Monatshefte für Chemie 116, 43—48 (1985)

Monatshefte für Chemie
Chemical Monthly

Effect of Ionic Solvation on the Polarographic Behaviour of Halide Ions in *N,N*-Dimethylformamide-Water Mixtures

J. Doménech[a] and **J. M. Costa**[b,*]

[a] Department of Physical Chemistry, Autonomous University of Barcelona, Bellaterra (Barcelona), Spain

[b] Laboratory of General Chemistry, University of Barcelona, Barcelona, Spain

(Received 24 February 1984. Accepted 27 April 1984)

The paloragraphic behaviour of chloride, bromide and iodide ions in several *DMF*-water mixtures at a temperature of 25 °C is reported. The half-wave potentials change linearly to more cathodic potentials with increasing *DMF* content of the solvent, up to *DMF*-rich compositions, where deviations are observed for chloride and iodide ions. On the other hand, the $D\eta$-product varies with solvent composition, showing a sharp maximum at water-rich compositions for the three halide ions and a smooth minimum for chloride and bromide ions at high *DMF* content of the solvent. These results are interpreted for different solvent mixtures in terms of the solvent structure and the ionic solvation nature of halide ions.

(Keywords: Halides; Ionic solvatation; Polarography; Solvent structure)

Effekt der Ionensolvatation auf das polarographische Verhalten von Halogenid-Ionen in N,N-Dimethylformamid-Wasser-Mischungen

Es wird über das polarographische Verhalten von Chlorid-, Bromid- und Iodid-Ionen in einigen *DMF*-Wasser-Mischungen bei 25 °C berichtet. Die Halbwellenpotentiale ändern sich mit ansteigendem *DMF*-Gehalt linear in Richtung zu kathodischen Potentialen, bei *DMF*-reichen Zusammensetzungen werden für Chlorid und Iodid Abweichungen beobachtet. Andererseits variiert das $D\eta$-Produkt mit der Lösungsmittelzusammensetzung: bei wasserreichen Mischungen zeigt es ein scharfes Maximum für die drei Halogenid-Ionen, bei hohem *DMF*-Gehalt ein glattes Minimum für Chlorid und Bromid. Die Ergebnisse werden in bezug auf Lösungsmittelstruktur und Ionensolvatation der Halogenid-Ionen interpretiert.

Introduction

The analysis of the polarographic behaviour of ions has been used for studying ionic solvation[1]. In mixed solvents, the half-wave potential and the diffusion current varies with solvent composition. This variation can be discussed in terms of changes of solvent structure as well as by changes of the solvation of the ions in the different solvent mixtures[2–4].

Recently, much attention has been paid to the study of the behaviour of electrolytes in mixed solvents and particularly in amide-water mixtures. These systems offer an interesting medium for reactions and they are used also as basis systems for biochemical studies. In the present paper, the polarographic behaviour of chloride, bromide and iodide ions in different dimethylformamide (*DMF*)-water mixtures at 25 °C are reported and the corresponding values of half-wave potential and diffusion current are analysed as a function structural characteristics of solutions.

Experimental

Sodium chloride, potassium bromide, potassium iodide, and potassium perchlorate were Merck of analytical grade. These salts were dried at 110–120 °C, except potassium perchlorate which was dried under vacuum at 60 °C. *N,N* dimethylformamide was Fluka, puriss *p.a.*, which was dried over 4 Å molecular sieves. The water content, determined by the *Karl-Fischer* method, was lower than 0,1% in weight.

The polarograms were recorded by means of a three electrode polarograph, Methrom, type 261 provided with an IR compensator. As a working electrode a dropping mercury electrode was used, with a drop-time of 5.7 s and a *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 satured calomel electrode (SCE), which was connected to the electrolytic cell through a salt bridge filled with the studied solution. Oxygen was eliminated by bubbling purified nitrogen through the solution, previously saturated with solvent vapours. All the measurements were carried out at 25 ± 0.1 °C.

Results and Discussion

The polarograms of 1 m*M* solutions of sodium chloride, potassium bromide and potassium iodide (with 0.1 *M* of potassium perchlorate as supporting electrolyte) in solutions of different solvent compositions were obtained. The polarograms of these solutions give a well defined wave which is diffusion controlled and correspond to the anodic oxidation of halide present in the solution. The half-wave potential and the diffusion current constant of this anodic process are given in Table 1 for different *DMF*-water mixtures. Furthermore, in a solution of water mole fraction 0.03, a second wave at more anodic potentials is observed. This wave also appears in the pure *DMF* solutions of halide[5–7] and is attributed to the formation of mercury(II) halide.

From Table 1 it is seen that the $E_{1/2}$-values for the three halide ions are shifted to less anodic potentials with increasing DMF content in the

Table 1. *Half-wave potentials (v. vs. SCE) and diffusion current constants* (μA mM^{-1} mg$^{-2/3}$ s$^{-1/6}$) *for chloride, bromide and iodide ions in different DMF-water mixtures at 25 °C*

Cl^-			Br^-			I^-		
x_{H_2O}	$E_{1/2}$	I	x_{H_2O}	$E_{1/2}$	I	x_{H_2O}	$E_{1/2}$	I
1.00	0.254	2.55	1.00	0.120	2.69	1.00	−0.029	2.74
0.949	0.240	2.31	0.956	0.108	2.44	0.948	−0.044	2.53
0.900	0.220	2.06	0.851	0.106	1.76	0.902	−0.055	1.77
0.782	0.197	1.52	0.800	0.098	1.42	0.802	−0.108	1.17
0.603	0.109	1.21	0.700	0.070	1.12	0.608	−0.164	0.91
0.397	0.070	1.21	0.632	0.020	1.00	0.414	−0.220	0.90
0.201	0.024	1.24	0.461	−0.041	1.04	0.199	−0.254	1.05
0.033	−0.122	1.51	0.353	−0.054	1.04	0.037	−0.254	1.18
0.00[a]	−0.17	1.17	0.201	−0.116	1.11	0.00[c]	−0.183	1.22
			0.035	−0.182	1.31			
			0.00[b]	−0.136	1.49			

[a] Ref.[5].
[b] Ref.[6].
[c] Ref.[7].

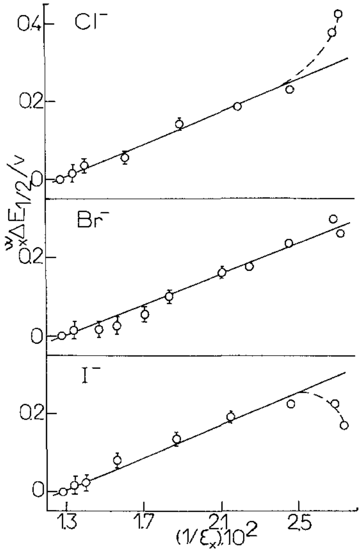

Fig. 1. ${}^{w}_{x}E_{1/2}$-values for Cl^-, Br^- and I^- ions as a function of $1/\varepsilon_x$ at 25 °C

solvent. This $E_{1/2}$-variation can be interpreted in terms of the changes in solvation of the depolarizers. The simplest model of ionic solvation, developed by *Born*[8], assumes that the solvation phenomena have electrostatic nature, changing with a change in the dielectric constant of the medium. Based on this model and disregarding the differences between the formal and the half-wave potential, one can deduce the following equation

$$ {}_{x}^{w}\Delta E_{1/2} = (E_{1/2})_w - (E_{1/2})_x = z_B e (1/\varepsilon_w - 1/\varepsilon_x)/8 \pi \varepsilon r_B \qquad (1)$$

where ${}_{x}^{w}\Delta E_{1/2}$ corresponds to the difference between the $E_{1/2}$-values in water and in the mixtures of mole fraction x, r_B is the ionic radius of electroactive species and ε is the solvent dielectric constant. In Fig. 1, the plots of the ${}_{x}^{w}\Delta E_{1/2}$-values vs. $1/\varepsilon_x$ for Cl^-, Br^- and I^- ions are represented. These values lie in a straight line, except for Cl^- and I^- ions at *DMF*-rich compositions, where deviations from linearity are observed. For the three species the slopes are practically the same, 20 v approximately, which is larger than predicted by equation (1). In fact the slopes are not so large because of the existence of a liquid junction potential which is positive and increases with the *DMF* content in the solvent[9, 10], making the $E_{1/2}$-values more anodic.

At *DMF*-rich compositions the ${}_{x}^{w}\Delta E_{1/2}$-variation with solvent composition for Cl^- ion shifts more rapidly to positive values, suggesting that the Cl^- ion suffers a sudden desolvation. Actually, in *DMF* it is assumed that interactions between halide ions and solvent molecules are sterically hindered[11], which implies that these ions are not solvated in pure *DMF*. On the other hand, the presumed dispersion forces in *DMF*[12–14] increase with increasing radius of the anion. This explains the shift of ${}_{x}^{w}\Delta E_{1/2}$-values for the I^- ion at high *DMF* content, as shown in Fig. 1. These observations are confirmed by emf measurements in *DMF* and *DMF*-water mixtures[12,13], where the differences between the standard free energies of transfer for halide ions are greater with increasing *DMF* content in the solvent.

From the height of the waves the diffusion current constants, *I*, at 25 °C for Cl^-, Br^- and I^- ions at different solvent compositions are calculated; the obtained values are given in Table 1. The *I*-constants change with solvent composition, showing a minimum at a water mole fraction of about 0.60. This minimum is mainly due to the increase in the viscosity of the solvent reaching the maximum near this mole fraction[14]. According to the *Ilkovic* equation the corresponding self-diffusion coefficients for the three halide ions in presence of 0.1 *M* potassium perchlorate can be determined. In order to avoid the influence of the bulk viscosity the results are discussed in terms of the $D\eta$-product. The products were calculated from the viscosity of solutions containing 0.1 *M* of potassium perchlorate at different solvent compositions[14]. According to the *Stokes-Einstein* law, the $D\eta$-product is inversely proportional to the solvated radius of diffusive species.

Fig. 2 shows the variation of the $D\eta$-product as a function of the *DMF*-water composition for Cl^-, Br^- and I^- ions. According to the *Stokes* law the $D\eta$-product should remain constant. However, it is apparent from Fig. 2 that the product $D\eta$ for the three halide ions varies with solvent composition. This variation can be interpreted in terms of changes in solvent structure.

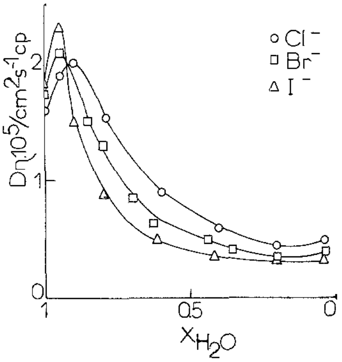

Fig. 2. Variation of $D\eta$-product with solvent composition for Cl^-, Br^- and I^- ions at 25 °C

From Fig. 2 it may be seen that the $D\eta$-product reaches a maximum at water-rich compositions, similarly to that observed in analogous systems[9,10,15–17]. This maximum decreases and shifts to the lower water content region with decreasing radius of the halide ion. On the other hand, a maximum of the *Walden* product and a minimum of the viscosity *B*-coefficient for simple salts are also observed at ca. $x_{H_2O} = 0.90$ (Ref.[18,14]). This behaviour can be explained considering that the solvent is more structured in these water-rich compositions[12,14], leading to an increase in the structure-breaking ability of the ions which is greater with increasing the ionic radius. This produces a decrease in the local viscosity around the ion favouring its mobility[19].

Having passed the region of more structured solvent, an increase in the proportion of *DMF* causes a decrease of the structure-breaking ability because the solvent behaves less structured[12,14]. This explains the decrease in $D\eta$ and also the decrease of this product with increasing ionic radius at a given solvent composition. At 0.2 mole fraction of water a smooth minimum in the $D\eta$-values for Cl^- and Br^- ions is observed. This behaviour can be attributed to the increasing desolvation in the *DMF*-rich region, which increases the ionic mobility. For the I^- ion, the $D\eta$-product remains practically constant in that range. In the latter case one may to consider dispersion forces which are greater with increasing the anion size, leading to a decrease in the mobility of the ion.

Finally, the $D\eta$-values for halide ions are greater than those for alkaline ions in the whole range of *DMF*-water mixtures[4], which suggests that the cations are more solvated. Actually, the alkaline ions are less hindered to interact with *DMF* molecules giving rise to a gradual substitution of water with *DMF* molecules in the solvation sheath of the ion, leading to an increase in volume.

References

[1] *Broadhead J., Elving P. J.*, J. Electrochem. Soc. **118**, 63 (1971).
[2] *Costa J. M., Vilarrasa M.*, An. Quím. **65**, 609 (1969).
[3] *Costa J. M., Miro J.*, An. Quím. **74**, 342 (1978).
[4] *Domenech J., Costa J. M.*, An. Quím. **79**, 553 (1983).
[5] *Given P. H., Peover N. E.*, J. Chem. Soc. **1959**, 1602.
[6] *Matsui Y., Kawakado R., Date Y.*, Bull. Chem. Soc. Jap. **41**, 2913 (1968).
[7] *Matsui Y., Kurosaki J., Date Y.*, Bull. Chem. Soc. Jap. **43**, 1707 (1970).
[8] *Born M.*, Z. Physik. **1**, 45 (1920).
[9] *Behr B., Borkowska Z., Elzanowska H.*, J. Electroanal. Chem. **100**, 853 (1979).
[10] *Broda J., Galus Z.*, J. Electroanal. Chem. **130**, 229 (1981).
[11] *Kawaizumi F., Zana R.*, J. Phys. Chem. **78**, 1099 (1974).
[12] *Das K., Bose K., Kundu K. K.*, Electrochim. Acta **26**, 479 (1981).
[13] *Cox B. G., Hedwig G. R., Parker A. J., Watts D. W.*, Aust. J. Chem. **27**, 477 (1974).
[14] *Domenech J., Costa J. M.*, An. Quím. **77**, 227 (1981); ibid. **78**, 59 (1982); ibid. **79**, 85 (1983).
[15] *Lipkowski J., Galus Z.*, J. Electroanal. Chem. **58**, 51 (1975).
[16] *Janiszewska L., Galus Z.*, Electrochim. Acta **27**, 1781 (1982).
[17] *Izutsu K., Adachi T., Fujinaga T.*, Electrochim. Acta **15**, 135 (1970).
[18] *Singh D., Bahadur L., Ramanamurti M. V.*, J. Solution Chem. **6**, 703 (1977).
[19] *Domenech J., Costa J. M.*, Electrochim. Acta **28**, 1789 (1983).