

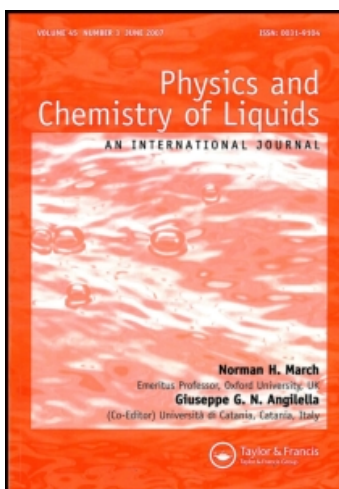
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CONDUCTIVITY PROPERTIES OF SOME TETRAALKYLAMMONIUM IODIDES IN THE WATER + N,N-DIMETHYLFORMA- MIDE MIXTURES AT 298.15 K.

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Conductance measurements are reported for iodides of tetramethylammonium (Me_4NI), tetraethylammonium (Et_4NI), tetrapropylammonium (Pr_4NI), tetrabutylammonium (Bu_4NI), and tetrahexylammonium (Hex_4NI), in the water + N,N-dimethylformamide (DMF) mixtures over the whole composition range, except for Me_4NI and Hex_4NI , where the composition range are 0–50 mol% and 50–100 mol% of DMF, respectively, at 298.15 K. The data obtained have been analyzed by the Fuoss-Justice equation, in terms of the limiting molar conductances (Λ_0), the Walden products ($\Lambda_0\eta$) and the association constant (K_A). Variation in the Walden products with solvent composition are briefly discussed. The results obtained here were also compared with the literature data.

Keywords: Conductances; solution of tetraalkylammonium salts; mixtures of water with N,N-dimethylformamide; walden products

1. INTRODUCTION

This work is a continuation of our earlier study on conductometric properties of univalent electrolytes in the water + DMF mixtures. The conductometric properties of some alkali metal chlorides have been published a few years ago [1]. Recently we have reported on the conductivities of some alkali metal bromides [2], and very recently we have studied the conductivities of some alkali metal iodides in the water + DMF system at 298.15 K [3]. The present work is an extension

of our previous studies and deals with the conductance data for Me_4NI , Et_4NI , Pr_4NI , Bu_4NI and Hex_4NI in the water + DMF mixtures at 298.15 K. These investigations were performed in the whole range of the mixed solvent composition except for Me_4NI and Hex_4NI , where the composition ranges are 0–50 mol% DMF and 50–100 mol% DMF, respectively, because their solubility becomes too low.

2. EXPERIMENTAL

The details of experimental procedures and apparatus used, have been described earlier [1]. The tetraalkylammonium iodides used in this work (Merck or Fluka) were of puris grade, and were further purified by recrystallisation to ensure maximum purity.

The recrystallised salts were dried under vacuum at elevated temperature for a long time immediately prior to use. The solvents used in this work i.e. water and DMF (Apolda, Germany) were purified according to the standard procedure, showing their specific conductance similar to those given in the literature, as it was explained earlier [2]. Solutions and mixed solvent compositions were prepared by weight.

The compositions were accurate to within ± 0.01 wt%. The measurements of the conductivity were performed in the range of 0.0002–0.01 mol dm^{-3} , usually for 16 or more concentrations. All data were corrected at 298.15 K with the specific conductance of the solvent. The values of relative permittivity and viscosity necessary for calculation were taken from the literature [4–6] as well as were numerically interpolated, when necessary. We estimated the accuracy of the measured values of conductivity as better than 0.05 per cent, taking into account the method of measurement, the temperature control and the purity of the reagent.

3. RESULTS AND DISCUSSION

As in the previously published paper [7–24] the conductance data obtained were analysed using the Fuoss-Justice equation [25–27] in the

following form:

$$\Lambda = \alpha[\Lambda_0 - S(\alpha c)^{1/2} + E(\alpha c)\ln(\alpha c) + J(\alpha c) + J_{3/2}(\alpha c)^{3/2}] \quad (1)$$

together with

$$K_A = (1 - \alpha)/(\alpha^2 c y_{\pm}^2) \quad (2)$$

and

$$\ln y_{\pm} = -(A\alpha^{1/2}c^{1/2})/(1 + BR\alpha^{1/2}c^{1/2}) \quad (3)$$

In these equations Λ_0 is the limiting molar conductance, α is the dissociation degree of an electrolyte, K_A is the ionic association constant, R is the distance parameter of ions and y_{\pm} is the mean activity coefficient of ions on the molar scale; (the activity coefficient of the ion pairs is assumed to be equal to unity, as usual for dilute solutions). A and B are the Debye-Hückel equation coefficients. The analytical form of the parameters S , E , J and $J_{3/2}$, are presented in papers [25–28]. The values of Λ_0 , K_A and R , were obtained with the use of the well known procedure given by Fuoss [29]. In this method, the optimized values of Λ_0 and K_A were acceptable, for which the function $\sigma_{\Lambda} = f(R)$ did have a sharp minimum (σ_{Λ} is the standard deviation of the experimental results). The error of the R value i.e. ΔR was estimated as corresponding to $0.1(\sigma_{\Lambda})_{\min}$. This means, that the values of R were closed in the interval for which $\sigma_{\Lambda} \leq 1.1(\sigma_{\Lambda})_{\min}$. The values of Λ_0 , K_A and R thus obtained together with their standard deviations are collected in Tables I–V, for Me_4NI , Et_4NI , Pr_4NI , Bu_4NI , Hex_4NI , respectively. The values of the Walden products ($\Lambda_0\eta$) for investigated here tetraalkylammonium salts are also presented in Tables I–V. The dependencies of limiting molar conductances (Λ_0) and viscosity (η) versus the mixed solvent composition are presented in Figure 1. The dependencies of the Walden products ($\Lambda_0\eta$) versus the mixed solvent composition are illustrated in Figure 2. As it is seen in Figure 1 the viscosity of the solvent mixtures increases rapidly with increasing of DMF, reaching a maximum of nearly 3 times the viscosity of water at about 25 mole % of DMF in the system. When the maximum of the viscosity is attained, then the values of the

TABLE I Limiting molar conductances (Λ_0), association constants (K_A), their standard deviations ($\sigma\Lambda_0$, σK_A), parameters R and their estimated errors (ΔR), and Walden products ($\Lambda_0\eta$) for Me_4NI in the water + DMF mixtures at 298.15

DMF/ mol%	Λ_0	$\sigma\Lambda_0$	K_A	σK_A	R	ΔR	$\Lambda_0\eta$
0.00	121.42	0.05	1.2	0.7	4.0	0.5	1.081
2.50	95.71	0.02	1.4	0.4	4.0	0.5	1.053
5.00	79.17	0.06	1.7	0.8	4.0	1.0	1.049
10.00	58.91	0.05	1.6	0.8	4.5	0.5	1.023
20.00	41.36	0.08	1.8	1.0	4.5	1.0	0.982
25.00	38.76	0.07	2.5	1.1	5.0	1.0	0.963
35.00	37.78	0.06	3.0	1.4	5.0	0.5	0.909
50.00	45.06	0.06	5.2	1.8	5.0	1.0	0.840

TABLE II Limiting molar conductances (Λ_0), association constant (K_A), their standard deviations ($\sigma\Lambda_0$, σK_A), parameters R and their estimated errors (ΔR) and Walden products ($\Lambda_0\eta$) for Et_4NI in the water + DMF mixtures at 298.15

DMF/ mol%	Λ_0	$\sigma\Lambda_0$	K_A	σK_A	R	ΔR	$\Lambda_0\eta$
0.00	109.20	0.04	2.1	0.9	4.0	0.5	0.972
2.62	85.58	0.04	2.0	0.8	4.0	0.5	0.954
5.72	67.79	0.02	2.0	0.7	4.0	0.5	0.936
9.42	54.55	0.01	2.1	0.4	4.5	0.5	0.916
19.52	38.71	0.02	2.0	0.7	4.5	0.5	0.907
27.14	35.32	0.02	2.2	0.6	4.5	0.5	0.884
37.48	36.47	0.01	2.8	0.4	5.0	0.5	0.849
50.67	43.45	0.01	5.1	0.9	5.0	0.5	0.798
68.42	58.28	0.02	6.4	0.9	5.5	0.5	0.749
81.86	71.09	0.01	9.2	1.2	6.0	0.5	0.720
88.09	77.23	0.05	9.8	2.3	6.0	1.0	0.714
100.00	88.07	0.08	12.2	2.9	6.0	1.0	0.700

viscosity decreased slower with the increasing of DMF content in the mixture, up to value of 0.00795 P [6] for pure DMF. From the data given in Tables I–V results, that the values of limiting molar conductances (Λ_0), of investigated in this paper salts increases in the order $\text{Hex}_4\text{NI} < \text{Bu}_4\text{NI} < \text{Pr}_4\text{NI} < \text{Et}_4\text{NI} < \text{Me}_4\text{NI}$. It seems that the mentioned above dependence results from the fact that the size of cations [30] and structure forming effect (hydrophobic solvation) [30] of cations (anion, I, being the same) increases in the reverse order. Similar dependencies for limiting molar conductances of tetraalkylammonium bromides in the water + N,N-dimethylacetamide (DMA)

TABLE III Limiting molar conductances (Λ_0), association constant (K_A), their standard deviations, ($\sigma\Lambda_0$, σK_A), parameters R and their estimated errors (ΔR) and Walden products ($\Lambda_0\eta$) for Pr_4NI in the water + DMF mixtures at 298.15

DMF/ mol%	Λ_0	$\sigma\Lambda_0$	K_A	σK_A	R	ΔR	$\Lambda_0\eta$
0.00	100.27	0.05	2.5	1.2	4.5	1.0	0.893
2.50	78.80	0.06	3.3	1.1	4.5	1.0	0.867
5.00	64.27	0.05	3.0	1.0	4.5	1.0	0.867
10.00	47.68	0.06	3.2	1.1	4.5	1.0	0.852
20.00	34.53	0.04	4.5	1.2	4.5	0.5	0.814
25.00	32.62	0.04	5.1	1.2	5.0	0.5	0.811
35.00	32.39	0.03	4.9	0.9	5.0	0.5	0.778
50.00	39.32	0.03	5.0	1.0	5.0	0.5	0.732
70.00	54.87	0.04	6.5	1.2	5.5	0.5	0.683
80.00	63.81	0.04	8.2	1.4	6.0	0.5	0.664
90.00	72.35	0.03	9.4	1.6	6.0	0.5	0.651
100.00	81.13	0.04	10.5	1.9	6.5	0.5	0.645

TABLE IV Limiting molar conductances (Λ_0), association constant (K_A), their standard deviations, ($\sigma\Lambda_0$, σK_A), parameters R and their estimated errors (ΔR) and Walden products ($\Lambda_0\eta$) for Bu_4NI in the water + DMF mixtures at 298.15

DMF/ mol%	Λ_0	$\sigma\Lambda_0$	K_A	σK_A	R	ΔR	$\Lambda_0\eta$
0.00	96.29	0.03	5.1	1.5	4.5	0.5	0.850
2.50	75.57	0.03	5.2	1.6	4.5	0.5	0.831
5.00	61.86	0.04	5.2	1.9	4.5	0.5	0.820
10.00	45.99	0.01	5.4	1.1	4.5	0.5	0.799
15.00	37.49	0.01	5.3	0.8	4.5	0.5	0.791
20.00	33.02	0.01	4.8	0.5	4.5	0.5	0.779
25.00	30.99	0.01	4.6	0.4	5.0	0.5	0.770
35.00	31.00	0.01	4.4	0.5	5.0	0.5	0.746
50.00	37.31	0.01	4.8	0.9	5.0	1.0	0.696
70.00	52.21	0.02	7.1	1.2	5.5	0.5	0.650
80.00	60.86	0.02	8.2	1.5	6.0	0.5	0.633
90.00	69.48	0.01	9.8	1.1	6.5	0.5	0.616
100.00	78.00	0.05	11.1	1.9	6.5	1.0	0.620

at 308.15 K are given in paper [30]. As it can be seen in Figure 1, the character of the dependencies ($\Lambda_0 = f(\text{composition})$) are similar for all investigated here tetraalkylammonium iodides. The addition of the small amounts of DMF to the water prove to the violent drop in the values of limiting molar conductances, reaching minimum at nearly 30 mol% DMF in the mixture, and subsequently, these values increases up the pure amide. In contrary, the macroscopic viscosity increases, when the small amounts of DMF are added to the water, reaching maximum at nearly 25 mol% DMF in the mixture (see also Figure 1).

TABLE V Limiting molar conductances (Λ_0), association constants (K_A), their standard deviations, ($\sigma\Lambda_0$, σK_A), parameters R and their estimated errors (ΔR) and Walden products ($\Lambda_0\eta$) for Hex_4NI in the water + DMF mixtures at 298.15

DMF/ mol%	Λ_0	$\sigma\Lambda_0$	K_A	σK_A	R	ΔR	$\Lambda_0\eta$
50.00	34.72	0.03	6.1	1.8	5.0	0.5	0.648
70.00	48.68	0.03	7.5	1.9	5.5	0.5	0.606
80.00	57.18	0.04	8.2	2.3	6.0	1.0	0.595
90.00	65.51	0.04	11.0	2.5	6.5	1.0	0.590
100.00	73.67	0.05	14.5	3.2	7.0	1.0	0.586

United in Tables I–V are: Λ_0 and $\sigma\Lambda_0/\text{S cm}^2\text{mol}^{-1}$; K_A and $\sigma K_A/\text{dm}^3\text{mol}^{-1}$; R and $\Delta R/10^{-8}\text{cm}$; $\Lambda_0\eta/\text{S cm}^2\text{mol}^{-1}\text{P}$.

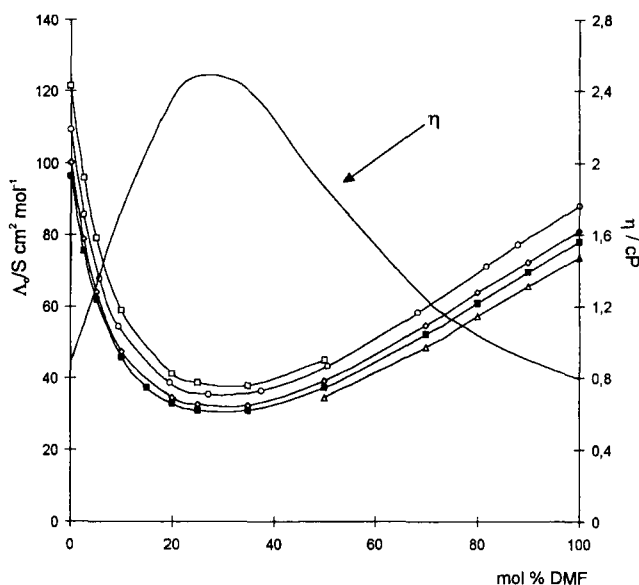


FIGURE 1 Viscosity (η) of water + DMF mixtures and limiting molar conductances (Λ_0) in water + DMF mixtures at 298.15 K for Me_4NI \square ; Et_4NI \circ ; Pr_4NI \diamond ; Bu_4NI \blacksquare and Hex_4NI \triangle .

So, one can supposed, that the changes of the macroscopic viscosity have the substantial influence on the conductivity of investigated electrolytes, according to the Stokes law. However, substantial influence on the ionic mobility have the effective ion size, which are connected with ion-solvent interaction. Therefore, the analyse of the changes of the values of the Walden products ($\Lambda_0\eta$) as the function of

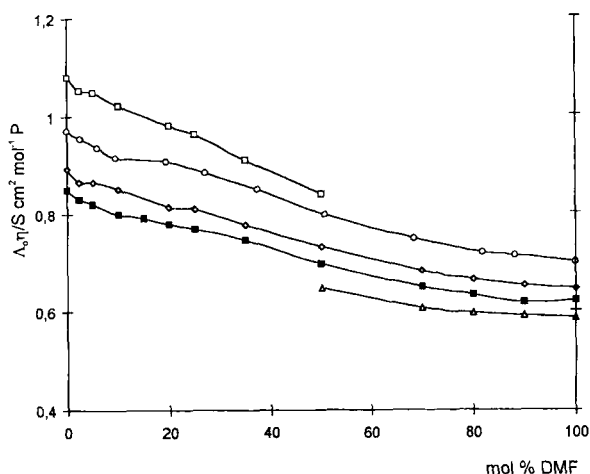


FIGURE 2 Walden product ($\Lambda_0\eta$) in water + DMF mixtures at 298.15 K for: Me₄NI (□); Et₄NI (○); Pr₄NI (◇); Bu₄NI (■) and Hex₄NI (△).

the mixed solvent composition (Fig. 2), seems more interesting. In fact, as it seen in Figure 2, the values of the Walden products for all five investigated here electrolytes decreases monotonically in the whole range of the mixed solvent composition. The differences in types of the dependencies $\Lambda_0\eta = f(\text{composition})$ for the tetraalkylammonium iodides studied here and the tetraalkylammonium bromides investigated in Ref. [30] in the water + N,N-dimethylacetamide (DMA) are evident.

As was mentioned in paper [30], both water + DMF and water + DMA mixtures indicate the close similarity. Even so, the dependencies $(\Lambda_0\eta) = f(\text{composition})$ for the salts of the type of R₄NBr, reach a maximum at nearly 10 mol% DMA. Bahadur and Ramanamurti [30] have analysed the maximum of the values of $(\Lambda_0\eta)$ with regard to the possibility of tetraalkylammonium cations to the hydrophobic solvation. Moreover, the authors [30] concluded, that height of the maxima in the Walden product are of the order Me₄N⁺ > Bu₄N⁺ > Et₄N⁺. On the other side, the ability of these cations to hydrophobic hydration varies in the order Bu₄N⁺ > Et₄N⁺ > Me₄N⁺, which in opinion of the authors of paper [30], can be attributed, to the fact, that Me₄N⁺ is a structure breaker, while greater cations such as Et₄N⁺, and Bu₄N⁺ are hydrophobic in nature. Owing to the conclusion given

in paper [30], we would like however to express our opinion, that the analysis of the dependencies $(\Lambda_0\eta) = f(\text{composition})$ could be unsatisfactory for the estimation of the nature of the interaction tetraalkylammonium cation with solvent.

The above mentioned opinion can be confirmed by the fact that in the case of tetraalkylammonium iodides, investigated by us the dependencies $(\Lambda_0\eta) = f(\text{composition})$ decrease monotonically. We would like also to express here our opinion, that the differences in the dependencies $(\Lambda_0\eta) = f(\text{composition})$ for tetraalkylammonium halides in the mixtures water + N,N-disubstituted amide, result in substantial differences between mobilities of chloride and bromide ions in these mixed solvents.

Moreover, the above mentioned maxima on the dependencies $(\Lambda_0\eta) = f(\text{composition})$ will not be observed, if the mobility of iodide ions decreases in the greater extent (or increases in the smaller extent) than the mobility of chloride ions, when the small amounts of N,N-disubstituted amide are added to the water. On the other hand, our opinion can be confirmed by the fact that the maximum of the values of the Walden products are present, when the small amounts of DMF are added to the water, in the case of alkali metal chlorides investigated earlier, but are not observed in the case of alkali metal iodides [3]. However, this fact, that these maxima are observed (or are not observed) in the case of the above mentioned alkali halides gives any connection with the hydrophobic solvation of ions. So, we can conclude that the more precise conclusions on the ion-mixed solvent molecule interaction could be drawn on the basis of the analysis of the dependencies $(\Lambda_0\eta) = f(\text{composition})$ for the single ions.

Furthermore, as results from the data given in Tables I–V, the values of the association constants (K_A) are relatively small and most frequently do not exceed the values of order of ten, so we can consider the electrolytes investigated here as practically completely dissociated. The results obtained in this paper of our investigations were only briefly discussed. However, nothing more can be said on the present state of investigations, and further studies are necessary on the conductances of other univalent ions in the water + DMF mixture. These results will be published in a subsequent paper.

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