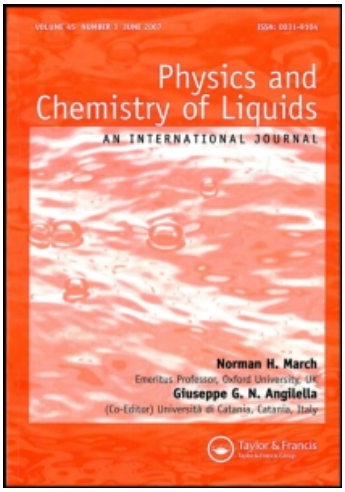

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CONDUCTANCE OF ASYMMETRIC IODIDES OF BUTYL-TRIETHYL-AMMONIUM IN TOLUENE-ACETONITRILE MIXTURES AT 25°C

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The conductance of ter-$BuEt_3NI$, sec-$BuEt_3NI$, iso-$BuEt_3NI$, *n*-$BuEt_3NI$ and Bu_4NI in toluene acetonitrile mixtures has been measured. The range of dielectric constant of the solvent mixtures covered from 9,4 to 35,9. The densities and viscosities of the solvent mixtures were also determined. The phoreograms of the ter-$BuEt_3NI$ and sec-$BuEt_3NI$ in the mixtures having molar fractions of toluene of 0,4, 0,5 and 0,6 and those of the iso-$BuEt_3NI$ and Bu_4NI in the molar fractions 0,3, 0,4 and 0,5 show similar shape. The phoreograms lie below the Onsager limit line. The conductance data for the salts having asymmetric cations were analyzed using the Fuoss Onsager equation for unassociated 1-1 electrolytes. The data for the salt *n*-BuEt3NI in mixtures of mole fraction 0,1, 0,2 and 0,4 of toluene were fitted to the equation. All other systems studied did not fit. This investigation suggests that the geometry of the hydrocarbons chains has an effect on the conductance behaviour of ammonium salts.

KEY WORDS: Fuoss-Onsager equation, mixed solvents, acetonitrile, toluene, asymmetric tetraalkylammonium salts.

1 INTRODUCTION

The decrease of molar conductance with increasing electrolyte concentration as a result of the effects of decreasing mobility of the free ions and of the relative concentration of free ions has been pointed out by the theories of electrolytes[1]. Also, for wide variety of electrolyte systems the phoreograms approach the Onsager tangent in the limit of infinite dilution[2], Fuoss[3] has shown that if the phoreograms lie below the limiting tangent (catabatic phoreograms); ion association or incomplete dissociation could provide a satisfactory explanation.

One of the main features of the theories of electrolytic conductance is the use of the model of rigid charged spheres in a continuum[4]. The latest models eliminate a number of artifacts that cannot be correlated unambiguously with the properties of a real physical systems; there is restriction to symmetrical ions. Unfortunately, this restriction has disregarded a great number of studies on non-symmetric electrolytes systems.

Table 1 Properties of Toluene acetonitrile mixtures at 25° C[1].

Molar fraction (x)	ρ *(g/cm³)*	η *(cP)*	ε^2
0,000	0,77664	0,3525	35,68
0,102	0,79289	0,3696	29,08
0,193	0,80528	0,3887	23,93
0,298	0,81737	0,4127	18,83
0,401	0,82764	0,4378	14,71
0,492	0,83562	0,4599	11,81
0,597	0,84302	0,4682	9,31

[1] ρ is the density, η is the viscosity. ε^2 is the relative permittivity calculated from Ref. 6.

The asymmetric alkylammonium salts offer a useful way to study the effect of a single hydrocarbon chain of the cation on the conductance behavior. In this case, we used the butyl isomers. The present study involves the determination of molar conductivities for a number of 1:1 asymmetric cation electrolytes in toluene-acetonitrile mixtures for the molar fractions 0,0 to 0,6 of toluene. Our interest is to evaluate the effect of the butyl isomers on the conductivity. Also in these mixtures of solvents of medium and low dielectric constant, one expects and should find association of ions to give nonconducting pairs.

2 EXPERIMENTAL

Bu_4NI (Sigma,puriss p.a) was recrystallized twice from a methanol-acetone mixtures and dried under vacuum over P_2O_5. Acetonitrile (Merck, puriss p.a.) was passed through 3 Å molecular sieves and fractionally distilled. Toluene (Merck, extra pure) was shaken with cold concentrated H_2SO_4 in order to remove traces of thiophene, next with water then with 5% aq.$NaHCO_3$, and finally with water again. It was dried with $CaSO_4$ and P_2O_5 and fractionally distilled from P_2O_5. The middle fraction of the distillate was used.

The salts were obtained and analyzed using methods described previously [5,6]. All salts were stored in a vacuum dessiccator protected from light. The melting points found of the salts are: iso-$BuEt_3NI$, 152,5°C; sec-$BuEt_3NI$, 175,5°C; ter-$BuEt_3NI$, 173,5°C; *n*-$BuEt_3NI$, 208,4°C; and Bu_4NI, 143,0°.

Conductance measurements were carried out using a LKB 3216 bridge, whose stated accuracy is 0,05%. All conductivity measurements were carried out in the laboratory using a water bath thermostated at 298,15 K controlled to $\pm$0,02K. Solutions of the salts for conductance measurements were made up by weight.

Densities of the mixed solvents were determined with a calibrated Sprengel pycnometer. The viscosities of the solvent mixtures were measured with an Ubbeholde viscometer. Toluene-acetonitrile mixtures were prepared by weight. Solvent specific conductance was lower than $10 \times 10^{-8}\,\Omega\text{-}1\,\text{cm}^{-1}$. In all weighings buoyancy corrections were applied. The dielectric constants of the solvent mixtures used for analysis were taken from the literature[7].

Table 2 Conductance data of ter-$BuEt_3NI$ in toluene-acetonitrile mixtures at 25°C.

Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C
X	0,0		0,1		0,2		0,3		0,4		0,5		0,6
203,303	2,38	207,206	2,05	123,401	3,35	124,103	1,36	44,973	2,60	34,024	2,07	12,180	1,04
198,856	3,36	203,625	2,69	117,753	4,55	117,874	1,68	40,753	3,12	32,921	1,66	8,674	1,52
197,283	3,37	199,694	3,33	117,282	4,80	110,971	2,06	39,036	3,73	22,540	3,37	3,215	2,58
195,344	4,29	199,763	3,37	105,604	8,00	103,122	2,79	36,562	4,72	18,345	4,55	2,762	4,96
192,392	5,46	195,664	4,34	101,736	9,30	96,773	3,73	32,235	5,92	16,467	5,44	2,584	9,25
179,885	10,27	193,993	4,50	95,845	11,70	85,891	4,93	30,735	7,74	9,604	14,97	2,085	94,94
150,403	31,76	191,204	5,30	86,894	15,90	79,175	6,87	29,133	8,74	6,712	27,40	2,132	19,21
131,744	54,98	189,685	5,50	79,815	20,58	67,930	8,27	27,591	9,81	6,281	30,34	2,084	94,94
120,066	65,93	162,733	20,20	55,905	45,00	56,703	12,06	23,112	13,48	4,074	80,72	1,611	71,51
94,045	144,74	118,854	46,00	50,393	61,80	54,304	12,80	19,554	17,14	3,642	108,17	1,203	95,68
92,632	150,43	112,314	64,80	41,884	102,44	47,871	15,61	12,973	32,60				
80,745	214,94	110,643	65,00	39,784	126,10	37,232	23,60	1,035	59,70				
77,603	236,90	91,976	118,70			34,151	27,37	0,852	96,90				

Λ: $Scm^2\ mol^{-1}$; C: $mol\ dm^{-3}$

Table 3 Conductance data of sec-$BuEt_3NI$ in de toluene-acetonitrile mixtures at 25°C.

Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C
X	0,0		0,1		0,2		0,3		0,4		0,5		0,6
215,374	1,69	263,965	1,85	120,505	2,52	83,166	0,58	80,825	0,65	31,294	1,89	20,856	1,10
205,426	3,24	237,503	4,14	116,043	3,11	79,647	1,06	45,003	3,47	15,425	4,95	13,142	2,20
198,777	5,01	192,002	12,25	112,505	3,72	72,903	2,01	42,283	4,15	11,703	8,70	5,415	3,66
175,502	13,54	162,684	16,80	103,792	5,48	64,985	4,74	29,372	8,23	11,004	14,40	3,145	2,20
168,503	18,50	128,682	45,40	94,054	8,28	57,184	7,71	25,464	9,19	8,705	18,90	2,703	5,17
141,681	39,64	123,404	52,80	76,414	12,61	50,652	12,19	22,425	12,78	6,305	37,30	2,005	14,82
131,094	47,47	111,221	67,80	70,352	19,00	50,275	15,14	21,525	14,00	5,213	54,61	1,855	12,20
129,202	53,30	109,714	75,67	66,585	27,20	42,221	20,06	18,332	17,79	5,906	43,20	1,601	32,36
118,095	69,97	109,845	74,70	65,585	22,10	34,386	29,80	13,674	30,16	4,402	82,30	1,254	43,48
110,042	90,85	87,453	147,60	56,823	33,10	29,254	37,60	12,013	57,29	4,206	96,60	0,783	114,80
107,924	95,40	83,645	102,01	45,615	49,28	26,146	53,80	10,384	77,71	3,704	127,60		
96,751	134,56			43,963	69,90	25,032	59,50						
				42,425	77,04								

Λ: $Scm^2\ mol^{-1}$; C: $mol\ dm^{-3}$

Table 4 Conductance data of iso-$BuEt_3NI$ in toluene-acetonitrile mixtures at 25°C.

Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C
X 0,0		0,1		0,2		0,3		0,4		0,5		0,6	
241,152	1,59	262,785	1,61	170,665	2,20	124,053	0,75	106,505	0,76	74,305	1,24	97,206	0,64
237,534	2,33	235,686	3,17	145,653	3,50	111,184	5,91	105,603	0,88	70,513	2,10	94,322	0,67
219,111	6,46	204,792	6,60	134,926	9,20	109,192	9,71	98,272	2,05	67,626	3,71	83,462	0,73
169,515	35,14	201,041	6,84	118,052	20,59	100,224	15,00	96,555	2,90	57,811	6,69	77,840	0,77
156,644	53,07	165,496	15,61	115,191	22,79	91,342	24,19	77,731	12,30	49,515	14,37	65,324	0,98
151,163	67,55	155,472	13,90	113,456	25,20	88,855	27,89	61,704	25,20	43,042	15,73	58,714	1,20
144,623	80,43	147,525	20,88	105,163	37,79	81,491	36,60	58,112	36,70	39,256	23,70	44,435	1,48
134,914	119,52	137,552	25,68	107,165	41,50	77,680	47,10	53,793	47,40	37,962	27,80	41,331	1,44
132,055	141,96	131,556	29,58	101,912	46,38	75,574	56,80	45,773	74,17	29,876	63,24	22,774	4,44
131,897	132,40	115,644	46,30	98,144	79,90	68,993	82,47	41,802	117,80	28,742	63,20	18,763	9,63
127,183	177,20	105,642	79,30			66,125	105,70			26,395	94,20	15,522	23,09

Λ: $Scm^2\ mol^{-1}$; C: $mol\ dm^{-3}$

Table 5 Conductance data of *n*-$BuEt_3NI$ in toluene-acetonitrile mixtures at 25°C.

Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C
X 0,0		0,1		0,2		0,3		0,4		0,5		0,6	
221,393	2,88	182,524	5,53	151,604	3,40	138,560	2,94	121,381	1,80	134,153	2,64	42,356	1,42
209,662	5,91	181,186	6,65	138,103	9,00	122,983	7,50	117,154	2,90	66,201	5,13	34,453	2,20
171,253	39,72	178,202	10,20	132,630	15,70	122,224	1,59	108,875	5,60	59,514	7,25	31,745	3,54
165,015	33,73	173,875	16,97	131,211	24,40	120,846	2,56	100,702	9,71	51,903	14,20	27,101	4,31
163,732	54,31	162,077	40,60	127,521	43,80	117,852	7,30	94,803	13,81	48,205	22,80	26,835	4,49
162,635	58,37	152,326	75,90	125,327	30,01	100,461	32,50	78,916	31,04	39,602	44,20	24,163	10,13
156,706	60,02	147,543	99,30	122,826	55,11	75,485	82,50	65,142	57,60	35,905	60,20	19,705	15,55
147,421	99,38	136,413	169,20	119,482	56,20	57,166	170,30	59,022	86,91	35,203	31,70	11,892	64,19
140,114	210,39	120,863	211,40	115,793	68,60	34,243	257,94	58,627	87,50	29,604	125,60	10,895	132,20
140,262	217,10			103,794	119,20							10,331	180,94

Λ: $Scm^2\ mol^{-1}$; C: $mol\ dm^{-3}$

Table 6 Conductance data of $BuEt_3NI$ in toluene-acetonitrile mixtures at 25°C.

Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C	Λ	10^4C
X 0,0		0,1		0,2		0,3		0,4		0,5		0,6	
158,432	2,73	149,824	0,76	137,161	0,35	127,912	0,41	97,251	2,91	73,704	2,08	35,402	0,82
158,093	2,13	148,652	1,20	134,272	1,06	125,613	0,76	91,371	4,32	67,425	3,18	29,504	1,59
156,654	4,17	147,054	2,05	132,453	1,67	122,254	1,48	85,095	6,57	59,362	5,28	21,031	1,59
155,531	5,65	145,053	3,51	130,671	2,46	114,685	4,37	78,941	9,56	56,791	6,02	20,902	4,29
154,170	7,55	143,212	5,12	128,342	3,66	111,686	5,60	77,063	10,72	52,630	7,62	18,995	5,21
151,105	12,11	141,661	6,62	127,761	4,01	109,852	6,59	64,832	26,78	53,735	7,14	10,495	35,72
152,253	10,36	139,563	9,18	124,533	6,21	108,283	7,64	64,263	30,14	51,433	8,21	11,403	14,91
148,615	17,07	136,224	14,30	120,245	9,94	106,351	8,76	64,041	30,72	50,831	8,51	16,662	65,10
147,432	19,64	133,742	18,77			105,360	9,71			42,073	15,04	15,401	72,90
										38,601	20,72	14,693	79,01

Λ: $Scm^2\ mol^{-1}$; C: $mol\ dm^{-3}$

Table 7 Conductance Parameters of n-$BuEt_3NI$.

X	Λ_0	S	E	$a°10^8$	$J(a°)$	$\sigma\Lambda$
0,1	194,01	437,03	1681,87	2,7	1972,20	0,7340
0,2	158,40	584,38	2976,52	4,06	7587,23	0,0014
0,4	133,69	660,25	9625,42	3,77	20384,19	0,0070

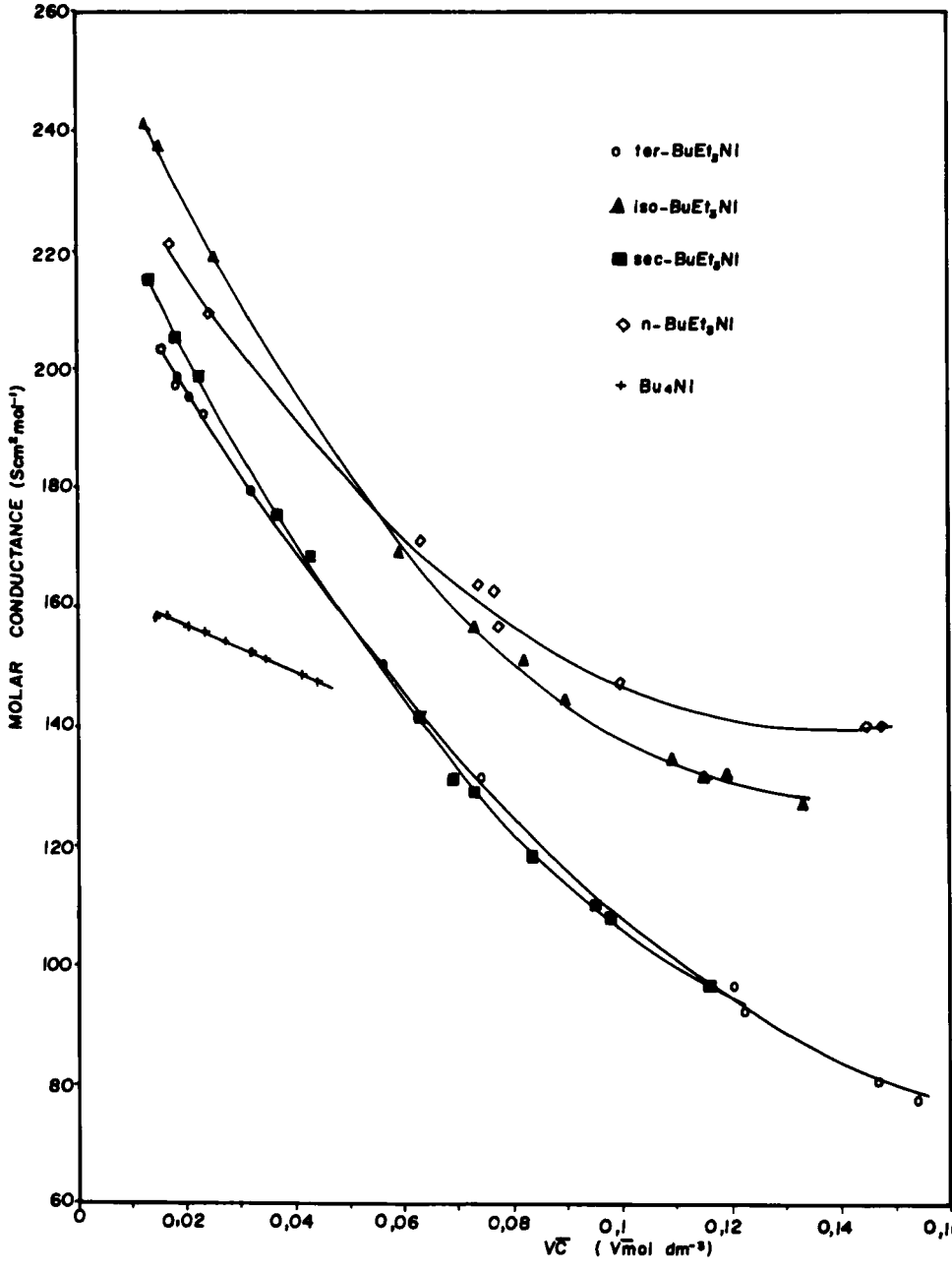

Figure 1 Comparative phoreograms of the asymmetric salts in the molar fraction of toluene 0,0 at 25°C(X:0,0).

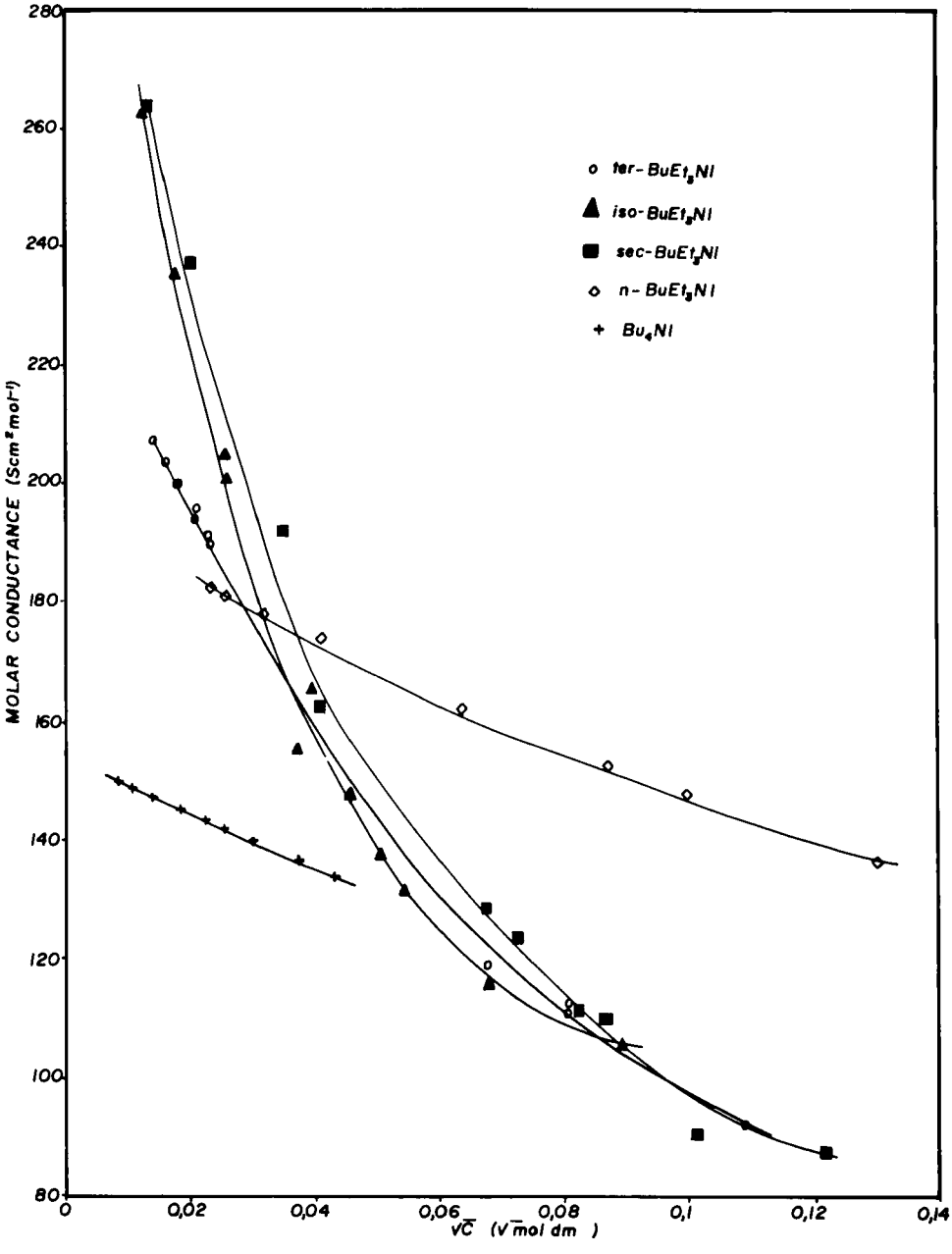

Figure 2 Comparative phoreograms of the asymmetric salts in the molar fraction of toluene 0,1 at 25°C (X:0,1).

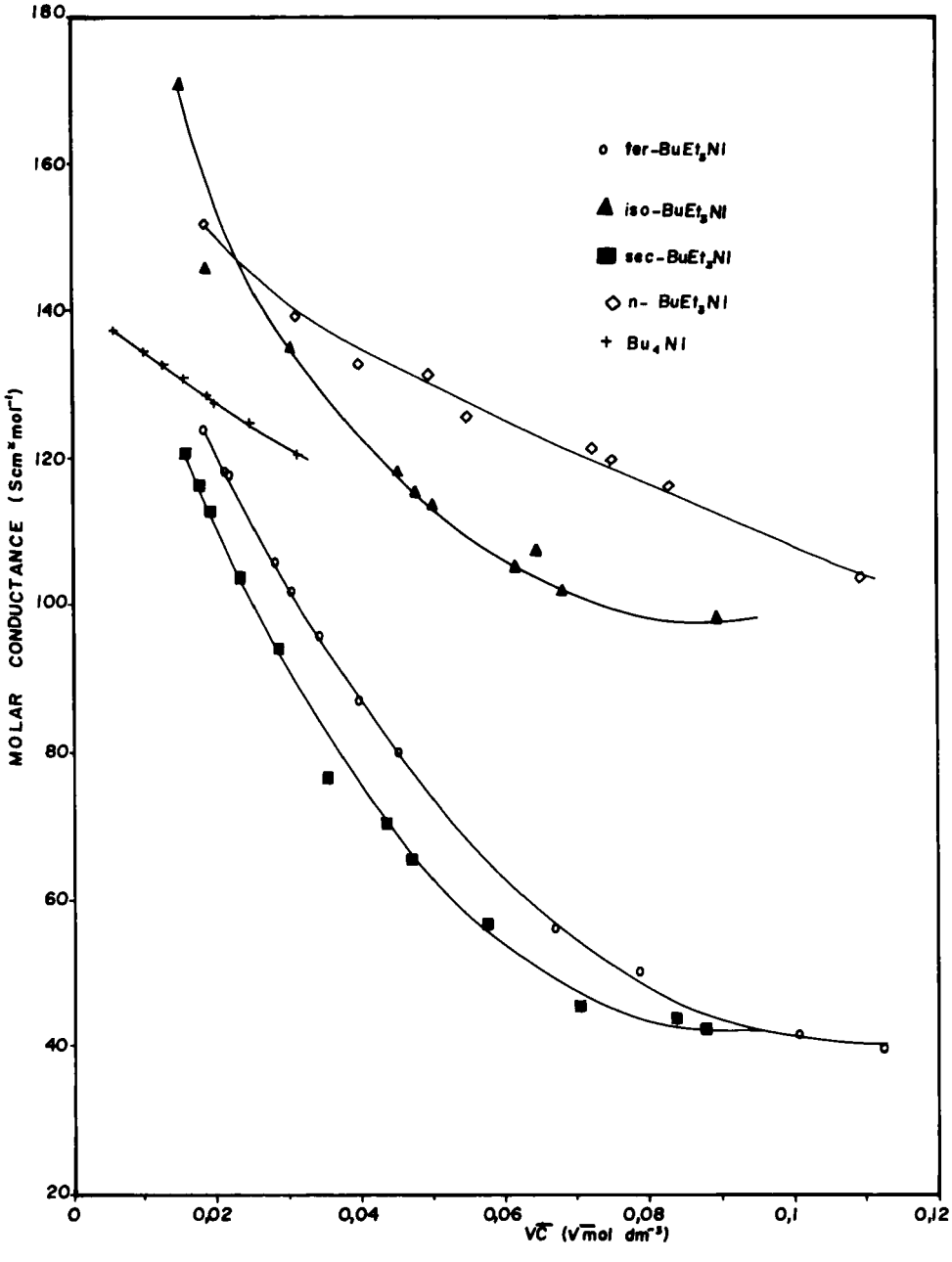

Figure 3 Comparative phoreograms of the asymmetric salts in the molar fraction 0,2 at 25 °C (X:0,2).

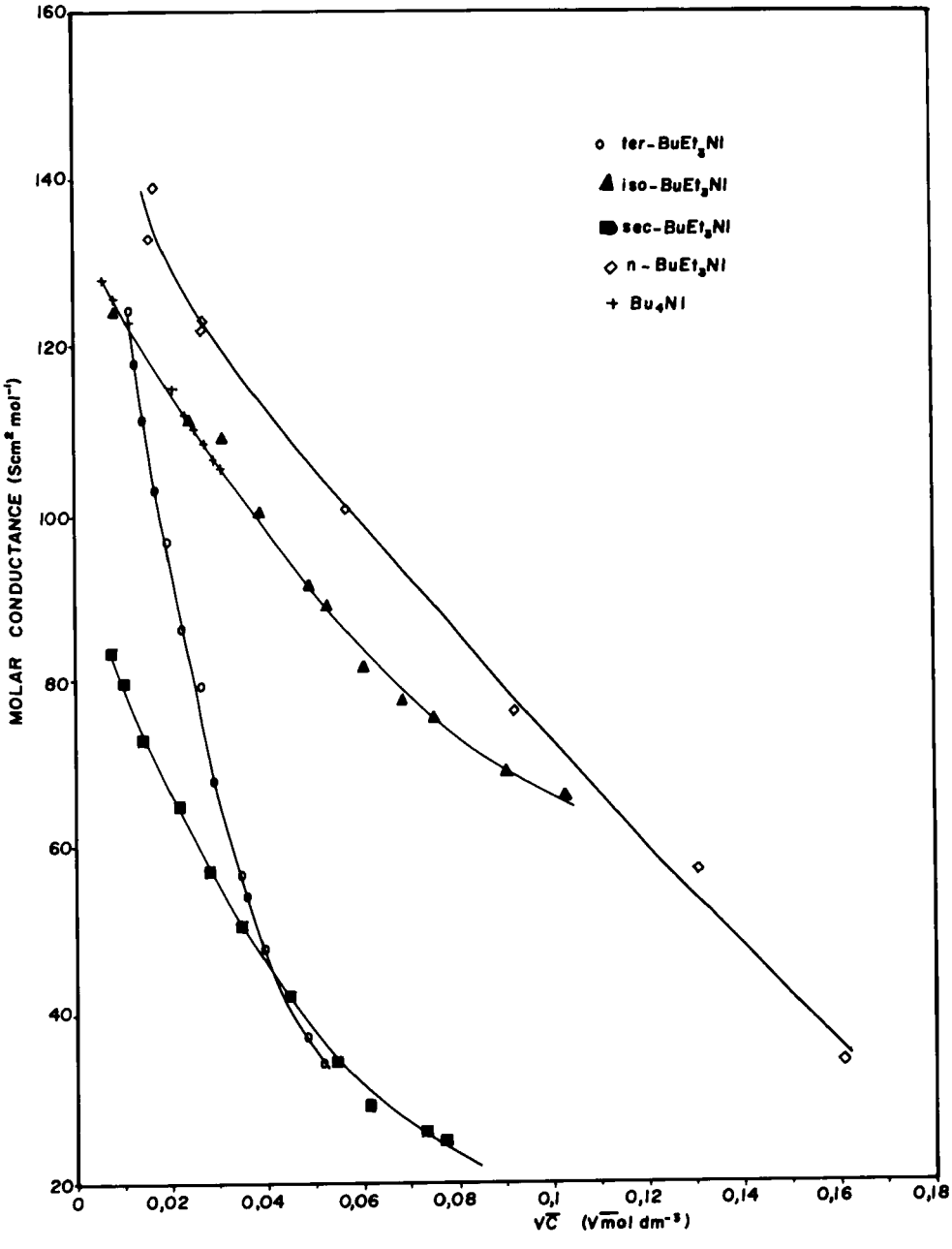

Figure 4 Comparative phoreograms of the asymmetric salts in the molar fraction of toluene 0,3 at 25°C (X:0,3).

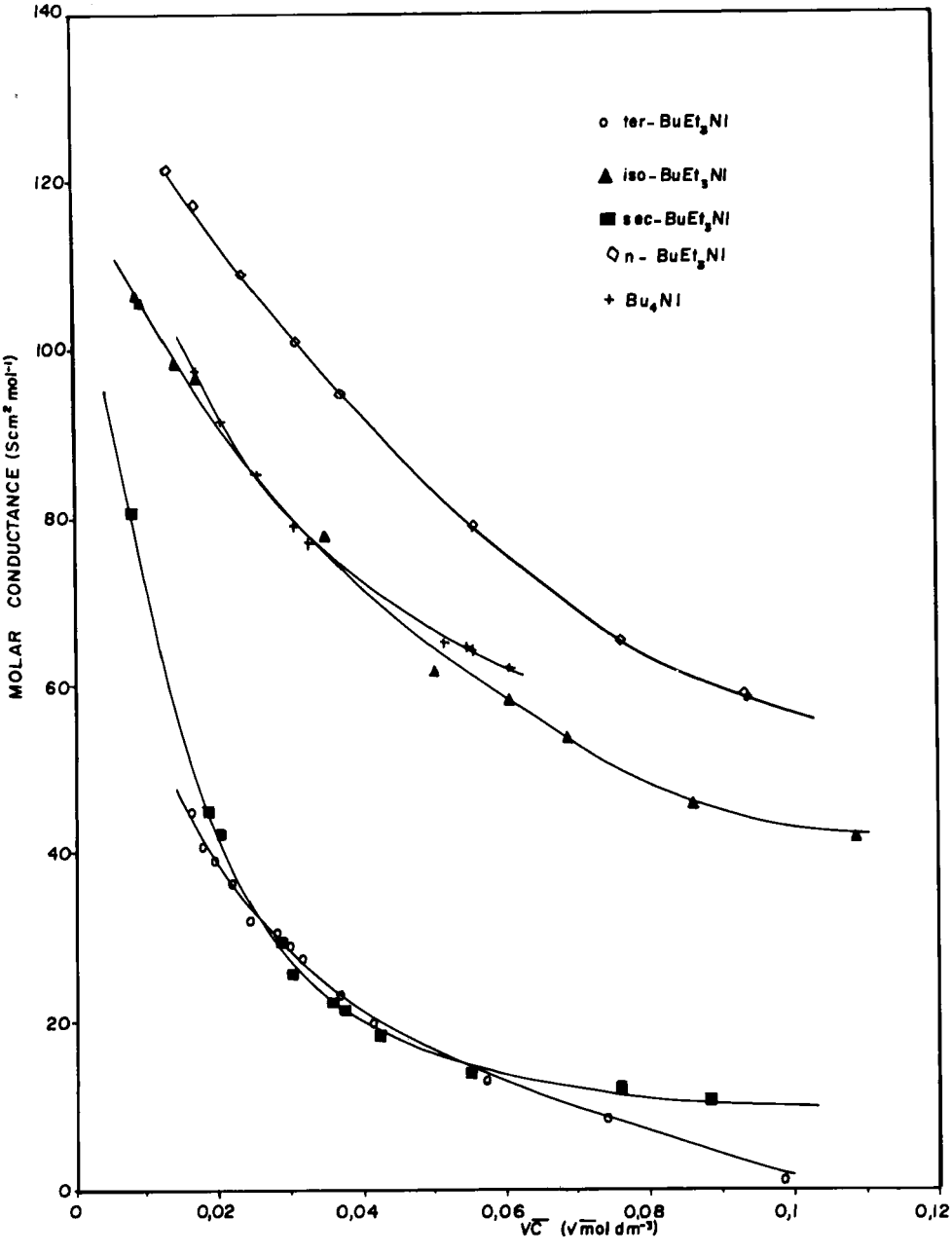

Figure 5 Comparative phoreograms of the asymmetric salts in the molar fraction of toluene 0,4 at 25°C (X:0,4).

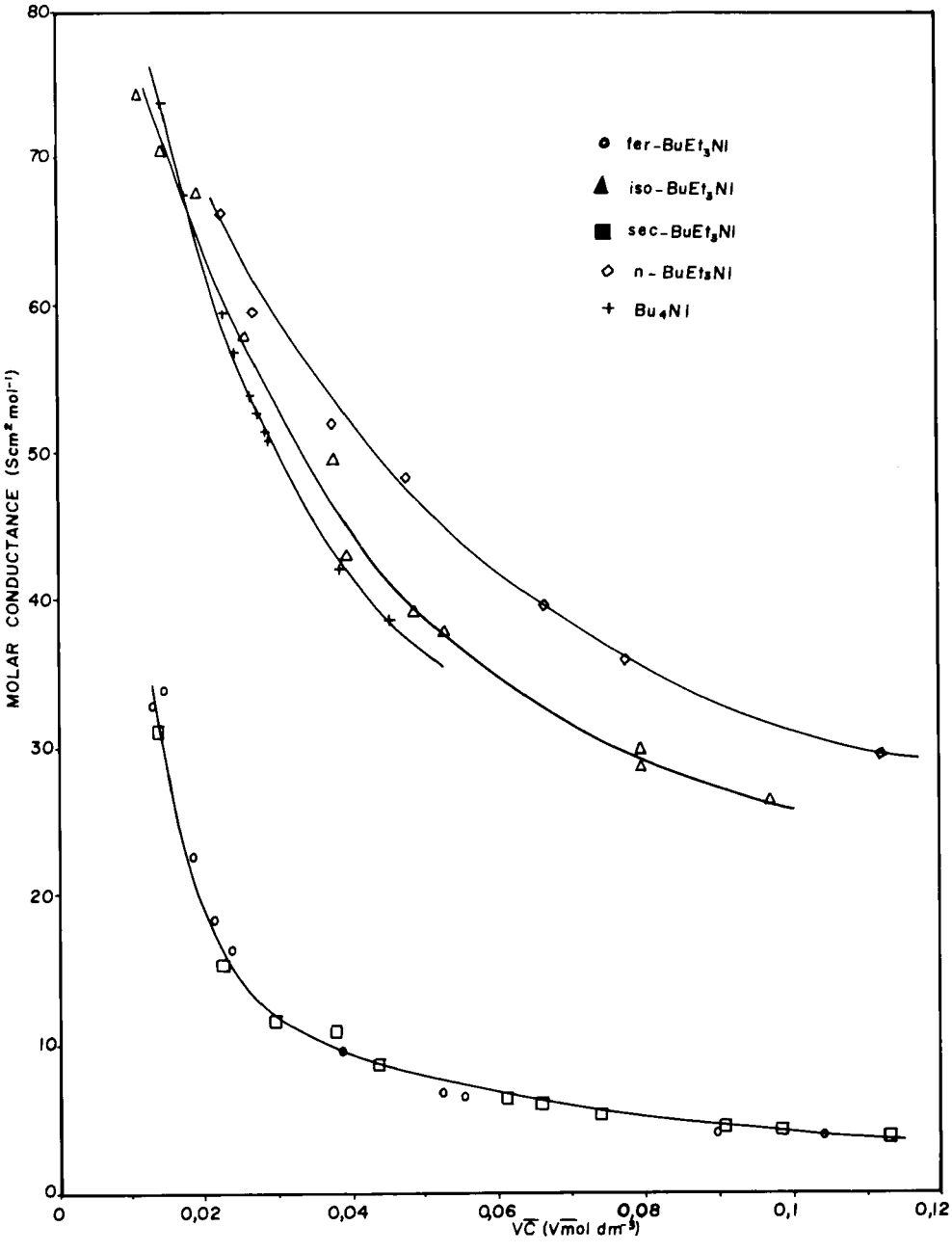

Figure 6 Comparative phoreograms of the asymmetric salts in the molar fraction of toluene 0,5 at 25°C (X:0,5).

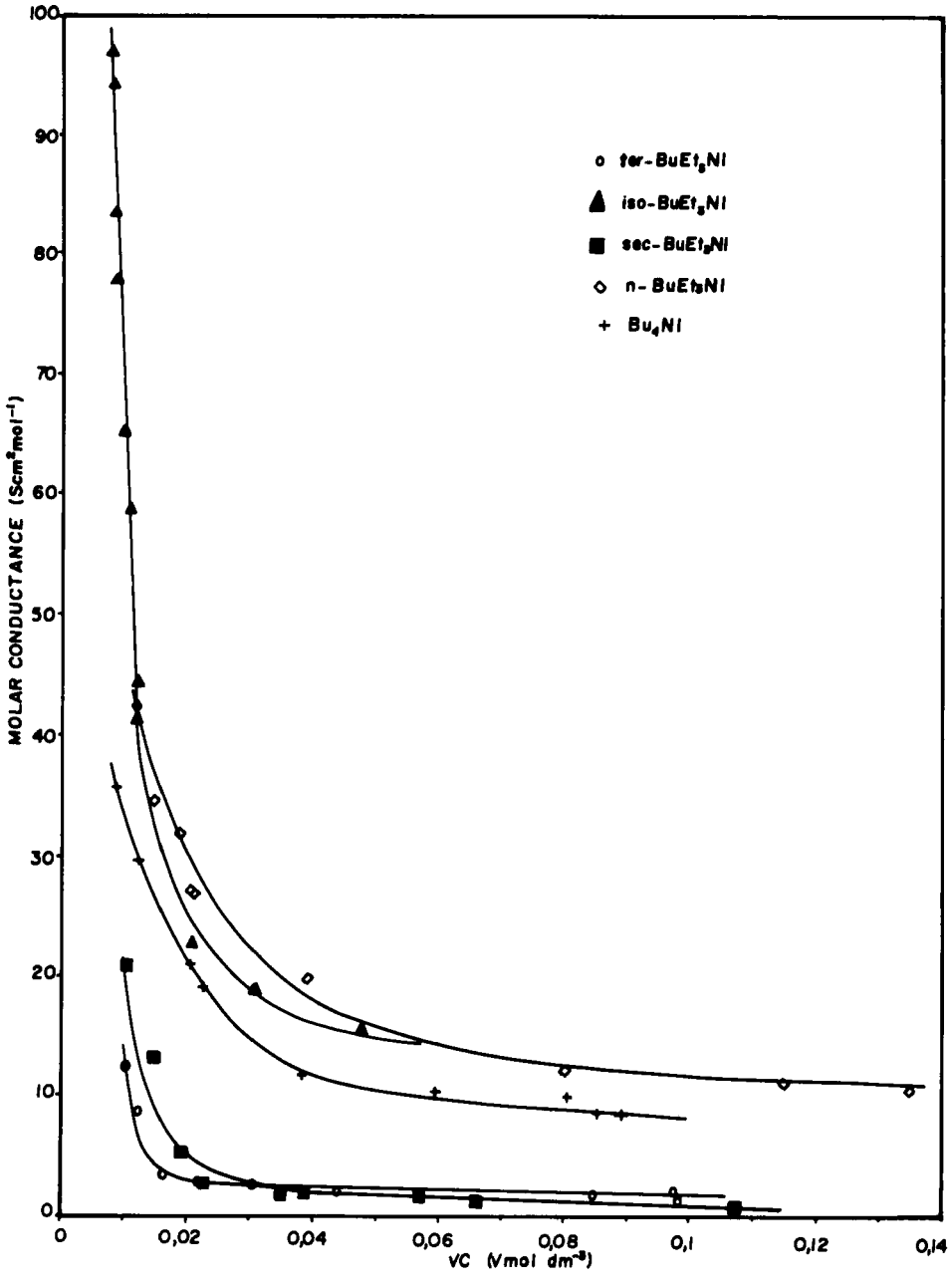

Figure 7 Comparative phoreograms of the asymmetric salts in the molar fraction of toluene 0,6 at 25°C (X:0,6).

3 CALCULATIONS

The physical properties of the solvent mixture used are given in Table 1. The molar conductance, $\Lambda(Scm^2mol^{-1})$ of Bu_4NI, sec-$BuEt_3NI$, iso-$BuEt_3NI$, ter-$BuEt_3NI$ and *n*-$BuEt_3NI$ in toluene-acetonitrile mixtures of different compositions, corrected for the conductivity of the solvent, are given in Tables 2 and 3 as a function of concentration, C(mol dm^{-3}) at 25°.

The conductance data of Bu_4NI in toluene acetonitrile mixtures at 25°C is given elsewhere [7]. The agreement of the results of Papadopoulus and Ritzoulis at 25° with those given here is within the precision of the measurements. The phoreograms of the Bu_4NI were compared with those of the asymmetric ammonium salts. To know if the asymmetric ammonium ions could behave as free ions only, the conductivity data for the asymmetric salts in toluene-acetonitrile were fitted to the Fuoss-Onsager equation[8] of unassociated electrolytes, Eq. (1).

$$\Lambda = \Lambda o - S\sqrt{c} + Ec \log c + Jc \tag{1}$$

In order to solve Eq. (1), the data of Λ in Tables 2, 3, 4, 5 and 6 were analyzed by the least squares method[9] to determine Λo and J. The values of S, E and J in Eq. (1), and those of standard deviation, $\sigma\Lambda$, are listed in Table 3.

A fit was obtained using the Fuoss Onsager equation for unassociated ions for the *n*-$BuEt_3NI$ only in the molar fractions 0,1, 0,2, and 0,4. The calculations are summarized in Table 4.

The values found for å: $X_{0,1}\,\dot{a} = 2,70$Å; $X_{0,2}\,\dot{a} = 4,06$Å; and $X_{0,4}\,\dot{a} = 3,77$Å, for the *n*-$BuEt_3NI$, could mean that å values are just either an arbitrary value or a solvent feature. Also, the fit of these systems could only be fortuituos and therefore without any physical meaning.

4 DISCUSSION AND CONCLUSION

The phoreograms of the asymmetric salts ter-$BuEt_3NI$ and *n*-$BuEt_3NI$, and of the Bu_4NI, show a decrease in conductance as the mixture is enriched in toluene. (Figs. 1 to 7). It could be caused as a consecuence of stronger interactions ion-ion and ion-solvent. The conductance behaviour of the different salts do not follow a unique pattern. Then, it is not possible to postulate a specific effect of the geometry of the butyl chains on the conductance. For instance: the phoreograms of the salt iso-$BuEt_3NI$, in the molar fractions 0,3 and 0,4, are analogous to those gotten for the symmetric salt Bu_4NI, within a restricted concentration range of the salts (Figs. 4 and 5)

The phoreograms of the salts sec-$BuEt_3NI$ and ter-$BuEt_3NI$, in the molar fraction 0,0, 0,4, 0,5 and less evidently for $X = 0,6$, show an analogous shape (Figs. 1, 5 and 6). Even though, the shape of the conductance curve is not a enough criterion to evaluate possible geometrical modifications of the cations due to association effects, we believe that the asymmetric salts could be grouped in two general groups: 1. The *n*-$BuEt_3NI$ and iso-$BuEt_3NI$ salts; 2. The ter-$BuEt_3NI$ and

sec-$BuEt_3NI$ salts. From the point of view of the geometry shape, our hypothesis is that there should be some geometric modifications of the cations due to changes of their charge density, as the dielectric constant decrease and the ion-ion and ion-solvent interactions increase.

On the premise that forces of eletrostatic attraction between ions should yield fairly high potential energies for ions pairs to diminish the asymmetric effect, the ionic association might be considered as a probable phenomena to explain the phoreograms. This study showed that the Fuoss-Onsager equation for unassociated electrolytes could not be used to explain the conductance behaviour of the asymmetric cations. The concept of symmetric ions has limited the extent to which data from asymmetric salts could be used to fit the conductimetric models as happened with the Fuoss-Hsia model.

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