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Diffusion coefficients of lead (II) nitrate in nitric acid aqueous solutions at 298 K

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Abstract

Interdiffusion coefficients of lead (II) nitrate in water and in nitric acid (10^{-5} – 10^{-2} M) mixtures at 298.15 K, and at concentrations from 0.001 to 0.1 M, have been measured using a conductimetric cell and an automatic apparatus to follow diffusion. The cell uses an open-ended capillary method and a conductimetric technique is used to follow the diffusion process by measuring the resistance of a solution inside the capillaries, at recorded times. The diffusion of lead (II) nitrate is clearly affected by the presence of HNO_3 as well as by the lead (II) hydrolysis. At the highest HNO_3 concentration (0.01 M) the effect of the hydrogen ions on the whole diffusion process has an important and main role, whilst at the highest Pb(II) concentration the presence of HNO_3 as well as the hydrolysis can be neglected. These values are supported by UV-spectroscopy as well as by pH measurements. The experimental interdiffusion coefficients are discussed on the basis of the Onsager–Fuoss model.

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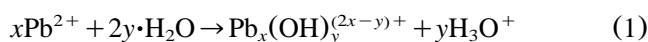
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1. Introduction

Heavy metals, with many useful applications in our life, are very harmful if discharged into natural water resources. Lead is an example of a heavy metal classified as priority pollutant by the US Environmental Protection Agency Metals [1]. Many industrial applications, e.g. surface treatment, still use lead in their components; it can also be absorbed by living beings; one interesting case is that cork used for many applications (as for example, sealing wine bottles and consequent diffusion of such metals to wine) can carry some amounts of lead absorbed by *Quercus Suber* L. In the last few years much work has been done in heterogeneous systems to remove lead from different environments [2,3]. Fundamental studies on Pb(II) solutions have been done often involving determination of self-diffusion coefficients by electrochemical techniques [4–8]. However, as far as

the authors know, no data on the mutual differential diffusion coefficients of Pb(II) salts are published [9].

Lead (II) nitrate aqueous solutions are slightly acidic if unbuffered. The general hydrolysis equation of Pb(II) may be



and the most prominent hydrolysed species are $\text{Pb}_4(\text{OH})_4^{4+}$ and $\text{Pb}_6(\text{OH})_8^{4+}$ [10]. The formation of a number of complex species creates difficulties in the measurements, and may justify the scarcity of diffusion data for lead (II) aqueous solutions.

In this study mutual diffusion coefficients, D , (interdiffusion coefficients) are reported for aqueous solutions of lead (II) nitrate in a concentration range 0.001 to 0.10 M, at different nitric acid conditions (0, 1.00×10^{-5} , 1.00×10^{-3} , 1.00×10^{-2} M). The open-ended conductimetric capillary cell [11,12] was used.

These data fulfil a gap in the literature for heavy metal ions and will help the understanding of the mechanism of sorption and release kinetics of these ions in polymeric systems.

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2. Experimental

2.1. Reagents

Lead (II) nitrate, $\text{Pb}(\text{NO}_3)_2$ and nitric acid (HNO_3) were obtained from Riedel-de-Haen, *pro analysis* grade. $\text{Pb}(\text{NO}_3)_2$ solutions were prepared from the solid salt, dried at 120 °C; distilled and degassed water, with an ionic conductivity lower than $1.0 \times 10^{-4} \Omega^{-1} \text{m}^{-1}$, was used.

2.2. Open-ended conductimetric capillary cell

An open-ended capillary cell, used to obtain mutual diffusion coefficients of a large amount of electrolytes [13], is described in great detail in previous papers [14–16]. Basically, it consists of two vertical capillaries, each closed at one end by a platinum electrode and positioned one above the other with the open ends separated by a distance of approximately 14 mm. The upper and lower tubes, initially filled with solutions of concentrations $0.75c$ and $1.25c$, respectively, are surrounded with a solution of concentration c . This ambient solution is contained in a glass tank $200 \times 140 \times 60$ mm immersed in a thermostat at 25 °C. Perspex sheets divide the tank internally and a glass stirrer creates a slow lateral flow of ambient solution across the open ends of the capillaries. Experimental conditions are such that the concentration at each of the open ends is equal to the ambient solution value c , i.e. the physical length of the capillary tube coincides with the diffusion path. In other words, the required boundary conditions described in the literature [12] to solve Fick's second law of diffusion are applicable. Therefore the so-called Δl effect [11,12] is reduced to negligible proportions. In a manually operated apparatus, diffusion is followed by measuring the ratio $w = R_t/R_b$ of resistances R_t and R_b of the upper and lower tubes by an alternating current transformer bridge. In an automatic apparatus, w is measured by a Solartron digital voltmeter (DVM) 7061 with 6.5 digits. A power source (Bradley Electronic Model 232) supplies a 30-V sinusoidal signal at 4 kHz (stable to within 0.1 mV) to a potential divider that applies a 250 mV signal to the platinum electrodes at the top and bottom capillaries. By measuring the voltages V' and V'' from top and bottom electrodes to a central electrode at ground potential, in a fraction of a second, the DVM calculates w .

In order to measure the differential diffusion coefficient D at a given concentration c , the bulk solution of concentration c is prepared by mixing 1 l of 'top' solution with 1 l of 'bottom' solution, measured accurately. The glass tank and the two capillaries are filled with c solution, immersed in the thermostat, and allowed to come to thermal equilibrium. The resistance ratio $w = w_\infty$ measured under these conditions (with solutions in

both capillaries at concentration c) accurately gives the quantity $\tau_\infty = 10^4/(1 + w_\infty)$.

The capillaries are filled with the 'top' and 'bottom' solutions, which are then allowed to diffuse into the 'bulk' solution. Resistance ratio readings are taken at recorded times, beginning 1000 min after the start of the experiment, to determine the quantity $\tau = 10^4/(1 + w)$ as τ approaches τ_∞ . The diffusion coefficient is evaluated using a linear least-squares procedure to fit the data and, finally, an iterative process using 20 terms of the expansion series of Fick's second law for the present boundary conditions. The theory developed for the cell has been described earlier [11].

2.3. Instruments

pH measurements were carried with a pH meter PHM 240 from Radiometer, with a pH conjugated electrode Ingold U457-K7; the electrode was calibrated immediately before each experimental set of solutions. From pH meter calibration results a zero pH of 6.897 ± 0.030 and sensitivity higher than 98.7%. pH was measured in fresh solutions and the buffers used were IUPAC-type of 4 and 7 pH. UV-spectra were obtained using a spectrophotometer *Jasco V-530*; the spectra were obtained between 345 and 265 nm with a bandwidth of 1.0 nm.

3. Results

Mutual diffusion coefficients of $\text{Pb}(\text{NO}_3)_2$ in aqueous solutions, D_{av0} , and in $\text{H}_2\text{O}-\text{HNO}_3$ mixtures, D_{av} , are shown in Tables 1–4, respectively. D_{av} is the mean diffusion coefficient, calculated on the basis of, at least, three independent measurements. Table 1 also shows the diffusion coefficients of $\text{Pb}(\text{NO}_3)_2$ and HNO_3 estimated by the Onsager–Fuoss equation Eq. (3), D_{of} [17].

The following polynomial in $c^{1/2}$ was fitted to the data by a least squares procedure

$$D = a_0 + a_1 c^{1/2} + a_2 c + a_3 c^{3/2} + a_4 c^2 \quad (2)$$

where the coefficients a_0 , a_1 , a_2 , a_3 and a_4 are adjustable parameters. Table 5 shows the coefficients a_0 to a_4 of Eq. (2). They may be used to calculate the values of diffusion coefficients at specified concentrations within the range of the experimental data shown in Tables 1–4. The goodness of the fit (obtained with a confidence interval of 98%) can be assessed by the correlation coefficient, R^2 .

4. Discussion

Tables 1–4 show that, decreasing the pH, the diffusion coefficients of lead(II) nitrate change to higher values (positive deviation in $(D_{\text{av}} - D_0)/D_0$). Such deviations

Table 1

Interdiffusion coefficients of lead (II) nitrate in aqueous solutions, D_{av0} , and those calculated from Onsager–Fuoss equation (Eq. (3)), D_{of} , at 25 °C

c/M	$D_{av0}/(10^{-9} \text{ m}^2 \text{ s}^{-1})^a$	$S_{D_{av0}}/(10^{-9} \text{ m}^2 \text{ s}^{-1})^b$	$D_{ofPb(NO_3)_2}/(10^{-9} \text{ m}^2 \text{ s}^{-1})$	$D_{of(HNO_3)}/(10^{-9} \text{ m}^2 \text{ s}^{-1})$
0	–	–	1.412	3.158
0.001	1.799	0.028	1.348	3.100
0.005	1.423	0.014	1.297	3.045
0.008	–	–	1.280	3.024
0.010	1.318	0.011	1.273	3.013
0.025	1.204	0.007	1.240	2.972
0.050	1.103	0.020	1.229	2.942
0.075	1.094	0.006	1.228	2.932
0.100	1.152	0.022	1.227	2.928

^a D_{av0} is the mean diffusion coefficient of three experiments.

^b $S_{D_{av0}}$ is the standard deviation of that mean.

Table 2

Interdiffusion coefficients of lead (II) nitrate in nitric acid (10^{-5} M) aqueous solutions, D_{av} , at 25 °C

$[Pb(NO_3)_2]/M$	$D_{av}/(10^{-9} \text{ m}^2 \text{ s}^{-1})$	$S_{D_{av}}/(10^{-9} \text{ m}^2 \text{ s}^{-1})^a$	$\frac{D_{av}-D_{av0}}{D_{av0}} \times 100/\%^a$
0.001	1.889	0.002	5.0
0.010	1.387	0.005	5.2
0.025	1.266	0.028	5.2
0.050	1.166	0.007	5.7
0.075	1.159	0.045	5.9
0.100	1.162	0.011	0.9

^a See Table 1.

Table 3

Interdiffusion coefficients of lead (II) nitrate in nitric acid (10^{-3} M) aqueous solutions, D_{av} , at 25 °C

$[Pb(NO_3)_2]/M$	$D_{av}/(10^{-9} \text{ m}^2 \text{ s}^{-1})$	$S_{D_{av}} (10^{-9} \text{ m}^2 \text{ s}^{-1})^a$	$\frac{D_{av}-D_{av0}}{D_{av0}} \times 100/\%^a$
0.001	1.900	0.001	5.6
0.010	1.393	0.016	5.7
0.025	1.315	0.007	9.2
0.050	1.218	0.001	10.4
0.075	1.178	0.006	7.7
0.100	1.170	0.001	1.6

^a See Table 1.

Table 4

Interdiffusion coefficients of lead (II) nitrate in nitric acid (10^{-2} M) aqueous solutions, D_{av} , at 25 °C

$[Pb(NO_3)_2]/M$	$D_{av}/(10^{-9} \text{ m}^2 \text{ s}^{-1})$	$S_{D_{av}} (10^{-9} \text{ m}^2 \text{ s}^{-1})^a$	$\frac{D_{av}-D_{av0}}{D_{av0}} \times 100/\%^a$
0.001	3.103	0.016	78.8
0.005	2.799	0.015	0.015
0.010	2.022	0.011	53.4
0.025	1.698	0.017	41.0
0.050	1.357	0.042	23.0
0.075	1.249	0.016	14.2
0.100	1.175	0.012	2.0

^a See Table 1.

can be neglected only at 0.1 M concentrations, probably due to other phenomena such as, for example, ion-pair formation [18–20]. Those deviations can be mainly due to two different factors: (a) alteration of free Pb (II) concentration with a decrease of hydrolysis products; and/or (b) effect of the free hydrogen ion concentration in solution.

To understand the transport process of this electrolyte in the above systems, it is necessary to know the behaviour of $\text{Pb}(\text{NO}_3)_2$ in aqueous solutions. For that the experimental interdiffusion coefficients were compared, as a first approach, with those estimated by the Onsager–Fuoss equation (Eq. (3))

$$D = 2000 RT \frac{\bar{M}}{c} \left(1 + c \frac{\partial \ln \gamma_{\pm}}{\partial c} \right) \quad (3)$$

where

$$\frac{\bar{M}}{c} = 1.0741 \times 10^{-20} \frac{\lambda_1^0 \lambda_2^0}{|z_1| \nu_1 \Lambda^0} + \frac{\Delta \bar{M}'}{c} + \frac{\Delta \bar{M}''}{c} \quad (4)$$

In Eq. (4), the first- and second-order electrophoretic terms are given by

$$\frac{\Delta \bar{M}'}{c} = \frac{(|z_2| \lambda_1^0 - |z_1| \lambda_2^0)^2}{|z_1 z_2| 2 (\Lambda^0)^2} \times \frac{3.132 \times 10^{-19}}{\eta_0 (ET)^{1/2}} \frac{c \sqrt{\tau}}{(1 + ka)}$$

and

$$\frac{\Delta \bar{M}''}{c} = \frac{(z_2^2 \lambda_1^0 - z_1^2 \lambda_2^0)^2}{(\Lambda^0)^2} \times \frac{9.304 \times 10^{-13} c^2}{\eta_0 (ET)^{1/2}} \phi(ka)$$

where $\tau = \sum c_i z_i^2$ is the ionic concentration, η_0 is the viscosity of the solvent, k is the ‘reciprocal average radius of ionic atmosphere’ (e.g. [21]), a is the mean distance of approach of ions, $\phi(ka) = |e^{2ka} E_i(2ka)/(1 + ka)|$ has been tabulated by Harned and Owen [21], and the other letters represent well-known quantities [21]. In this equation, phenomena such as ion association and hydrolysis are not taken into consideration.

Comparing the estimated diffusion coefficients of $\text{Pb}(\text{NO}_3)_2$, D_{of} , with the related experimental values (Table 1), an increase in the experimental D values is

Table 6

Estimated percentage of hydrogen ions, α , resulting from the hydrolysis of Pb^{2+} in aqueous solutions of lead (II) nitrate at 298.15 K, using Eqs. (5) and (6)

$[\text{Pb}(\text{NO}_3)_2]/(\text{M})$	$\alpha/\%$
0.001	26.0
0.005	7.2
0.01	2.5
0.05	^a

^a For this concentration we can consider α as non-relevant.

found in lead(II) nitrate concentrations below 0.025 M. This can be explained not only by the initial $\text{Pb}(\text{NO}_3)_2$ gradient, but also by a further H_3O^+ flux, according to Eq. (1). Consequently, as H_3O^+ diffuses more rapidly than NO_3^- or Pb^{2+} , the lead(II) nitrate gradient generates ‘its own’ HNO_3 flux. Thus, the $\text{Pb}(\text{NO}_3)_2$ /water mixture should be considered a ternary system. However, in the present experimental conditions we may consider the system as pseudo-binary, mainly for $c \geq 0.01$ M. For $c < 0.01$ M, we can estimate the concentration of H_3O^+ produced by hydrolysis of $\text{Pb}(\text{II})$ using Eqs. (5) and (6) assuming that: (a) the fluxes of the species, HNO_3 and $\text{Pb}(\text{NO}_3)_2$, are independent; (b) the values of the diffusion coefficients, D_{of} , come from Eq. (3). The percentages of H_3O^+ (or the amount of acid that would be necessary to add to one solution of $\text{Pb}(\text{NO}_3)_2$ in the absence of hydrolysis, resulting in this way a simulation of a more real system) are estimated from the following equations

$$\alpha D_{\text{of}}(\text{HNO}_3) + \beta D_{\text{of}}(\text{Pb}(\text{NO}_3)_2) = D_{\text{av}} \quad (5)$$

$$\alpha + \beta = 1 \quad (6)$$

where $\alpha \times 100$ and $\beta \times 100$ are the percentages of nitric acid and lead nitrate, respectively. From Table 6 we can conclude that, for $c \geq 0.01$ M, α becomes very low, suggesting that either the hydrolysis effect or the contribution of $D_{\text{of}}(\text{HNO}_3)$ to the whole diffusion process, can be neglected.

Another limit situation occurs in the HNO_3 (0.01 M)– $\text{Pb}(\text{NO}_3)_2$ systems (Table 4). At 0.001 M $\text{Pb}(\text{NO}_3)_2$ the experimental interdiffusion coefficient is approximately the same as the diffusion coefficient of nitric acid in aqueous solution of 0.01 M concentration ($D = 3.013 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$); however, at 0.1 M

Table 5

Coefficients a_0 to a_4 of Eq. (2) for interdiffusion coefficients of $\text{Pb}(\text{NO}_3)_2$ at H_2O – HNO_3 mixtures, at 25 °C

$[\text{HNO}_3]/\text{M}$	a_0	a_1	a_2	a_3	a_4	R^2
0	2.33×10^{-9}	-2.14×10^{-8}	1.61×10^{-7}	-5.63×10^{-7}	7.32×10^{-7}	1.00
1×10^{-5}	2.22×10^{-9}	-1.23×10^{-8}	4.77×10^{-8}	-6.21×10^{-9}	–	0.99
1×10^{-3}	2.24×10^{-9}	-1.25×10^{-8}	5.25×10^{-8}	-7.47×10^{-8}	–	0.99
1×10^{-2}	3.49×10^{-9}	-8.97×10^{-9}	-8.45×10^{-8}	5.61×10^{-7}	-8.79×10^{-7}	0.98

$\text{Pb}(\text{NO}_3)_2$, D_{av} is very close to the interdiffusion coefficient of lead(II) nitrate in aqueous solution, for the same concentration (see Table 1). While in the first case the nitric acid is the species that controls the diffusion process, in the latter is the lead (II) nitrate. Having in mind these considerations, we can also use Eqs. (5) and (6) to estimate the percentages of nitric acid and lead nitrate, which are, in each concentration range, controlling the diffusion process (Table 7). For that, we took the experimental values of diffusion coefficients of lead nitrate in aqueous solutions (Table 1) due to limitations of the Onsager–Fuoss theory for $c > 0.01$ M [18,21].

From Tables 6 and 7, we may conclude that for $[\text{Pb}(\text{NO}_3)_2] \leq 0.01$ M the percentage of nitric acid responsible for contribution of the diffusion of lead nitrate in aqueous solutions at 0.01 M nitric acid, are the result of the sum of two contributions: the hydrolysis of lead nitrate and the added HNO_3 . For the other values of HNO_3 mixtures (0.001 M and 0.00001 M) the contribution of the percentage of nitric acid is very small and in some cases can even be neglected. For $[\text{Pb}(\text{NO}_3)_2] > 0.01$ M the percentage of nitric acid directly results from HNO_3 (see Table 8), being more relevant to 0.01 M. From the estimated values of α and β shown in Tables 6 and 7, we may conclude that the applicability of Eqs. (5) and (6) is only reliable at 0.005 M $< [\text{Pb}(\text{NO}_3)_2] < 0.1$ M.

Those estimations are in good agreement with other experimental results. UV-spectra of $\text{Pb}(\text{NO}_3)_2$ 0.001 M solutions at different nitric acid concentrations were obtained. The normalised absorbance, A , of Pb(II), at 300 nm, in a solution of HNO_3 0.01 M, is approximately five times higher ($A = 0.089$) than that found for Pb(II) solution without and with HNO_3 1×10^{-5} M ($A = 0.018$). When the nitric acid concentration increases to 1×10^{-4} M and 1×10^{-3} M only a slight absorbance increase is found, 0.021 and 0.026, respectively. This shows that only in $\text{HNO}_3 \times 10^{-2}$ M mixture the concentration of Pb(II) is closer to the initial concentration of $\text{Pb}(\text{NO}_3)_2$, and on these conditions the measured diffusion coefficient becomes close to the interdiffusion coefficient of lead(II) nitrate (without hydrolysis prod-

Table 8
pH values of $\text{Pb}(\text{NO}_3)_2$ aqueous solutions with different concentrations of HNO_3 at 25 °C

[$\text{Pb}(\text{NO}_3)_2$]/M	[HNO_3]/M			
	0	1×10^{-5}	1×10^{-3}	1×10^{-2}
0.001	5.11	4.95	3.11	2.22
0.005	4.78	4.71	3.04	2.08
0.010	4.67	4.63	3.01	2.03
0.025	4.58	4.59	2.98	1.99
0.050	4.47	4.56	2.95	1.97
0.075	4.44	4.53	2.93	1.94
0.10	4.41	4.49	2.91	1.94

ucts). However, comparing the fitting equations (Table 5) of the experimental results to the $\text{Pb}(\text{NO}_3)_2 + \text{HNO}_3$ (10^{-2} M) system, the limiting diffusion coefficient, D^0 , obtained by extrapolation of the mentioned fitting equation is significantly higher ($2.327 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) than the D^0 of $\text{Pb}(\text{NO}_3)_2$, which is $1.407 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. The Nernst limiting diffusion coefficient was computed from $D^0(\text{Pb}^{2+}) = 0.925 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ and $D^0(\text{NO}_3^-) = 1.903 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [18]. Although the hydrolysis can be neglected at such conditions, this cannot explain such D_{av} values. However, at the lowest Pb(II) concentrations and HNO_3 0.01 M, D_{av} values approach the diffusion coefficients of nitric acid in aqueous solution. This suggests that in these conditions, the hydrogen ions will have an important contribution to the measured diffusion coefficient. The analysis of the pH values in lead(II) nitrate fresh aqueous solutions, with different HNO_3 concentrations (Table 8), shows that the hydrogen ions change with Pb(II) concentration according to the following fitting equations: $[\text{H}_3\text{O}^+] = 5.358 \times 10^{-5} + 6.831 \times 10^{-6} \ln [\text{Pb}(\text{II})]$ ($R^2 = 0.988$), $[\text{H}_3\text{O}^+] = 4.123 \times 10^{-5} + 4.213 \times 10^{-5} \ln [\text{Pb}(\text{II})]$ ($R^2 = 0.983$), $[\text{H}_3\text{O}^+] = 1.414 \times 10^{-3} + 9.329 \times 10^{-5} \ln [\text{Pb}(\text{II})]$ ($R^2 = 0.989$), $[\text{H}_3\text{O}^+] = 1.453 \times 10^{-2} + 1.197 \times 10^{-3} \ln [\text{Pb}(\text{II})]$ ($R^2 = 0.989$), to mixtures of Pb(II) and HNO_3 at concentrations 0, 10^{-5} , 10^{-3} and 10^{-2} M, respectively.

Table 7

Estimated percentage of nitric acid, α , responsible for a further contribution to the diffusion of lead nitrate in aqueous solutions at different HNO_3 concentrations, using Eqs. (5) and (6)

[$\text{Pb}(\text{NO}_3)_2$]/M	$\alpha/\%$		
	[HNO_3] = 0.01 M	[HNO_3] = 0.001 M	[HNO_3] = 0.00001 M
0.001	~ 100	–	–
0.005	86.5	–	–
0.010	41.5	6.6	3.8
0.025	27.3	4.0	3.2
0.050	13.3	5.8	3.1
0.075	8.1	4.2	3.1
0.100	~ 0.0	~ 0.0	~ 0.0

From the experimental fitting equations (of $[H_3O^+]$ as a function of initial concentration of Pb(II)) described above, and from the open-ended conductimetric initial conditions, it is possible to conclude that in $HNO_3 \times 10^{-2}$ M mixtures, the hydrogen ions bulk concentration, at $[Pb(NO_3)_2] = 10^{-2}$ M, is approximately 6.26×10^{-3} M, whilst at $[Pb(NO_3)_2]$ equal to 0.01 M and 0.1 M that concentration increases to 9.10×10^{-3} and 1.18×10^{-2} M, respectively. However, it is clear that the ionic strength at the $Pb(NO_3)_2$ lowest concentration is controlled by the acid [18].

In the unbuffered $Pb(NO_3)_2$ solutions the hydrolysis can also be noted by the analysis of the pH values, but the contribution of the H_3O^+ for the whole diffusion process is not so significant as before: the hydrogen ion concentration changes from 6.39×10^{-6} ($[Pb(NO_3)_2] = 0.001$ M) to 3.78×10^{-5} M ($[Pb(NO_3)_2] = 0.1$ M). Although, in this case, only tracer H_3O^+ concentration gradients occur (1.9×10^{-6} to $[Pb(NO_3)_2] = 0.001$ M and 3.3×10^{-6} M to $[Pb(NO_3)_2] = 0.1$ M), they can be neglected in the $Pb(NO_3)_2$ highest concentrations, but justify the increase of D_{av0} when the $Pb(NO_3)_2$ concentration increases.

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