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Electrical Conductivities of Sodium Bromide in Formamide-Water Mixtures

Javier Doménech and **Sergio Rivera**

Departament de Química Física, Universitat Autònoma de Barcelona, Bellaterra (Barcelona), Spain

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The limiting equivalent conductances for sodium bromide in formamide-water mixtures of different composition have been determined at 25 °C. The diffusion coefficient for Br^- ion has also been determined by the polarographic technique in various solvent compositions at 25 °C. From these data the corresponding limiting equivalent conductances for Na^+ and Br^- ions were calculated. The results are discussed in terms of structural changes of the solvent and specific acid-base interactions between the ions and solvent molecules. Finally, the influence of the cation size on the ionic solvation in the different formamide-water mixtures is analysed.

(Keywords: Acid-base interactions; Conductances of ions; Polarography; Solvent interactions)

Elektrische Leitfähigkeit von Natriumbromid in Formamid/Wasser-Mischungen

Es wurden die Grenzäquivalentleitfähigkeiten für Natriumbromid in verschiedenen Formamid/Wasser-Gemischen bei 25 °C bestimmt. Der Diffusionskoeffizient für Br^- wurde ebenfalls für verschiedene Lösungsmittelgemische bei 25 °C mittels einer polarographischen Methode erhalten. Aus diesen Daten wurden die entsprechenden Grenzäquivalenzleitfähigkeiten für Na^+ und Br^- berechnet. Die Ergebnisse werden als Resultat von Strukturänderungen des Lösungsmittels und von spezifischen Säure-Base-Wechselwirkungen zwischen den Ionen und den Lösungsmittelmolekülen interpretiert. Zusätzlich wird der Einfluß der Kationengröße auf die Ionen-Solvatation in den verschiedenen Formamid/Wasser-Mischungen diskutiert.

Introduction

Much attention has been given to the structural properties of electrolytic solutions in mixed solvents, and particularly, in amide-water mixtures owing to their interesting properties as reactive medium which cover a large range of dielectric constants. In addition, the amide-water system is important to elucidate the behaviour of peptides in aqueous solutions.

The formamide (*FA*)-water mixtures are an interesting system owing to the high dielectric constant of the *FA* ($\varepsilon = 109.58$) and its capacity to form hydrogen bonds. In a recent work the solvation of Na^+ and Br^- ions in *FA* water mixtures has been studied from the analysis of the viscosity *B*-coefficient[1]. In the present paper a deeper insight is given from conductivity measurements. With this aim, the electrical conductivities of sodium bromide solutions and the polarographic characteristics of Br^- ion have been determined in different *FA*-water mixtures at 25 °C. From these measurements a tentative separation of the equivalent limiting conductance of the salt into the ionic contributions are performed. The results are discussed in terms of structural aspects of the solvent molecules. Finally, the influence of the cation size on the ionic solvation in the different solvent mixtures is analysed together with the results of a previous work[2].

Experimental

Conductances were measured with a Beckman conductivity bridge, model AC-18 A, operating at a frequency of 3 000 Hz. A *Jones*-type cell with bright platinum electrodes, supplied by Metrhom (model EA 655-C), was used. The cell constant determined from reference solutions of KCl was 0.8360 cm^{-1}.

The polarograms were recorded by means of a three electrode polarograph Metrhom, model 261, provided with an IR compensator. As a working electrode, a dropping mercury electrode was used, with a dropp-time of 5.75 and *m*-value of 1.45 mg s^{-1} under a mercury head of 35 cm at open circuit. Platinum was used as an auxiliar electrode. The half-wave potentials were referred to an aqueous saturated calomel electrode (SCE) which was connected to the electrolytic cell through a salt bridge filled with the solution of interest. Oxygen was eliminated by bubling purified nitrogen—previously saturated with solvent vapours—through the solution.

The technique and procedure for the viscosity and density measurements have been described before[3]. All solutions were prepared by weight and the determinations were carried out at 25 ± 0.01 °C.

All chemicals were of analytical grade. *FA* and potassium perchlorate were from Merck and sodium bromide was from Fluka. *FA* was purified as described previously[4], and sodium bromide and potassium perchlorate were dried at 80 °C and used without further purification.

Results

Table 1 summarises the measured equivalent conductances, Λ, for some salt concentrations in different *FA*-mixtures at 25 °C. The conductance data were analysed by the *Shedlovsk* method[5,6], using the following equation:

$$1/S(z)\Lambda = 1/\Lambda_0 + c\Lambda S(z) f_{\pm}^{2} K_A/\Lambda_0^{2}$$

Table 1. *Equivalent conductances for* NaBr *in formamide-water mixtures at 25 °C*

X_{H_2O}	$\Lambda/\Omega^{-1}\,cm^2\,eq^{-1}$	$c/10^{-3}M$	X_{H_2O}	$\Lambda/\Omega^{-1}\,cm^2\,eq^{-1}$	$c/10^{-3}M$
0.90	105.7	4.624	0.40	48.20	5.776
	104.5	14.90		46.96	15.33
	103.6	25.77		45.90	25.68
	103.6	25.77		45.58	35.43
	102.2	34.42		45.42	45.64
	101.2	57.08		45.08	56.99
	100.5	66.94		44.77	66.04
	100.2	75.53		44.43	75.24
	99.70	85.73		44.14	85.73
	99.23	95.28		43.83	95.89
0.80	90.27	5.476	0.20	35.04	5.929
	88.42	14.90		33.95	18.46
	88.23	24.30		33.32	24.65
	87.43	34.45		33.18	34.17
	86.91	44.65		32.59	44.48
	86.15	55.82		32.61	55.08
	85.65	64.75		32.25	64.46
	84.72	83.50		32.06	77.42
	84.50	85.09		31.80	86.30
				31.51	95.73
0.60	66.91	3.969			
	64.60	14.70			
	63.48	25.42			
	62.86	36.27			
	62.71	45.44			
	62.22	55.56			
	61.65	64.70			
	61.34	75.64			
	60.26	87.25			
	59.89	95.12			

where for 1 : 1 electrolytes:

$$S(z) = 1 + z + z^2/2 + z^3/8 + \dots .$$

$$z = \beta(\Lambda c)^{1/2}\Lambda_0^{-3/2}$$

$$\beta = 8.204\,10^5\,\Lambda_0\,(\varepsilon T)^{-3/2} + 82.5\,\eta^{-1}\,(\varepsilon T)^{-1/2}$$

$$\log f = -\frac{1.8246\,10^6\,(c\alpha)^{1/2}\,(\varepsilon T)^{-3/2}}{1 + 50.29\,10^8\,R(c\alpha)^{1/2}\,(\varepsilon T)^{-1/2}}$$

$$\alpha = \Lambda/\Lambda_0\,S(z)$$

The R parameter needed for determining the mean-ion activity coefficient ($f_{\pm}$) can be substituted by the *Bjerrum* critical distance ($q = e^2/2\varepsilon kT$) as it has been suggested by *Justice*[7].

Table 2. *Viscosites of FA-warer mixtures at 25 °C*

X_{H_2O}	η/cp
1.00	0.8904
0.90	0.9993
0.80	1.1310
0.75	1.1991
0.70	1.2808
0.65	1.3605
0.60	1.4542
0.40	1.8748
0.20	2.4481
0.00	3.2904

Table 3. *Limiting equivalent conductances for* NaBr *in different FA-water mixtures at 25 °C*

X_{H_2O}	$\Lambda_0/\Omega^{-1}\,eq^{-1}\,cm^2$
1.00[a]	128.6
0.90	108.6 ± 0.2
0.80	92.4 ± 0.2
0.60	69.1 ± 0.2
0.40	50.0 ± 0.1
0.20	36.3 ± 0.1
0.00[b]	27.8

[a] *Kay L., Evans O. F.,* J. Phys. Chem. **70**, 2325 (1966).
[b] Ref.[10].

The limiting equivalent conductance (Λ_0) was obtained from the intercept of the $1/S(z)\Lambda$ vs. $C\Lambda f_{\pm}^2/S(z)$ representations, and the association constant (K_A) was evaluated from the corresponding slope. These parameters were determined with a least-squares iterative method, using a computer program (Digital Vax, 11-750). The dielectric constants (ε) of the solvents, needed for determining K_A and Λ_0 values, were taken from the literature[8]. The viscosities (η) of the different solvent mixtures at 25 °C are indicated in Table 2. In Table 3 the values for NaBr in various *FA*-water mixtures at 25 °C together with their standard deviations are summarised. The K_A values are near zero, indicating absence of noticeable ionic association.

The polarograms of 1 m*M* solutions of sodium bromide with 0.1 *M* of potassium perchlorate as supporting electrolyte were recorded in a solvent

Table 4. *Half-wave potentials (v vs. SCE), diffusion current constants* ($\mu A\, mM^{-1}\, mg^{-2/3}\, s^{1/2}$) *and diffusion coefficients* ($cm^2\, s^{-1}$) *for* Br^- *ion in different FA-water mixtures at 25 °C*

X_{H_2O}	$E_{1/2}$	I	$D \cdot 10^5$
0.90	0.142	2.44	1.62
0.80	0.139	2.19	1.35
0.75	0.139	2.18	1.30
0.70	0.137	2.12	1.22
0.65	0.134	2.05	1.14
0.60	0.131	1.97	1.05

Table 5. *Limiting equivalent conductances* ($\Omega^{-1}\, eq^{-1}\, cm^2$) *for* Na^+ *and* Br^- *ions at different FA-water mixtures at 25 °C*

X_{H_2O}	$\lambda_0^{Na^+}$	$\lambda_0^{Br^-}$
1.00[a]	50.20	78.22
0.90	46.4	60.1
0.80	41.9	50.1
0.75	37.9	48.3
0.70	34.9	45.3
0.65	31.9	42.3
0.60	38.2	39.0
0.00[b]	10.1	17.7

[a] *Kay L., Evans D. F.*, J. Phys. Chem. **70**, 2325 (1965).
[b] Ref.[10].

composition range between 1 and 0.60 water mole fraction at 25 °C. The polarograms for solutions at higher *FA* contents were not obtained due to the oxidation of dropping mercury electrode. The polarograms of these solutions give a well defined wave which is diffusion controlled and corresponds to the anodic oxidation of the bromide ion. Table 4 gives the half-wave potential ($E_{1/2}$) and the diffusion current constant (I) for this process in different solvent compositions. Table 4 gives also the diffusion coefficient (D) of Br^- ion calculated from the *Ilkõvic* equation.

From the diffusion coefficient and the *Nernst-Einstein* equation ($\lambda_0 = Ze_0 FD/KT$), the limiting equivalent conductance for Br^- ion was obtained at different *FA*-water mixtures. The limiting equivalent conductance for the Na^+ ion was obtained from the difference between the corresponding values for NaBr and Br^- ion. The results are indicated in Table 5 for different solvent compositions at 25 °C.

Discussion

The Λ_0 values for NaBr decrease as the *FA* content in the solvent increases (Tab. 2). This behaviour can be attributed mainly to the gradual increase of the solvent viscosity with adding *FA* (Table 2). For this reason it is more convenient to discuss the results in terms of the *Walden* product ($\Lambda_0 \eta$). Fig. 1 shows the *Walden* product for NaBr as a function of the water mole fraction. The $\Lambda_0 \eta$ values decrease gradually as the *FA* content increases, reaching a minimum at 0.2 water mole fraction. At a first glance, this variation can be attributed to the loss of solvent structure by adding the organic component[4,9]. Though *FA* can form hydrogen bonds giving way to certain compatibility between both solvents[10], the overall effect corresponds to a decrease of solvent structure[4,9]. This fact leads to a decrease in the excess mobility due to the breaking properties of the ions which produces a diminution of the $\Lambda_0 \eta$ product. At 0.2 water mole fraction, a minimum in the *Walden* product variation is observed (Fig. 1). As we will discuss later on, this minimum can be explained taking into account the existence of specific interactions between the ions and one of the two solvent components.

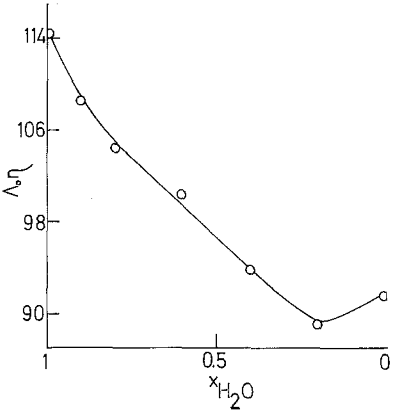

Fig. 1. Variation of the $\Lambda_0 \eta$-product ($\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{eq}^{-1}\,\mathrm{cp}$) for NaBr with solvent composition at 25 °C

Further information can be obtained from the analysis of the ionic *Walden* product. Fig. 2 shows the $\lambda_0 \eta$-products for Br^- and Na^+ ions at different solvent compositions within the range 1 to 0.6 of water mole fractions. One observes a strong decrease of $\lambda_0 \eta$-product for Br^- ion in water-rich regions as far as $X_{H_2O} = 0.8$, and from this composition $\lambda_0 \eta$

remains practically constant with a value similar to the corresponding one in pure *FA* ($58.2\,\Omega^{-1}\,cm^2\,eq^{-1}\,cp$)[11]. Upon adding *FA* to water, a high disruption of the water structure is produced initially[12,13], leading to a strong loss of excess mobility characteristic for structure breaking ions, as for example Br^-. This produces a clear diminution of the $\lambda_0\eta$-product for this ion at high water contents (Fig. 2). The constancy of the *Walden* product in higher *FA* compositions can be explained assuming a progressive desolvation of the Br^- ion when adding *FA*. In pure *FA* the Br^- ion has a small *Stokes* radius which is lower than the crystallographic radius[14] and a small viscosity *B*-coefficient[1,15]. These facts allow us to conclude the Br^- ion is not solvated in pure *FA*, despite its possibility to form hydrogen bonds with solvent molecules. Thus the progressive desolvation of the Br^- ion when increasing the *FA* content counteracts the loss of excess mobility of the ion, leading to a constancy of the $\lambda_0\eta$—product in relation to the solvent mole fraction.

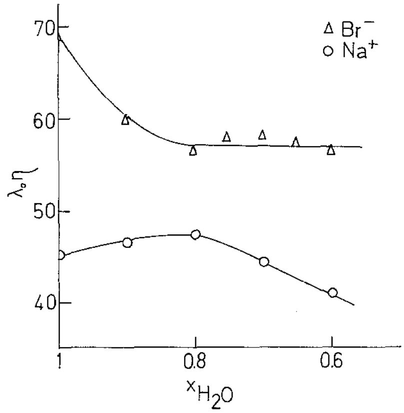

Fig. 2. Variation of the $\lambda_0\eta$-product for Na^+ and Br^- ions with solvent composition at 25 °C

The Na^+ ion presents an opposite behaviour. In this case, a slight increase of the *Walden* product in the water-rich region is observed (Fig. 2), decreasing subsequently as increases the *FA* content. The initial increase of the $\lambda_0\eta$-product when adding *FA* to water can be explained by taking into account the existence of a weak preferential solvation of Na^+ by water, which seems to be due to specific acid-base interactions. The Na^+ ion which has an acid feature interacts with water increasing its basicity due to the hydrogen bond with *FA* ("averaging effect"[16]). This leads to a lower local viscosity around the ion with respect to the bulk viscosity, producing an increase in the mobility of the Na^+ ion. From $X_{H_2O} = 0.80$ to higher *FA* contents the $\lambda_0 \eta$—product gradually decreases. When increasing the *FA* content in the solvent, a substitution of the more voluminous *FA* molecules for those of water in the solvation shell of Na^+ ion is produced, resulting in a decrease of ionic mobility.

Finally it is interesting to compare the *Walden* product variation in dependence of solvent composition for cations of different size. Fig. 3 shows the variation of *R* [$R = (\lambda_0 \eta)_S/(\lambda_0 \eta)_W$] for lithium[2], sodium and cesium[2] bromides as a function of the solvent mole fraction. As it is observed, *R* decreases in the order $Cs^+ > Na^+ > Li^+$ at a given solvent composition, except at *FA*-rich regions where the opposite trend is observed. For CsBr, *R* decreases as increasing the *FA* content, being more pronounced at the *FA*-rich regions. Whereas for LiBr and NaBr, the *R*-variation presents a minimum which is located at higher *FA* contents for NaBr.

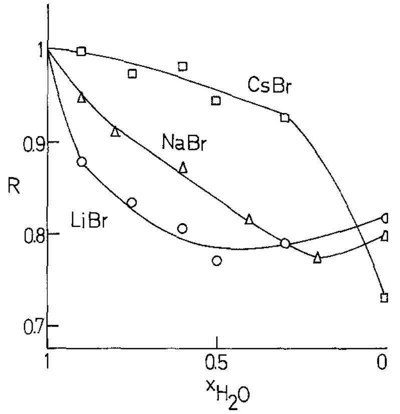

Fig. 3. *R*-values for LiBr, NaBr, and CsBr as a function of solvent composition at 25 °C

The minimum in the *R*-variation for LiBr and NaBr can be explained taking into account the existence of specific acid-base interactions between Na^+ and Li^+ ions and *FA* molecules, leading to a preferential solvation. This tendency of the ion to be surrounded selectively by *FA* produces a local viscosity around the ion greater than in the bulk solution, which decreases its mobility and consequently *R*. Bearing in mind that the Li^+ ion is more acid than the Na^+ ion, the preferential solvation of the former for *FA* holds out to higher water contents in the solvent. In fact, the strong decrease of *R* at water-rich compositions for LiBr cannot be explained only in terms of the decrease of the structure-breaking effect of

Br^- ion when adding *FA*, but furthermore by a preferential solvation of the Li^+ ion for *FA* which leads to a more voluminous kinetic entity and a viscosity around the ion greater than in the bulk.

As it has been mentioned above, Na^+ ion presents a slight preferential solvation for water at high water compositions. On the other hand, from the viscosity *B*-coefficient analysis[1], it has been deduced the existence of a preferential solvation of Na^+ ion for *FA* at *FA* rich compositions, which is in accordance with the minimum observed in the *R*-variation with solvent composition (Fig. 3). For the remaining solvent compositions it can be assumed that there is no preferential solvation for either of the two solvents. These observations contrast with those of *Holz* and *Rau* derived from RMN measurements, who did not consider preferential solvation for the whole range of solvent compositions[17].

As far as CsBr is concerned we have to take into account the low acidity of the Cs^+ ion to produce acid-base interactions. Then we may consider the possibility of a progressive desolvation of Cs^+ ion when adding *FA* in order to explain the high *R*-values near the one observed in a large range of solvent compositions (Fig. 3). This gradual desolvation gives rise to a decrease in the size of the kinetic entity increasing its mobility, counteracting thus the structure breaking effect of Br^- ion. However, at high *FA* contents the Cs^+ ion seems to be preferentially solvated by *FA* regarding the drastic decrease of the *R*-value for these solvent compositions (Fig. 3).

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