



Ionic self-diffusion coefficients and structure of the trivalent lanthanide ion europium ¹⁵²Eu(III) in concentrated aqueous solutions and similarity with the transamericium ion ²⁴⁴Cm(III).



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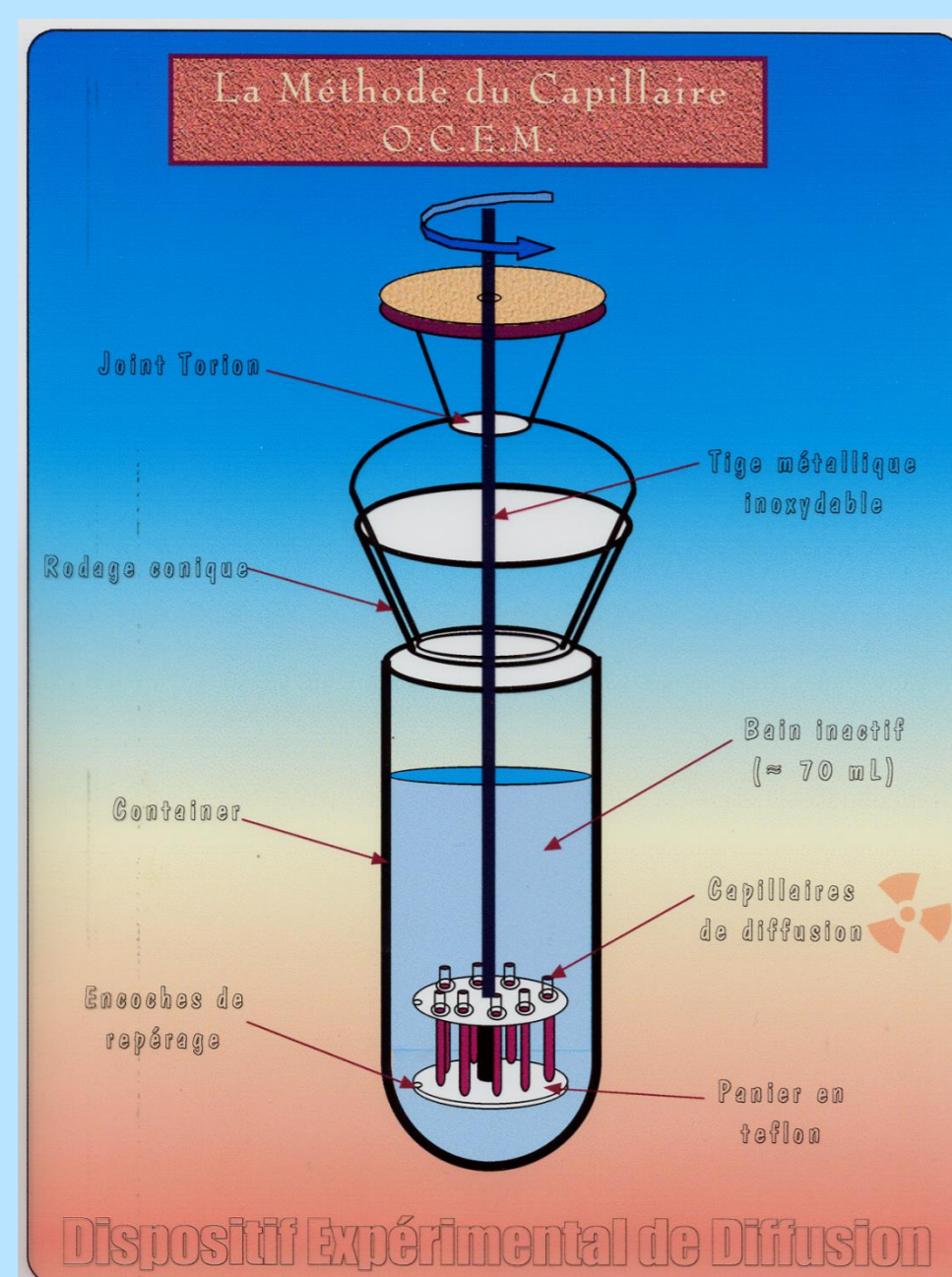
* Corresponding Author, E-mail: nouerfelli@yahoo.fr. This paper is dedicated to the memory of J. Oliver.

EAEA, Egyptian Atomic Energy Authority

Introduction

Ionic self-diffusion coefficients *D* of the lanthanide trivalent trace ion ¹⁵³Gd (III) have been determined in supporting aqueous solutions of Gd(NO₃)₃-HNO₃ over a large range of concentration in acidic medium (pH = 2.50) at 25°C by the open-end capillary method (O.E.C.M.). The method measures the transportation time of ion across a fixed distance. We optimized the pH in order to avoid the hydrolysis, pairing and complexing trivalent 4f ions. The diffusion data obtained in large range of concentration as well as the physicochemical properties, allow to derive the following information: (i) the limiting value *D*⁰ at zero ionic strength, as 5.985 10⁻⁶ cm².s⁻¹ for ¹⁵³Gd (III), (ii) the validity of the Onsager limiting law, (iii) the ionic self-diffusion coefficient as a function of the ionic strength for asymmetrical 3:1 electrolytes in dilute solutions, (iv) a competition between ion-ion interaction and ion-solvent interaction and (v) a more extended law available for an intermediate range of concentration up to 0.114 mol.L⁻¹ and for a concentrated range up to 1.5 mol.L⁻¹. This study contributes to demonstrate similarities transport and structure properties between ¹⁵³Gd (III) and ²⁴⁴Cm (III) trivalent ions explained by a similar electronic configuration, ionic radius and same hydration number. These properties could also result from a long-range structuration of the concentrated ionic solution.

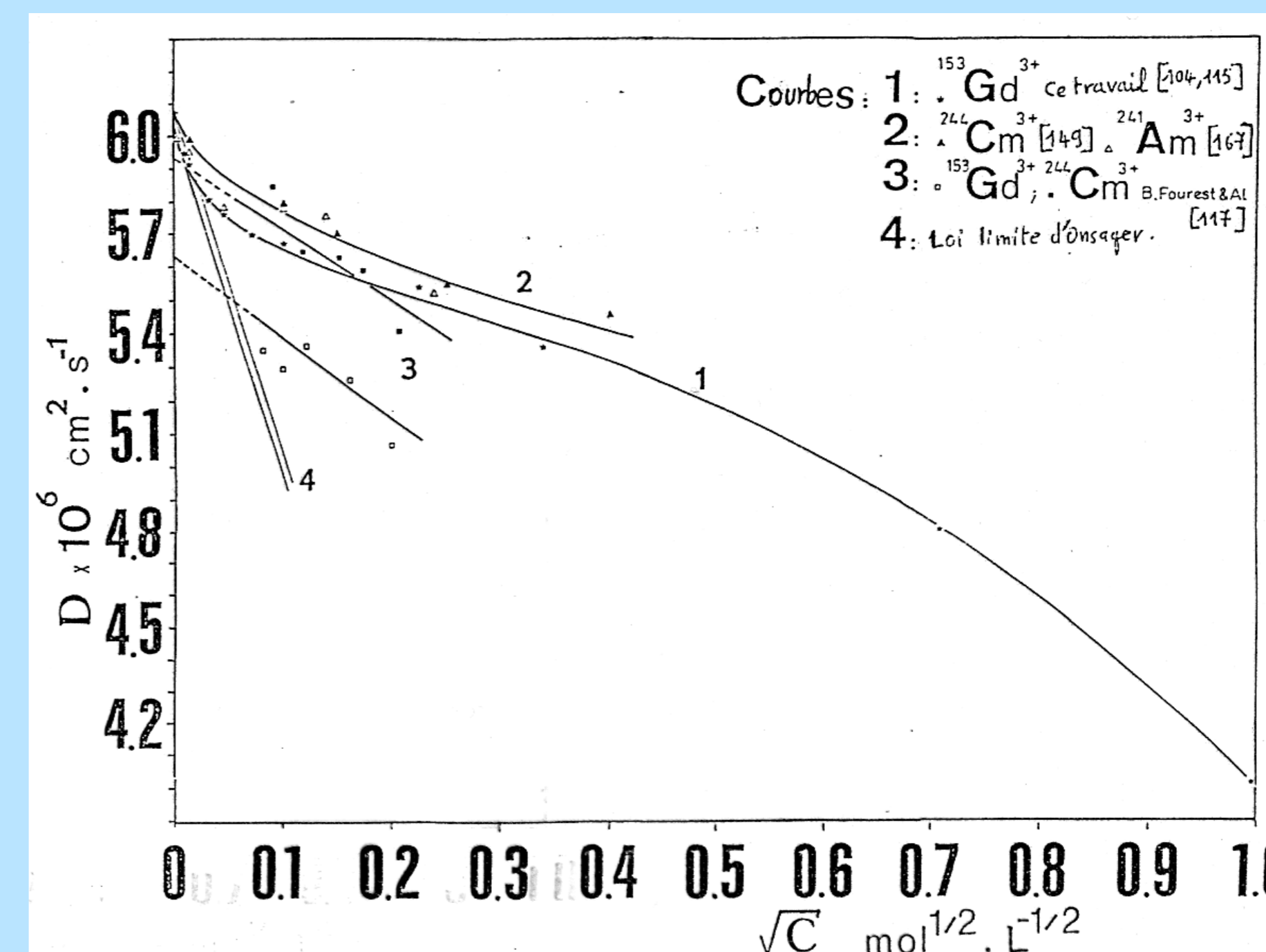
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Activity ratio :
 $\Gamma = A(t) / A(0)$

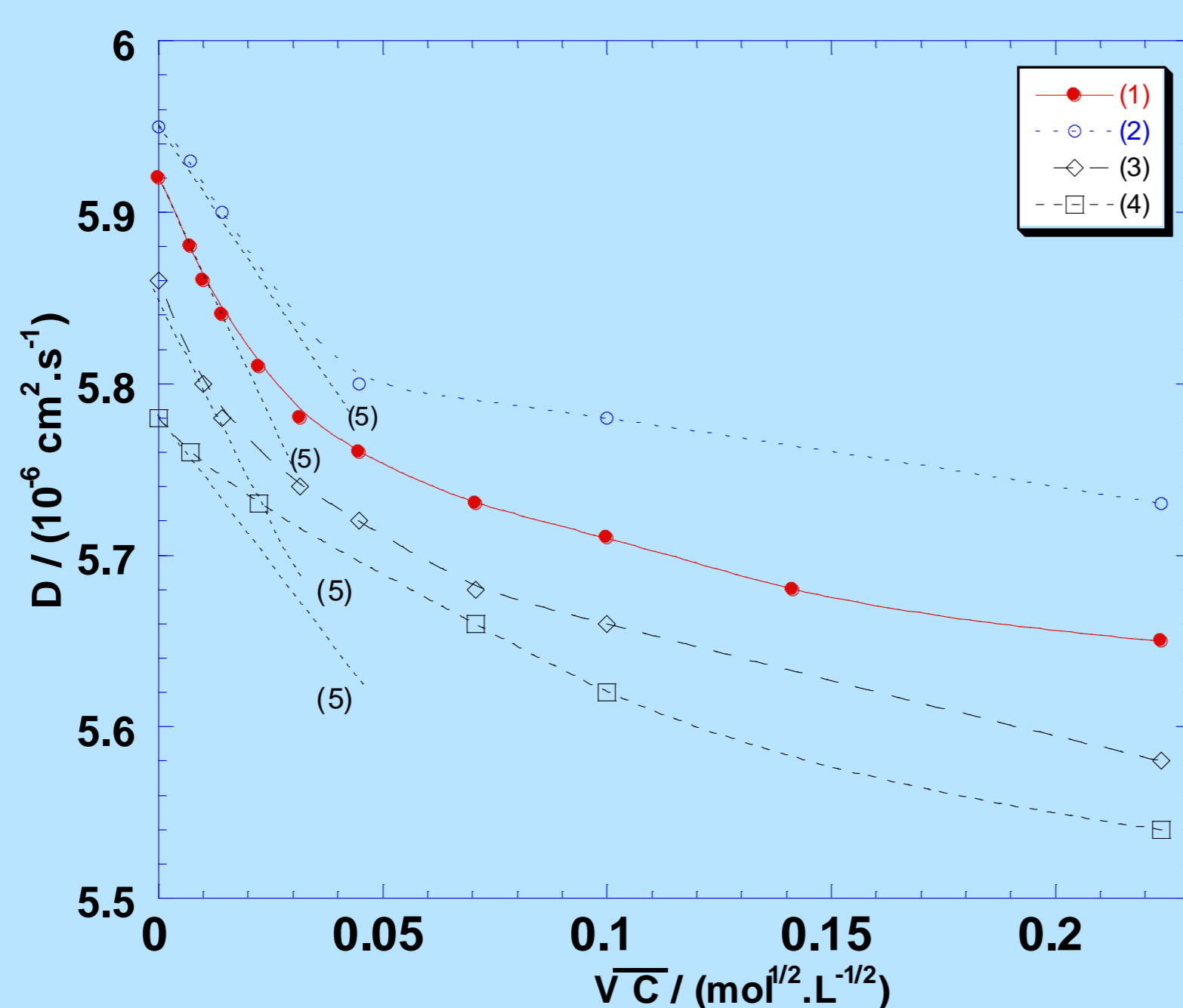
$$\Gamma = \sum_0^{\infty} \frac{8}{\pi^2 (2n+1)^2} \exp\left(\frac{-\pi^2 (2n+1)^2 Dt}{4l^2}\right)$$

$$D = 0.4053 \frac{l^2}{t} \ln\left(\frac{0.8106}{\Gamma}\right)$$



Self-diffusion cell *** Open end capillary method

Self-diffusion coefficients *D* / (10⁻⁶ cm².s⁻¹) in mean and concentrated solutions at 25°C of some trivalent lanthanide and actinide ions as a function of square root of molarity *C* / (mol.L⁻¹).



Lanthanide ion	λ°_S	D°_S	λ°_M	D°_M	D°_F	D°_L	D°_W	D°_{exp}
La (III)	69.7	6.19	67.0	5.95	-	-	6.19	-
Eu (III)	67.8	6.02	67.1	5.96	6.02	6.15		6.11(a)
Gd (III)	67.3	5.97	67.9	6.02	5.74	-		6.04 (b)
Tm (III)	65.4	5.80	-	-	-	-		5.96 (b)

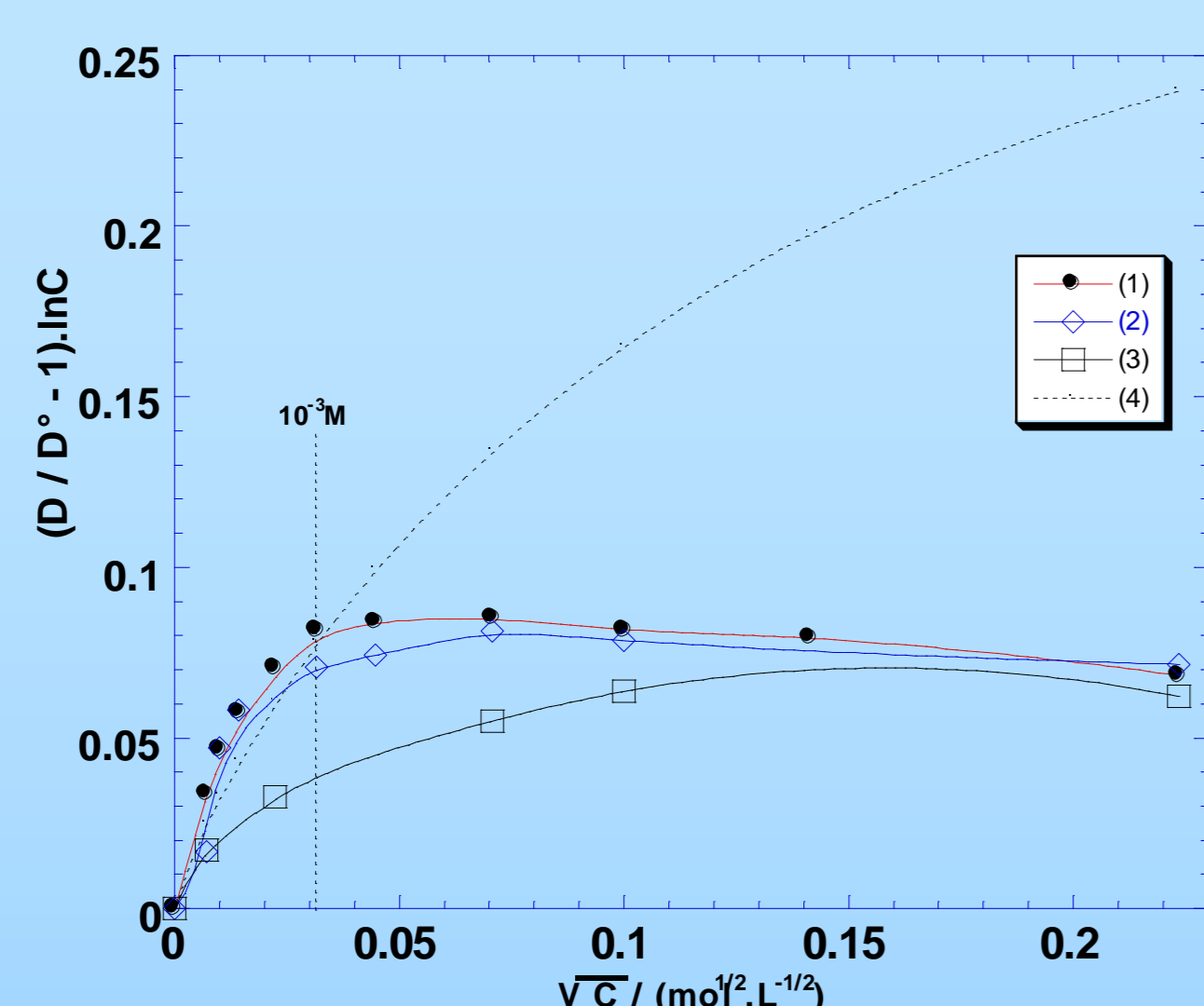
Ionic self-diffusion coefficients *D* / (10⁻⁶ cm².s⁻¹) at 25°C in dilute aqueous solutions of some lanthanide trivalent ions versus square root of the concentration of supporting electrolytes of gadolinium nitrates solutions at pH 2.50, m / mol.kg⁻¹; (1): present work (¹⁵²Eu (III) in Gd(NO₃)₃-HNO₃); (2): ¹⁵²Eu (III) in Eu(NO₃)₃-HNO₃; (3): ¹⁵³Gd (III); (4): ¹⁷⁰Tm (III); (5): Onsager limiting law.

Nernst-Einstein expression at infinite dilution :

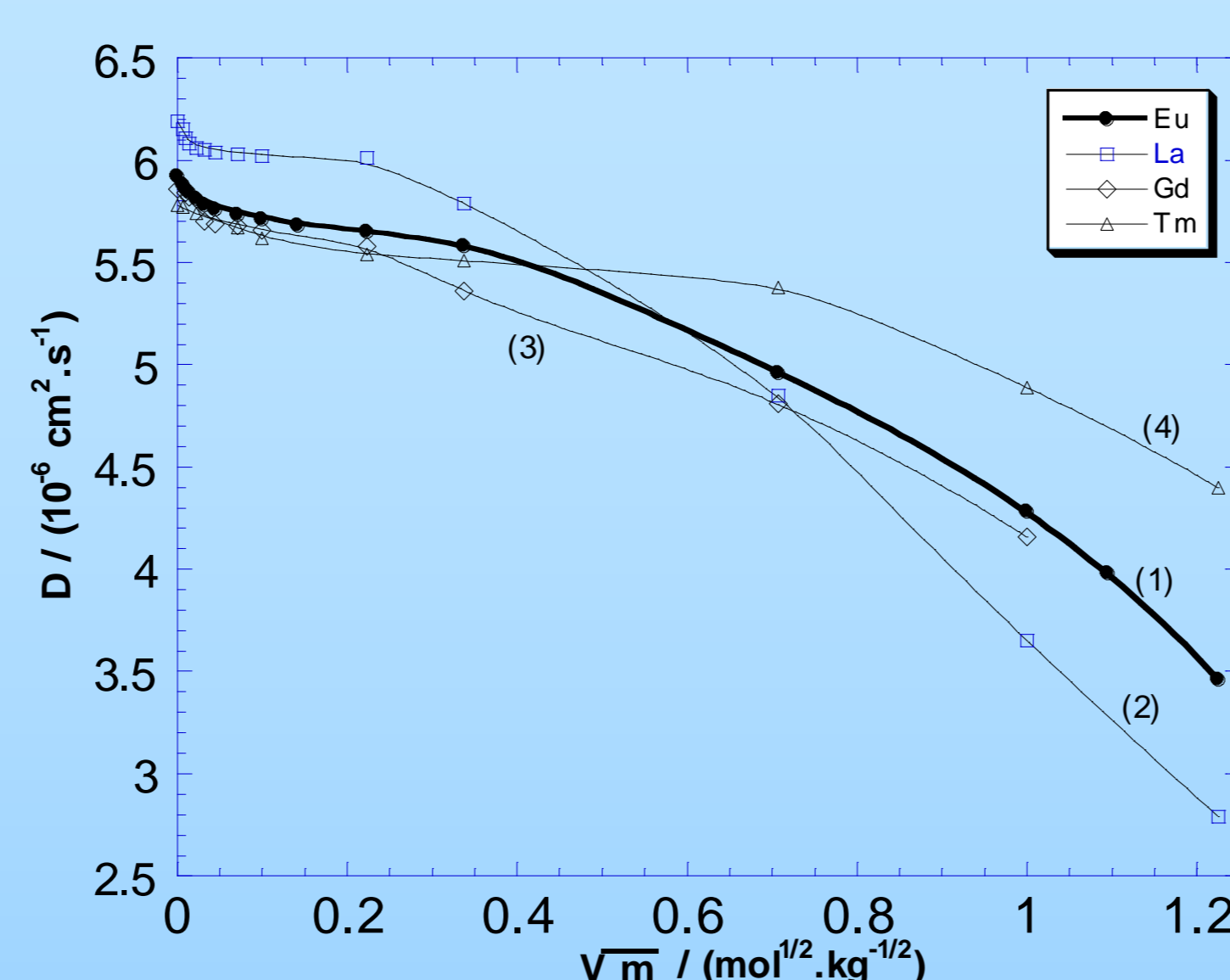
$$D_i^0 = 2.66110^{-7} \cdot \frac{\lambda_i^0}{|z_i|}$$

Onsager limiting law : $D = D^0 \cdot [1 - 0.7816 \cdot (1 - \sqrt{d}) \cdot z_2 \cdot \sqrt{I}]$

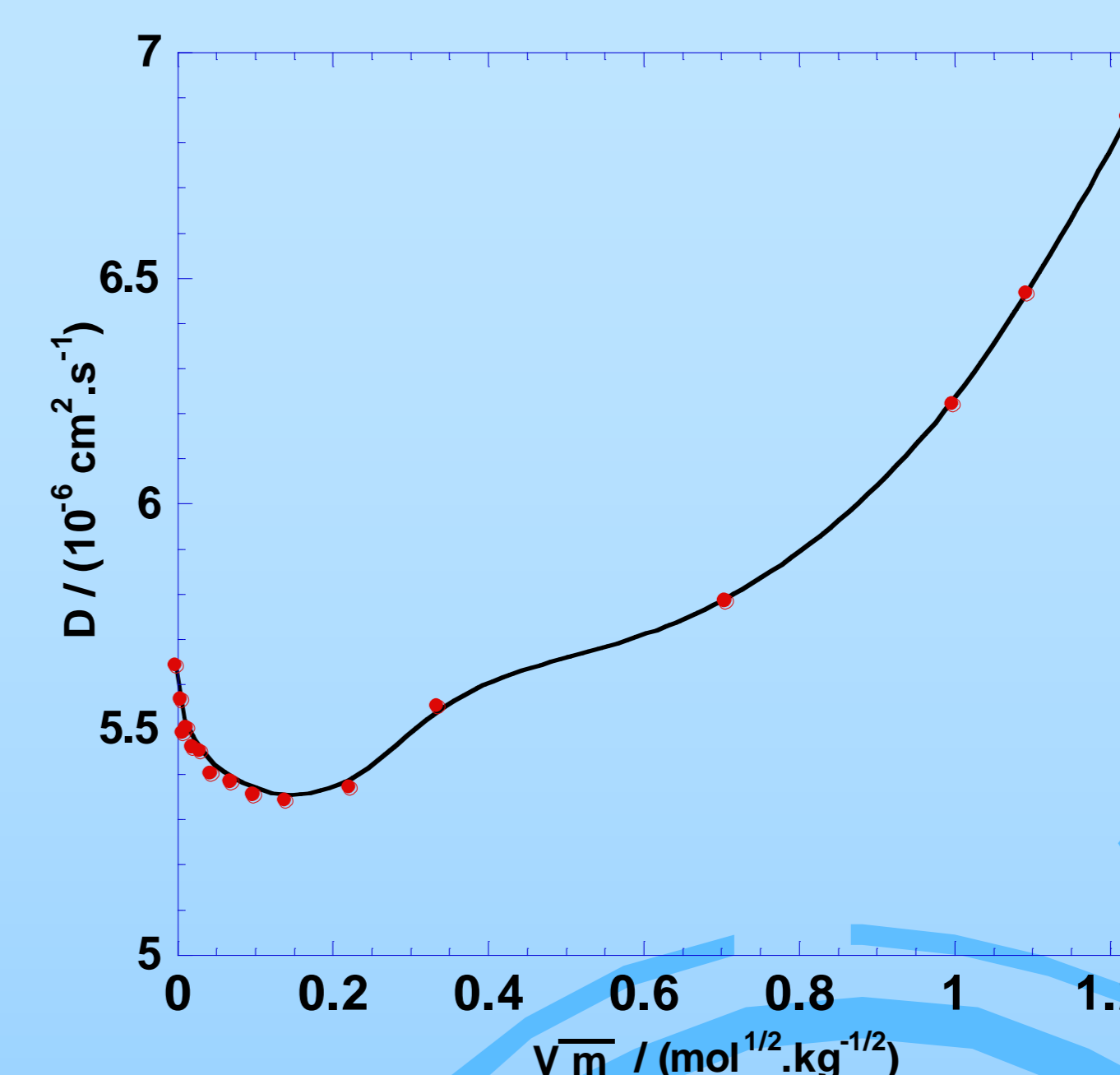
$$d_i = \frac{|z_1|}{|z_2| + |z_3|} \cdot \left[\frac{|z_2| \cdot \lambda_2^0}{|z_1| \cdot \lambda_2^0 + |z_2| \cdot \lambda_1^0} + \frac{|z_3| \cdot \lambda_3^0}{|z_1| \cdot \lambda_3^0 + |z_3| \cdot \lambda_1^0} \right]$$



Variation of (D/D⁰ - 1).lnC as a function of square root of supporting electrolyte (\sqrt{c}) in dilute solutions and deviation to linear Onsager limiting law; (1): present work (¹⁵²Eu (III) in Gd(NO₃)₃-HNO₃); (2): ¹⁵³Gd (III); (3): ¹⁷⁰Tm (III); (4): Onsager limiting law.



Self-diffusion coefficients *D* / (10⁻⁶ cm².s⁻¹) in mean and concentrated solutions at 25°C of trivalent lanthanide ions as a function of square root of molarity *m* / (mol.kg⁻¹); (1) : ¹⁵²Eu (III) present work ; (2) : ¹⁴⁰La (III) ; (3) : ¹⁵³Gd (III) and (4) : ¹⁷⁰Tm (III).



Walden's product *D*. η versus square root of molarity *m*.
D : self-diffusion coefficients of tracers ¹⁵²Eu (III) ions ;
 η : viscosity of supporting electrolytes of Gd(NO₃)₃-HNO₃.

$$D = D^0 \left[1 - \frac{A\sqrt{c}}{(1 + b\sqrt{c})} \right]$$

Extension of the
Onsager limiting
model

Conclusion

In this work, we have used the O.E.C.M. for determining the self-diffusion data of the lanthanide trivalent ion ¹⁵³Gd (III) over a large range of concentration of supporting lanthanide electrolytes. In order to minimize the hydrolysis, association and complexing, we have used an acidic medium (pH 2.50).

An interesting comparison can be made between limiting diffusion coefficients obtained data by different methods. Results from different studies show satisfactory agreement. By means of the study of (D/D⁰ - 1).lnC variation as a function of \sqrt{c} we have clearly delimited the upper limit of validity of the Onsager limiting law as being. However, in the intermediate and concentrated solution domains, we ascertain that the variation of *D* is not linear. In this context, we have proposed and discussed a semi-empirical model with two adjustable parameters and performed new accurate values of limiting self-diffusion coefficient *D*⁰ for some trivalent lanthanide ions. We conclude that in the case of self-diffusing in concentrated aqueous solution when hydrolysis and pairing are avoided, the extended model with molality as a variable is advised to use even in dilute range. We also note that the behaviour of the 4f and 5f ions is similar in the case where there is neither hydrolysis phenomenon nor pairing and nor complexing. In going to the concentrated domain, we observe a changing of concavity of the variation of *D* versus the square root of concentration, and a rapid decrease of the self-diffusion coefficients, whereas the viscosity rises even more sharply. These properties could result from a long-range structuration of the concentrated ionic solution.