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# Electrical Conductivities of Halide Salts in Aqueous Formamide Solutions

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The electrical conductivities of sodium chloride and sodium iodide solutions in formamide-water mixtures of different composition have been measured at 25 °C. From these data, the limiting equivalent conductances for these salts have been determined. The corresponding *Walden* products are compared together with the one reported for sodium bromide in the same solvent mixtures, and they are analysed as functions of the anion size. Further, the limiting ionic equivalent conductances are estimated for the different ions. The variation of the ionic *Walden* products with solvent composition is discussed in terms of ionic solvation and solvent structure.

*(Keywords: Ionic conductance; Aqueous formamide; Sodium halides)*

*Elektrische Leitfähigkeit von Halogensalzen in wäßrigen Formamid-Lösungen*

Es wurden die elektrischen Leitfähigkeiten von Natriumchlorid- und Natriumjodidlösungen in Formamid-Wasser-Mischungen verschiedener Zusammensetzung bei 25 °C gemessen. Aus diesen Daten wurden die Grenzäquivalenzleitfähigkeiten für diese Salze bestimmt. Die entsprechenden *Walden*-Produkte wurden mit den für Natriumbromid in den gleichen Lösungsmittelgemischen berichteten verglichen und hinsichtlich der Anionengrößen analysiert. Außerdem wurden die ionischen Grenzäquivalenzleitfähigkeiten für die einzelnen Ionen abgeschätzt. Die Variation der ionischen *Walden*-Produkte mit der Lösungsmittelzusammensetzung wurde bezüglich Ionensolvatation und Lösungsmittelstruktur diskutiert.

## Introduction

Studies about the properties of electrolyte solutions in mixed solvents have recently received much attention regarding to their use as reactive medium in technical applications. Formamide-water mixtures are of special interest because they cover a wide range of dielectric constants (109.58–78.30). Formamide is considered as a three-dimensionally structured solvent as well as water. Then, one can expect that in their mixtures with water a certain degree of structuration may be preserved. In this way, it has been showed that the hydrogen bond energies of formamide-water and water-water bonds are similar [1]. This fact can explain that only small departures from ideality are observed for several physico-chemical properties of the formamide-water mixtures [2].

In the present work, the electrical conductivities of sodium chloride and sodium iodide solutions have been measured in different formamide-water mixtures at 25 °C. The results, together with those corresponding to sodium bromide obtained in a previous work [3], are discussed in terms of the variation of the ionic *Walden* product with solvent composition.

## Experimental

Sodium chloride and sodium iodide were Merck of analytical grade. The salts were dried at 110 °C for 24 h before use. Formamide (*FA*) was Fluka, analytical grade, and it was purified as has been described previously [4]. All solutions were made up by weight using conductivity water equilibrated with atmospheric $CO_2$. Large enough samples were used, so errors in weighing were limited, and the volume concentrations were calculated from weight concentrations and density values.

Conductances were measured with a Beckman AC-18A and a Crison 525 conductivity bridge, operating at frequencies of 3 000 and 3 800 Hz, respectively. Two cells were used for the conductance measurements: a *Jones*-type cell with bright platinum electrodes, supplied by Methrom (model EA 655-C), and a cell designed by us. The cell constants were determined by the *Lind-Zwolenik-Fuoss* method [5], using the polynomial equation obtained by *Chiu* and *Fuoss* [6], with aqueous solutions of KCl ranging from $5.1 \cdot 10^{-5} M$ to $1.7 \cdot 10^{-2} M$. The resulting constants were 0.836 and $0.944 \mathrm{cm}^{-1}$. For the conductance runs, the dilution method was used starting with the pure solvent. After the measurement of the solvent conductance (when the thermal equilibrium has been achieved) the stock solutions were added from a weight burette and the conductance was measured after 20–30 min, in order to reach the homogeneity of the solution and to reestablish thermal equilibrium. All measurements were made at 25 ± 0.01 °C by placing the cells in a oil-filled thermostated bath. A temperature probe was used to set the temperature inside the cell.

## Results and Discussion

The measured equivalent conductances, $\Lambda$, of sodium chloride and sodium iodide solutions of different concentrations in *FA*-water mixtures are reported in Tables 1 and 2, respectively. From these results, the limiting equivalent conductances, $\Lambda_0$, have been determined using the *Shedlovsky* method [7, 8]. As it has been suggested by *Justice* [9], the *Bjerrum* critical distance ($q = e^2/2\varepsilon kT$) has been used in order to determine the mean-ion activity coefficient needed for the evaluation. The viscosities and the dielectric constants of the different solvent mixtures

Table 1. *Equivalent conductances of* NaCl *in formamide-water mixtures at 25 °C*

| $x_{H_2O}$ | $\Lambda/\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{eq}^{-1}$ | $c/10^{-3}\,M$ |
|---|---|---|
| 0.897 | 105.5 | 15.04 |
| | 104.5 | 18.50 |
| | 104.0 | 21.80 |
| | 102.9 | 25.60 |
| | 102.5 | 28.20 |
| | 101.5 | 32.37 |
| | 101.0 | 37.55 |
| | 99.30 | 44.59 |
| | 98.75 | 56.91 |
| | 97.84 | 58.50 |
| 0.800 | 92.70 | 13.46 |
| | 92.50 | 16.38 |
| | 92.33 | 19.22 |
| | 91.13 | 25.95 |
| | 89.93 | 32.40 |
| | 87.85 | 38.35 |
| | 87.35 | 48.22 |
| | 86.57 | 62.71 |
| | 85.32 | 75.03 |
| 0.599 | 66.80 | 12.54 |
| | 66.42 | 15.38 |
| | 66.03 | 21.15 |
| | 65.04 | 26.71 |
| | 64.75 | 33.42 |
| | 64.09 | 40.65 |
| | 63.35 | 47.35 |
| | 63.02 | 51.36 |
| | 62.95 | 57.60 |
| 0.500 | 56.82 | 15.17 |
| | 56.43 | 18.22 |
| | 56.14 | 21.29 |
| | 55.86 | 27.08 |
| | 55.28 | 33.87 |
| | 55.00 | 40.01 |
| | 54.45 | 51.37 |
| | 53.86 | 61.11 |
| | 53.47 | 77.27 |
| 0.203 | 35.01 | 13.22 |
| | 34.75 | 15.38 |
| | 34.60 | 29.68 |
| | 34.31 | 28.90 |
| | 34.00 | 35.91 |
| | 33.71 | 45.16 |
| | 33.70 | 50.80 |
| | 33.50 | 54.95 |
| | 33.01 | 62.36 |
| | 32.99 | 69.37 |

Table 2. *Equivalent conductances of* NaI *in formamide-water mixtures at 25 °C*

| $X_{H_2O}$ | $\Lambda/\Omega^{-1}\,cm^2\,eq^{-1}$ | $c/10^{-3}\,M$ |
|---|---|---|
| 0.900 | 96.23 | 2.818 |
| | 96.09 | 3.721 |
| | 95.90 | 4.606 |
| | 95.69 | 8.794 |
| | 95.63 | 9.977 |
| | 95.58 | 10.36 |
| | 95.57 | 11.13 |
| | 95.45 | 12.62 |
| | 95.41 | 14.06 |
| | 95.33 | 14.76 |
| | 95.26 | 15.45 |
| 0.800 | 79.98 | 27.72 |
| | 79.74 | 30.47 |
| | 79.73 | 33.07 |
| | 79.62 | 34.32 |
| | 79.31 | 44.09 |
| | 79.26 | 45.97 |
| | 79.18 | 51.08 |
| | 79.17 | 58.20 |
| | 78.89 | 62.36 |
| | 78.85 | 63.45 |
| | 78.74 | 65.51 |
| 0.750 | 76.33 | 6.856 |
| | 75.98 | 8.653 |
| | 75.74 | 10.38 |
| | 75.35 | 12.06 |
| | 75.22 | 13.67 |
| | 74.98 | 15.61 |
| | 74.86 | 16.73 |
| | 74.37 | 20.28 |
| | 74.25 | 22.28 |
| | 74.22 | 24.18 |
| | 74.14 | 25.40 |
| | 73.93 | 28.86 |
| | 73.83 | 29.94 |
| | 73.79 | 32.02 |
| | 73.62 | 33.50 |
| | 73.52 | 35.39 |
| | 73.37 | 36.74 |
| | 73.32 | 38.05 |
| 0.500 | 51.86 | 9.179 |
| | 51.30 | 12.61 |
| | 50.86 | 17.52 |
| | 50.50 | 22.18 |

Table 2 *(continued)*

| $X_{H_2O}$ | $\Lambda/\Omega^{-1}\,cm^2\,eq^{-1}$ | $c/10^{-3}\,M$ |
|---|---|---|
| | 50.13 | 26.59 |
| | 50.11 | 31.05 |
| | 49.83 | 35.02 |
| | 49.72 | 38.80 |
| | 49.68 | 42.17 |
| | 49.25 | 48.91 |
| | 49.16 | 53.89 |
| | 49.03 | 58.71 |
| | 48.85 | 64.26 |
| | 48.80 | 69.04 |
| | 48.65 | 71.30 |
| 0.200 | 35.68 | 2.914 |
| | 35.03 | 8.336 |
| | 34.72 | 13.28 |
| | 34.39 | 17.80 |
| | 34.10 | 23.90 |
| | 33.93 | 27.57 |
| | 33.80 | 30.98 |
| | 33.55 | 37.08 |
| | 33.54 | 39.83 |
| | 33.27 | 50.22 |
| | 33.14 | 54.02 |
| | 32.98 | 58.21 |

were taken from the literature [3, 10]. The $\Lambda_0$-values for NaCl and NaI, together with their standard deviations obtained with a least-squares iterative method using a computer program (Digital Vax, 11-750 and PDP-11/03), are summarized in Table 3 in different *FA*-water mixtures at 25 °C.

As it is shown in Table 3, the values of $\Lambda_0$ for NaCl and NaI decrease gradually with increasing *FA* content in the solvent. This behaviour can be attributed mainly to the increase of the viscosity of the solvent with increasing *FA* mole fraction [3]. For this reason, it is better to discuss the results in terms of the *Walden* product ($\Lambda_0\eta$), in order to analyse the structural changes of the solutions when varying the solvent composition. In Fig. 1, the *Walden* products for NaCl and NaI are represented as a function of the water mole fraction. In the same figure, $\Lambda_0\eta$-products for NaBr obtained in a previous work [3] are also represented. According to the *Walden* rule, the $\Lambda_0\eta$-product should remain constant for a given electrolyte in different solvents. However, as it can be seen in Fig. 1, the $\Lambda_0\eta$-products depend on solvent composition. In fact, the departures of

Table 3. *Limiting equivalent conductances* ($\Omega^{-1}$ $cm^2$ $eq^{-1}$) *of* NaCl *and* NaI *in different FA-water mixtures at 25 °C*

| | $\Lambda_0$ | |
|---|---|---|
| $X_{H_2O}$ | NaCl | NaI |
| 1.00[a] | 126.54 | 127.18 |
| 0.90 | 114.4 ± 0.2 | 99.05 ± 0.03 |
| 0.80 | 99.5 ± 0.2 | 86.07 ± 0.02 |
| 0.75 | — | 79.90 ± 0.02 |
| 0.60 | 71.3 ± 0.2 | — |
| 0.50 | 60.5 ± 0.05 | 54.54 ± 0.03 |
| 0.20 | 36.4 ± 0.1 | 36.89 ± 0.03 |
| 0.00[b] | 27.2 | 26.8 |

[a] *Kay L, Evans DF* (1966) J Phys Chem 70: 2325
[b] *Thomas J, Evans DF* (1970) J Phys Chem 74: 3812

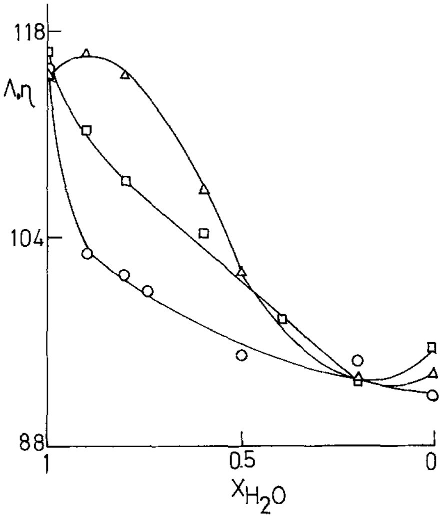

Fig. 1. Variation of the $\Lambda_0\eta$-product ($\Omega^{-1}$ cm$^2$ eq$^{-1}$ cp) for NaCl (△), NaBr (□) and NaI (○) with solvent composition at 25 °C

the *Walden* rule can be ascribed to changes of ion solvation and of solvent structure. In this way, the diminution of the $\Lambda_0\eta$-product observed for the three salts with increasing *FA* content in the solvent, except in *FA*-rich compositions, and in water-rich regions for NaCl, can be explained considering the breaking of the water structure by adding *FA* [11]. Consequently, for NaI and NaBr a decrease of the excess mobility of the ions in the solvent mixtures is produced, due to their lower structure-breaking ability, which leads to a decrease of $\Lambda_0\eta$-products. The lower structure-breaking role of the ions in *FA*-water mixtures is more pronounced by increasing the anion size. The order $Cl^- > Br^- > I^-$ for the $\Lambda_0\eta$-product at a given solvent composition supports this claim. The differences between $\Lambda_0\eta$-products for NaCl and NaBr and for NaBr and NaI take maximum values in the water-rich region. In fact, it has been suggested from heat capacities and NMR studies [12, 13] that, initially, by adding *FA* to water, a strong disruption of the water structure is produced. Then, the loss of the excess mobility of the ions is more pronounced with increasing the anion size in this region of solvent composition.

Table 4. *Limiting equivalent conductances* (*$\Omega^{-1}$ cm$^2$ eq$^{-1}$*) *of* $Cl^-$, $Br^-$ [3], $I^-$ *and* $Na^+$ [3] *ions in different FA-water mixtures at 25 °C*

| | $\lambda_0$ | | | |
|---|---|---|---|---|
| $X_{H_2O}$ | $Na^+$ | $Cl^-$ | $Br^-$ | $I^-$ |
| 1.00[a] | 50.20 | 76.34 | 78.22 | 76.8 |
| 0.90 | 46.4 | 68.0 | 60.1 | 52.6 |
| 0.80 | 41.9 | 57.6 | 50.1 | 44.1 |
| 0.75 | 37.9 | — | 48.3 | 42.0 |
| 0.65 | 31.9 | — | 42.3 | (36.1) |
| 0.60 | 30.2 | 41.2 | 39.0 | — |
| 0.00[b] | 10.1 | 17.1 | 17.7 | 16.7 |

[a] *Kay L, Evans DF* (1966) J Phys Chem 70: 2325
[b] *Thomas J, Evans DF* (1970) J Phys Chem 74: 3812

In a previous work, the separation of $\Lambda_0$ for NaBr into its ionic components in different *FA*-water mixtures was achieved [3]. Then, the limiting ionic conductances ($\lambda_0$) for $Cl^-$ and $I^-$ ions can be obtained by the difference between the corresponding $\Lambda_0$-values for sodium halide salts and sodium ion. The $\lambda_0$-values for $Cl^-$ and $I^-$ ions obtained in this manner, together with those for $Na^+$ and $Br^-$ ions, in different *FA*-water mixtures at 25 °C, are summarized in Table 4. In Fig. 2 the corresponding ionic *Walden* products are represented as a function of solvent composition. As can been observed each $\lambda_0\eta$-product for $Na^+$ ion is lower than the corresponding for halide ions, despite of the smaller size of the former. Then, one can assume that $Na^+$ ion is more solvated than halide ions in the different solvent mixtures. Actually, $Na^+$ does not show preferential solvation in either of the two solvents, as it is evidenced from NMR and viscosity studies [14, 15]. So, with increasing *FA* content in the solvent, a substitution of water molecules by the more voluminous ones of *FA* in the ionic solvation shell takes place, resulting in a gradual diminution of the $\lambda_0\eta$-product. However, in the water-rich region, an increase of the *Walden* product for $Na^+$ ion is noticed when *FA* is added to water (see Fig. 2). As it is discussed elsewhere [3], this behaviour is a consequence of the existing specific acid-base interactions between $Na^+$ and water molecules. The basic feature of water molecules in the mixtures is increased due to the hydrogen bond formation between *FA* and water molecules ("averaging effect" [16]). Consequently, $Na^+$ becomes preferentially solvated by water molecules in the water-rich regions of the solvent mixtures. The greater proportion of water molecules around the ion with respect to the bulk leads to a lower local viscosity and a greater ionic mobility [17].

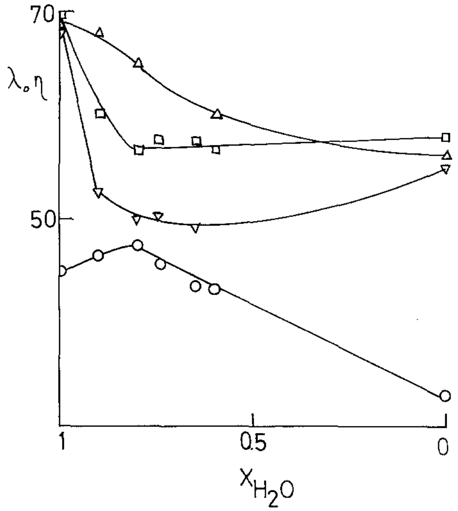

Fig. 2. Variation of the $\lambda_0\eta$-product for $Na^+$ (○), $Cl^-$ (△), $Br^-$ (□) and $I^-$ (▽) ions as a function of solvent composition at 25 °C

In pure *FA*, a great difference of the $\lambda_0\eta$-product between $Na^+$ and halide ions is noticed (see Table 4). There are two reasons explaining such a difference. First, the halide ions are presumably not solvated by *FA* molecules, as it is suggested by the low viscosity *B*-coefficients showed by these anions in pure *FA* [15, 18], and also by the fact that the *Stokes* radii for the halide ions in pure *FA* are lower than their crystallographic radii, while for $Na^+$ the opposite is true [19]. Second, *FA* is a protic solvent which shows a certain degree of structuration; in this way, *FA* can be considered as formed by chains of *FA* molecules which are associated by hydrogen bonds [10]. Thus, ions with large size, such as halide ions, act as structure-breakers. The breaking of the solvent structure, which occurs around these structure-breaking ions, leads to an increase of their mobilities, increasing consequently the $\lambda_0\eta$-products. The addition of small amounts of water to the pure *FA* causes the breaking of the chain structure of *FA* [10]. This explains the slight decrease of the $\lambda_0\eta$-product for $I^-$ and $Br^-$ ions upon adding water to *FA*. However, water produces little destruction of the *FA* structure because the $\lambda_0\eta$-product for $Cl^-$ ion, which exhibits low structure-breaking properties, increases steeply by increasing the water content in the solvent, being insensible to solvent structure changes. In this case, the augmentation of the $\lambda_0\eta$-product as the water mole fraction is increased can be ascribed probably to a preferential solvation of $Cl^-$ by water. Then, the gradual entry of water molecules in the solvation shell of $Cl^-$, which may take place when the water content in the solvent increases, produces a lower local viscosity around the ion, rising its mobility.

On the other hand, a decrease of the $\lambda_0\eta$-product for the $Br^-$ and $I^-$ ions with increasing the *FA* mole fraction in the water-rich region is observed (Fig. 2). The decrease is more pronounced with increasing anion size. As it is mentioned above, upon adding *FA* to water, a strong disruption of the water structure is produced. Then, a high loss of the excess mobility of the ion takes place, and the loss is more important for those structure-breaking ions.

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