



Solvation of Ions. Part XXIX. Ionic Conductances in Acetonitrile-Water and Pyridine-Water Mixtures

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The limiting conductance of various salts of Na^+ , Ag^+ , Cu^+ , Cu^{2+} and Ph_4As^+ in acetonitrile-water ($\text{AN-H}_2\text{O}$) and pyridine-water ($\text{Py-H}_2\text{O}$) mixtures are reported. Single ion values are calculated for $\text{AN-H}_2\text{O}$ mixtures using the TATB assumption [$\lambda_0(\text{Ph}_4\text{As}^+) = \lambda_0(\text{Ph}_4\text{B}^-)$]. The trends observed for the limiting Walden products ($\lambda_{\infty}\eta$) of the electrolytes and individual ions are discussed in terms of specific ion-solvent interactions and the structural effects of the solvent mixtures.

KEY WORDS: Conductance; Walden product; tetraphenylarsonium and tetraphenylboride ions; pyridine-water and acetonitrile-water mixtures; alkali metal salts; copper salts; ion-solvent interactions; structural effects.

1. INTRODUCTION

Certain d¹⁰ cations such as Ag^+ and Cu^+ show heteroselective solvation by acetonitrile in acetonitrile-water ($\text{AN-H}_2\text{O}$) solvent mixtures whereas other ions like Na^+ , Cu^{2+} , Cl^- and NO_3^- are selectively solvated by H_2O in the solvent mixture.⁽¹⁻³⁾ Bulky ions with low charge density such as Ph_4As^+ and Ph_4B^- are virtually unsolvated in aquo and organic solvents.⁽⁴⁾ This observation has applications to copper and silver hydrometallurgy and forms the basis of several patents.^(3,5) Due to the applications of this solvent mixture ($\text{AN-H}_2\text{O}$) we have been interested in understanding the solvation mechanism of various ions especially Cu^{2+} , Cu^+ and Ag^+ in the solvent mixture. We have investigated the energetics⁽⁶⁾ and partial molal volumes⁽⁷⁾ of transfer of these

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ions from H_2O to AN- H_2O mixtures; this paper considers the ionic conductivities. Kay *et al.*⁽⁸⁾ and others^(9,10) have shown that ionic mobilities in solvent mixtures yield information on solvation mechanism in terms of the influence of solvent structure and solvent sorting in the ionic solvation shell. Since the influence of AN on the structure of H_2O is well characterized^(11,13) and the chemical interactions of the ions of interest with AN are also known,⁽³⁾ the ionic conductance investigation in AN- H_2O is highly appropriate.

Strehlow *et al.*⁽¹⁴⁾ investigated the conductance of Ag^+ and NO_3^- ions in AN- H_2O using an ionic transport method. Petrella *et al.*⁽⁹⁾ recently extended this study to Na^+ , K^+ , Cl^- , Br^- and I^- ions in the same solvent mixture, but their ionic values were based on the Coplan-Fuoss split⁽¹⁵⁾ (the TAB assumption) in which $\lambda_o[(i\text{-Am})_3\text{BuN}^+] = \lambda_o(\text{Ph}_4\text{B}^-)$. Due to our specific interest in copper and silver ions, we measured the conductivities of copper and silver nitrates in AN- H_2O and obtained the individual ion contributions by using the TATB assumption that $\lambda_o(\text{Ph}_4\text{As}^+) = \lambda_o(\text{Ph}_4\text{B}^-)$. For comparative purposes we obtained data for Na^+ , Cl^- , I^- and NO_3^- ions by using the same TATB assumption. Pyridine-water (Py- H_2O) solvent mixtures are also included in this study because Py can interact with cations through Lewis acid-base interactions and form strong coordinate bonds particularly with Ag^+ , Cu^+ , and Cu^{2+} .

2. EXPERIMENTAL

Water was doubly deionized and distilled from alkaline KMnO_4 to give a specific conductance of $2 \times 10^{-7} \text{ S-cm}^{-1}$. Laboratory grade AN was distilled twice from potassium permanganate and left standing over calcium hydride for 48 hours. After decantation it was refluxed over fresh calcium hydride for six hours, fractionally distilled from calcium hydride under high purity nitrogen and stored under nitrogen. Pyridine (Baker, A. R.) was fractionally distilled twice from KOH by using the technique of Ralph and Gilkerson.⁽¹⁶⁾

Analytical grade $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, AgNO_3 , NaNO_3 , NaCl and NaI were recrystallized from conductivity water. Ph_4AsCl , Ph_4AsI and NaPh_4B were purified as described in the literature.⁽⁷⁾ Solutions of CuNO_3 were prepared by stirring AgNO_3 in the solvent mixture with excess copper powder under nitrogen and the precipitated silver and excess copper were removed. Solutions of CuNO_3 were standardized by titration with KMnO_4 or by oxidation with HNO_3 and iodometric determination of Cu^{2+} . All CuNO_3 solutions were handled in a dry

Table I. Limiting Molar Conductances of Various Electrolytes in Acetonitrile-Water Mixtures at 25 °C

w/w %	mole %		Λ_0^a						
	AN	AN	Ph ₄ AsCl	Ph ₄ AsI	NaPh ₄ B	NaI	NaNO ₃	CuNO ₃	$\frac{1}{2}$ Cu(NO ₃) ₂
0.0		0	97.4	-	-	-	-	-	-
5.52		2.5	88.9	-	-	-	116.0	108.0	121.2
10.7		5.0	84.5	-	-	-	114.0	101.5	119.0
15.6		7.5	84.1	-	-	-	113.5	97.5	118.4
20.21		10.0	-	84.0	-	-	113.5	97.5	120.2
36.57		20	-	87.6	67.5	-	117.0	101.0	128.8
53.60		33.6	-	95.0	74.7	114.9	121.5	106.5	138.4
75.91		58.0	-	114.0	96.3	129.2	136.5	126.0	-
90.24		80.2	-	138.5	116.0	154.0	158.0	150.0	-
97.08		93.6	-	151.5	127.2	169.8	175.0	164.5	-
100.00		100.0	-	-	-	-	183.3	171.4	-

^a Units: S-cm²-mol⁻¹

Table II. Limiting Molar Conductances of Nitrates in Pyridine-Water Mixtures at 25 °C

Mole %		Λ_0			
Py	$10^2 \eta^a$	NaNO ₃	AgNO ₃	CuNO ₃	$\frac{1}{2}\text{Cu}(\text{NO}_3)_2$
0.0	0.890	121.6 ^b	133.4 ^b	-	125.1 ^b
2.4	1.116	100.8	76.0	75.7	-
5.3	1.336	85.0	62.0	62.0	68.0
12.8	1.800	63.0	44.2	46.0	50.2
25.6	2.190	50.5	37.5	36.3	39.5
47.8	1.895	51.5	40.0	36.6	38.2
100.0	0.885	79.0 ^c	86.9 ^d	-	-

^a Viscosities in poise. A. E. Dunstant, F. B. T. Thole, and J. S. Hunt, *J. Chem. Soc.* 91, 1728 (1907). ^b *Electrolyte Solutions*, 1st edn., R. A. Robinson and R. H. Stokes, eds., (Butterworths, London, 1955). ^c D. S. Burgess and C. A. Kraus, *J. Am. Chem. Soc.* 70, 706 (1948). ^d W. F. Luder and C. A. Kraus, *J. Am. Chem. Soc.* 69, 2481 (1947).

nitrogen glove bag to exclude air and CO₂.

The solutions of other electrolytes for conductivity measurements were prepared by diluting known weights of a concentrated solution (1-2 molar) of the electrolyte in the required solvent. The conductivities of solutions of at least five different concentrations in the range $1 \times 10^{-2} - 1 \times 10^{-4}$ molar were measured at 25 ± 0.001 °C by using a Phillips PW 9501/01 bridge and a PW 9511 cell of cell constant 0.725 cm⁻¹. Molar conductances Λ for Ph₄AsCl, Ph₄AsI, NaPh₄B, NaI, NaNO₃, CuNO₃, and Cu(NO₃)₂ in various AN-H₂O mixtures and for NaNO₃, AgNO₃, CuNO₃, and Cu(NO₃)₂ in various Py-H₂O mixtures were measured. The corresponding limiting molar conductances Λ_0 of the electrolytes were obtained by extrapolation of the measured molar conductance values to infinite dilution using Λ vs. $C^{1/2}$ plots. The Λ_0 values of various electrolytes thus obtained were used to calculate the limiting ionic conductances via the TATB assumption, *i.e.* by using the relationships

$$\lambda_0(\text{Ph}_4\text{As}^+) = \lambda_0(\text{Ph}_4\text{B}^-) = \frac{1}{2}[\lambda_0(\text{Ph}_4\text{AsPh}_4\text{B})] \quad \text{and}$$

$$\Lambda_0(\text{Ph}_4\text{AsPh}_4\text{B}) = \Lambda_0(\text{Ph}_4\text{As X}) + \Lambda_0(\text{NaPh}_4\text{B}) - \Lambda_0(\text{NaX})$$

where X is any anion.

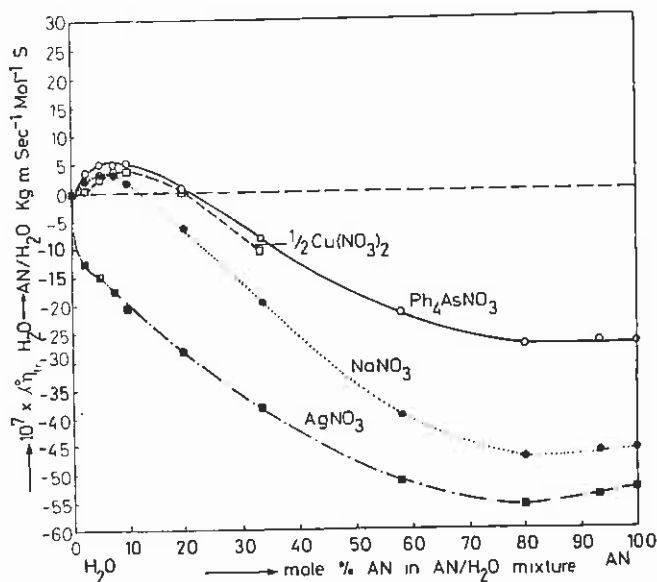


Fig. 1. Walden products of transfer of Ag^+ , Na^+ , Cu^{2+} and Ph_4As^+ nitrates from water to acetonitrile-water at 25 °C.

3. RESULTS AND DISCUSSION

3.1. Electrolyte Conductance

The limiting molar conductances of various electrolytes in AN- H_2O and Py- H_2O are shown in Tables I and II, respectively. The corresponding Walden products of transfer $(\Lambda_0\eta)_t [= (\Lambda_0\eta)_B - (\Lambda_0\eta)_A]$; for transfer from solvent A to B] for copper(II), silver(I) and sodium nitrates are shown in Figs. 1 and 2, respectively. For comparison the Walden products of transfer of Ph_4AsNO_3 , which were calculated from the data in Table I and Ref. 9 by using the expression

$$(\Lambda_0\eta)_t, \text{Ph}_4\text{AsNO}_3 = (\Lambda_0\eta)_t, \text{Ph}_4\text{AsX} - (\Lambda_0\eta)_t, \text{NaX} + (\Lambda_0\eta)_t, \text{NaNO}_3$$

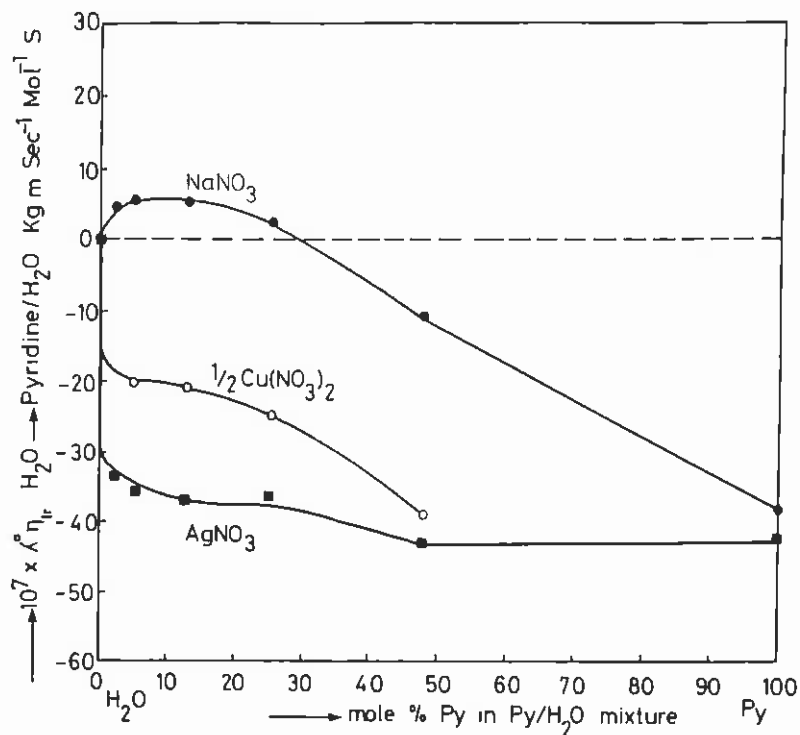


Fig. 2. Walden products of transfer of Ag^+ , Na^+ , and Cu^{2+} nitrates from water to pyridine-water at 25 °C.

where X is Cl^- or I^- , are also included in Fig. 1. The results are analyzed in terms of the Walden products of transfer with the hope of a better cancellation of viscosity effects.

In concentrated AN- H_2O and Py- H_2O mixtures (> 30 mole %) all the nitrates examined exhibit lower Walden product values than in water. At lower concentrations of organic solvents in the solvent mixtures, the figures show that the conductance of nitrates of those cations which do not form strong complexes with the organic solvent, initially rise and pass through a maximum, while the conductance of nitrates whose cations form strong complexes with the organic solvent show a sharp decrease. The Ag^+ ion forms strong complexes with both AN, through $p\pi-d\pi$ back bonding interactions, and Py through Lewis acid-base interactions. By contrast Cu^{2+} only forms strong coordination complexes with Py and remains solvated by water in AN- H_2O . Since the Walden product is inversely dependent on the radius of the solvated ion

$$(\lambda_0 \eta) = FeZ/6\pi r_s$$

Table III. Comparison of the Limiting Ionic Conductances in AN-H₂O at 25 °C Obtained by the TATB and the TAB Assumptions and by the Transference Method^{a,b}

Mole % AN	Ph ₄ As ⁺		Na ⁺		I ⁻		Cl ⁻		NO ₃ ⁻	
	TATB	TATB	TATB	Transf. ^c	TATB	Transf. ^c	TATB	Transf. ^c	TATB	Transf. ^c
0.0	20.4	49.5	50.8	50.1 ^d	71.4	76.1	75.7	76.4 ^d	72.1	71.5 ^d
2.5	19.2	47.8	48.3		70.0	69.5	69.2		68.2	67.5
5.0	18.9	46.3	46.8		66.2	65.7	65.1		67.7	63.0
7.5	19.7	44.5	45.8		65.5	64.1	63.1		69.0	62.6
10.0	19.7	44.2	44.8		64.3	63.7	62.3		69.3	62.4
20.2	23.2	44.3	44.0		64.5	64.8	58.4		72.7	61.7
33.6	27.4	47.3	-		67.6	-	-		74.2	63.6
58.0	40.6	55.7	-		73.5	-	-		80.8	72.2
80.2	50.3	65.7	-		88.3	-	-		92.3	86.1
93.6	54.5	72.7	-		97.1	-	-		102.3	100.2
100.0	57.2 ^e	78.3	76.9	76.9 ^f	101.7	102.5	-	98.7 ^g	105.0	106.4 ^h

^a The TATB assumption is based on $\lambda_0(\text{Ph}_4\text{As}^+) = \lambda_0(\text{Ph}_4\text{B}^+) = \frac{1}{2}[\lambda_0(\text{Ph}_4\text{AsPh}_2\text{B}^+) + \lambda_0(\text{Ph}_4\text{AsX}^+) + \lambda_0(\text{NaPh}_4\text{B}) - \lambda_0(\text{NaX})]$, where X is any anion. ^b The TAB assumption is based on $\lambda_0(\text{i-Am}_3\text{BuN}^+) = \lambda_0(\text{Ph}_4\text{B}^+)$, with data from Ref. 9. ^c Ionic conductances obtained with aid of precise transference data. ^d *Electrolyte Solutions*, 1st edn., R. A. Robinson and R. H. Stokes, eds., (Butterworths, London, 1955). ^e Precise transference data from Ref. 23 gives $\lambda_0 = 55.8$ for the Ph₄As⁺ ion in pure acetonitrile at 25°C. ^f Ref. 23. ^g Ref. 23 with conductance data listed in Ref. 24. ^h Data for $\lambda_0(\text{NaCl})$ from Ref. 9.

where F is the Faraday Constant, Z the absolute ionic valence, e the electronic charge and r_s the radius of the solvated ion. The sharp decrease in $(\lambda_o\eta)_i$ upon transfer of AgNO_3 from H_2O to $\text{AN-H}_2\text{O}$ or $\text{Py-H}_2\text{O}$ and of Cu^{2+} from H_2O to $\text{Py-H}_2\text{O}$ is an indication of a large increase in the radius of the solvated ion. Because of the large molar volumes of pyridine and acetonitrile, the nitrile or pyridine solvated ions are bulkier than the water solvated ions. Na^+ ion has no specific coordination interaction with AN or Py and thus NaNO_3 behaves differently from AgNO_3 in $\text{AN-H}_2\text{O}$ and $\text{Py-H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2$ in $\text{Py-H}_2\text{O}$ mixtures. It may be noted that only in those solvent mixtures in which Ag^+ shows specific coordination interactions with the organic component does AgNO_3 shows a trend different from that of NaNO_3 . For example, in aqueous ethanol⁽¹⁶⁾ and aqueous dioxane,⁽¹⁷⁾ Ag^+ , like Na^+ , has no specific interaction with the organic component of the solvent mixture and the salts of both of these cations show similar conductivity behavior in these solvents. Likewise Cu^{2+} behaves more like Na^+ in $\text{AN-H}_2\text{O}$ and like Ag^+ in $\text{Py-H}_2\text{O}$ mixtures.

It is surprising that the observed behavior of Ph_4AsNO_3 in $\text{AN-H}_2\text{O}$ is similar to that of NaNO_3 in this solvent mixture since the solvation shell compositions of Na^+ and Ph_4As^+ are expected to be quite different in the solvent mixture. Individual ion values are necessary to explain this observation.

4. INDIVIDUAL ION CONDUCTANCE

The effect of solvation and solvent structure on conductance can be better understood in terms of individual ion contributions. The values in $\text{AN-H}_2\text{O}$ mixtures presented in Table III have been derived from the data in Table I and Ref. 9 by applying the TATB assumption. For comparison, the literature values for the NO_3^- ion obtained by Strehlow⁽¹⁴⁾ are also included in Table III.

Our λ_o values for Na^+ , I^- , and Cl^- are in close agreement with those reported by Petrella.⁽⁹⁾ The λ_o ion values in pure AN and pure H_2O also agree well with those obtained by others using transport methods (Table III). However, in spite of the fact that our $\lambda_o(\text{NO}_3^-)$ values in H_2O and AN are very close to those reported by Strehlow,⁽¹⁴⁾ the agreement is not good for $\text{AN-H}_2\text{O}$ mixtures. Since our method gives acceptable values for most ions we question the Strehlow results and use our $\lambda_o(\text{NO}_3^-)$ values for computing other λ_o ion values and the corresponding ionic $\lambda_o\eta$ values (Table III). The ionic Walden products of transfer from H_2O to $\text{AN-H}_2\text{O}$ for cations are plotted in Fig. 3 and

Table IV. Additional Single Ion Limiting Conductances for Acetonitrile-Water Mixtures at 25°C^a

Mole % AN	η (cP) ^c	Ag ⁺ ^b	λ_0 Cu ⁺	$\frac{1}{2}\text{Cu}^{2+}$
0.0	0.8903	61.3	-	53.0
2.5	0.9497	43.8	39.8	53.0
5.0	0.9779	38.8	33.8	51.3
7.5	0.9826	34.5	28.5	49.4
10.0	0.9704	32.2	28.2	50.9
20.2	0.8706	31.3	28.3	56.1
33.6	0.729	36.3	32.3	64.2
58.0	0.503	54.0	45.2	-
80.2	0.387	70.2	57.7	-
93.6	0.355	80.2	62.2	-
100.0	0.341	87.6	66.4	-

^a Values based on the TATB assumption, i.e., $\lambda_0(\text{Ph}_4\text{As}^+) = \lambda_0(\text{Ph}_4\text{B}^-)$. See Table III. ^b TATB assumption data from Ref. 14. ^c Refs. 9 and 21.

Table V. Limiting Walden Products for Ions in Acetonitrile-Water Mixtures at 25°C^a

Mole %	AN	Ph ₄ As ⁺	Na ⁺	Ag ⁺	$\lambda_{0.77}$ Cu ⁺	$\frac{1}{2}$ Cu ²⁺	NO ₃ ⁻	Cl ⁻	I ⁻
0		18.2	44.1	54.6	-	47.2	64.2	68.6	68.91
2.5		18.2	45.4	41.6	37.8	50.3	64.8	66.2	66.5
5.0		18.5	45.3	37.9	33.1	50.2	66.2	64.2	64.7
7.5		19.4	43.7	33.9	28.0	48.5	67.8	63.3	64.4
10.0		19.1	42.9	31.3	27.4	49.4	67.2	61.0	62.4
20.2		20.2	38.6	27.2	24.6	48.8	63.3	50.6	56.1
33.6		20.0	34.5	26.5	23.6	46.7	54.1	-	49.3
58.0		20.4	28.0	27.2	22.7	-	40.6	-	37.0
80.2		19.5	25.4	27.2	22.3	-	35.7	-	34.2
93.6		19.3	25.8	28.5	22.1	-	36.3	-	34.5
100.0		19.4	26.7	29.9	22.6	-	35.8	-	34.7

^aSee Table IV for viscosity data.

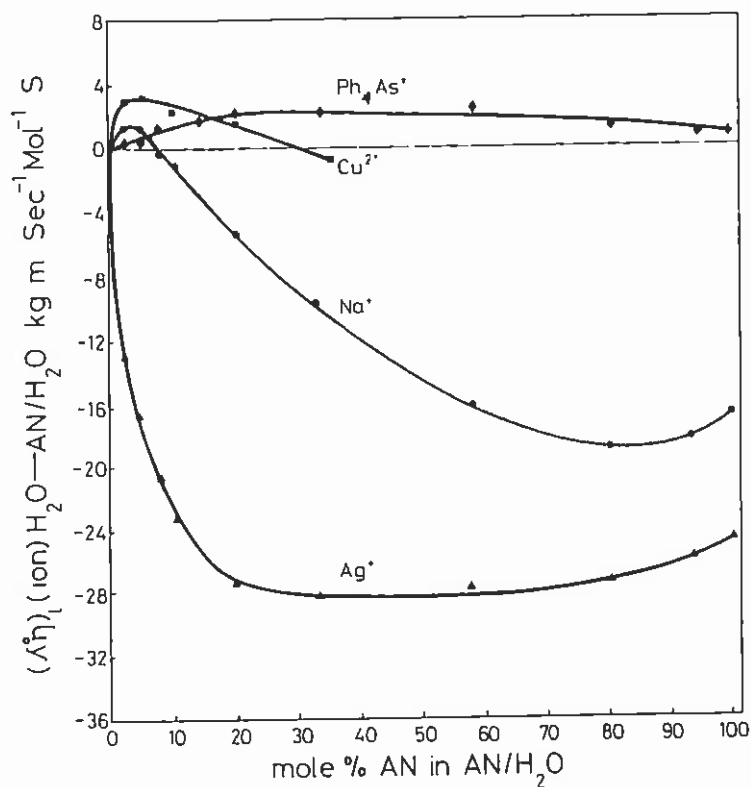


Fig. 3. Ionic Walden products of transfer of Ag^+ , Na^+ , Cu^{2+} , and Ph_4As^+ from water to acetonitrile-water at 25 °C.

those for anions in Fig. 4 to facilitate comparison.

4.1. Cations

As shown in Fig. 3, the change in single ion $(\lambda_0\eta)_1$ values with solvent composition for Na^+ and Cu^{2+} which are solvated by water in AN-H₂O is similar to that observed for their nitrate salts, but Ph_4As^+ shows different behavior. The values of $(\lambda_0\eta)_1$ for Na^+ pass through a small sharp maximum at about 3 mole % AN and then show gradual decrease while those for Cu^{2+} pass through a similar maximum at the same composition but decrease more slowly with the solvent composition change. By contrast $(\lambda_0\eta)_1$ for Ag^+ drops very sharply up to 20 mole % AN and thereafter remains virtually constant. The behavior of Na^+ in AN-H₂O is similar to that observed by Kay *et al.* for alkali metal

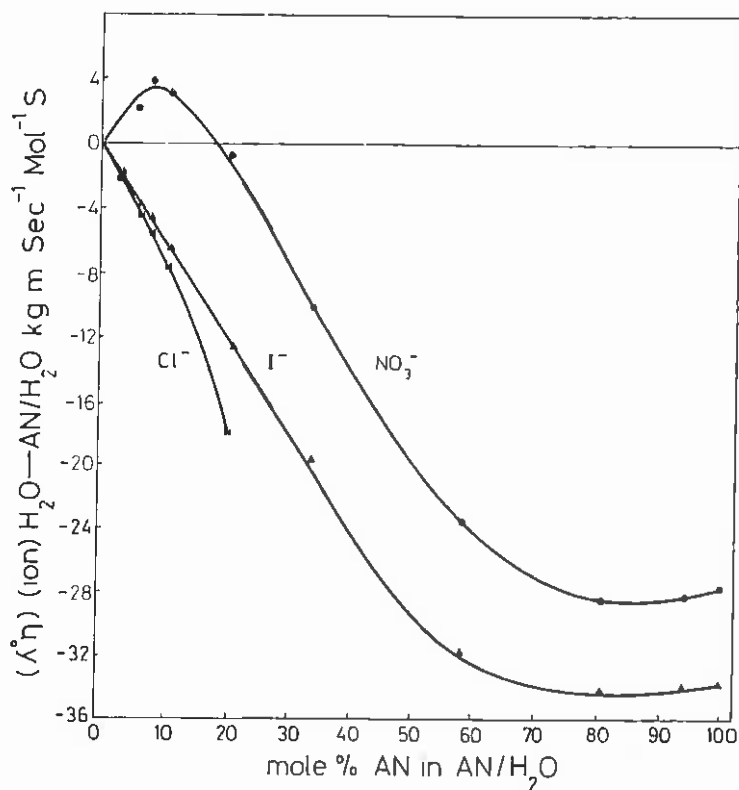


Fig. 4. Ionic Walden products of transfer of Cl^- , I^- , and NO_3^- from water to acetonitrile-water at 25 °C.

cations and halide ions in other mixed aqueous solvent mixtures including dioxane,⁽¹⁷⁾ *t*-butanol,⁽¹⁸⁾ and ethanol.⁽⁸⁾ Kay rationalized this behavior by proposing a 'solvent-sorting' model.⁽⁸⁾ He noted that the viscosity of these solvent mixtures goes through a maximum in the water rich region. Due to the preferential solvation of these ions by water in this region of the solvent mixture, the viscosity of the solvent in the vicinity of these ions is lower than that of the bulk solvent. Since the bulk viscosity value is used in the calculation of the Walden products of transfer, the values of the calculated $(\lambda^\circ\eta)_i$ are too high up to the point corresponding to the viscosity maximum after which they are low and therefore a maximum in the Walden product occurs. The bulk viscosity of AN-H₂O mixtures also goes through a maximum (see Fig. 5), and since the Na^+ and Cu^{2+} have water rich solvation shells in dilute AN-H₂O mixtures, the observed behavior of these ions is consi-

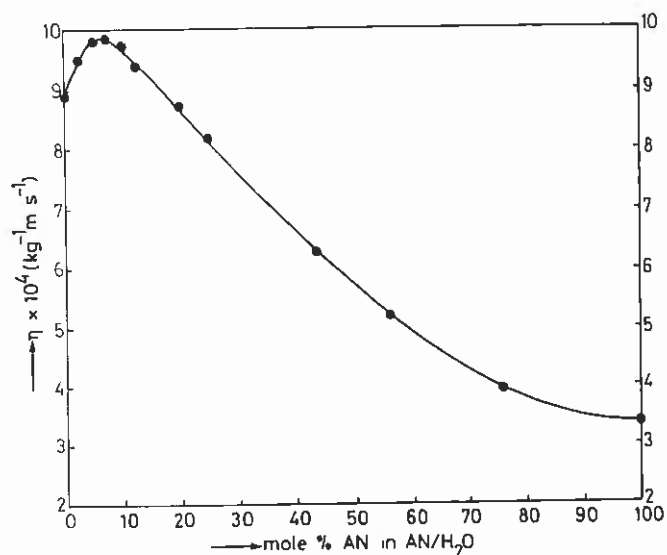


Fig. 5. Viscosity of acetonitrile-water mixtures at 25 °C. Data from Refs. 9 and 21.

tent with Kay's model. At higher concentrations of AN (> 30 mole %), the polymeric structure of water is broken down⁽¹³⁾ and bulkier nitrile molecules replace water in the solvation shell of Na⁺. This leads to low ionic conductivities so that the $(\lambda_{\sigma\eta})_i$ for the Na⁺ ion from water to nitrile rich mixtures is negative.

The magnitude of the $(\lambda_{\sigma\eta})_i$ for the Ag⁺ ion for transfer from water to dilute AN-H₂O mixtures cannot be explained in terms of the difference in viscosities of the bulk solvent and the solvent in the vicinity of the ion. The silver ion as discussed earlier is preferentially solvated by AN even in dilute nitrile mixtures. Thus, the solvodynamic radius of Ag⁺ is greater in AN-H₂O than in H₂O and $(\lambda_{\sigma\eta})_i$ Ag⁺ is negative. Once the solvation shell is saturated with AN, further addition of AN to the solvent mixture does not effect the transfer function.

The effect of solvent composition on $(\lambda_{\sigma\eta})_i$ Ph₄As⁺ is interesting. The Ph₄As⁺ is a bulky hydrophobic ion and carries no definite solvent molecules in its primary solvation shell. However, due to its

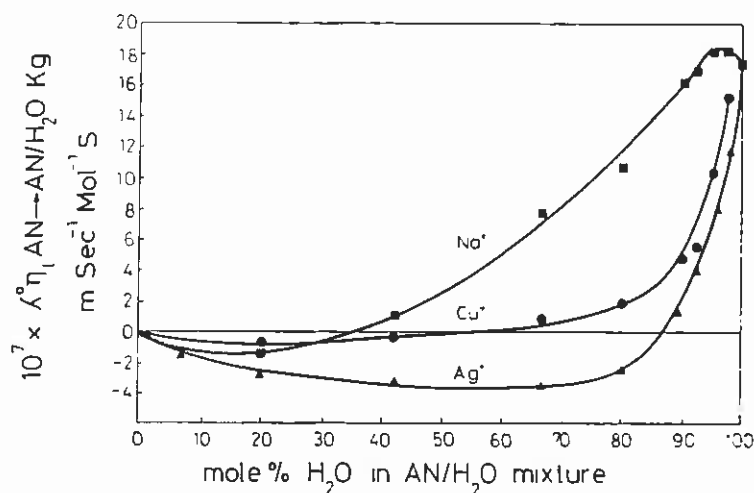


Fig. 6. Ionic Walden products of transfer of Ag^+ , Na^+ , and Cu^+ from acetonitrile to acetonitrile-water mixtures at 25 °C.

hydrophobic interactions⁽¹⁹⁾ (solvation of the second kind), a sheath of tightly packed water molecules is formed around the ion which offers resistance to its mobility. The magnitude of the hydrophobic interactions decreases as the three dimensional water structure is broken down by the addition of acetonitrile⁽¹¹⁻¹³⁾ and hence should result in an increase in mobility of the Ph_4As^+ as AN is added to water. Thus, the $(\lambda_{\sigma\eta})_1 \text{Ph}_4\text{As}^+$ from water to AN- H_2O is positive throughout the solvent composition range as was found by Kay *et al.*⁽⁸⁾ for the hydrophobic Bu_4N^+ ion in ethanol-water mixtures.

The conductance of Cu^+ in AN- H_2O mixtures is important to several hydrometallurgical applications and warrants special attention. Like Ag^+ , Cu^+ also interacts strongly with nitriles $p\pi-d\pi$ back bonding interactions. It incorporates two strongly bonded AN molecules in its solvation shell even in very dilute nitrile solutions and a further two weakly bound AN molecules in more concentrated nitrile solutions. Its solvation shell remains virtually constant for much of the range of the solvent composition. Since Cu^+ is unstable in water, the Walden product of transfer of Cu^+ from H_2O to AN- H_2O cannot be determined. In order to compare the behavior of Cu^+ with other ions, the $(\lambda_{\sigma\eta})_1$ values from pure AN to AN- H_2O mixtures are plotted in Fig. 6. The figure shows that Cu^+ behaves very similar to Ag^+ and differs from Na^+ , up to 70 mole % H_2O in AN- H_2O . The $(\lambda_{\sigma\eta})_1 \text{Cu}^+$ is approximately zero suggesting that the solvation shell which is essentially

acetonitrile $[\text{Cu}(\text{AN})_4^+]$ remains unchanged up to this solvent composition. Thereafter water replaces AN so that the solvodynamic radius becomes smaller and the $(\lambda_{\sigma\eta})_1$ increases. In contrast to Cu^+ , the Ag^+ has only two AN molecules in its solvation shell even in dry AN. It is more hydrophilic than $\text{Cu}(\text{AN})_4^+$ and thus when H_2O is added to AN, water enters the solvation shell of $\text{Ag}(\text{AN})_2^+$ without displacing any AN. This gives a slightly larger solvodynamic unit than $\text{Ag}(\text{AN})_2^+$ in pure AN, so that $(\lambda_{\sigma\eta})_1 \text{Ag}^+$ initially decreases as H_2O is added to AN and then remains virtually constant over a wide range of solvent composition.

4.2. ANIONS

Figure 4 shows that the conductance behavior of anions in AN- H_2O mixtures is quite complex. The NO_3^- ion shows similarities to the Na^+ and Cu^{2+} ions so that the solvent sorting mechanism used for Na^+ could explain its $(\lambda_{\sigma\eta})_1$ values from H_2O to AN- H_2O . However, both Cl^- and I^- are distinctly different and show a sharp decrease in $(\lambda_{\sigma\eta})_1$ even in dilute AN- H_2O mixtures. Our observation concerning Cl^- and I^- ions in AN- H_2O is in agreement with that observed by Petrella.⁽⁹⁾ Kay *et al.* found that the halide ions go through a maximum resembling alkali metal cations in aqueous dioxane,⁽¹⁷⁾ *t*-butanol,⁽¹⁸⁾ and ethanol⁽⁸⁾ solvent mixtures. Petrella *et al.*⁽²⁰⁾ observed that in aqueous sulfolene the halide ions differed from the alkali metal cations which show behavior similar to that observed in AN- H_2O mixtures. The halide ions seem to vary in their conductance behavior in different solvent mixtures. Petrella⁽⁹⁾ suggests that these observations are related to the solvent structure changes due to solvent mixing. The fact that NO_3^- differs from halide ions is surprising. Oxyanions generally show stronger specific interactions in aqueous mixtures which may be one reason why NO_3^- differs from halide ions in AN- H_2O . It would appear from these results that the conductance behavior of anions cannot be explained simply by invoking solvent sorting or solvent structure making/breaking mechanisms. Further work is needed to clarify the situation.

5. CONCLUSION

The results discussed in this paper show that the conductivity of ions in aqueous solvent mixtures show a complex dependence on a number of factors. They are strongly influenced by the mechanism of

solvation and the solvent structure. Ions like Ag^+ and Cu^+ , which show specific ion-solvent interaction with one component of the solvent mixture such as with AN or Py show large decreases in their conductance due to significant changes in their solvation shell composition. Solvent sorting in the solvation shells of ions like Na^+ lead to changes in viscosity of the solvent in their near vicinity which influence their conductance. Large hydrophobic ions like Ph_4As^+ which interact with water through solvation of the second kind show dependence on the structural changes of water when water is mixed with solvents. The behavior of anions is quite complex and may be influenced by a combination of factors, most importantly 'solvent sorting' and solvent structural changes due to solvent mixing.

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