Ionic Mobility of Some Inorganic Ions in Mixed Solvents from Electromigration on Paper

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Measurements of ionic mobilities of a number of cations and anions in nonaqueous and mixed solvents were made from electromigration on filter paper, and the apparent advantages of the ionophoretic method over other modern techniques have been explained. The values so obtained have been corrected for (a) electroosmotic and (b) tortuosity (*i.e.*, 'added migration path length') effects, in order to compare them with those in free solution. Considering the combined effect of dielectric constant and viscosity the ionic mobilities obtained by the electrophoretic method are considered to be of correct order of magnitude. The ionic mobilities at constant dielectric constant when plotted against reciprocal of viscosity show a slight deviation from linearity.

A number of direct and indirect methods are available for the determination of ionic mobilities in liquid media under an applied electric field. Of the earlier ones, the methods of Lodge,1) Whetham,2) and Hittorf3) should be mentioned. The most precise one is the moving boundary method, developed by MacInnes,4) Longsworth,5) Shedlovsky,6) and Tiselius.7)

Whatever the method, the less accurate one of Hittorf or the more precise moving boundary method, they are all time-consuming and require accurate chemical analysis and elaborate techniques. By comparison, the ionophoretic technique lends itself to less complicated equipments which are easy to manipulate. It has also become apparent that it provides fairly accurate values of ionic mobility within a comparatively short time. The promise of paper ionography as an elegant and simple means of measuring ionic mobilities has come to the fore recently. However, a sufficient amount of data is not yet available for the purpose of establishing the potentialities of the technique. Although simple, its degree of reproducibility under varying working conditions has to be accurately ascertained.

Data on ionic mobilities in nonaqueous and mixed media are conspicuous for their paucity. In spite of some inherent difficulties of nonaqueous solutions, ionic mobilities of several alkali metal ions and of a few halide ions have been measured by Gordon and his collaborators8) in anhydrous methanol and ethanol at 25°C from a combined study of transference number and the equivalent conductivity. Measurement of individual ionic mobilities in formamide ($D=109$) has also been reported.9) The ionophoretic technique allows more convenient measurements in nonaqueous and/or mixed media, and hence this possibility has been explored to a large extent. Mixed solvents have been preferred because they permit a continuous variation of macroscopic parameters, namely the dielectric constant and the viscosity.

Principle

The factors governing the ionic migration in solution in an electric field can be classified as:

(a) Characteristics related to the particular ion under investigation, namely its charge (sign and magnitude), size, shape, tendency to dissociate, and tendency for complex formation and amphoteric behaviour, if any.

(b) Environmental factors such as electrolyte concentration, ionic strength, dielectric properties, pH, temperature, viscosity, etc.

(c) The uniformity and intensity of the applied field.

In addition, two other important factors often called "barrier effects", influencing the speed of ions are: (i) electroosmotic effect caused by the movement of charged medium, and (ii) tortuosity factor of 'added migration path length' owing to the winding nature of the path created by the fibrous structure of the filter paper. These two factors and consequent corrections according to McDonald and Bermes10) have been discussed in an earlier communication.11) McDonald and Bermes have shown that acceptable values of mobility of small as well as macro ions may be obtained after making these two corrections.

As mentioned earlier,11) four measurements are required for each set of experimental conditions. These include measurement of ionographic mobility,

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7) A. Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937); *Kolloid.-Z.*, **85**, 129 (1938).

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10) H. J. McDonald and E. W. Bermes, Jr., *J. Chromatogr*, **4**, 34 (1960).

11) M. M. Lahiri, *J. Indian Chem. Soc.*, **42**, 843 (1965).

and R_D, a modified R_f as in classical chromatography of the migrant and of the electroosmotic indicator.

The general expression:

$$U = \frac{U_E}{R_D{}^M} \pm \frac{U_{el}}{R_D{}^{el}}$$

(where U_E denotes the ionographic mobility of the migrant and U_{el} that of the indicator and $R_D{}^M$ and $R_D{}^{el}$ denote the R_D values of the migrant and the indicator, respectively) has been utilised for the determination of free solution mobilities of some inorganic ions in mixed solvents. The negative sign is used if the migrant is positively charged, the positive sign if it is charged negatively.

Experimental

In the present communication are included the results for Cu^{2+}, Ni^{2+}, SCN^-, HSO_4^-, $[Fe(CN)_6]^{3-}$ and $[H_2Fe(CN)_6]^{2-}$ ions. HSO_4^- and $[H_2Fe(CN)_6]^{2-}$ actually resulting from the conversion of SO_4^{2-} and $[Fe(CN)_6]^{4-}$ respectively, in the back ground electrolyte having 0.05M acidity. The concentrations used were of the order 10^{-2}M prepared from reagent grade chemicals.

The reagents employed for detecting the ionic species on paper were as follows. Copper and nickel were detected by first spraying the paper with a saturated solution of rubeanic acid in ethanol and then holding the strip over ammonia vapour. Copper gave a dirty green colour and nickel a blue colour. Ferrocyanide and thiocyanate ions on paper were detected by spraying with a dilute solution of ferric chloride. The former gave a deep blue and the latter, a deep red colour· Ferricyanide was detected by spraying the strip with a dilute solution of ferrous sulphate when a blue colour was obtained. Sulphate was detected first by spraying the neutral paper with a 0.05 per cent solution of sodium rhodizonate in water, drying it, and then with a 0.02 per cent aqueous solution of $BaCl_2$, when a colourless spot on a reddish background was obtained. The electroosmotic indicator, glucose (concentration 0.005 g/ml), was detected on paper by spraying the neutral paper strip with an alcoholic solution of aniline oxalate and then heating it to 120°C when a brown spot appeared.

Micropipettes (1 ml capacity, graduated up to 10^{-3} ml) were used to spot a small volume of the substance under investigation on chromatographic paper. The Precision Ionograph (designed by Research Specialties Co., Richmond, California) which utilises the horizontal paper strip in the electrolyte-saturated condition was used with Whatman chromatographic paper No. 1 and the appropriate electrolyte solutions.

The media consisted of solvent mixtures having different dielectric constants. For this purpose, pure and distilled methanol, ethanol, 2-propanol, acetone, dioxane, and ethylene glycol were mixed with water and hydrochloric acid in definite proportions by weight so as to obtain mixtures of known dielectric constants at a particular temperature and of known acidity (0.05M). The "barrier effects" for the above-mentioned ions were evaluated by measureing the R_D values of the migrants and of the electroosmotic indicator in solvent mixtures of different dielectric constants with the help of a locally fabricated Ionograph similar to that proposed by McDonald and Bermes[10] under conditions identical with those above.

To start with an ionographic experiment, two strips (3.8× 57 cm) were simultaneously moistened with the electrolyte from both ends taking care to avoid excess electrolyte and then pressed gently between two dry filter paper sheets in order to make them, as far as possible, uniformly wet. The strips were then placed in position inside the chamber so that they were pulled horizontally taut by pressing gently the graphite electrodes on each end inside the electrolyte vessels. In order that each strip might offer the same resistance towards current flow, which could be observed from the equal length of each strip exposed above the solvent level, the strips were so placed that the mid-point line of each strip just touched the pointed end of a narrow plastic stick on which it rested. Electrolyte was then poured to the same level in each electrode vessel in order to avoid hydrodynamic flow of fluid in the paper, which was independent of electrical potential. A direct current at 200 V was applied for five minutes in order to drain out any excess solvent. The flow of current was then stopped, and to the marked mid-point of each strip, 0.002 ml of a mixture of the solutions of salt and glucose was carefully spotted. The chamber was then made gas-tight virtually by placing a cover and then closing the points of junction of the cover and the top of the base by means of cellophane adhesive tape. The temperature of the chamber was maintained constant at 25°C, thus reducing evaporation of the solvent from the strip to a minimum. A direct current at 200 V was applied for 30 min. The strips were then dried and sprayed with the reagent specific for the particular ion and again dried. The distance of migration of the ion together with the R_D values were utilised for calculation of free solution mobilities.

For ionographic experiments carried out in pure organic media such as formamide, special care was taken to use completely dehydrated copper and nickel salts for preparing solutions in formamide. Anhydrous sulphates of copper and nickel were obtained in the following processes.

(a) Reagent quality $CuSO_4 \cdot 5H_2O$ was heated in an air-oven first at 100°C to obtain the compound of stoichiometric composition $CuSO_4 \cdot H_2O$. This was further heated to 250°C when almost colourless and dehydrated $CuSO_4$ was obtained. The latter sample was finally heated to 360°C to result in anhydrous $CuSO_4$.

(b) Reagent quality $NiSO_4 \cdot 7H_2O$ was heated in an air-oven first at 120°C to obtain a compound having the stoichiometric composition $NiSO_4 \cdot 2H_2O$ which was further heated to 290°C when yellow and anhydrous $NiSO_4$ was obtained.

Anhydrous sulphates of copper and nickel thus obtained were dissolved separately in anhydrous formamide containing HCl upto the acidity of 0.05M and the respective solutions were used in the electromigration experiments in formamide.

Attempts were also made to use, as far as possible, moisture-free formamide which was obtained by lime-distillation under reduced pressure.[12] The boiling point of the moisture-free formamide prepared was 137.5°C under a reduced pressure of 40 mmHg.

Dry hydrogen chloride gas obtained by the action of reagent quality sulphuric acid on analytically pure sodium chloride (previously dried at 120°C overnight) was bubbled into the distilled formamide upto the acidity of 0.05M. Precautions were taken to avoid moisture-contamination as far as possible by keeping the solvent in an all-glass air-tight vessel and reducing the time between the initial preparations and final electromigration experiments.

The purity (particularly with regard to water content) of the sample of formamide was confirmed spectroscopically using IR and NMR techniques. Further information regarding the purity of the sample was obtained from a study

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12) L. R. Dawson, T. M. Newell, and W. J. McCreary, *J. Amer. Chem. Soc.*, **76**, 6024 (1954).

of vapour phase chromatography.

IR spectra of (a) formamide, (b) formamide containing HCl upto the acidity of 0.05M (vide experiments) and (c) formamide previously kept under moist atmosphere were studied separately. The spectra of (a) and (b) showed no free water band and intermolecular hydrogen bonded water, and hydrogen bonded-NH group could not be distinguished from the spectra because both absorb practically in the same region. IR spectra of sample (c) suggests that formamide is not highly susceptible to moisture absorption. Moreover, a high resolution NMR spectrum of the sample of formamide taken by a Varian spectrometer (operating frequency 56.445 MHz) showed no line for the water proton even at considerably high gain of the amplifier. A vpc study of the formamide sample further confirmed the absence of water.

Results and Discussion

Details of composition by weight of the different solvent mixtures and the values of their dielectric

TABLE 1(A). (Room temperature: 25°)

Constituents of the solvent mixture	Composition of the solvent mixture (% by weight)		Dielectric constant of the solvent mixture	Viscosity (100 η) cp
	Organic liquid	Water–HCl		
1. Methanol: Water: 0.05M HCl	80	20	40.1	1.007
	40	60	59.6	1.599
	20	80	69.2	1.391
2. Ethanol: Water: 0.05M HCl	70	30	38.0	2.007
	50	50	49.0	2.903
	30	70	61.1	2.084
3. 2-Propanol: Water: 0.05M HCl	60	40	35.3	2.693
	40	60	49.7	3.052
	20	80	64.1	1.908
4. Acetone: Water: 0.05M HCl	50	50	48.2	1.229
	30	70	61.0	1.339
	10	90	73.0	1.09
5. Dioxan: Water: 0.05M HCl	70	30	17.69	1.927
	45	55	38.48	1.518
	20	80	60.79	1.275
6. Ethylene glycol: Water: 0.05M HCl	40	60	66.6	1.46
	20	80	72.8	1.453
	10	90	75.6	1.14
7. Water			78.54	0.8937

TABLE 1(B). DETERMINATION OF R_D VALUES IN DIFFERENT MIXED SOLVENTS[a)]

Substances	Methanol: water: HCl dielectric constant.			Ethanol: water: HCl dielectric constant			2-Propanol: water: HCl dielectric constant		
	40.1	59.6	69.2	38.0	49.0	61.1	35.3	49.7	64.1
Cu^{2+}	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ni^{2+}	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
SCN^-	0.97	0.95	0.90	1.0	1.0	0.92	1.0	1.0	1.0
HSO_4^-	0.67	0.91	0.95	0.84	0.86	0.89	0.88	1.0	1.0
$[Fe(CN)_6]^{3-}$	0.91	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$[H_2Fe(CN)_6]^{2-}$	0.95	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

Substances	Acetone: water: HCl dielectric constant			Dioxan: water: HCl dielectric constant			Ethylene glycol: water: HCl dielectric constant		
	48.2	61.0	73.0	17.7	38.4	60.8	66.6	72.8	75.6
Cu^{2+}	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Ni^{2+}	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
SCN^-	1.0	1.0	1.0	1.0	0.92	0.92	1.0	0.96	0.94
HSO_4^-	0.92	1.0	1.0	0.85	0.90	0.90	1.0	1.0	1.0
$[Fe(CN)_6]^{3-}$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$[H_2Fe(CN)_6]^{2-}$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0

a) Since the electrophoretic movement of glucose (used as the electroosmotic indicator) in each of the above-mentioned mixed solvents (Table 2) was zero, determination of R_D value (used as the correction for tortuosity effect of a migrant through the paper) was not done. The electroosmotic effect has been found to be negligible in different nonaqueous solvents[13)]

Table 2.
(Experimental conditions: potential gradient=3.508 V/cm; time=30 min; temperature=25°C)

Solvent mixtures with appropriate dielectric constants (*D*)		Cu^{2+}		Ni^{2+}		SCN^-	
		Distance of migration (mm)	Mobility × 10^4 (computed) (cm²/Vsec)	Distance of migration (mm)	Mobility × 10^4 (computed) (cm²/Vsec)	Distance of migration (mm)	Mobility × 10^4 (computed) (cm²/Vsec)
Methanol: water: 0.05M HCl	40.1	7.5	1.19	8.5	1.35	8.5	1.39
	59.6	11.0	1.74	12.0	1.90	12.5	2.09
	69.2	12.5	1.98	13.5	2.14	14.0	2.46
Ethanol: water: 0.05M HCl	38.0	7.0	1.11	8.0	1.26	7.5	1.19
	49.0	9.0	1.43	10.0	1.58	10.0	1.58
	61.1	11.0	1.74	12.0	1.90	12.0	2.07
2-Propanol: water: 0.05M HCl	35.3	6.0	0.95	7.5	1.19	7.0	1.12
	49.7	8.0	1.26	9.5	1.50	10.5	1.66
	64.1	10.5	1.66	12.0	1.90	13.0	2.06
Acetone: water: 0.05M HCl	48.2	8.5	1.35	10.0	1.58	12.0	1.90
	61.0	10.0	1.58	11.5	1.82	15.0	2.40
	73.0	12.0	1.90	13.5	2.14	18.5	2.93
Dioxane: water: 0.05M HCl	17.69	7.0	1.11	8.0	1.26	7.5	1.19
	38.48	10.0	1.58	11.0	1.74	10.0	1.72
	60.79	13.0	2.06	14.0	2.22	14.0	2.40
Ethylene glycol: water: 0.05M HCl	66.6	7.0	1.11	7.5	1.19	8.0	1.30
	72.8	11.0	1.74	11.0	1.74	14.0	2.30
	75.6	12.5	1.98	13.0	2.06	17.5	2.95

Solvent mixtures with appropriate dielectric constants (*D*)		HSO_4^-		$[Fe(CN)_6]^{3-}$		$[H_2Fe(CN)_6]^{2-}$	
		Distance of migration (mm)	Mobility × 10^4 (computed) (cm²/Vsec)	Distance of migration (mm)	Mobility × 10^4 (computed) (cm²/Vsec)	Distance of migration (mm)	Mobility × 10^4 (computed) (cm²/Vsec)
Methanol: water: 0.05M HCl	40.1	6.0	1.41	9.5	1.61	5.0	0.84
	59.6	10.5	1.81	15.0	2.38	7.5	1.19
	69.2	12.5	2.09	18.0	2.85	9.0	1.43
Ethanol: water: 0.05M HCl	38.0	5.5	1.04	7.5	1.19	4.0	0.63
	49.0	7.5	1.38	10.0	1.58	5.0	0.79
	61.1	9.5	1.70	12.0	1.90	7.0	1.11
2-Propanol: water: 0.05M HCl	35.3	6.0	1.08	9.0	1.43	4.5	0.71
	49.7	9.0	1.43	13.0	2.06	7.0	1.11
	64.1	11.0	1.74	17.0	2.69	9.0	1.43
Acetone: water: 0.05M HCl	48.2	9.5	1.63	14.0	2.22	8.5	1.35
	61.0	12.0	1.90	17.5	2.77	10.0	1.58
	73.0	14.0	2.22	21.0	3.32	12.0	1.90
Dioxane: water: 0.05M HCl	17.69	6.0	1.11	8.5	1.35	3.5	0.55
	38.48	9.0	1.58	13.0	2.06	6.0	0.95
	60.79	11.5	2.02	18.0	2.85	8.5	1.35
Ethylene glycol: water: 0.05M HCl	66.6	6.0	0.95	7.5	1.19	3.5	0.55
	72.8	10.0	1.58	15.0	2.40	8.0	1.26
	75.6	12.5	1.98	19.0	3.00	11.00	1.74

constants are given in Table 1(A), the R_D values of ions studied in various solvent mixtures in Table 1(B) and the calculated mobilities in Table 2. The ionic mobility varies linearly with the dielectric constant of the medium as shown in Fig. 1. We see that with decreasing dielectric constant of the mixed solvents the ionic mobility gradually decreases. Except for the mixtures containing ethylene glycol, the variations of ionic mobility in the others are more or less similar. The graphs in Fig. 1 when extrapolated to the dielectric constants of the pure organic components give values of the ionic mobilities at a finite concentration (10^{-2}M) and at a particular acidity (0.05M HCl) in these different media. However, verification of these values by direct measurement has not been possible owing to the high resistance in the nonaqueous solvents which as a result evaporate quickly. The ethylene glycol graphs, to be noted, extrapolate to an absurdly negative value.

In each of the mixed media, glucose used as an electroosmotic indicator was found to be practically immobile. This does not mean necessarily that electroosmosis is absent, but under such conditions the ionic

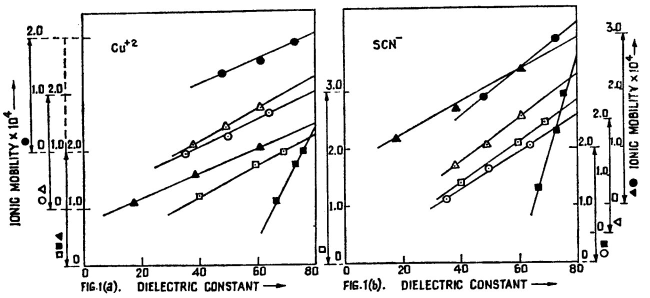

Fig. 1. Ionic mobilily *vs*. dielectric constants.
Solvent mixtures:

1) 2-Propanol: Water: HCl (○)
2) Ethanol: Water: HCl (△)
3) Methanol: Water: HCl (□)
4) Acetone: Water: HCl (●)
5) Dioxan: Water: HCl (▲)
6) Ethylene glycol: Water: HCl (■)

mobilities have to remain uncorrected for this effect. Glucose is therefore unsuitable as an indicator in mixed media, where the magnitude of electroosmotic effect may in reality be very small. Actually Strickler and Mathews[13] found the electroosmotic effect to be negligible in different nonaqueous solvents.

Table 3.

(Experimental conditions: electrolyte medium: formamide–hydrogen chloride mixture (0.05M); (dielectric constant=109.5 and viscosity=0.033 Poise at 25°C); temperature=25°C; potential gradient=3.508 V/cm; time=30 min.)

Migrant	Distance of migration (mm)	R_D value[a)]	Computed mobility $\times 10^4$, (cm²/Vsec)	Computed mobility $\times 10^4$ (cm²/Vsec)	
				0.1M HCl	0.1M $HClO_4$
Glucose	0.0	—	—	—	—
Cu^{2+}	2.0	1.0	0.32(0.89)	2.35	—
Ni^{2+}	3.0	1.0	0.48(1.11)	2.61	—
Br^-	8.0	1.0	1.27(1.36)	—	3.61
I^-	8.5	1.0	1.35(1.36)	—	3.61
SCN^-	7.5	1.0	1.19(1.09)	—	2.89
$Cr_2O_7^{2-}$	8.0	0.95	1.33(1.19)	—	3.14
$[Fe(CN)_6]^{3-}$	8.5	1.0	1.35(1.33)	—	3.51

a) Since the electrophoretic movement of glucose (used as the electroosmotic indicator) in the above-mentioned medium was zero, determination of its R_D value was not done. The values in parentheses in the fourth column are the theoretical mobilities.

Of pure organic media, measurements in formamide ($D=109$) could be successfully made for Cu^{2+}, Ni^{2+}, Br^-, I^-, SCN^-, $Cr_2O_7^{2-}$, $[Fe(CN)_6]^{3-}$ ions in hydrochloric acid. The results are shown in Table 3. Comparing these with the values of ionic mobilities in aqueous media containing HCl and $HClO_4$, it is noted that the ionic mobilities are considerably lower in formamide, particularly for Cu^{2+} and Ni^{2+} ions. The expected increase in ionic mobility in formamide due to its high dielectric constant has apparently not been made due to other factors. One such factor is the viscosity of formamide solutions but it alone cannot explain the decrease observed for Cu^{2+} and Ni^{2+} ions. Even in aqueous mixtures of organic solvents where viscosities are of this order (2-propanol: water–HCl, 40: 60), the ionic mobilities are not so low. One plausible explanation may be as follows: In the aqueous mixtures of organic solvents, the cations remain preferentially hydrated in view of the high polarity and dielectric constant of water and hence the observed mobilities in these mixtures are essentially those of hydrated Cu^{2+} and Ni^{2+} ions. In formamide, the anions remain perhaps unsolvated as in other solvent mixtures and are not therefore much affected, in so far as their mobilities are concerned. This expectation receives support from theoretically computed mobilities[14] which agree fairly well with those observed for these anions in formamide medium. But Cu^{2+} and Ni^{2+} ions are perhaps solvated as usual, and because of the bulkier formamide molecule being attached to these cations thus forming complex basic salts[16] the mobilities are considerably reduced. The solvation of Cu^{2+} and Ni^{2+} ions by formamide is supported by the fact that formamide and its mono- and di-alkyl derivatives and the corresponding compounds derived from acetic acid are known to form complexes with the first group transition elements. Drago *et al.* have actually prepared hexacoordinated complexes of Ni^{2+} and Cr^{3+} ions with the above-mentioned ligands and have studied their spectra and other properties.[17] It is to be noted that care was taken to use completely dehydrated copper and nickel salts for preparing solutions in formamide (vide experiments).

From the graphs in Fig. 1, the mobilities of ions corresponding to any particular value of dielectric constant of the media can be read off. The mobilities corresponding to one such value of $D=60$ are recorded in Table 4, showing that they are different even though measured, so to say, at the same dielectric constant. Considering the combined effect of viscosity and dielectric constant the ionic mobilities recorded in Tables 2 and 4 are considered to be of correct order of magnitude except in ethylene glycol–water–HCl mixture of dielectric constant 60, where ionic mobilities are absurdly low even a negative value is shown for $[H_2Fe-$

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[13] A. Strickler and J. H. Mathews, *J. Amer. Chem. Soc.*, **44**, 1647 (1922).

[14] The mobilities have been calculated from the quation $U_1=\eta_{H_2O}/\eta_1 \cdot \varepsilon_1/\varepsilon_{H_2O}\, U_{H_2O}$ where U_1 is the ionic mobility in mixed medium, η_1 and ε_1 are respectively the viscosity and the dielectric constant of the medium. This expression has been obtained from Walden equation $U=Ze/6\pi\eta r$, assuming that the Stokes ionic radii remain unaltered on changing the medium and the mobility is linearly proportional to the dielectric constant (*cf*. Fig. 1). In calculating the mobilities we have assumed that the mobilities of anions in 0.05M HCl will be close to those in 0.1M $HClO_4$ at the same anion concentration. The mobilities observed of Cu^{2+} and Ni^{2+} ions in 0.05M HCl are 2.37 and 2.93.[15]

[15] M. M. Lahiri and S. K. Mukherjee, *J. Indian Chem. Soc.*, **44**, 980 (1967).

[16] L. F. Audrieth and J. Kleinberg, "Non-Aqueous Solvents," John Willy & Sons, Inc., New York, Chapman & Hall, Ltd., London, p. 144.

[17] R. S. Drago, D. W. Meek, M. D. Joeston, and L. La Roche, *Inorg. Chem.*, **2**, 124 (1963).

Table 4(a).
(Dielectric constant=60.)

Solvent system	Viscosity (millipoise)	Fluidity	Isodielectric mobility × 10^4 (cm²/Vsec)					
			Cu^{2+}	Ni^{2+}	SCN^-	HSO_4^-	$[Fe(CN)_6]^{3-}$	$[H_2Fe(CN)_6]^{2-}$
2-Propanol: water: 0.05M HCl	23.00	0.0435	1.55	1.80	1.92	1.63	2.37	1.34
Ethanol: water: 0.05M HCl	21.75	0.0460	1.70	1.87	1.95	1.67	2.00	0.98
Methanol: water: 0.05M HCl	16.00	0.0625	1.74	1.90	2.12	1.85	2.37	2.20
Acetone: water: 0.05M HCl	13.38	0.0747	1.60	1.85	2.35	1.88	2.73	1.60
Dioxane: water: 0.05M HCl	12.88	0.0776	2.05	2.20	2.37	2.00	2.80	1.34
Ethylene glycol: water: 0.05M HCl	12.00	0.0833	0.60	0.62	0.15	0.25	0.00	−0.30

Table 4(b).

Solvent system	Dielectric constant	Viscosity cp	Mobility × 10^4 (cm²/Vsec)				
			Cu^{2+}	Ni^{2+}	HSO_4^-	$[Fe(CN)_6]^{3-}$	$[H_2Fe(CN)_6]^{2-}$
Ethylene glycol: water: 0.05MHCl	75.6	1.14	1.98(1.86)	2.06(2.3)	1.98(2.07)	3.0 (2.75)	1.74(1.64)
Ethylene glycol: water: 0.05M HCl	72.8	1.453	1.74(1.46)	1.74(1.8)	1.58(1.62)	2.40(2.16)	1.26(1.29)

a) The values in parentheses are the theoretical mobilities.

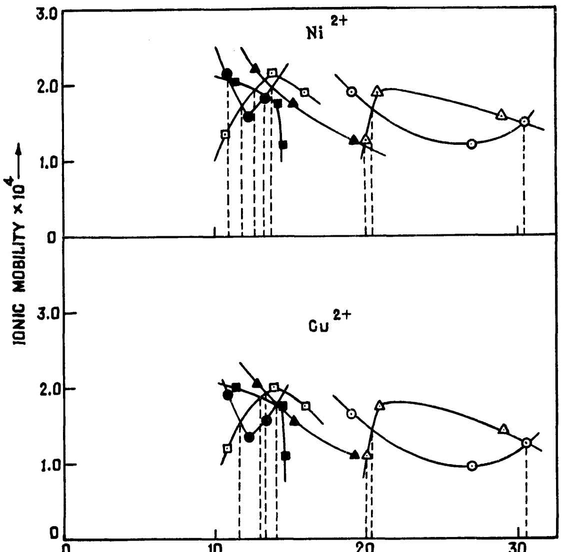

Fig. 2. Ionic mobility *vs*. η.
Solvent mixtures:
1) 2-Propanol: Water: HCl (○)
2) Ethanol: Water: HCl (△)
3) Methanol: Water: HCl (□)
4) Acetone: Water: HCl (●)
5) Dioxan: Water: HCl (▲)
6) Ethylene glycol: Water: HCl (■)

$(CN)_6]^{2-}$. Consequently the nature of the solvent medium and the ionic size in this medium are both going to influence the measured mobilities.

Viscosity is another factor influencing ionic mobility. The latter has been plotted in Fig. 2 against the viscosity of each of the solvent mixtures, from which it is seen that the curves are more or less smooth. Two

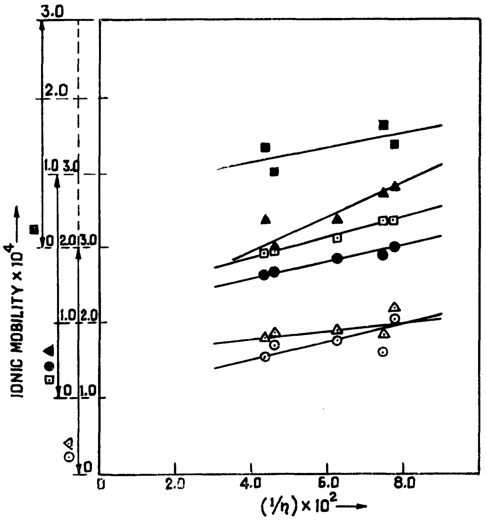

Fig. 3. Ionic mobility *vs*. $1/\eta$.
○: Cu^{2+}, △: Ni^{2+}, □: SCN^-, ●: HSO_4^-,
▲: $[Fe(CN)_6]^{3-}$, ■: $[H_2Fe(CN)_6]^{2-}$.

and sometimes three or more curves intersect; these points being iso-viscous the corresponding mobilities may be termed iso-viscous mobilities. It is probable that irrespective of the nature of the ion, the curvature of the graphs is characteristic of the particular solvent system. The effect of viscosity under iso-dielectric condition ($D=60$) is shown by the data given in Table 4. If, however, the ionic mobilities at $D=60$ are plotted against the fluidity of the media assuming that Stokes ionic radii remain unaltered on changing the medium we have the graphs shown in Fig. 3 which are more linear than those in Fig. 2. The dielectric constants of two ethylene glycol: water: 0.05M HCl systems are close to that of water. Consequently any effect on ionic mobility in these media will be purely a viscosity effect. Accordingly we calculated the mobilities of ions in these media knowing those in water, on the assumption that the Stokes ionic radii remain unaltered. The agreement between the observed and calculated mobilities is, in view of the assumptions made, considered satisfactory. The results are shown in Table 4(b).

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