

Electrolytic Behaviour of Acetylcholine Halides & Perchlorate in Aqueous Solutions

N H EL-HAMMAMY*, M F AMIRA, S A ABOU EL-ENEIN & F M ABD EL-HALIM

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

Received 30 March 1983; revised and accepted 27 July 1983

Conductance measurements are reported for acetylcholine halides and perchlorate in water at 25°C. The data have been analyzed using the Fuoss-Onsager equation for 1:1 associated electrolytes, and the characteristic functions, Λ_0 , a° , and K_A have been derived. The association constant K_A has been analyzed on the basis of the solvent separated-ion pair model.

The Fuoss-Onsager equation for 1:1 electrolytes¹ has been applied to study the electrolytic behaviour of a large number of salts. We have measured conductances of acetylcholine halides and perchlorate in water at 25°C and the results are presented in this paper. The effect of anionic size on the conductance of these salts has been discussed in the light of the variation of both the association constant (K_A) and the closest distance of approach (a°). The solvent separated ion pair model has been applied in an attempt to analyze the values obtained for K_A .

Materials and Methods

All the acetylcholine salts were crystallized twice from ethyl alcohol and were dried *in vacuo* over P_2O_5 . KCl (AR) was crystallized twice from conductivity water and dried in an air oven at 120°C to constant weight and used after powdering in a quartz mortar.

Conductivity water was prepared by passing distilled water over a 60 cm long Elgastat deionizer and guarded against atmospheric CO_2 by sodalime tubes. Its specific conductance, γ_0 was 5.7×10^{-7} ohm⁻¹ cm⁻¹.

All the solutions were prepared by weight. Dilution was carried out successively in the cell itself by siphoning off the solvent using a dispenser.

A Pye conductivity bridge (model 11700) was used for measuring the conductances of the solutions at 5 kHz. All the measurements were carried out at $25 \pm 0.02^\circ C$ using a water thermostat.

The conductivity cell was of pyrex glass and of conventional design (Erlenmeyer Type) with un-platinized electrodes². Calibration of the cell was made using aqueous potassium chloride solutions in the concentration range (7.25×10^{-4} equiv/litre). The conductivities of these solutions were calculated using Lind, Zwolenik and Fuoss equation³. The cell constant was found to be 0.05443 ± 0.0043 . In order to test the reproducibility of this value, a successive run for

potassium chloride in water at 25°C was made using a Pye conductivity bridge (model 11700) at 5 kHz, and the data obtained were compared with those previously published^{4,5}.

The solvent constants used in all calculations were taken as³: the density (d_{25}) = 0.99704 gml⁻¹, the viscosity (η_{25}) = 0.8903×10^{-2} P, and the dielectric constant (D) = 78.54.

Results and Discussion

The equivalent conductances Λ (ohm⁻¹ equiv⁻¹ cm²) measured at the corresponding concentrations C (equiv/litre of solution) are shown in Table 1. A preliminary value of Λ_0 was estimated from the plot of Λ versus $C^{1/2}$.

Table 1—Conductances of Acetylcholine Halides and Perchlorate in Water at 25°C

10 ⁴ C (equiv/lit)	Λ (ohm ⁻¹ cm ² equiv ⁻¹)	10 ⁴ C (equiv/lit)	Λ (ohm ⁻¹ cm ² equiv ⁻¹)
Acetylcholine chloride		Acetylcholine bromide	
22.211	97.173	23.523	102.000
17.016	98.800	17.766	103.393
12.764	100.382	12.959	104.698
8.3404	102.347	9.5935	105.676
6.5798	103.288	7.5065	106.596
5.5035	103.941	6.6363	106.946
4.3604	104.489	6.1360	107.100
3.5156	105.200	5.2971	107.510
Acetylcholine iodide		Acetylcholine perchlorate	
16.818	96.915	17.824	88.769
13.073	98.473	15.477	89.727
9.9891	100.198	13.294	90.727
8.6048	100.874	11.472	91.342
7.3682	101.639	8.7113	92.457
6.6223	102.188	8.0379	92.923
5.5744	102.883	6.5965	93.569
4.8408	103.399	5.6490	94.261

A more accurate value of Λ_0 was estimated from the Fuoss-Kraus-Shedlovsky equation⁶,

$$1/\Lambda S_{(Z)} = 1/\Lambda_0 + (c\Lambda S_{(Z)}f^2)/K_D\Lambda_0^2 \quad \dots (1)$$

where, K_D is the dissociation constant and $S_{(Z)}$ is the Shedlovsky's function which was introduced by Daggett⁷ for various values of Z . The value of Z could be calculated from the equation,

$$Z = \alpha(C\Lambda)^{1/2}/\Lambda_0^{3/2}$$

in which α is the limiting tangent. The plot of $1/\Lambda S_{(Z)}$ against $(C\Lambda S_{(Z)}f^2)$ gives $1/\Lambda_0$ as the intercept and $1/K_D\Lambda_0^2$ as the slope. Fig. (1) illustrates the (FKS) plots for the studied salts.

The true values of the parameters Λ_0 , a° , and K_A were calculated using a computer programme on a PDP 11/70 machine. The accuracies required in these computations for the absolute value deviations are ± 0.02 for Λ_0 ; ± 2 for $J < 200$; ± 5 for $J = 200-1000$; and ± 10 for $J > 1000$. Fig. (2) shows the variation of a° with J , from which a° can be determined by interpolation.

The small values of the standard deviation σ_{Λ} show that the Fuoss-Onsager¹ equation expresses all the experimental data. This indicates that the value of $J_2(C\gamma)^{3/2}$ term in the 4-parameter equation proposed by D'Aprano and others⁸⁻¹¹ may be neglected.

It can be readily seen from Table 2 that Λ_0 increases from acetylcholine chloride to bromide, while it decreases from bromide to iodide to perchlorate according to the ionic equivalent conductance of anions. On the other hand, J and a° decrease with

increasing size of anions. This supports the opinion that¹² for salts with a common cation, the size of anion becomes the controlling factor of the extent of ion pairing since the solvation of the anions increases in the direction: acetylcholine $\text{Cl}^- > \text{Br}^- > \text{I}^- > \text{ClO}_4^-$, which is in accordance with the trend of a° values. From electrostatic point of view, since the distance between cation and anion increases as the anion size decreases, the force of attraction would increase in the order: $\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$, and hence K_A would increase as the anion size increases.

The same behaviour was observed for S-alkylisothiuronium bromides and iodides^{13,14} and tetraethylammonium bromide and iodide¹⁵ in water at 25°C indicating that for salts with a common anion the size of the cation becomes the controlling factor for the extent of ion-pairing.

D'Aprano *et al.* found for some alkali metal ion perchlorates⁸ and chlorates¹⁶ that the extent of ionic association increased with increasing cationic size for any given anion in water at 25°C. They explained these results by taking into account the effect of solvation on ion-pairing¹⁷⁻²⁰.

Evans and Kay²¹ measured the conductances of quaternary ammonium salts of Cl^- , Br^- , and I^- in water at 25°C. They found that the order of a° solvation was $\text{Cl}^- > \text{Br}^- > \text{I}^-$ which is in agreement with the results in Table 2.

In the present case the trend of a° values gives a good support to Sadek's²² conclusion that a° represents the contact distance between the solvated ions. This view is

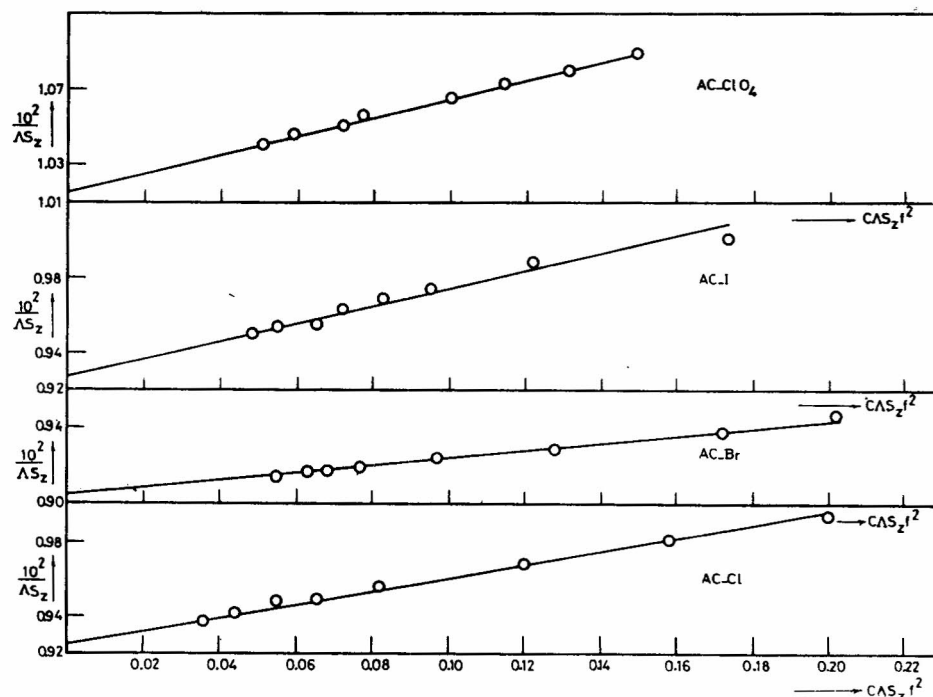
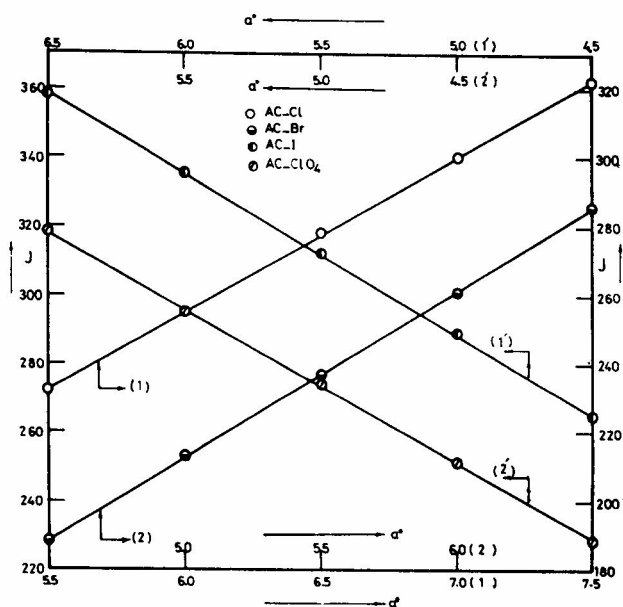


Fig. 1—FKS plots for acetylcholine halides and perchlorate in water at 25°C

Fig. 2—Variation of J with a° in water at 25°C Table 2—The Characteristic Parameters for Acetylcholine Halides and Perchlorate in Water at 25°C

Salt	[Derived from Fuoss-Onsager Equation]				
	Λ_0 (ohm ⁻¹ cm ² equiv ⁻¹)	J	a° (Å)	K_A	σ_Λ
Acetylcholine chloride (Ac.Cl)	107.70 ± 0.09	326	6.69	36.19	0.088
Acetylcholine bromide (Ac.Br)	110.49 ± 0.23	278	5.55	20.86	0.085
Acetylcholine iodide (Ac.I)	107.55 ± 0.12	276	5.59	50.92	0.089
Acetylcholine perchlorate (Ac.ClO ₄)	98.21 ± 0.09	235	5.04	42.84	0.069

in contrast to the original Fuoss' statement that a° represents the distance between unsolvated ions.

The extent of ionic association was found to increase with increasing size of the anion and was discussed in terms of a multiple-step association process²³.

It may be concluded that the sphere in the continuum model is adequate to describe these systems and the simple equation²⁴, $K_A = 4\pi Na^{\circ 3} e^b / 3000 = 2.524 \times 10^{-3} a^{\circ 3} e^b$, where the closest distance of approach a° is in angstroms, does not suffice to describe association. Additional effects must be involved which are specific for a given ion-solvent system.

First, the energy of solvent molecule with respect to two free ions and with respect to the pair which they can make is different; a factor of the form $\exp(-Es/kT)$ calculated by Gilkerson²⁵ is therefore included. The evidence for this point of view was provided by Sadek and Fuoss²⁶ who proposed the expression,

Table 3—Calculated Values of K_2 and U for Acetylcholine Halides and Perchlorate in Water at 25°C

Salt	K_A	K_1	K_2	U
Acetylcholine chloride	36.19	2.19	15.51	2.80
Acetylcholine bromide	20.86	1.56	12.38	2.59
Acetylcholine iodide	50.92	1.58	31.28	3.47
Acetylcholine perchlorate	42.84	1.33	31.24	3.47

$$\ln K_A = \ln(4\pi Na^{\circ 3}/3000) + e^2/a^\circ DkT - Es/kT$$

They found that Es/kT , which allows for ion-dipole interaction in case of Bu_4NBr in $\text{phNO}_2\text{-CCl}_4$, EtOH-CCl_4 , and MeOH-CCl_4 mixtures, equaled -2.0 , -1.5 , and -0.6 respectively. Secondly, the arrangement of the solvent molecules will in general be different around free ions and around pairs, so an entropy factor $\exp(\Delta S/k)$ is also needed.

Accascina, D'Aprano and Triolo¹⁷ developed a more general expression than the one based only on charge-charge interactions,

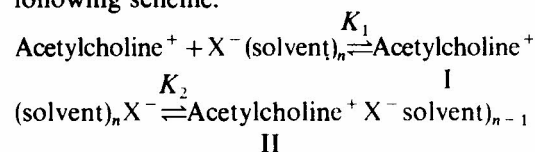
$$\ln K_A = \ln(4\pi Na^{\circ 3}/3000) + e^2/a^\circ DkT + U$$

where, U can be calculated using the relation $U = \Delta S/k - Es/kT$ in which $\Delta S/k$ (the entropy/Boltzmann constant ratio) denotes the probability of the orientation of solvent molecules around free ions and Es/kT includes the energy of solvent molecules with respect to the free ions and the pair which they can make. This equation is consistent with the results obtained for the ClO_3^- ion in $\text{phNO}_2\text{-CCl}_4$, EtOH-CCl_4 and MeOH-CCl_4 .

The values of U for acetylcholine halides and perchlorate salts in water are given in the last column of Table 3.

It can be easily seen from Table 3 that in case of water, U increases slowly as the anionic size increases, i.e., the ratio $\Delta S/k$ increases with increasing anionic size.

Finally, a solvent separated-ion pair model is applied. This model was introduced by Evans and Gardam²³ in the case of tetraalkylammonium salts with a common cation and varying anions in EtOH , PrOH , and BuOH . The same model was also applied in the case of S-alkylisothiuronium iodides in water-methanol²⁷ mixture at 25°C . In this model a multiple step association occurs, where solvent separated and contact ion pairs are involved as presented in the following scheme.



The association constant is given by the equation,

Table 4—Calculation of the Radius of the Ions in Water at 25°C

Parameter	Acetylcholine chloride	Acetylcholine bromide	Acetylcholine iodide	Acetylcholine perchlorate
Λ_0 (ohm ⁻¹ cm ² equiv ⁻¹)	107.70	110.49	107.55	98.21
$\lambda_+^0 \eta^0$ (ohm ⁻¹ cm ² equiv ⁻¹ poise)	0.6804	0.7002	0.6791	0.5974
λ_-^0 (ohm ⁻¹ cm ² equiv ⁻¹)	76.42	78.65	76.28	67.10
λ_-^0 (ohm ⁻¹ cm ² equiv ⁻¹)	31.28	31.84	31.27	31.11
A.V. λ_+^0		31.37 ± 0.28		
R^+ (Å)	2.93	2.93	2.93	2.93
R^- (Å)	1.20	1.17	2.94	2.96
$R^+ + R^-$ (Å)	4.14	4.10	5.88	5.89
a^0 (Å)	6.69	5.55	5.59	5.04

$$K_A = K \Sigma = \frac{C_{(\text{ion pairs})}}{(C_{\text{Acetylcholine}^+}) (C_{X^- (\text{solvent})_n})} = K_1 (1 + K_2)$$

where, $K \Sigma = K_A$ obtained from conductance measurements, and

$$K_1 = 4 \pi N a^{03} / 3000 e^b$$

Thus, K_2 may be calculated. The results are presented in Table 3. It can be readily seen from Table 3 that K_2 increases as anionic size increases, i.e., the formed ion pair prefers the more desolvated form (case II) than the completely solvated one (case I). Accordingly, it may be concluded that, the orientation of solvent molecules surrounding the ion occurs rapidly for large anions. This supports the increase in U on increasing the size of anion.

The electrostatic radii R^+ and R^- can be determined by using the Stokes' equation in the following forms:

$$R^+ = 0.8194 \times 10^{-8} / \lambda_+^0 \eta^0 \text{ and}$$

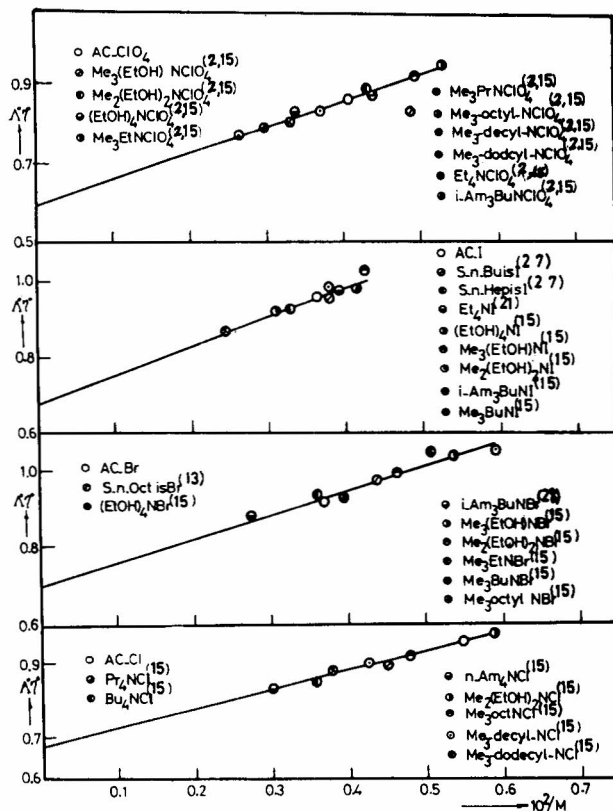
$$R^- = 0.8194 \times 10^{-8} / \lambda_-^0 \eta^0$$

It is clear that the application of these equations necessitates the determination of the true values of ionic conductance. Sadek and Hafez¹³ made a successful attempt, which is based on the plot of the Walden product $\Lambda_0 \eta^0$ against the reciprocal of the molecular weight of a series of electrolytes with a common anion. The same method can also be applied in pure solvents.

The Walden product $\Lambda_0 \eta^0$ for different salts with a common anion is plotted against the reciprocal of the molecular weight of solute in the same solvent (Fig. 3). Straight lines are obtained in which the intercept gives the value $\lambda_-^0 \eta^0$, and hence λ_-^0 can be calculated.

These values are found to be 76.42, 78.65, 76.28 and 67.10 for the Cl^- , Br^- , I^- and ClO_4^- respectively, which are in good agreement with the values 76.39², 78.22², 76.80⁴ and 67.20² reported in literature.

The interpolated λ_-^0 and calculated λ_+^0 were introduced in the Stokes' equation in order to determine the ionic radii and the results are recorded in Table 4. It can be readily seen from Table 4 that the


 Fig. 3—Evaluation of λ_-^0 in water at 25°C

values of a^0 are greater than the electrostatic radii ($R^+ + R^-$) obtained from Stokes' equation. The electrostatic radius of the anion (R^-) is found to increase with increasing anionic size in the following order: $\text{ClO}_4^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$.

References

- 1 Fuoss R M & Onsager L, *J phys Chem*, **61** (1957) 668; Fuoss R M, *J Am chem Soc*, **81** (1959) 2659.
- 2 Robinson R A & Stokes R H, *Electrolyte solutions*, 2nd edn (Butterworths, London), 1959.
- 3 Lind J E, Zwolenik J J & Fuoss R M, *J Am chem Soc*, **81** (1959) 1557.
- 4 Shedlovsky T, *J Am chem Soc*, **54** (1932) 1411.
- 5 Chambers J F, Stokes J M & Stokes R H, *J phys Chem*, **60** (1956) 985.

- 6 Fuoss R M & Kraus C A, *J Am chem Soc*, **55** (1933) 476; Fuoss R M, *J Am chem Soc*, **57** (1935) 488; Fuoss R M & Shedlovsky T, *J Am chem Soc*, **71** (1949) 1496.
- 7 Daggett H M, *J Am chem Soc*, **73** (1951) 4977.
- 8 D'Aprano A, *J phys Chem*, **75** (1971) 3290.
- 9 Hsia K L & Fuoss R M, *Proc Natl Acad Sci*, **59** (1967) 1550.
- 10 Fernandez Prini R & Prue J E, *Z phys Chem*, **228** (1965) 373.
- 11 Justice J C, *J chem Phys*, **65** (1968) 353.
- 12 Evans D F & Gardam P, *J phys Chem*, **72** (1968) 3281.
- 13 Sadek H & Hafez A M, *Electrochim Acta*, **21** (1976) 767.
- 14 Hafez A M, Sadek H & El-Hammamy N H, *Conference on electrochemistry, held in Yugoslavia from 1 to 4 June 1977*.
- 15 Evans D F, Cunningham G P & Kay R L, *J phys Chem*, **70** (1966) 2974.
- 16 D'Aprano A & Donato I D, *Electrochim Acta*, **17** (1972) 1175.
- 17 Accascina F, D'Aprano A & Triolo R, *J phys Chem*, **71** (1967) 3469.
- 18 D'Aprano A & Fuoss R M, *J phys Chem*, **67** (1963) 1704, 1877.
- 19 Gilkerson W R & Ezell B, *J Am chem Soc*, **87** (1965) 3812; **88** (1966) 3484.
- 20 Bodenseh H K & Ramsey J B, *J phys Chem*, **69** (1965) 543.
- 21 Evans D F & Kay R L, *J phys Chem*, **70** (1966) 366.
- 22 Sadek H, Hafez A M & Khalil F Y, *Electrochim Acta*, **14** (1969) 1089.
- 23 Evans D F & Gardam P, *J phys Chem*, **73** (1969) 158.
- 24 Fuoss R M, *J Am chem Soc*, **80** (1958) 5059.
- 25 Gikerson W R, *J chem Phys*, **25** (1956) 1199.
- 26 Sadek H & Fuoss R M, *J Am chem Soc*, **81** (1959) 4507.
- 27 Sadek H, Hafez A M & El-Hammamy N H, *Pakistan J Sci Res*, **29** (1977) 100.
- 28 Kay R L & Evans D F, *J phys Chem*, **70** (1966) 2325.