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Interaction between lactose and cadmium chloride in aqueous solutions as seen by diffusion coefficients measurements

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ABSTRACT

Diffusion coefficients of an aqueous system containing cadmium chloride 0.100 mol · dm^{-3} and lactose at different concentrations at 25 °C have been measured, using a conductimetric cell and an automatic apparatus to follow diffusion. The cell relies on 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. From these results and by *ab initio* calculations, it was possible to obtain a better understanding of the effect of lactose on transport of cadmium chloride in aqueous solutions.

1. Introduction

Lactose (disaccharide derived from the condensation of galactose and glucose, behaving as a typical non-electrolyte) is technologically a relevant compound and it is often used in medical, pharmaceutical, food and biological biomedical applications. The interactions of these compounds with metal ions are of major biological interest, having in mind that these systems play a dominant role in many biochemical interactions. Among them, we are particularly interested on systems containing this carbohydrate and cadmium ions, justified by the exposure of the population to these metal ions through different sources (*e.g.*, drinking water, food, excipients, and dental casting alloys) (*e.g.*, [1,2] and also, by their possible adverse effects on human health (*e.g.*, carcinogenic effects, toxic, and allergic ones) [3]. In fact, as a result of long-term exposure to cadmium in contaminated food and water (*e.g.*, from agricultural soils, where cadmium compounds are readily taken up by plants, and accumulated in edible parts due to their high solubility, and, consequently entering into the food chain), some research is on-going regarding the estrogen mimicry that may induce breast cancer [3,4]. However, the understanding of these complex systems has not yet been well established, and consequently, their characterization is very important, helping us to understand better their structure, and to model them for practical applications. While numerous studies have been carried out on the thermodynamic properties of aqueous lactose solutions (*e.g.*, [5,6]), few have taken into account the transport behaviour of these systems (*e.g.*, [7–9]). We have been particularly interested in data on these properties for chemical systems, particularly on the diffusion of the systems containing lactose and cadmium ion as cadmium chloride.

A few diffusion coefficients for binary aqueous systems containing lactose and cadmium, respectively, have been reported (*e.g.*, [9,10]) but, as far as the authors know, after careful literature search, no data on diffusion coefficients are available in literature for systems containing cadmium salts and lactose at $t = 25$ °C.

Thus, we have measured the diffusion (interdiffusion) coefficients D, for aqueous solutions of cadmium chloride 0.100 mol · dm^{-3} plus lactose in the concentration range from (0.005 to 0.200) mol · dm^{-3}, using the open-ended conductimetric capillary cell, at $t = 25$ °C.

To better understand the structure of the chemical species formed and the main biochemical mechanisms involved, we have complemented these studies using *ab initio* calculations.

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2. Experimental

2.1. Materials

The solutes used in this study were lactose monohydrate and cadmium chloride (table 1). They were used as received without further purification. The solutions for the diffusion measurements were prepared in calibrated volumetric flasks using bi-distilled water. The solutions (concentration in molarity) were freshly prepared and de-aerated for about 30 min before each set of runs.

2.2. Mutual diffusion coefficients, D, measured by the open-ended conductimetric capillary cell

The open-ended capillary cell, which has been used to obtain mutual diffusion coefficients for a wide variety of electrolytes (*e.g.*, [11–14]) is described in great detail in paper [13]. 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 about 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 bath 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, that is, the physical length of the capillary tube coincides with the diffusion path. This means that the required boundary conditions described in the literature [13] to solve Fick's second law of diffusion are applicable. Therefore, the so-called Δl effect [13] is reduced to negligible proportions. In our automatic 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 a Solartron digital voltmeter (DVM) 7061 with 6 1/2 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 in 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 molarity is prepared by mixing 1 dm^3 of "top" solution with 1 dm^3 of "bottom" solution, accurately measured. 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 various 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 is applied 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 previously [13].

TABLE 1
Provenance and purity of the materials studied.

Chemical name	Source	Mass fraction purity
Cadmium chloride	Merck	>0.970
Lactose monohydrate	BDH	>0.970

2.3. Methods: ab initio studies

Calculations were performed in a HP Z620 workstation using the HyperChemv7.5 software package from Hypercube Inc., 2000, USA. The geometry optimization used a Polak-Ribiere conjugated gradient algorithm for energy minimization in vacuum, with a final gradient of 4.18 $kJ \cdot nm^{-1} \cdot mol^{-1}$. The potential surfaces were calculated after an *ab initio* geometry minimization using a RHF method with a small (3-21G) basis set.

3. Results and discussion

3.1. Measurements of diffusion coefficients

Diffusion coefficients, D, and their respective standard deviations, S_D, of $CdCl_2$ 0.100 $mol \cdot dm^{-3}$ in aqueous solutions of lactose (0.005 $mol \cdot dm^{-3}$, 0.010 $mol \cdot dm^{-3}$, 0.025 $mol \cdot dm^{-3}$, 0.050 $mol \cdot dm^{-3}$, 0.100 $mol \cdot dm^{-3}$ and 0.200 $mol \cdot dm^{-3}$) at 25 °C are shown in table 2 and figure 1. For brevity, we will indicate as 1 and 2 (not including the solvent, component 0), the lactose and $CdCl_2$ species, respectively. D is the mean value of, at least, three independent measurements, and the error limits of our results should be close to the imprecision, therefore giving an experimental uncertainty of (1 to 3) percent.

The following polynomial in $c_1^{1/2}$ was used to fit our data by a least squares procedure (table 2),

$$D/(10^{-9}\ m^2 \cdot s^{-1}) = 0.892 + 0.991\,c_1^{1/2} - 5.426\,c_1, \quad R^2 = 0.999, \tag{1}$$

where c_1 and D represent the molarity concentration of lactose and the diffusion coefficients of cadmium chloride in different aqueous solutions containing this carbohydrate, respectively. The goodness of the fit (obtained with a confidence interval of 98%) was assessed by the excellent correlation coefficient, R^2, and the low standard deviation (<1%). Moreover, the deviation between the limiting D^0 value calculated by extrapolating experimental results to $c_1 \rightarrow 0$ ($D^0 = 0.892 \cdot 10^{-9}\ m^2 \cdot s^{-1}$) and the measured D value for solutions containing only $CdCl_2$ for $c = 0.100\ mol \cdot dm^{-3}$ ($D = 0.902 \cdot 10^{-9}\ m^2 \cdot s^{-1}$) is also acceptable (−1.1%).

From our results (table 2), we can verify that the diffusion behaviour of cadmium chloride in aqueous solutions at 25 °C is affected by the presence of the lactose molecules. In fact, under the present experimental conditions, the decrease of the diffusion

TABLE 2
Experimental diffusion coefficients, D, of systems containing lactose, c_1, and cadmium chloride ($c_2 = 0.100\ mol \cdot dm^{-3}$) at 25 °C.[a]

$c_1/(mol \cdot dm^{-3})$[b]	$D \pm S_D/10^{-9}\ m^2 \cdot s^{-1}$[c]	$(\Delta D/D)/(\%)$[d]
0.200	0.274 ± 0.022	−69.6
0.100	0.669 ± 0.015	−25.8
0.050	0.847 ± 0.010	−6.1
0.025	0.915 ± 0.010	+1.4
0.010	0.931 ± 0.015	+3.2
0.005	0.924 ± 0.010	+2.4
0.000	0.902 ± 0.028[e]	0.0

[a] $u(T) = 0.01$ K.
[b] $u(c) = 0.001\ mol \cdot dm^{-3}$.
[c] D is the mean diffusion coefficient of three experiments and S_D is the standard deviation of that mean.
[d] $(\Delta D/D)/\%$ represent the deviation between the diffusion coefficients of system (Lactose + $CdCl_2$ + H_2O) and the diffusion coefficients, D, of system ($CdCl_2$ + H_2O) [9].
[e] Experimental value of the diffusion coefficient of aqueous solutions of cadmium chloride at $c_2 = 0.100\ mol \cdot dm^{-3}$ for $c_1 = 0$ [9].