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A STUDY OF CONDUCTOMETRIC BEHAVIOR OF $NaClO_4$ AND Et_4NClO_4 IN ISOPROPANOL-METHANOL MIXTURES AT 25° C.

by

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Abstract: *Conductivity measurements of dilute solutions of* $NaClO_4$ *and* Et_4NClO_4 *in various mixtures of isopropanol-Methanol at 25°C arc reported. The experimental data were analyzed by mcans of Fuoss-Onsager-Skinner equation. The values of limiting equivalent conductance, the association constants and ion-size parameters are given. Variations in the Walden products of* $NaClO_4$ *and* Et_4NClO_4 *with solvent composition are reported. In this paper it is also discussed the effect of the decreasing amount of methanol in solvent mixtures on the solvation of the ion. Dielectric constants and viscosities of the mixed solvents used are also given.*

Zusammenfassung: *Leitfähigkeitsmsesnngen von verdünnten* $NaClO_4$*-bzw* Et_4NClO_4 *-Lösungen in Isopropanol-Methanol-Gemischen von verschiedener Zusammensetzung bei 25°C werden durchgeführt. Die Versuchsergebnisse werden mit Hilfe der Fnoss-Onsager-Skinner'schen Gleichung ausgewertet. Die Werte dcr Äquivalentleitfähigkeit bei unendlicher Verdünnung, die Assoziationskonstanten und die Ionengrössen, sowie auch Änderungen im Walden'schen Produkt von* $NaClO_4$ *und* Et_4NClO_4 *mit der Zusammensetzung des Lösungsmittels werden angegeben. Es wird zunächst die Einwirkung von der abnehmenden Methanolmenge im Lösungsmittel auf die Ionensolvatation diskutiert. Die Dielektrizitätskonstanten und die Viskositätskoeffizienten der untersuchten gemischten Losungsmittel werden ebenfalls angegeben.*

INTRODUCTION

The use of non aqueous solvents in electrochemical studies, as well as mixed solvents, for studying the effect of the solvent on solvation of the ions, ion-ion interaction and ionic behavior in general, is of increasing interest.

In this work has been studied the conductance of dilute solutions of $NaClO_4$ and Et_4NClO_4 in solvent mixtures of isopropanol-methanol at 25° C.

The selection of the above mentioned solvents was succeeded between substances with 1) a similar chemical behavior so that the influence of the chemical factor reaches the minimum and 2) a remarkable difference to the physical properties so that the effect of the physical factor on the conductometric behavior of the salts mentioned can be mainly studied.

The values of the limiting equivalent conductance, of the association constant and the «ion-size» parameter have been calculated in all mixtures studied.

It was found that in methanol solutions the ionic conductance of alkalimetal ions is proportional to their crystallographic radius[1,2], because of the solvation effect, while the ionic conductance of tetraalkylammonium ions decreases when the crystallographic radius of the cation increases[3]. Therefore we have done a comparative study of the equivalent conductance of the two salts in the above mentioned solvent system as the methanol is replaced in steps by isopropanol.

EXPERIMENTAL SECTION

The $NaClO_4$ (Carlo Erba) was recrystallized three times from distilled water and dried in vacuum[4]. The Et_4NClO_4 was recrystallized twice from n-butanol and dried at 150°C in vacuum[5].

Methanol (Fluka) was purified according to the Evers-Knox[6] method. The value of specific conductance was found between $2{\cdot}10^{-7}$ and $4{\cdot}10^{-7}$ $mho{\cdot}cm^{-1}$ being in accordance to the values given in bibliography[3,7].

The isopropanol (Aldrich)-i-prOH- was used after two distillations and the value of specific conductance was $2{\cdot}10^{-7}$—$3{\cdot}10^{-8}$ $mho{\cdot}cm^{-1}$.

During the measurments the temperature was kept constant at 25.000±0.002° C by means of an oil bath thermostat made by Leads and Northrup Co., and it was checked with a Beckmann thermometer with an accuracy of 0.001° C.

The conductivity bridge used to measure the resistance of the various solutions was a Beckman bridge Type RC-18A.

Resistance measurments were made on a frequency of 3000 c/sec. Measurments made on a 1000 c/sec frequency showed that the corresponding values of equivalent conductance were identical in both frequencies.

The dielectric constants (D) of the various isopropanol-methanol mixtures were determined by means of a Dipolmeter WTW type DM 01, which is based on the heterodyne principle.

The densities were measured at 25° C using a Sprengel pycnometer and the viscosities (η) using an Ubbehlode viscometer, calibrated with conductivity water ($\eta = 8.903 \cdot 10^{-3}$ poise, $d = 0.99707 g.cm^{-3}$ at 25° C)[8].

The two conductance cells used, were similar to that discribed by Dagget Bair and Kraus[9]. Their constants were determined by the Jones and Bradshaw[10] method and were found equal to 1,024 cm^{-1} and 1,031 cm^{-1}.

In brief the working procedure was as follows: A quantity of freshly prepared solvent was set into the conductance cell and quantities of concentrated stock solution of the salt were added to it.

Each time the concentration of the salt in the solution was calculated and the corresponding resistance was measured; then the equivalent conductance of the solution was calculated. Special care was taken to avoid contact between the solution and the free atmosphere.

RESULTS AND DISCUSSION

The values of viscosity and of dielectric constant are listed in table I.

TABLE I

Physical Properties of Isopropanol-Methanol Mixtures at 25°C.

Isopropanol v/v%	$\eta \cdot 10^2$poise	D
0	0.544	32.75
10	0.608	31.40
20	0.668	30.00
30	0.734	29.20
40	0.824	27.25
50	0.922	26.47
60	1.056	24.55
70	1.209	23.26
80	1.422	22.00
90	1.681	20.70
100	2.070	19.45

In figure 1 is represented the rate of change of the viscosity with the percentage of isopropanol in isopropanol-methanol mixtures at 25°C. It shows that viscosity increases smoothly with the amount of isopropanol.

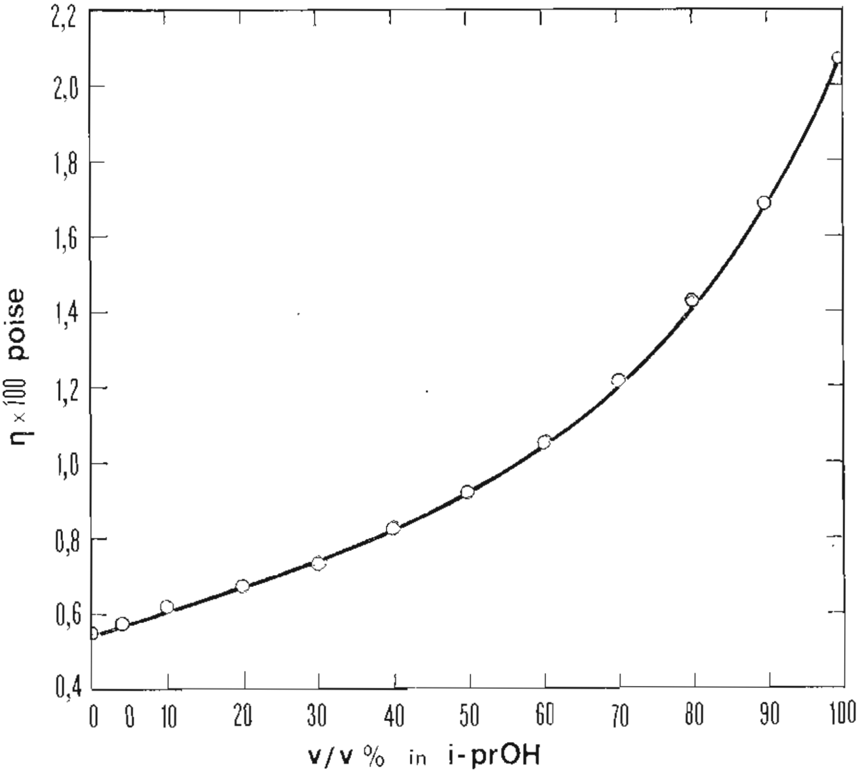

Fig. 1. Variation of the viscosity of isopropanol-methanol mixtures vs. isopropanol percentage at 25°C.

The concentrations and equivalent conductances are summarized in table II and III. Solvent correction was made, substracting the specific conductances of solvents from the specific conductances of solutions.

Because of the low solubility of Et_4NClO_4 in isopropanol, measurments for this salt over 50% isopropanol were not made.

The resulting values were analyzed by meaus of Fuoss-Onsager-Skinner[11] conductance equation:

$$\Lambda = \Lambda^0 - Sc^{1/2}\gamma^{1/2} + E' c\gamma \ln (6E'_1 c\gamma) + Lc\gamma - K_A c\gamma f^2 \Lambda \qquad (1)$$

for associated electrolytes, and by the equation

$$\Lambda = \Lambda_0 - Sc^{1/2}\gamma^{1/2} + E' c \ln (6E'_1 c) + Lc \qquad (2)$$

TABLE II

Conductances of $NaClO_4$ in Isopropanol-Methanol Mixtures at 25°C.

$C\cdot10^4$ gm.equiv· lit^{-1}	Λ Mho·cm^2· equiv^{-1}	$\Delta\Lambda$	$C\cdot10^4$ gm. equiv· lit^{-1}	Λ Mho·cm^2· equiv^{-1}	$\Delta\Lambda$
0% in i-prOH			10% v/v in i-prOH		
6.0503	110.77	0.02	6.5440	99.85	0.00
11.905	108.16	0.01	12.877	97.22	0.04
17.574	106.25	0.02	19.008	95.38	-0.01
23.067	104.76	-0.01	24.949	93.86	0.01
33.552	102.47	-0.07	36.289	91.63	-0.09
43.420	100.70	-0.10	46.963	89.86	-0.08
52.724	99.31	-0.14	57.026	88.43	-0.06
61.512	98.11	-0.11	66.531	87.28	-0.06
69.824	97.11	-0.10	75.552	86.26	0.00
77.699	96.22	-0.04	84.039	85.40	0.05
85.170	95.45	0.01			
20% v/v in i-prOH			30% v/v in i-prOH		
5.0291	90.23	-0.16	5.6535	79.50	-0.07
9.8960	87.95	-0.08	11.124	77.21	0.03
14.608	86.25	0.00	16.422	75.48	0.14
19.173	84.92	0.04	21.554	74.32	0.01
27.888	82.94	0.00	31.351	72.32	-0.02
36.091	81.40	-0.01	40.572	70.81	-0.07
43.825	80.15	-0.02	49.266	69.55	-0.05
51.129	79.11	-0.01	57.477	68.49	-0.03
58.039	78.20	0.01	65.245	67.58	0.00
64.584	77.39	0.07	72.603	66.82	0.02
70.794	76.71	0.11	79.584	66.17	0.02

$C\cdot10^4$ gm.equiv· lit^{-1}	Λ Mho·cm^2· equiv^{-1}	$\Delta\Lambda$	$C\cdot10^4$ gm.equiv· lit^{-1}	Λ Mho·cm^2· equiv^{-1}	$\Delta\Lambda$
40% v/v in i-prOH			50% v/v in i-prOH		
4.9369	69.92	0.13	5.7655	60.25	-0.17
9.7146	67.99	0.06	11.345	58.03	-0.03
14.340	66.56	0.01	16.747	56.41	0.05
18.822	65.37	0.02	21.981	55.13	0.11
27.377	63.52	0.00	31.972	53.24	0.07
35.429	62.11	-0.03	41.376	51.82	0.01
43.021	60.96	-0.04	50.243	50.65	0.00
50.192	60.02	-0.06	58.616	49.70	-0.02
56.974	59.16	-0.03	66.538	48.90	-0.01
63.400	58.46	-0.03	74.042	48.21	-0.02
69.496	57.84	-0.01	81.161	47.61	-0.02

60% v/v in i-prOH

7.2688	50.58	-0.14
14.303	48.08	0.03
21.114	46.35	0.08
27.712	45.02	0.07
34.107	43.91	0.08
40.309	43.01	0.04
52.164	41.56	-0.03
63.342	40.40	-0.05
73.900	39.47	-0.06
83.886	38.71	-0.07
93.347	38.04	-0.03
102.323	37.47	0.01

70% v/v in i-prOH

9.9719	40.65	-0.15
19.622	37.88	0.01
28.966	36.00	0.07
38.017	34.59	0.06
46.791	33.48	0.04
55.298	32.56	0.00
63.552	31.79	-0.03
71.563	31.14	-0.07
86.898	30.07	-0.12
101.381	29.23	-0.12
115.081	28.53	-0.06
128.060	27.94	0.01
140.373	27.46	0.10

80% v/v in i-prOH

7.3225	32.98	0.03
14.408	30.52	0.10
21.270	28.85	0.11
27.917	27.61	0.08
40.606	25.82	0.04
52.550	24.59	-0.03
63.810	23.66	-0.08
74.445	22.93	-0.10
84.506	22.33	-0.09
94.036	21.83	-0.06
103.078	21.40	-0.02

90% v/v in i-prOH

5.6687	25.44	-0.04
11.154	23.15	0.03
16.466	21.65	0.05
21.612	20.54	0.06
31.435	19.03	0.00
40.681	17.97	-0.04
49.398	17.17	-0.05
57.632	16.54	-0.03
65.420	16.03	0.00
72.798	15.61	0.01
79.798	15.26	0.05

$C\cdot 10^4$ gm. equiv· lit^{-1}	Λ Mho·cm^2· equiv.$^{-1}$	$\Delta\Lambda$
100% i-prOH		
6.2079	16.99	0.00
12.215	14.67	0.01
18.032	13.30	0.01
23.667	12.36	0.00
34.425	11.13	-0.03
44.550	10.32	-0.03
54.097	9.74	-0.02
63.114	9.30	0.00
71.642	8.96	0.01
79.723	8.67	0.05
87.738	8.44	0.01

TABLE III

Conductances of Et_4NClO_4 in Isopropanol-Methanol Mixtures at 25°C.

$C \cdot 10^4$ gm.equiv·lit^{-1}	Λ Mho·cm^2·equiv^{-1}	$\Delta\Lambda$	$C \cdot 10^4$ gm.equiv·lit^{-1}	Λ Mho·cm^2·equiv^{-1}	$\Delta\Lambda$
0% i-prOH			10% v/v in i-prOH		
2.8867	125.60	0.09	4.1513	112.66	-0.02
5.6803	122.76	0.02	8.1687	109.02	0.08
8.3853	120.52	0.02	12.058	106.33	0.08
11.005	118.67	0.01	15.827	104.11	0.11
16.008	115.78	-0.07	23.021	100.72	0.00
20.716	113.47	-0.11	29.792	98.05	-0.02
25.155	111.54	-0.10	36.176	95.89	-0.04
29.348	109.90	-0.06	42.205	94.11	-0.07
33.314	108.48	-0.02	47.908	95.58	-0.07
37.071	107.16	0.12	53.312	91.24	-0.03
40.636	106.12	0.10	58.438	90.02	0.05
20% v/v in i-prOH			30% v/v in i-prOH		
3.3898	101.43	0.04	3.3713	89.66	-0.06
6.6704	98.42	0.01	6.6338	86.43	0.05
9.8467	96.11	-0.02	9.7928	84.03	0.06
12.923	94.16	0.00	12.853	82.12	0.02
18.798	91.10	-0.02	18.695	79.07	-0.02
24.327	88.61	0.06	24.194	76.70	-0.05
29.504	86.74	-0.06	29.378	74.76	-0.03
34.463	85.00	0.03	34.275	73.18	-0.06
39.121	83.61	-0.01	38.906	71.78	0.00
43.533	82.39	-0.02	43.294	70.62	-0.01
47.719	81.32	-0.04	47.457	69.55	0.06

$C \cdot 10^4$ gm.equiv·lit^{-1}	Λ Mho·cm^2·equiv^{-1}	$\Delta\Lambda$	$C \cdot 10^4$ gm.equiv·lit^{-1}	Λ Mho·cm^2·equiv^{-1}	$\Delta\Lambda$
40% v/v in i-prOH			50% v/v in i-prOH		
1.6628	81.71	-0.06	2.4546	69.47	-0.03
3.2720	79.45	-0.02	4.8300	66.71	0.00
4.8301	77.65	0.04	7.1301	64.60	0.03
6.3395	76.21	0.03	9.3582	62.90	0.04
7.8025	74.97	0.04	11.517	61.52	-0.01
9.2211	73.88	0.04	13.612	60.26	0.01
11.933	72.09	-0.01	17.615	58.26	-0.03
14.490	70.60	-0.02	21.390	56.63	-0.05
16.905	69.34	-0.03	24.955	55.25	-0.01
19.189	68.22	0.02	28.327	54.12	-0.02
21.354	67.31	-0.01	31.522	53.12	0.00
23.407	66.48	0.00	34.553	52.27	0.00
			37.433	51.50	0.04
			40.172	50.88	-0.03

for non associated electrolytes,
in which S ($=\alpha\Lambda_0+\beta$) is the Onsager limiting slope, $E=E'_1\Lambda_0-E'_2$ the Fuoss-Onsager constant, L a constant-which is a function of the «ion-size» å-γ the degree of dissociation, f the activity coefficient and K_A the association constant.

The computation of the three parameters Λ_0, K_A, L (or å) was done on an Univac 1106 Computer, by means of a program which finds the values of Λ_0, K_A, and å, which values minimise the sum of $(\Delta\Lambda_i)^2$, where

$$\Delta\Lambda_i = \Lambda_{obs.} - \Lambda_{calc.}$$

In the cases where there is no association the analysis of the data were done by means of the equation (2).

The results of the analysis are listed in tables IV and V.

TABLE IV

Conductance Parameters and Constants for $NaClO_4$ in Isopropanol-Methanol Mixtures at 25°C.

i-prOH v/v %	Λ_0	K_A	å	L	σ_Λ	$\Lambda_0\eta$
0	117.38		3.4	692.6	0.07	0.638
10	106.34		3.3	604.8	0.05	0.646
20	95.48		3.3	556.7	0.07	0.637
30	84.80		3.1	435.7	0.05	0.629
40	74.87		3.1	371.9	0.05	0.617
50	65.01	6	3.0	286.5	0.07	0.599
60	55.92	14	3.0	205.1	0.07	0.590
70	46.76	29	2.9	105.1	0.08	0.565
80	38.65	99	3.1	106.2	0.07	0.549
90	30.66	242	3.3	103.4	0.04	0.515
100	23.95	806	3.7	139.5	0.02	0.495

TABLE V.

Conductance Parameters and Constants for Et_4NClO_4 in Isopropanol-Methanol Mixtures at 25°C.

i-prOH v/v %	Λ_0	K_A	å	L	σ_Λ	$\Lambda_0\eta$
0	131.72	44	4.4	1108.5	0.08	0.716
10	119.89	48	3.4	678.6	0.06	0.728
20	107.64	50	2.8	374.5	0.03	0.719
30	95.80	76	3.2	489.6	0.04	0.703
40	85.89	122	4.6	950.6	0.03	0.707
50	74.64	144	3.5	475.9	0.03	0.688

As is shown in tables IV and V the limiting equivalent conductances, Λ_0 for $NaClO_4$ as well as for Et_4NClO_4 are decreasing smoothly with isopropanol enrichment of the solvent, because of the increasing viscosity of the mixtures. As shown in Figure 2 the Walden products, $\Lambda_0 \cdot \eta$, for the two salts show no constancy, but they increase smoothly with the dielectric constant of the solvent. These curvatures can be explained as follows:

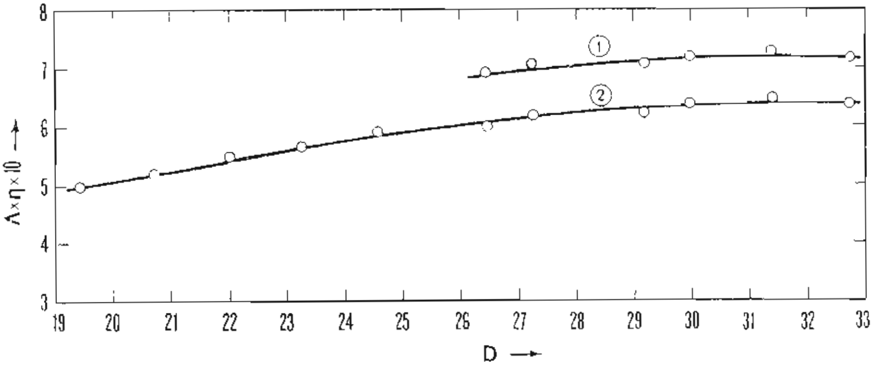

Fig. 2. $\Lambda_0 \cdot \eta$ *vs. D for* $NaClO_4$ *(1) and* Et_4NClO_4 *(2) in isopropanol-methanol mixtures at 25°C.*

As an ion moves in the solution, it orients the dipoles of the solvent in its vicinity. There will be an orientation of solvent molecules in front of the moving ion and a relaxation to a random orientation behind it. The steady state will correspond to a net excess of oriented dipoles behind the moving ion and a deficiency in front, and therefore the moving ion will be retarted in any polar solvent. This effect is at least a reason why $\Lambda_0 \cdot \eta$ is not constant[12].

Comparison of the limiting equivalent conductance values between $NaClO_4$ and Et_4NClO_4 shows that the cations (at least the Na^+) undergo intensive solvation. Although the crystallographic radius of Et_4N^+ is much greater than that of the Na^+ radius the limiting equivalent conductances of $NaClO_4$ are always much less than the corresponding values of Et_4NClO_4. This result can be explained by the decrease of mobility owning to the solvation of Sodium ion.

In pure methanol, Et_4NClO_4 shows significant association, which increases as the dielectric constant decreases, while $NaClO_4$ in pure methanol as well as in mixted solvents up to 50% in isopropanol-that is up to a dielectric constant 26.47 behaves as non associated electro-

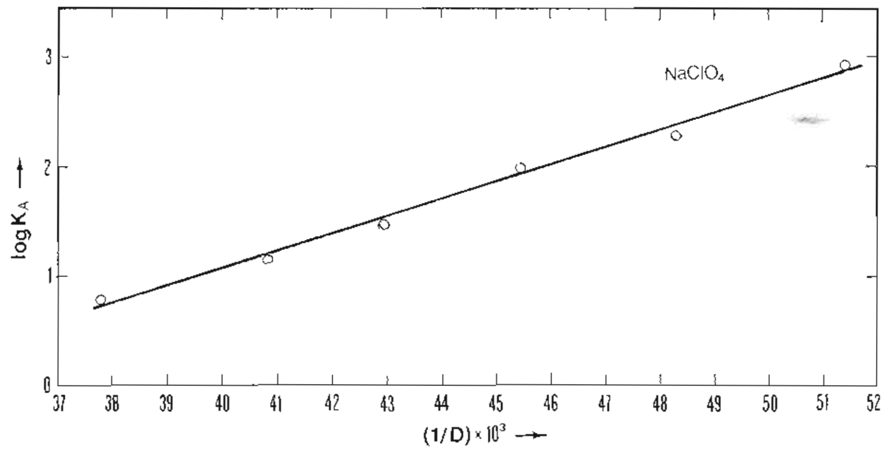

Fig. 3. Dependence of the $\log K_A$ *of* $NaClO_4$ *on reciprocal of dielectric constant in isopropanol-methanol mixtures.*

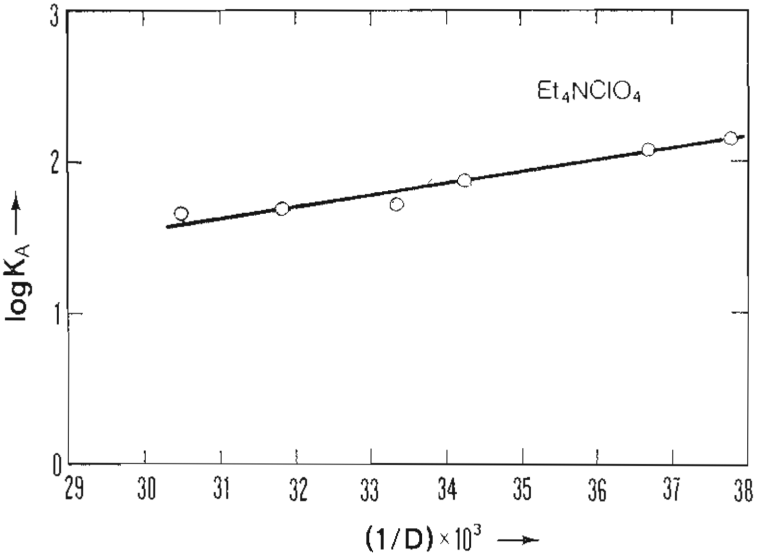

Fig. 4. Dependence of the $\log K_A$ *of* Et_4NClO_4 *on resiprocal of dielectric constant in isopropanol-methanol mixtures.*

lyte; however for lower dielectric constant values, association increases rapidly. The K_A for $NaClO_4$ reaches the value 806 (in pure isopropanol), although the dielectric constant has increased only seven units. In Fig. 3 and 4 is shown the dependence of $\log K_A$ on the reciprocal dielelecrric constant, and it will be seen that the points average to a satisfactory straight line. The linearity means that the Denison-Ramsay[13] relation.

$$\log K_A = \log K_0 + \frac{e^2}{2.303kDaT}$$

holds true,

but the values of a_x -computed from the slopes of the lines-are smaller than the sum of crysrallographic radii and smaller than the values that we get from the term L of the Fuoss-Onsager-Skinner equation. This is an indication that between the ions which form the ionic pairs no molecules of solvents exist[14].

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ΠΕΡΙΛΗΨΙΣ

ΜΕΛΕΤΗ ΤΗΣ ΑΓΩΓΙΜΟΜΕΤΡΙΚΗΣ ΣΥΜΠΕΡΙΦΟΡΑΣ ΤΩΝ $NaClO_4$ καὶ Et_4NClO_4 ΕΝΤΟΣ ΜΙΚΤΩΝ ΔΙΑΛΥΤΙΚΩΝ ΣΥΣΤΗΜΑΤΩΝ ΙΣΟΠΡΟΠΑΝΟΛΗΣ - ΜΕΘΑΝΟΛΗΣ

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Μελετᾶται ἡ ἀγωγιμομετρικὴ συμπεριφορὰ ἀραιῶν διαλυμάτων $NaClO_4$ καὶ Et_4NClO_4 εἰς διαλυτικὰ συστήματα ἰσοπροπανόλης-μεθανόλης διαφόρων περιεκτικοτήτων εἰς ἰσοπροπανόλην. Τὰ πειραματικὰ δεδομένα ἀνελύθησαν διὰ τῆς ἐξισώσεως τῶν FUOSS-ONSANGER-SKINNER καὶ δίδονται αἱ τιμαὶ τῆς ἰσοδυνάμου ἀγωγιμότητος ἀπείρου ἀραιώσεως, τῆς σταθερᾶς συζεύξεως καὶ τῆς παραμέτρου τοῦ ἰονικοῦ μεγέθους α. Μελετᾶται ἡ ἐξάρτησις τοῦ γινομένου WALDEN τῶν διαλυμάτων τοῦ $NaClO_4$ καὶ Et_4NClO_4 ἐκ τῆς συστάσεως τοῦ διαλύτου. Ἐπίσης ἐξετάζεται ἡ ἐπίδρασις τῆς σταδιακῆς ἀντικαταστάσεως τῆς μεθανόλης ὑπὸ τῆς ἰσοπροπανόλης εἰς τὸν διαλύτην ἐπὶ τοῦ φαινομένου τῆς ἐπιδιαλυτώσεως τῶν ἰόντων.

Δίδονται αἱ διηλεκτρικαὶ σταθεραὶ καὶ τὰ ἰξώδη τοῦ συστήματος ἰσοπροπανόλης-μεθανόλης εἰς ὅλην τὴν ἔκτασιν τῶν μελετηθεισῶν περιεκτικοτήτων.