. 1. This figure shows that D_{OH^-} increases from a low value as the concentration of hydroxide ion increases and then reaches a steady-state value. It has been shown earlier that in aqueous solution of CsNO_3 and LiNO_3 , D_{OH^-} is almost independent of OH^- concentration within the concentration range investigated [10].

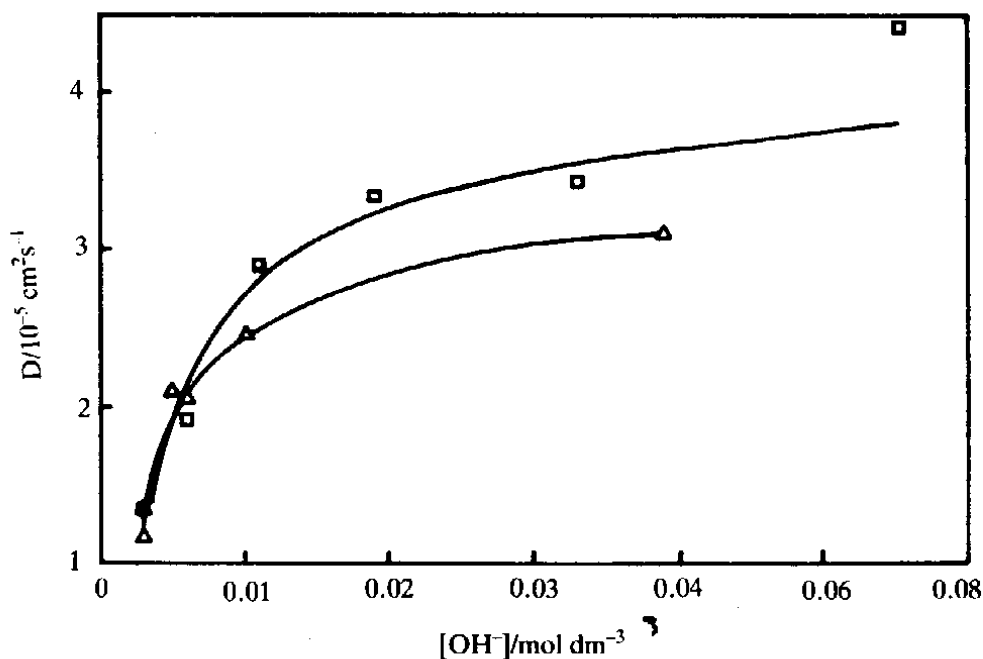


Fig. 1. Effect of hydroxide ion concentration on its diffusion coefficient in Me_4NNO_3 (□); Bu_4NNO_3 (△) at a constant ionic strength of 0.50 mol dm^{-3} (▲) using a platinum microelectrode.

Similar behavior of the proton diffusion coefficient in $0.100 \text{ mol dm}^{-3} \text{ NaClO}_4$ has been observed [11]. D_{H^+} increases from 5×10^{-5} to $10 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ when the proton concentration is increased from 5×10^{-4} to $8 \times 10^{-3} \text{ mol dm}^{-3}$. This behavior

was attributed to the increasing contribution of the proton migration as its concentration increases resulting in a higher diffusion coefficient. In the present study the effect of the ohmic drop due to the solution resistance is probably small since D_{OH^-} at zero Bu_4NNO_3 concentration is in good agreement with the theoretical value calculated from the limiting molar conductivity using the Nernst limiting law [12] (see Table 1). Moreover, D_{OH^-} in Bu_4NNO_3 and Me_4NNO_3 in the plateau region (see Fig. 1) remains lower than D_{OH^-} as expected whereas in NaClO_4 it exceeds that value [11]. Also microelectrode technique was used to cross check D_{OH^-} in Bu_4NNO_3 at the lowest OH^- concentration studied. Therefore, it may be concluded that the observed behavior is not due to ohmic drop.

Table 1. The diffusion coefficient of OH^- ion in aqueous solutions of LiNO_3 and Bu_4NNO_3 at 25 °C

m/mol dm ⁻³	$D_{\text{OH}^-}/10^{-5} \text{ cm}^2 \text{ s}^{-1}$	
	LiNO_3	Bu_4NNO_3
0	5.29*	5.29*
0.10	4.77	3.77
0.20	—	3.01
0.30	4.36	2.45
0.50	4.12	2.01
0.90	3.60	—
2.00	3.05	—

* Calculated from equation (11.49) in ref. [12].

Extensive studies on solutions of tetraalkylammonium salts made clear that these salts are capable of forming ion-pairs in both aqueous and non-aqueous solutions [13-18]. Wirth [13] explained the decrease of the apparent molar volume of R_4NBr in aqueous solutions as the solute concentration increases by an association process. For Me_4NBr , a single association reaction was sufficient to interpret the observed concentration dependence and K_a was found to be $1.24 \text{ mol}^{-1} \text{ dm}^3$ whereas for Et_4NBr and Pr_4NBr in addition to ion association dimer formation was considered too. K_a for Et_4NBr and Pr_4NBr were 2.40 and $3.10 \text{ mol}^{-1} \text{ dm}^3$, respectively. Conductance measurements [14] for aqueous Bu_4NNO_3 solutions have shown that the salt is associated with a single water molecule between the cation and the anion and K_a at 25°C is equal to $3.5 \text{ mol}^{-1} \text{ dm}^3$. Measurement of ^{35}Cl NMR spectra in aqueous Et_4NCl and KCl showed that Cl^- are associated directly with Et_4N^+ ions in the form $\text{Et}_4\text{N}^+ \text{Cl}^- (\text{H}_2\text{O})_{n-1}$ with an association constant of about $10 \text{ mol}^{-1} \text{ dm}^3$ [15]. Bromide ions at 0.9 mol kg^{-1} were found to be bounded to the hydrophobic hydration spheres of Et_4N^+ ions [16]. In methanolic solution, proton resonance of N-methylene groups of

Bu_4NX (where $\text{X} = \text{I}^-$, Br^- and SCN^-) was found to shift to low field as the salt concentration increased. The anion with part of its solvation shell was found to form contact ion pairs [17]. Contact ion-pairs are mostly visualized by NMR method [18]. It is possible that the decrease noticed for D_{OH^-} in aqueous Bu_4NNO_3 and Me_4NNO_3 is due to ion pair formation.

D_{OH^-} in aqueous LiNO_3 and Bu_4NNO_3

The effect of ion-pair formation on D_{OH^-} may be elucidated better by studying the dependence of D_{OH^-} on Bu_4NNO_3 concentration as an associated electrolyte and on LiNO_3 concentration which is considered as non-associated electrolyte [19, p.24].

From Fig. 2, it is clear that D_{OH^-} decreases linearly with increasing square root of electrolyte concentration. The relative diffusion coefficient in these two systems are compared with the predictions of the Onsager limiting law [12] in Fig. 2. The experimental data for Bu_4NNO_3 deviates considerably from theoretical one, no agreement can be observed at lower concentrations. $D_{\text{OH}^-}/D_{\text{OH}^-}^\circ$ in LiNO_3 approaches the calculated values below 0.20 mol dm^{-3} . The relative diffusion coefficient of Br^- in Bu_4NBr is well below that predicted by the limiting law. Woolf and Weingartner [20] attributed this to specific interactions between cations and anions present in the solution due to the hydrophobic nature of the cation.

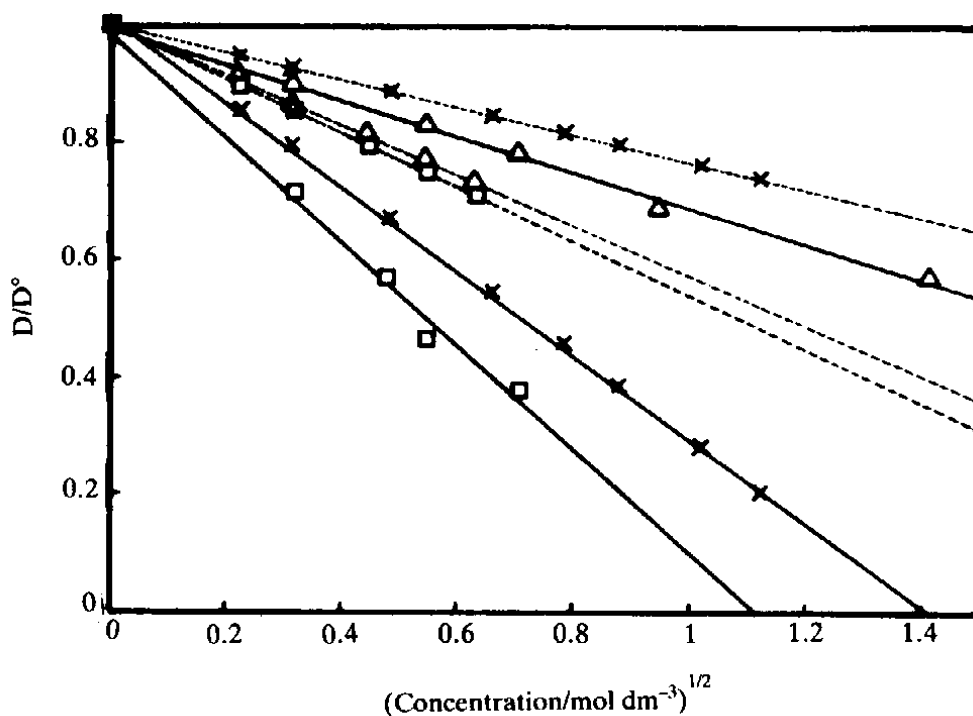


Fig. 2. Effect of concentration on the diffusion coefficient of OH^- ion and Br^- ion; solid line represent observed data and dotted line for calculated data. (\times) Br^- in Bu_4NBr ; (Δ) OH^- in LiNO_3 ; (\square) OH^- in Bu_4NNO_3 .

In general, the change of relative diffusion coefficient with concentration of solute may be attributed to two effects. One effect can be related to specific interaction between the diffusing ion and certain other ions present in the solution which leads to a decrease in diffusion coefficient. Also, diffusion can be retarded due to large size particles. In this process, large size particles effectively block part of the diffusion path and therefore ions have to go round the large particles; this would lengthen the diffusion pathway and consequently decreases the diffusion coefficient of the ion. This is known as the obstruction effect and it was suggested first by Wang [21] to explain diffusion of water in protein solutions, assuming that the obstructions are immobile and large compared with the solvent molecules and the diffusing species. The degree of obstruction depends on the volume fraction of the obstructing particles and their shape. The decrease in the self-diffusion coefficient is given by Wang's relation as

$$D = D^{\circ} (1 - 1.5 \phi) \quad (4)$$

where D° is the self-diffusion coefficient in pure solvent and ϕ is the volume fraction of the obstructing particles. It is possible to use this relation to explain the rapid decrease of D_{OH^-} in Bu_4NNO_3 since the Bu_4N^+ ion is larger than the water molecule. The volume fraction was estimated from the partial molar volume V_p of Bu_4N^+ ion [22] and the concentration m using the relation [23].

$$\phi = V_p m \quad (5)$$

A comparison of the experimental relative diffusion coefficient with that calculated from relation (4) is shown in Fig. 3. $D_{\text{OH}^-}/D^{\circ}_{\text{OH}^-}$ is noticeably much lower than the prediction of Wang's theory. For comparison, the diffusion coefficient of Br^- ion in Bu_4NBr [20] is shown in the figure and it is clear that a similar decrease occurs in the later system. The ratio $D_{\text{OH}^-}/D^{\circ}_{\text{OH}^-}$ is not changing linearly with the volume fraction and therefore a factor must be operating in addition to the obstruction effect [24]. This new factor may be the hydrophobic hydration of Bu_4N^+ ions.

Jönsson and co-workers [25] have presented another equation for the obstruction of an array of immobile obstructing particles as

$$D = D^{\circ} (1 - f) \left(1 + \frac{\phi}{2}\right)^{-1} \quad (6)$$

where f is the fraction of water that is bound to the particles and ϕ is the effective volume fraction of the obstructing particles [26]. This equation was successful in predicting the dependence of the diffusion coefficient of water on the concentration of the diffusion coefficient of water on the concentration of tetraalkylammonium chlorides

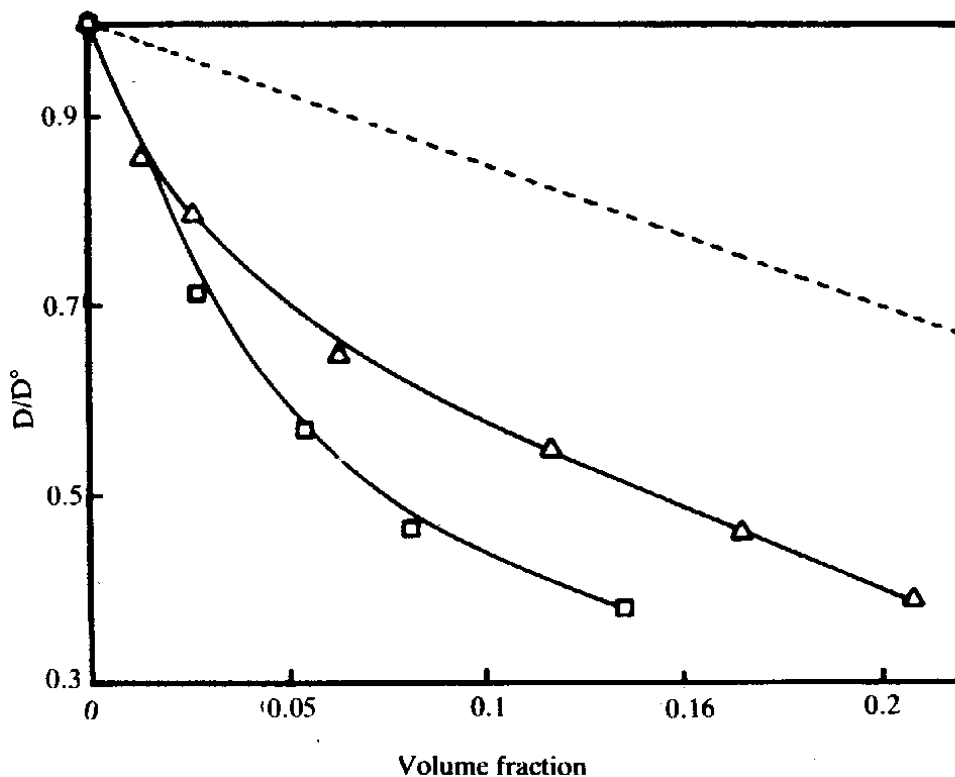


Fig. 3. Variation of diffusion coefficient of OH⁻ ion in Bu₄NNO₃ with volume fraction of Bu₄N⁺ ion.

The dashed line is calculated from Wang's relation.

Δ, for Br⁻ in Bu₄NBr; □, for OH⁻ in Bu₄NNO₃.

and *t*-butanol [26]. On the other hand, Wang's relation was not able to explain the decrease of the water diffusion in *t*-butanol, the calculated values were higher than the experimental values [27]. The situation was the same for the diffusion of water in aqueous *p*-Ethylbenzene sulfonate [23].

In order to explain here the rapid reduction of D_{OH^-} with increasing concentration of Bu₄NNO₃, equation 6 was used. f is given by

$$f = \frac{m n_{\text{H}}}{55.5 \text{ mol dm}^{-3}} \quad (7)$$

where m is the concentration of solute and n_{H} is the hydration number. When the partial molar volume (V_{p}) of Bu₄N⁺ ion was taken as 303 cm³ mol⁻¹ and the hydration number n_{H} was taken as 24 [26], the calculated $D_{\text{OH}^-}/D_{\text{OH}^-}^{\circ}$ values were close to the experimental results. It is possible that cation interaction is present in solution as shown by several workers [20,28]. On this basis, V_{p} and n_{H} were successively tested as the sums for two, three and four cations, the best fit between the calculated and experimental values was when the obstructing particle consists of three cations together as shown in Fig. 4. It has been stated that n_{H} is the only adjustable parameter

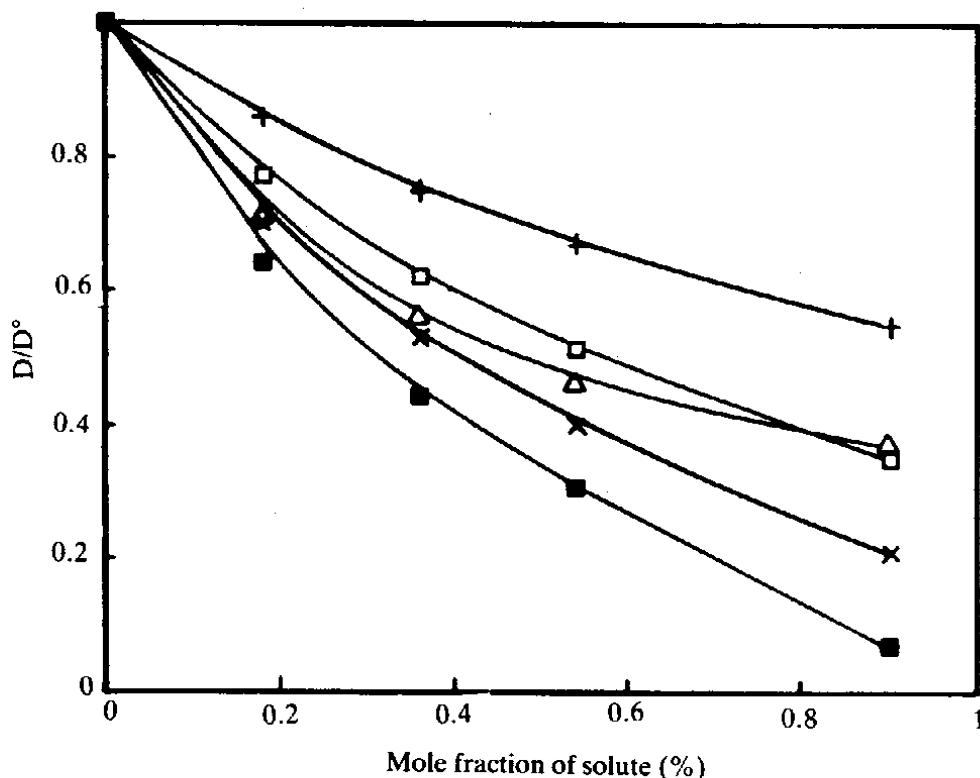


Fig. 4. Effect of changing V_p on the diffusion coefficient of OH^- ion. Δ , experimental line; +, $V_p=303 \text{ cm}^3 \text{ mol}^{-1}$; \square , $V_p=606$; \times $V_p=909$; \blacksquare , $V_p=1212$.

in the model [26], so consequently we have selected n_H to give the best fit for the experimental data. The n_H values selected at the four concentrations studied are, in increasing concentration order, 68, 60, 58 and 44.

Around each ion there is a hydration cosphere as a result of the overall influence of the ion on the water structure. As concentration increases, distances between ions decrease and the sum of their hydration cospheres is reduced due to overlapping. This effect is known from other studies [16].

The value of n_H which gives the best fit to experimental data which decreases with increasing solute concentration suggests that the obstructing particle consists of three Bu_4N^+ ions, interacting with each other in a hydrophobic manner to give hydration cosphere overlap. Streng and Wen [29] have presented an equation which calculates the mean number of water molecules per interacting ion which return from the cosphere to the bulk because of cosphere overlap. They have also calculated this number for tetraalkylammonium chlorides and bromides at several concentrations. A linear relationship is found between the displaced water molecules and the solute concentration. The ability of NO_3^- ion to destroy the water structure is found to lie between those of Br^- and Cl^- ions [30]. As a result the number of water molecules that leave the cosphere to rejoin the bulk water due to two Bu_4N^+ cospheres overlapping can be estimated approximately as the average of those of Bu_4NCl and Bu_4NBr .

Therefore, it was found that the number of water molecules resulting from subtracting the leaving water molecules from the sum of the hydration numbers of the three ions, *i.e.* 72, agrees well with the value of n_H used to calculate $D_{OH^-}/D_{OH^-}^\circ$ to fit the measured D_{OH^-} . This may show that in the concentration range of 0.10 to 0.50 mol dm⁻³ studied, Bu₄NNO₃ forms aggregates consisting of three cations. Anions are likely to be part of these aggregates because otherwise this would result in an unstable energy state because of positive charge accumulation, as stated by Kabisch [28]. On this basis, the effect of Bu₄N⁺ concentration increase is mainly due to the obstruction effect and the structure making effect of the solute need not be invoked.

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العوامل المؤثرة على معامل انتشار أيون الهيدروكسيد في المحاليل المائية لنترات رباعي ألكيل الأمونيوم

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(سُلّم في ٢٩ ربيع أول ١٤١٤هـ، وقُبل للنشر في ٢٩ شعبان ١٤١٤هـ)

ملخص البحث. لقد تمت دراسة تأثير تركيز أيون الهيدروكسيد على معامل انتشاره في المحاليل المائية لكل من نترات رباعي ميثيل الأمونيوم و نترات رباعي بيوتيل الأمونيوم وذلك عند شدة أيونية ثابتة قدرها ٠,٥ مولار. وقد وجد أن معامل الانتشار يزداد من قيمة منخفضة ويصل بعد ذلك إلى قيمة ثابتة. وقد نوقشت احتمالية تكون الأزواج الأيونية وأثرها على انتشار أيون الهيدروكسيد. فقد وجد أن حركية أيون الهيدروكسيد تكون أقل في محلول نترات رباعي بيوتيل الأمونيوم منها في محلول نترات الليثيوم وقد أرجع السبب في ذلك إلى تميؤ أيون رباعي بيوتيل الأمونيوم الهيدروفوبيي (hydrophobic) ففي نطاق التركيز من ٠,١ - ٠,٥ مولار من نترات رباعي بيوتيل الأمونيوم وجد أن معامل الانتشار يتناقص بدرجة كبيرة مع زيادة تركيز الالكتروليت وقد عزى ذلك إلى تأثير الإعاقة الناتج عن تجمع أيونات رباعي بيوتيل الأمونيوم على هيئة ثلاثة أيونات تتداخل أغلفة التميؤ الهيدروفوبيي لها مع بعضها البعض ولم يكن ضرورياً إدخال أي تأثيرات تركيبية على جزيئات الماء لتفسير سلوك أيون الهيدروكسيد في تلك المحاليل.