

Ionic self-diffusion coefficients of  $^{153}\text{Gd}$  (III) in  $\text{Gd}(\text{NO}_3)_3$  solutions in water - dioxan mixtures at 25 °C

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1996 J. Phys.: Condens. Matter 8 8173

(<http://iopscience.iop.org/0953-8984/8/43/013>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.207

The article was downloaded on 14/05/2010 at 04:23

Please note that [terms and conditions apply](#).

## Ionic self-diffusion coefficients of $^{153}\text{Gd}$ (III) in $\text{Gd}(\text{NO}_3)_3$ solutions in water–dioxan mixtures at $25^\circ\text{C}$

N Ouerfelli†, M Ammar‡ and H Latrous

Laboratoire de Chimie Analytique et de Diffusion, Département de Chimie, Faculté des Sciences de Tunis, Campus Université 1060 Belvédère, Tunisia

Received 30 October 1995, in final form 14 May 1996

**Abstract.** The measurement of ionic self-diffusion coefficients of the lanthanide ions  $^{153}\text{Gd}(\text{III})$  in asymmetrical electrolytes (3:1) solutions of  $\text{Gd}(\text{NO}_3)_3$  in hydro-organic water–dioxan mixtures (at a low dielectric constant) gives evidence of the progressive association of ion pairs.

The study of different physical–chemical properties in all the domains of composition shows the existence of three regions with distinct behaviours.

The application of association theory to such an asymmetrical electrolyte (3:1) with a polyvalent cation enables us to delimit the validity of the Bjerrum and Fuoss theories.

### 1. Introduction

Studies of ionic association phenomena are generally made by conductimetric methods for symmetrical electrolytes and especially for 1:1 electrolytes [1–3]. The ionic self-diffusion methods are rarely used for giving evidence of association, and particularly for the asymmetrical electrolytes [4–6]. The detection of ion pair formation in asymmetrical electrolyte solutions is more difficult than in symmetrical electrolytes [7], even by conductimetric methods. In fact, in the case of asymmetrical electrolytes, the ion pair is charged and, consequently, it takes part in the transport of electricity. Likewise, the decrease in conductivity caused by this charged pair is smaller than that brought about by the neutral pairs in the case of symmetrical electrolytes. On the other hand, the correctness of the simplifying assumptions introduced in the Debye–Hückel–Onsager theory is not certain in polyvalent ion solutions even for lower concentrations [8]. Using the solubility measurements of asymmetrical electrolytes, Monk and co-workers [9] give evidence of ion formation ( $\text{Na}(\text{SO}_4)^-$  and  $\text{La}(\text{SO}_4)^+$ ). By UV absorption spectrometry, the pair formation of  $\text{PbCl}^+$  ion was detected in [10], and this was proved by the study of the solubility of lead chloride in the framework of a modified Pitzer model [11]. The electrostatic theory of ionic association introduced by Bjerrum is generally in qualitative agreement with experiments, essentially in the 1:1 electrolyte case [12]. However, this theory includes uncertain conclusions, and it can be accepted only as a first approximation [8]. In fact, in this theory [13], the ions are considered as hard spheres, which can approach mutually to a distance  $a$ . The calculation of the decrease in the coulombic forces is based on the macroscopic dielectric constant. Furthermore, the use of the dielectric constant in polyvalent

† Author to whom correspondence should be addressed and from whom reprints are available.

‡ Deceased in 1990.

ion solutions can hardly be considered as shown by Anderson and Saddington [14]. In the present work, we have applied the study of the ionic self-diffusion coefficients of  $^{153}\text{Gd(III)}$  to the study of the ionic association phenomena in water–dioxan mixtures. Some reasons for this choice are as follows.

(1) These mixtures permit a large variation in the dielectric constant ( $2.2 \leq \epsilon \leq 78.4$ ); thus, a more associated domain of low dielectric constant values can be reached.

(2) Asymmetrical electrolytes of high-valency cation and very rich domains in dioxan are not practically treated by diffusion or conductimetric methods.

In addition to the reasons mentioned above, we must also consider the appreciable modification of liquid structure for greater than 68 wt% dioxan ( $\text{C}_4\text{H}_8\text{O}_2 \cdot 2\text{H}_2\text{O}$ ) [8].

## 2. Experimental methods

### 2.1. Determination of self-diffusion coefficients

The measurement of the self-diffusion coefficients of the  $\text{Gd}^{3+}$  ion and of the associated entities ( $\text{Gd}(\text{NO}_3)_3^{2+}$ ,  $\text{Gd}(\text{NO}_3)_2^+$ , etc) in the water–dioxan mixtures was made by the tracer  $^{153}\text{Gd(III)}$ , with the open-end capillary method, which was used by Anderson and Saddington [14], developed by Mills and Godbole [23] and adapted by Turq *et al* [2]. This method allows the study of the variation in the self-diffusion coefficients (at a constant temperature of  $25 \pm 0.01$  °C) for different compositions of water–dioxan mixture at a constant global concentration of  $\text{Gd(III)}$  entities. The quartz capillaries of length  $l$  were filled with an electrolyte solution of concentration  $c = 2 \times 10^{-4}$  M  $\text{Gd}(\text{NO}_3)_3$ , labelled with the tracers  $^{153}\text{Gd(III)}$ . The radioactive solution in the capillaries was in contact with an inactive solution of the same composition in the container.

We denote by  $A(0)$  the total activity in the capillary at time  $t = 0$ . After a diffusion time  $t$ , the final average activity will be  $A(t)$ . By solving Fick's equation with the appropriate limiting conditions, the ratio

$$\Gamma = A(t)/A(0) \quad (1)$$

can be related to the self-diffusion coefficient  $D$  by the following equation:

$$\Gamma = \sum_0^{\infty} \frac{8}{\pi^2(2n+1)^2} \exp\left(\frac{-\pi^2(2n+1)^2Dt}{4l^2}\right). \quad (2)$$

Generally, we restrict ourselves to the first term in these rapidly converging series:

$$D = 0.4053(l^2/t) \ln(0.8106/\Gamma). \quad (3)$$

The total activity was measured using a Packard Tri-Carb liquid scintillation spectrometer. For optimal accurate measurements, we stop the diffusion when  $\Gamma$  is approximately equal to 0.5. In fact, the ionic self-diffusion coefficient as measured is an average coefficient of different diffusion entities in the solution [7]. In the case of  $\text{Gd}(\text{NO}_3)_3$  solutions, there are four diffusion entities, namely  $\text{Gd}^{3+}$ ,  $\text{Gd}(\text{NO}_3)_2^+$ ,  $\text{Gd}(\text{NO}_3)_2^+$  and  $\text{Gd}(\text{NO}_3)_3$  for which  $D_0$ ,  $D_1$ ,  $D_2$  and  $D_3$  respectively are their self-diffusion coefficients. The mean experimental coefficient  $D$  is related to the individual coefficients  $D_i$  by the following equation:

$$D = \sum_0^3 \frac{D_i [\text{Gd}(\text{NO}_3)_i^{3-i}]}{[\text{Gd}^{3+}]_0} = \left( D_0 + \sum_1^3 D_i \beta_i [\text{NO}_3^-]^i \right) / \left( 1 + \sum_1^2 \beta_i [\text{NO}_3^-]^i \right). \quad (4)$$

The square brackets indicate the molar concentration, and  $[\text{Gd}^{3+}]_0$  is the total concentration of  $\text{Gd}(\text{NO}_3)_3$  used in our solution ( $2 \times 10^{-4} \text{ mol kg}^{-1}$ ). The conditional constant  $\beta_i$  of complexation or association which is given by

$$\beta_i = [\text{Gd}(\text{NO}_3)_i^{3-i}] / [\text{Gd}(\text{NO}_3)_{i-1}^{4-i}][\text{NO}_3^-] \quad (5)$$

is in principle calculated according to the ionic association of the Bjerrum theory if this association has a predominantly electrostatic character.

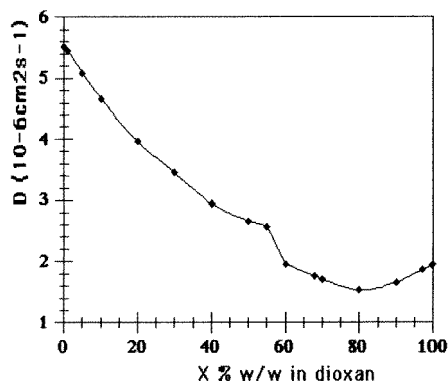
In the chemical complexation case, we must resolve an equation system of seven unknowns, namely  $D_0$ ,  $D_1$ ,  $D_2$ ,  $D_3$ ,  $\beta_1$ ,  $\beta_2$  and  $\beta_3$ , at a given composition in dioxan.

## 2.2. Density and viscosity

The kinematic viscosity  $\nu$  is determined for each weight composition of water–dioxan mixture, using an automatic viscometer (AVS/N-Chott Gerate). The densities  $d$  were measured in a digital densitometer DMA 46 (PAAR, Graz, Austria); the precision of density obtained is  $\pm 10^{-4} \text{ g cm}^{-3}$ . The shear viscosity  $\eta$  of the mixture at  $25^\circ\text{C}$  was determined from the product of density  $d$  and kinematic viscosity  $\nu$ :

$$\eta(\text{cP}) = \nu(\text{cSt}) \quad d(\text{g cm}^{-3}). \quad (6)$$

Those values led us to the calculation of the Walden product  $D\eta$  which gives a structural indication of the diffusing entities.



**Figure 1.** Ionic self-diffusion coefficient  $D$  of  $^{153}\text{Gd(III)}$  in water–dioxan mixtures versus the weight percentage  $X$  in dioxan.

## 3. Results and discussion

### 3.1. Self-diffusion coefficients of $^{153}\text{Gd(III)}$ in 'water–dioxan mixtures $+2 \times 10^{-4} \text{ M Gd}(\text{NO}_3)_3$ '

The self-diffusion coefficient  $D$  relative to the different entities of  $\text{Gd(III)}$  is determined for different weight percentages  $X$  in dioxan. The values obtained for  $D$  are shown in table 1 and plotted in figure 1. The examination of the curve representing  $D$  versus  $X$ , shows the existence of approximately three branches.

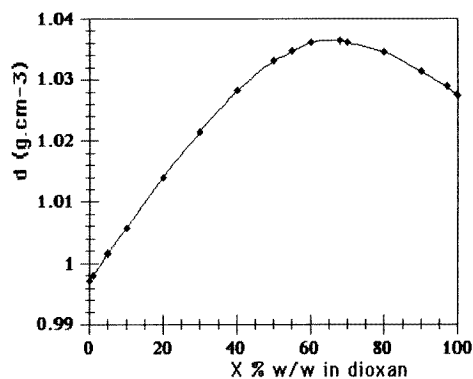
**Table 1.** Density  $d$ , viscosity  $\eta$ , self-diffusion coefficient  $D$  and the Walden product  $D\eta$  versus the weight percentage  $X$  at 25 °C.

$X$	$d$ (g cm <sup>-3</sup> )	$\eta$ (cP)	$D$ (10 <sup>-6</sup> cm <sup>2</sup> s <sup>-1</sup> )	$D\eta$ (10 <sup>-8</sup> g cm s <sup>-2</sup> )
0	0.9971	0.8916	5.52	4.922
1	0.9980	0.9188	5.45	5.008
5	1.0016	0.9903	5.08	5.031
10	1.0057	1.1076	4.67	5.173
20	1.0140	1.2960	3.96	5.132
30	1.0215	1.5094	3.45	5.207
40	1.0282	1.7300	2.94	5.086
50	1.0331	1.9176	2.66	5.101
55	1.0347	1.9505	2.56	4.993
60	1.0361	1.9718	1.96	3.865
68	1.0364	1.9309	1.76	3.397
70	1.0361	1.8985	1.71	3.246
80	1.0346	1.6912	1.53	2.588
90	1.0314	1.4310	1.66	2.375
97	1.0289	1.2090	1.86	2.249
99.7	1.0275	1.1640	1.94	2.259
99.9	1.0273	1.1549	1.95	2.252

*Branch 1.* This branch ( $X < X_1 \approx 55$  wt%) shows a rapid decrease in  $D$  versus  $X$  up to  $X_1$ , which corresponds to 0.2 in molar fraction (i.e. C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>.4H<sub>2</sub>O).

*Branch 2.* In this branch (55 wt%  $< X < X_2 \approx 80$  wt%),  $D$  undergoes a slow decrease from  $X = X_1$  to  $X = X_2$  which approximately corresponds to 0.5 in molar fraction (i.e. C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>.H<sub>2</sub>O).

*Branch 3.* This (80 wt%  $< X$ ) corresponds to the domain very rich in dioxan, where  $D$  varies very slowly.

**Figure 2.** Density  $d$  versus  $X$  in dioxan.

### 3.2. Viscosity and density

Experimental values of dynamic viscosity  $\eta$  and density  $d$  are shown in table 1, and the variations in their magnitudes with  $X$  are plotted in figures 2 and 3. Our data are in

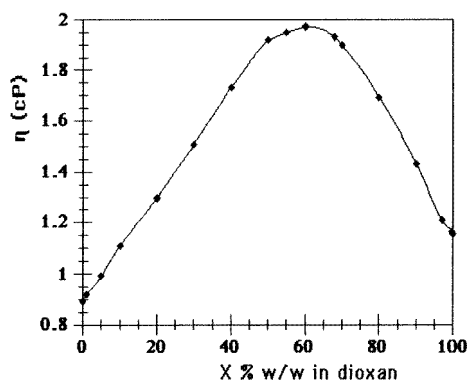


Figure 3. Shear viscosity  $\eta$  versus  $X$  in dioxan.

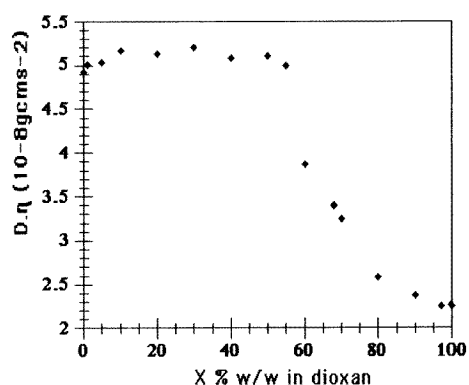


Figure 4. Walden product  $D\eta$  as a function of the weight percentage  $X$  in dioxan.

excellent agreement with those found in the literature [8, 15]. At  $X_0 \approx 62$  wt% (0.25 in molar fraction) the shear viscosity presents a maximum having a value double that of the pure solvent. Furthermore, around this composition we observe a maximal volume contraction, showing interaction between water and dioxan molecules due to the hydrogen bond [16].

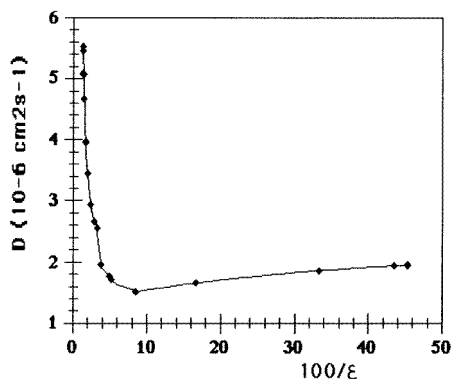
### 3.3. Walden product

We have to bear in mind that the Walden product  $D\eta$  expresses a given structural state of solvation. The variation in  $D\eta$  versus the weight percentage  $X$  in dioxan (figure 4) gives evidence of the three regions as follows.

*Branch 1.* The product  $D\eta$  starts from the value  $4.92 \times 10^{-8} \text{ g cm s}^{-2}$  and reaches rapidly a mean value  $5.14 \times 10^{-8} \text{ g cm s}^{-2}$ . This stabilization of  $D\eta$  around the Walden product of pure water shows a preferential water solvation. We also remark that this quasi-constancy is ascertained by similarity to the Walden product  $\lambda^0\eta$  relative to the conductivity of the lanthanum ferricyanide  $\text{LaFe(CN)}_6$  in some hydro-organic mixtures at dielectric constants  $\epsilon$  less than 53 [8] ( $X < 30$  wt% for the water–dioxan mixture).

*Branch 2.* Going to this region, we observe a change in concavity in the variation in the  $D\eta$  product with the weight percentage  $X$  in dioxan. What is more, we note a rapid decrease, showing competing solvation between dioxan and water.

*Branch 3.* The Walden product presents a plateau of very low slope and shows then a preferential solvation by the dioxan. We remark that the curves representing  $D$ ,  $\eta$  and  $D\eta$  as functions of  $X$  present globally a behaviour approximately similar to those obtained by Ammar *et al* [17] and Bouanz and Gharbi [24] for  $^{137}\text{Cs(I)}$  and  $^{153}\text{Gd(III)}$  in water–isobutyric acid mixtures far from the critical temperature.



**Figure 5.** Self-diffusion coefficient  $D$  versus the reciprocal  $1/\epsilon$  of dielectric constant of the water–dioxan mixture.

#### 4. Association discussion

As seen in figure 5, when  $D$  is represented as a function of the reciprocal dielectric constant, decreasing  $\epsilon$  reduces the self-diffusion coefficient and shows qualitatively the three regions previously mentioned. In fact, we observe a rapid decrease in branch 1 and a pseudo-plateau of small values in branch 3. Between these two regions, we can consider the phenomenon as competition between solvation and a structure change. The appreciable decrease in  $D$  (from 5.5 to 1.5) shows the existence of the association phenomenon. Owing to deficiency in the experimental data on  $D$  at different concentrations of the rare-earth salt  $\text{Gd}(\text{NO}_3)_3$ , we cannot resolve equations (4) and (5) related to conditional constants  $\beta_i$  of association. So, we proceed to some approximations for examining the limitations of the Bjerrum and Fuoss theories for the asymmetrical 3:1 electrolytes, especially in the dioxan-rich domains. When we progressively add dioxan to water, we can restrict, as a first approximation, the situation to the first association:



We roughly estimate a value for the self-diffusion coefficient  $D_p$  of the pair  $\text{Gd}(\text{NO}_3)^{2+}$ , when we adopt the viscosity correction ( $D_p = D_{p0}\eta_0/\eta$ ). We obtain then

$$D_{\text{exp}} = \alpha_A D_p \eta / \eta_0 + (1 - \alpha_A) D_{fi} \eta / \eta_0 \quad (8)$$

where  $\alpha_A$  is the associated fraction and  $D_{fi}$  the self-diffusion coefficient of the free  $\text{Gd(III)}$  ions far from hydrolysis, association or complexation. At  $c = 2 \times 10^{-4}$  M  $\text{Gd}(\text{NO}_3)_3$  we obtained, in previous work [18],  $D_{fi} = 5.82 \times 10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>.

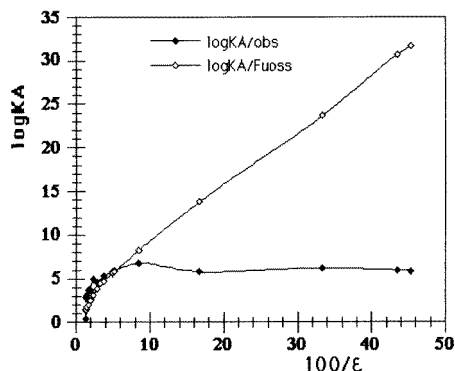
Using the Fuoss theory [8, 12, 19] in the water-rich region, we can estimate a value for the association constant  $K_A$ :

$$K_A = \frac{4\pi N_A a^3 \exp b}{3000} \quad (9)$$

where  $N_A$  is the Avogadro number ( $N_A = 6.0238 \times 10^{23} \text{ mol}^{-1}$ ) and  $b$  is given by

$$b = |z_1 z_2| e^2 / \epsilon k_B T a \quad (10)$$

where  $e$  is the electron charge ( $4.80233 \times 10^{-10} \text{ eu}$ ),  $k_B$  is Boltzmann's constant ( $1.380257 \times 10^{-16} \text{ erg K}^{-1}$ ) and  $T$  is the absolute temperature (259.15 K). The minimum separation distance  $a$  of ions in the Bjerrum theory [13] is evaluated as the sum of the hydrated radii of  $\text{Gd}^{3+}$  and  $(\text{NO}_3)^-$  deduced from the limiting conductivity and the Stokes law [12]; we have approximately  $a \approx 8 \text{ \AA}$ .



**Figure 6.** Estimated and calculated association constant  $\log K_A$  versus reciprocal dielectric constant  $1/\epsilon$  of the water-dioxan mixture.

When we substitute  $\alpha_A$  in equation (8) for  $X = 1$  and  $X = 5$ , we can adopt a value of  $D_p$  approximately equal to  $1.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . Considering the slow variation in  $D_p$ , the association constant  $K_{Aobs}$  (table 2), according to the law of mass action becomes

$$K_{Aobs} = \alpha_A / (1 - \alpha_A)(3 - \alpha_A) \tau^2 c \quad (11)$$

where  $c$  is the global electrolyte concentration and  $\tau$  the activity coefficient of diffusing species. If we neglect in a first approximation the relaxation electrostatic effects [8, 20], we can suppose that the activity coefficient of ion pairs does not deviate too much from unity. The variation in the logarithm of the observable association constant,  $\log K_{Aobs}$ , with  $1/\epsilon$  (figure 6) is quasi-linear only for branches 1 and 2 ( $1/\epsilon \leq 0.1$ ). In the third region (very rich in dioxan, maximum 83 wt%),  $\log K_{Aobs}$  varies very slowly and presents a quasi-plateau. We attributed this to the modification of the liquid structure. However, we remark that the Bjerrum model [8, 12, 13] necessitates an adjustment of the minimum distance  $a$  for each composition of mixture (i.e. for each  $\epsilon$ -value):

$$\alpha_A = (4\pi N_A c / 1000) (2q)^3 Q(b) \quad (12)$$

with  $q = |z_1 z_2| e^2 / 2\epsilon k_B T$  and  $Q(b) = \int_2^b x^{-4} \exp x \, dx$ . However, the adjustment of  $a$  gives very low values of  $\alpha_A$  and does not reflect the phenomena studied. An improvement in the value of  $\alpha_A$  for a given composition necessitates an adjustment approximately equal to  $1 \text{ \AA}$  (i.e. around the crystallographic radius of the cation). Therefore, we cannot consider



**Table 2.** Dielectric constant  $\epsilon$ , association degree  $\alpha_A$  and logarithm  $\log K_A$  of the association constant.

$X$	$\epsilon$	$100/\epsilon$	$\alpha_A$	$\log K_{Aobs}$	$\log K_{AFuoss}$
0	78.42	1.275	0.0032	0.38	1.40
1	77.75	1.286	0.0171	1.39	1.42
5	74.0	1.351	0.1073	2.83	1.53
10	70.31	1.422	0.182	3.08	1.74
20	61.5	1.626	0.381	3.69	2.02
30	52.5	1.905	0.422	3.79	2.50
40	43.75	2.286	0.788	4.93	3.07
50	35.35	2.837	0.698	4.57	3.86
55	31.0	3.226	0.722	4.65	4.46
60	27.0	3.704	0.868	5.38	4.75
68	20.5	4.878	0.917	5.81	5.64
70	19.0	5.21	0.929	5.95	5.86
80	11.75	8.51	0.973	6.81	8.31
90	6.0	16.67	0.915	5.78	13.79
97	3.0	33.33	0.946	6.20	23.69
99.7	2.30	43.48	0.934	5.97	30.71
99.9	2.21	45.25	0.922	5.87	31.65

that  $a$  is a minimum approach distance of the solvated lanthanide cations. Moreover, the Bjerrum model is somewhat better when we replace the effective hydrodynamic radius  $r$  (the corrected Stokes radius) with distance  $a$ , for each composition. Nevertheless, going to the dioxan-rich regions, the values of  $\alpha_A$  and  $\log K_A$  diverge rapidly and can cause aberration (such as  $\alpha_A > 1$ ). However, the phenomenon is better illustrated by the Fuoss model (equations (9)–(10)). Therefore, the variation in  $\log K_A$  with  $1/\epsilon$  is linear for a fixed parameter  $a$  [21] according to

$$\log K_A = A + B(1/\epsilon) \quad (13)$$

or quasilinear for a parameter adjusted to the effective radius  $r$  (figure 6). Equation (13) can be transformed in this case to the following equation, when our experimental conditions are considered:

$$\log K_A = -2.60 + 3 \log[a \text{ (\AA)}] + 730.12/\epsilon a \text{ (\AA)}. \quad (14)$$

This monotonic variation in  $\log K_A$  is similar to those obtained for many alkali halides at 25 °C by Fuoss and co-workers [15, 22] for  $1/\epsilon < 0.08$ , that is for the first two regions, but it cannot provide for an eventual quasi-plateau in branch 3. However, at low dielectric constants, the solubility of  $\text{Gd}(\text{NO}_3)_3$  in water–dioxan is very small. Consequently, we suppose that the observed aberration is also due to neutral ion pairs.

## 5. Conclusion

The study of ionic self-diffusion coefficients in electrolytes provides direct evidence of the influence of the solvent as well as its physical–chemical properties on the individual transport properties of ions. The set of calculated and measured parameters leads us to a coherent structure description of the medium. Similarly by the measurement of self-diffusion coefficients of ions we have an indication about the preferential solvation which is modified when the solvent composition varies.

Study of the asymmetrical electrolyte  $\text{Gd}(\text{NO}_3)_3$  in hydro-organic solutions (at low dielectric constants) shows distinctive regions having generally different behaviours. We note that these domains are approximately separated by the following molar fractions: 0.2 and 0.5, i.e.  $(\text{C}_4\text{H}_8\text{O}_2.4\text{H}_2\text{O})$  and  $(\text{C}_4\text{H}_8\text{O}_2.\text{H}_2\text{O})$ , respectively. Generally, the extreme regions show the preponderance of the effects of each pure solvent on the different properties and physical magnitudes; the intermediate region shows competition between the specified effects of each solvent, as well as the structure changes and correlations between the molecules of water and dioxan.

We have also shown in this study the validity of the Bjerrum and the Fuoss theories relative to association in asymmetrical electrolytes of polyvalent ions in all the domains of composition (i.e. even for a low dielectric constant of medium). In conclusion, an improvement in these theories requires taking into consideration the microscopic dielectric constant and the structural modification of the solvent.

### Acknowledgments

We thank Professor M Chemla (Paris VI) and Professor G Kessling (Göttingen) for helpful discussions and suggestions. I am grateful to Dr A Mgaidi and Dr A Cherni (Faculté des Sciences de Tunis) who helped us to improve this study, and T Labassi (Faculté des Sciences de Tunis) for reading the manuscript.

### References

- [1] Turq P 1972 *Chem. Phys. Lett.* **15** 579
- [2] Turq P, Lantelme F and Chemla M 1969 *Electrochim. Acta* **14** 1081
- [3] Turq P, Lantelme F, Roumegous Y and Chemla M 1971 *J. Chim. Phys.* **68** 527
- [4] Turq P, Deloncle R and Chemla M 1971 *J. Chim. Phys.* **68** 1305
- [5] Latrous H, Turq P and Chemla M 1972 *J. Chim. Phys.* **69** 1650
- [6] Turq P, Ilzyer D and Chemla M 1974 *J. Chim. Phys.* **2** 233
- [7] Latrous H, M'Halla J and Chemla M 1979 *Radiochem. Radioanal. Let.* **38** 355
- [8] Erdey-Gruz T 1958 *Transport Phenomena in Aqueous Solutions* (London: AHPB)
- [9] Jenkins I L and Monk C B 1950 *J. Am. Chem. Soc.* **72** 2695
- [10] Vosburgh W C and Cooper G R 1941 *J. Am. Chem. Soc.* **63** 437  
Foley R T and Anderson R C 1949 *J. Chem. Soc.* **71** 909
- [11] Mgaidi M, Fürst W and Renon H 1991 *Metall. Trans. B* **22** 491
- [12] Robinson R A and Stokes R H 1959 *Electrolyte Solutions* (London: Butterworth)
- [13] Bjerrum N 1918 *Z. Electrochem.* **24** 321; 1926 *Danske. Vidensk. Selsh.* **7** 9
- [14] Anderson J A and Saddington K 1949 *J. Chem. Soc.* **5** 381
- [15] Fabry T L and Fuoss R M 1964 *J. Phys. Chem.* **68** 971–4
- [16] Goates J R and Sullivan J R 1958 *J. Phys. Chem.* **62** 188
- [17] Ammar M, Bouanz M and M'Halla J 1990 *J. Chim. Phys.* **87** 233–54
- [18] Ouerfelli N, Ammar M and Latrous H 1994 *J. Chim. Phys.* **91** 1786–95
- [19] Fuoss R M 1958 *J. Am. Chem. Soc.* **80** 5059
- [20] Debye P and Hückel E 1923 *Phys. Z.* **24** 185
- [21] Fuoss R M and Kraus C A 1957 *J. Am. Chem. Soc.* **79** 3304
- [22] Lind J E and Fuoss R M 1961 *J. Phys. Chem.* **65** 99, 1414; 1962 *J. Phys. Chem.* **66** 1727  
Kunze R W and Fuoss R M 1963 *J. Phys. Chem.* **67** 911, 914  
Justice J C and Fuoss R M 1963 *J. Phys. Chem.* **67** 1707
- [23] Mills R and Godbole A W 1958 *Aust. J. Chem.* **11** 1
- [24] Bouanz M and Gharbi A 1994 *J. Phys.: Condens. Matter* **6** 4429–35