

Conductance of *S*-Alkylisothiuronium Iodides in Methanol at 25° C

Amina M. Hafez, H. Sadek, and N. H. El-Hammamy

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

Received January 31, 1977

Equivalent conductivities are reported for *S*-Methyl-, *S*-*n*-Butyl, *S*-*n*-Amyl- and *S*-*n*-Heptylisothiuronium iodides in methanol ($D = 32.63$) at 25 °C. The data were analyzed by the Fuoss-Onsager equation for 1:1 associated electrolytes. The characteristic constants: the equivalent conductance at infinite dilution Λ_0 , the closest approach distance a^0 and the association constant K_A are derived.

INTRODUCTION

In 1959 Fuoss and Onsager¹ suggested the 3-parameter conductance equation for 1:1 associated electrolytes

$$\Lambda = \Lambda_0 - S(c\gamma)^{1/2} + E(c\gamma) \log(c\gamma) + J(c\gamma) - K_A(c\gamma) \Lambda f^2 \quad (1)$$

where Λ is the equivalent conductance, c is the concentration in equiv./l and γ is the degree of dissociation and can be calculated from the following relation

$$\gamma = \Lambda / (\Lambda_0 - S \sqrt{\frac{c\Lambda}{\Lambda_0}})$$

while, S and E are theoretically predicted constants depending on the dielectric constant D , the viscosity η and the absolute temperature T , and J is a term which includes the ion-ion and ion-dipole interactions and is given by the equation

$$J = \sigma_1 \Lambda_0 + \sigma_2$$

where, σ_1 and σ_2 are functions of the closest approach distance a^0 in addition to η and D .

In derivation of equation (1) Fuoss and Onsager took into account both the decrease in mobility due to long-range interionic forces and the decrease in the concentration of free ions as a result of electrostatic attraction between oppositely charged ions due to short-range forces. The model used in their calculations is the sphere-in-continuum.

In the present work the conductance measurements are reported for 4 *S*-Alkylisothiuronium iodides in methanol which is a protic solvent at 25 °C. The possibility of application of the F—O equation to these electrolytic solutions will be studied by the derivation of the characteristic constants Λ_0 , a^0 and K_A . The effect of cationic size on the conductance of the studied salts can be discussed from the variation of both K_A and a^0 .

EXPERIMENTAL

Preparation of Salts

S-Methyl-, *S*-*n*-Butyl-, *S*-*n*-Amyl- and *S*-*n*-Heptylthiuronium iodides were synthesized and purified as described in previous papers^{2,3}. Table I shows the melting points and analysis of salts.

TABLE I
Analysis and M.P. of S-Alkylthiuronium Iodides

Salt	M. P./°C		I/%		N/%		S/%	
	Found	Calc'd.	Found	Calc'd.	Found	Calc'd.	Found	Found
<i>S</i> -Methylthiuronium iodide (<i>S</i> -MeisI)	109—110	58.21	58.22	12.85	12.88	14.70	14.70	
<i>S</i> - <i>n</i> -Butylthiuronium Iodide (<i>S</i> - <i>n</i> -BuisI)	105—106	48.80	48.76	10.77	10.82	12.33	12.21	
<i>S</i> - <i>n</i> -Amylthiuronium iodide (<i>S</i> - <i>n</i> -AmisI)	59—60	46.30	46.20	10.22	10.29	11.70	11.60	
<i>S</i> - <i>n</i> -Heptylthiuronium iodide (<i>S</i> - <i>n</i> -HeptisI)	60—61	42.01	42.06	9.27	9.34	10.61	10.58	

Purification of Solvent

Analar analytical reagent methanol (BDH) was kept in contact with molecular sieves 4A (BDH) for about 24 hours with frequent shaking, then distilled and refluxed with analar silver nitrate for 24 hours. After distillation it was refluxed again with analar magnesium turnings for 24 hours and then distilled. The distillate was kept in contact with activated alumina for 24 hours with frequent shaking and then distilled. In all distillations a fractionating column was used and only the middle portion at 65.5 °C/760 mmHg* was collected. Its properties at 25 °C are: density $d = 0.78657 \text{ g ml}^{-1}$ and viscosity $\eta = 0.54448 \text{ cp}$. Its specific conductance κ_0 amounts to $(4-7 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1})$.

Conductance Measurements

An Erlenmeyer conductivity cell with bright platinum electrodes was used. The cell constant is $0.04056 \pm 0.33\%$. A Beckman conductivity bridge Model No. 18A was used for measuring the resistance of the solution at 3 Kc/s. All solutions were prepared by weight reduced to vacuo.

RESULTS AND DISCUSSION

The measured equivalent conductances $\Lambda (\Omega^{-1} \text{ equiv.}^{-1} \text{ cm}^2)$ and the corresponding concentrations c in equiv./l of solution are shown in Table II.

Values of Λ_0 were estimated from the Fuoss-Kraus-Shedlovsky equation⁴.

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

* mmHg = 133 322 Pa

TABLE II

Conductance of S-Alkylisothiuronium Iodides in Methanol at 25 °C

(1) S-MeisI		(2) S-n-BuisI	
10 ⁴ c	Λ	10 ⁴ c	Λ
27.555	96.97	16.618	94.32
22.436	98.26	13.219	95.38
16.157	100.08	10.285	96.34
13.205	101.11	8.1064	97.26
11.484	101.72	6.7135	97.84
9.9196	102.31	5.4893	98.44
8.5392	102.96	4.4538	98.98
6.5190	103.89	3.5428	99.52

(3) S-n-AmisI		(4) S-n-HeptisI	
10 ⁴ c	Λ	10 ⁴ c	Λ
18.476	92.99	17.234	90.61
15.136	93.96	13.584	91.73
11.651	95.07	10.645	92.73
9.0631	96.00	8.0423	93.74
7.5598	96.61	6.8093	94.36
6.1633	97.27	5.6846	94.85
4.9267	97.88	4.7338	95.35
4.1576	98.30	3.9125	95.79

(The deduced Λ_0 values from (FKS) equation for these salts are: (1) 110.62, (2) 104.38, (3) 103.62 and (4) 100.91).

where, K_D is the dissociation constant and $S_{(Z)}$ is the Shedlovsky's function which was tabulated by Dagest⁵ for various values of Z. A compact representation of the data is shown by Figure 1.

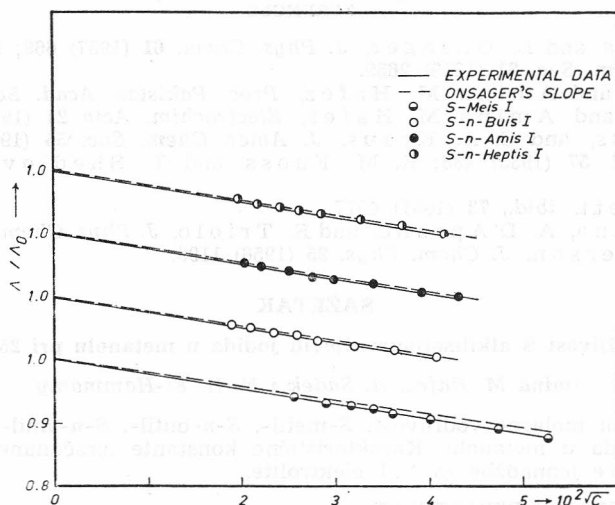


FIG. 1: REDUCED CONDUCTANCES OF S-ALKYLISOTHIURONIUM IODIDES IN METHNAOL AT 25 °C

A computer program on an IBM 1620 machine was used to determine true values of Λ_0 , a^0 and K_A . The accuracies required in these computations are ± 0.02 for Λ_0 , ± 10 for $J < 1000$ and ± 20 for $J > 1000$.

It can be readily seen from Table III that, the standard deviation, σ_A , is small indicating that our computations are correct.

Table III also shows that, there is a sudden decrease in K_A value from 18.18 (S-MeisI) to 6.87 (S-n-BuisI) and it remains almost constant for other normal salts having large cations; while a^0 decreases as the cationic size increases.

This behaviour can be interpreted in the light of the interaction energy U term which is given by the relation⁶:

$$\ln K_A = \ln(4\pi Na^{03}/3000) + e^2/a^0 D kT + U \quad (3)$$

where

$$U = \Delta S/k - E_s/kT$$

in which S/k is an entropy term responsible for the rearrangement of solvent molecules around free ions and around pairs and E_s/kT , a term which allows for ion-dipole interaction⁷.

TABLE III
Constants Derived from Conductance Data Using Equation (3)

Salt	Λ_0	J	a^0	K_A	σ_A	U
S-MeisI	111.03	2408	6.45	18.18	0.069	0.629
S-n-BuisI	104.34	2009	5.48	6.87	0.049	-0.326
S-n-AmisI	103.50	1993	5.48	7.24	0.045	-0.374
S-n-HeptisI	100.83	1810	4.98	6.68	0.052	-0.381

From the last column of Table III, the U term for S-MeisI is higher than for the other salts. This indicates that, the term responsible for the orientation of solvent molecules near the ion is higher than the ion-dipole interaction term for this salt.

REFERENCES

1. R. M. Fuoss and L. Onsager, *J. Phys. Chem.* **61** (1957) 668; R. M. Fuoss, *J. Amer. Chem. Soc.* **81** (1959) 2659.
2. H. Sadek and Amina M. Hafez, *Proc. Pakistan Acad. Sci.* **11** (1974) 1.
3. H. Sadek and Amina M. Hafez, *Electrochim. Acta* **21** (1976) 767.
4. R. M. Fuoss, and C. A. Kraus, *J. Amer. Chem. Soc.* **55** (1933) 476; R. M. Fuoss, *ibid.* **57** (1935) 488; R. M. Fuoss and T. Shedlovsky, *ibid.* **71** (1949) 1496.
5. H. M. Dagett, *ibid.*, **73** (1951) 4977.
6. F. Accascina, A. D'Aprano, and R. Triolo, *J. Phys. Chem.* **71** (1967) 3469.
7. W. R. Gilkerson, *J. Chem. Phys.* **25** (1956) 1199.

SAŽETAK

Vodljivost S-alkilisotouronijevih jodida u metanolu pri 25 °C

Amina M. Hafez, H. Sadek i N. H. El-Hammamy

Određene su molarne vodljivosti S-metil-, S-n-butil-, S-n-amil- i S-n-heptilzotouronij jodida u metanolu. Karakteristične konstante izračunane su s pomoću Fuoss-Onsagerove jednadžbe za 1:1 elektrolite.