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Solvent Effects on the Polarographic Behaviour of Halobenzenes in Aprotic Media

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The polarographic behaviour of fluoro, chloro, bromo and iodobenzene in dimethylformamide, dimethylsulfoxide and acetonitrile at 25 °C is reported. The viscosities and densities of these species in the three solvents have been measured and the corresponding viscosity B-coefficients and molar partial volumes at infinite dilution for halobenzenes are reported. The results, which show a clear dependence upon solvent nature, are analysed in terms of solute-solvent interactions and solvent structure.

(Keywords: Diffusion; Halobenzenes; Aprotic solvents)

Lösungsmitteleffekte des polarographischen Verhaltens von Halogenbenzolen in aprotischen Medien

Es wird über das polarographische Verhalten von Fluor-, Chlor-, Brom- und Iodbenzol in Dimethylformamid, Dimethylsulfoxid und Acetonitril bei 25 °C berichtet. Viskositäten und Dichten wurden in diesen drei Lösungsmitteln gemessen und die entsprechenden Viskositäts-B-Koeffizienten und die molaren partiellen Volumina für unendliche Verdünnung der Halogenbenzole bestimmt. Die Ergebnisse, die eine starke Abhängigkeit vom Lösungsmittel zeigen, werden mittels der Wechselwirkung Lösungsmittel —gelöster Stoff und Lösungsmittelstruktur interpretiert.

Introduction

The electrochemical cleavage of the carbon-halogen bond is a process with a well established mechanism[1]. However, little attention has been paid to the study of the influence of the solvent in this process. The main effect is related with the transport process of diffusing species. This process has been shown to be influenced by solvent structure and solute —solvent interactions[2–5].

Viscosity measurements are used as an indication of solute – solvent interactions. For dilute solutions, the relative viscosity, η_r, can be expressed as a function of the concentration according the *Jones-Dole* equation[6],

$$\eta_r = 1 + Ac^{1/2} + Bc$$

where A and B are two constants. The A-coefficient is a measure of ion – ion interactions, being zero for non-ionic solutes. The B-coefficient is a function of solute – solvent interactions which takes values depending on the "structure making" or "structure breaking" ability of the solutes[7].

In the present work the polarographic behaviour, the viscosity B-coefficients, and the partial molar volumes at infinite dilution of the halobenzenes in dimethylformamide (*DMF*), dimethylsulfoxide (*DMSO*) and acetonitrile (*AN*) at 25 °C are reported and are analysed in terms of solute and solvent nature.

Experimental

The fluoro, chloro, bromo and iodobenzenes were from Merck. The tetraethylammonium bromide, Fluka of analytical grade, was dried at 60 °C under reduced pressure for 24 h. *DMF* was Fluka of analytical grade; it was dried over molecular sieves (3 Å) for 18 h and then destilled. *AN*, Carlo Erba of RP-grade, was dried over Na_2SO_4, then was purified by refluxing for 5 h over P_2O_5 and finally destilled. *DMSO*, Scharlau of analytical grade, was used without further purification. The water contents of the solvents, determined by the *Karl-Fischer* method, was lower than 0.1%.

The polarograms were recorded by means 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 a auxiliar electrode. The half-wave potentials were referred to a Ag/AgI electrode made as follows: a silver wire, electrolytically covered with silver iodide, was immersed in a 0.1 *M* tetrabutylammonium iodide solution in the specific solvent used for each measurement. The reference solution made contact with the test solution through an asbestos fiber sealed in a glass probe. Oxygen was eliminated by bubbling purified nitrogen, previously saturated of solvent vapours, through the solution. All measurements were carried out at 25.0 ± 0.05 °C.

The experimental techniques and procedures for the measurement of the viscosities and densities, have been described in detail before[8].

Results

The polarograms of 1 m*M* solutions of fluoro, chloro, bromo and iodobenzenes in *DMF, DMSO* and *AN*, with tetraethylammonium bromide 0.1 *M* as supporting electrolyte, were obtained. The polarograms of these solutions give a single wave which is indeed diffusion controlled and corresponds to the reduction of the halobenzenes. In Table 1 the half wave potentials and the diffusion current constants at 25.0 °C correspond-

Table 1. *Half-wave potentials* ($E_{1/2}$) *and diffusion current constants* (I_d) *for halobenzenes in DMF, DMSO and AN, at 25 °C*

Species	$-E_{1/2}$/V vs. Ag/AgI			I_d/μ A m M^{-1} mg$^{-2/3}$ s$^{1/2}$		
	DMF[21]	*DMSO*	*AN*	*DMF*[21]	*DMSO*	*AN*
C_6H_5F	1.98	2.28	–	0.6	1.2	–
C_6H_5Cl	2.16	2.13	2.21	2.8	2.0	5.4
C_6H_5Br	1.87	1.84	1.86	4.3	2.3	5.4
C_6H_5I	1.24	1.20	1.12	6.1	3.1	5.9

ing to the polarographic reduction of the halobenzenes in the different solvents are reported.

The densities and viscosities of halobenzene solutions in *DMF, DMSO* and *AN* were measured within a concentration range from 0.01 *M* to 0.16 *M* at 25.0 °C. The relative viscosities of these solutions were analysed in terms of the "extended" *Jones-Dole* equation[9]:

$$\eta_r = 1 + Ac^{1/2} + Bc + Dc^2$$

Assuming that the *A*-coefficient is zero for the halobenzenes, the *B*-coefficient was evaluated from the intercept of $(\eta_r - 1)/c$ vs. c plots. The *B*-coefficients for the halobenzenes in the three solvents at 25.0 °C are summarized in Table 2.

Table 2. *Viscosity B-coefficients for halobenzenes in DMF, DMSO, and AN at 25 °C*

Species	B/dm^3 mol^{-1}		
	DMF	*DMSO*	*AN*
C_6H_5F	0.00	− 0.09	0.02
C_6H_5Cl	0.04	0.04	0.05
C_6H_5Br	0.06	0.05	0.08
C_6H_5I	0.10	0.27	0.24

From density measurements the partial molar volumes of the halobenzenes at infinite dilution, $\bar{V}_2^\circ$, were obtained according to the *Root* equation[10], which for dilute solutions takes the following form:

$$d_r = 1 + [(M_2 + \bar{V}_2^\circ d)/1\,000\,d]\,c$$

where d_r is the relative density, d the density of the solvent and M_2 the molecular weight of the solute. In Table 3 the $\bar{V}_2^\circ$-values of the halobenzenes in *DMF, DMSO,* and *AN* at 25 °C are reported.

Table 3. *Molar partial volumes at infinite dilution for halobenzenes in DMF, DMSO, and AN, at 25 °C*

Species	$\bar{V}_2^0$/ml mol^{-1} *DMF*	*DMSO*	*AN*
C_6H_5F	90	94	93
C_6H_5Cl	100	102	102
C_6H_5Br	108	107	105
C_6H_5I	117	114	110

Discussion

Basically, the *B*-coefficient is made up of three contributions[11]: a positive contribution related to the shape and size of the solute, which can be evaluated from the *Einstein* equation[12], a positive increment due to the solute–solvent interactions which increases the order in the solvent structure, leading to an increase in the local viscosity around the solute, and finally, a negative contribution due to the breaking of solvent–solvent associations, which leads to a decrease in the solvent order and consequently, a decrease in the local viscosity. Thus, the sign and the absolute value of the solute *B*-coefficient will depend on the value of these different contributions.

As can be seen from Table 2, the *B*-coefficient varies with the size of the solute and also with the solvent nature. The low *B*-values for the halobenzenes, which are voluminous, in *DMF, DMSO,* and *AN,* and specially for fluorobenzene in *DMF* and *DMSO* (zero and negative, respectively) compared with different electrolytes in the same solvents[13–16] suggest the scarce solvation of the halobenzenes and its greater ability as structure breakers.

Further evidence of the low solvation of these solutes is found when one compares the *B*-values in *DMF* and *AN.* For these solvents with similar dielectric constants, the *B*-values for the halobenzenes in *AN* are greater than those in *DMF,* in spite of the greater molar volume of *DMF.*

The $E_{1/2}$-values show no dependence with solvent nature (see Table 1). For a given solvent, the $E_{1/2}$-values shift to more cathodic potentials in the order iodo > bromo > chloro > fluorobenzene (except for fluorobenzene in *DMF*). The diffusion current constants show a certain dependence with the solvent nature (see Table 1). The I_d values in *AN* show a little variation changing the halobenzene, whilst in *DMSO* and *DMF,* I_d increases significantly with increase of the size of halobenzene.

Recently a linear relation between I_d and the *B*-coefficient has been shown for some ions in water[3] and *DMF*–water mixtures[17] evidencing the influence of solute – solvent interactions in the diffusion of electroactive species. In the present case one also observes this linearity between I_d and *B*-values for the halobenzenes in *DMF, DMSO* and *AN,* as can be seen in Fig. 1. The slopes of these straight lines change with solvent nature. In contrary to expectation these slopes are positive. while a greater *B*-value (due to a greater size of the solute, as has been mentioned above) would produce a slower diffusion of the species.

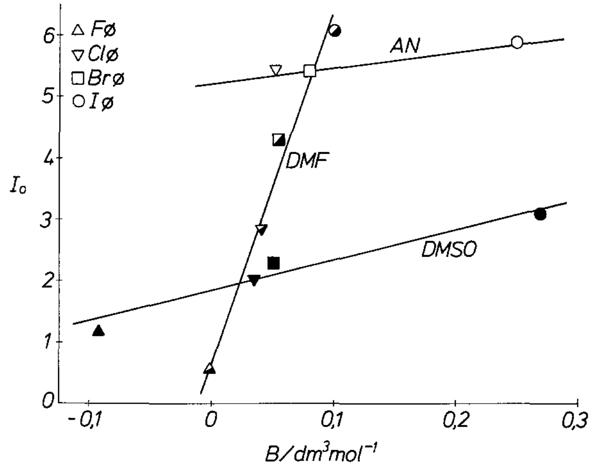

Fig. 1. I_d-values as a function of *B*-coefficients for halobenzenes at 25 °C; solid symbols, *DMSO* half-solid symbols, *DMF* open symbols, *AN*

In fact, the diffusion phenomena arise from the *Brown*ian movement of particles, resulting in a net transfer from a region of high to a region of low concentration[18]. This random motion of the particles depending on the number of collisions that are poduced in the trajectory will be greater as the empty space originated by the particles increases. In the present case, since the halobenzenes are scarcely solvated in *DMF, DMSO* and *AN,* the partial molar volume at inifinite dilution can be considered as the sum of the *Van der Waals* volumes plus the empty space originated by the solute ("free volume")[19]. From $\bar{V}_2^\circ$-values (Table 3), together with the *Van der Waals* volumes, V_w, taken from the literature[20], the free volumes were calculated with 1 ml mol^{-1} acurancy. From this data we can see that with increasing $\bar{V}_2^\circ$-value of the halobenzenes the free volume originated increases as well, and consequently, its diffusion rate.

In this way, one would expect the existence of a linear relation between the diffusion and the free volume associated with the solute. In Fig. 2, the

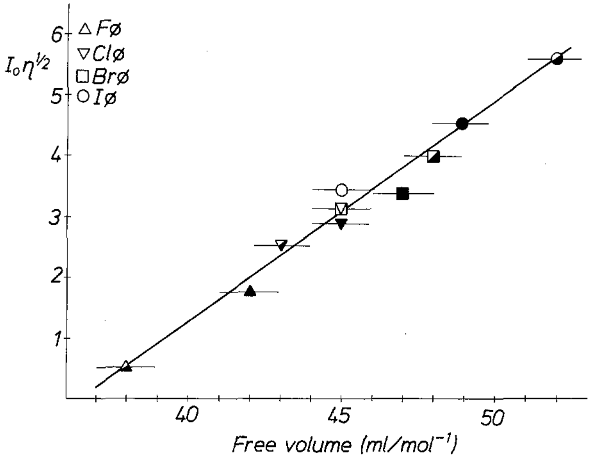

Fig. 2. $I_{\eta}^{1/2}$-products against free volume for halobenzenes at 25 °C; solid symbols, *DMSO* half-solid symbols, *DMF* open symbols, *AN*

$I_d\eta^{1/2}$-product* as a function of the free volume for the halobenzenes in the three solvents is represented. As can be seen from the figure that a straight line is obtained which evidences the effect of the free volume associated to the solute on its diffusion.

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* $I_d\eta^{1/2}$-products are used in order to avoid the effect of the bulk viscosity on the diffusion of species.

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