Concentration-dependent diffusion of lithium, sodium, potassium, and cesium hydroxides in water

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Abstract. The diffusion coefficients of aqueous solutions of lithium, sodium, potassium, and cesium hydroxide in a concentration range of 0 to 3.0 mol/L were obtained at 25 °C and normal pressure. The Fizeau interferometer and the spatial phase-shifting method were used to measure the spatial distribution of concentration of the investigated substances. The concentration dependence of the diffusion coefficient was determined from the Matano–Boltzmann analysis. The experimental setup and techniques, as well as the image and data processing procedure, were tested using an aqueous solution of nitric acid. The comparison made for lithium, sodium, and potassium hydroxides indicated good agreement between the obtained results and the data collected from the literature. The concentration dependence of the diffusion coefficient for cesium hydroxide in water was found experimentally for the first time.

1. Introduction

Diffusion is usually considered in physics as a dissipative process leading to spontaneous equalization of concentration throughout the volume. However, in hydrodynamics, there are situations when diffusion in multicomponent solutions can lead to the development of instability and the formation of convective structures even in an initially stable liquid system. This was first discovered in oceanology, where different rates of diffusion of heat and salt can lead to disruption of the initially stable stratification of the density of sea water and the emergence of convective motion [1]. This type of hydrodynamic instability was called the instability of double (or differential) diffusion. It was later discovered that this phenomenon is the main mechanism responsible for the development of convective motion in chemically reacting liquid [2]. In particular, the stability of a two-layer system in the presence of a frontal neutralization reaction was studied in [3]. It was shown that the results of numerical calculations are consistent with the results of experimental observations only when the concentration dependence of the diffusion coefficient of both the reactants and the reaction product is taken into account in the theoretical model. Unlike acids and salts, measurements of the diffusion coefficient of alkaline metal hydroxides in aqueous solutions are surprisingly rare. Most of the available measurements have dealt with either diluted solutions or have been performed in narrow concentration ranges [4-9]. No data on the diffusion coefficient of cesium hydroxide can be found in the
literature. The absence of the data needed to study the chemo-hydrodynamic problem motivated us to make measurements ourselves.

In this paper, we present the results of measurements of the diffusion coefficient in the aqueous solutions of lithium, sodium, potassium, and cesium hydroxides in a concentration range of 0 to 3.0 mol/L at 25 °C and normal pressure. Digital interferometry (Fizeau scheme) was used to visualize and measure the temporal evolution of the spatial concentration distribution, and the Matano–Boltzmann (MB) analysis was applied to calculate a concentration dependence of the diffusion coefficient. To test the experimental setup and techniques, as well as the image and data processing procedure, we measured the concentration dependence of the nitric acid diffusion coefficient in water for which data are available in the literature. The results obtained for the alkali metal hydroxides are also compared, where is it possible, with the results of other researchers.

2. Experimental section

2.1. Materials and experimental setup

All chemicals used in this research were analytical grade or better (Merck, Germany) and applied without further purification. The solutions in bi-distilled water were prepared by weighing each component using electronic balances (accuracy 0.01 g). The final concentration of each solution was checked before the experiment by measuring its density and by comparing it with the available density data [10].

The diffusion cell (Fig. 1a) was formed by two glass plates. The plates are separated by a thin glass spacer of 0.132 cm thickness, which assigned the form and inner size of the diffusion cell, width 1.0 cm and height 3.5 cm. To form an initial two-layer system with a sharp transition zone, the “counter flow” technique was applied. This method was first described in [11] and later successfully used in a series of diffusion measurement experiments [12]. First, the cell was filled with water and then the water and an aqueous solution of one of the studied substances were pumped through the inflow ports (positions 1 and 2 in Fig. 1a) located on the upper and lower boundaries of the cell, respectively. The liquid from the transition zone was drained from the cell through two outflow ports (positions 3 and 4 in Fig. 1a). The diffusion cell had rounded corners to avoid the formation of stagnant zones for flow during pumping the liquids. After a thin transition zone corresponding to the vertical concentration distribution close to a step-wise one was formed, the inflow and the outflow ports were closed and the experiment started. The initial step-wise concentration profile is necessary since the experimental concentration profile is compared to an analytical solution, based on Fick's law, in which the initial profile is a step function by default. The initial thickness of the transition zone was approximately 0.03 cm. All experiments were performed at (25.0±0.1) °C. The temperature distribution in the cell was controlled with three thermocouples the location of which is indicated in Fig. 1a.

To visualize and measure the spatial concentration distribution, the interferometric scheme shown in Fig. 1b was applied. The He-Ne laser with a wavelength of $\lambda = 632.8$ nm was used as a light source. The diffusion cell was placed between two plane-parallel glass plates of interference quality which formed the measuring cell of the Fizeau interferometer assembled according to an autocollimation scheme. The interference pattern in reflected light was observed by a CCD camera (IDS UI-3250ML-C-HQ) with a 1600×1200 pixels sensor.
Figure 1. Experimental setup. (a) Sketch of the diffusion cell. 1, 2 – inflow ports; 3, 4 – outflow ports. The points A, B, and C indicate the location of thermocouples. (b) Scheme of the optical part: 1–He-Ne laser, 2, 4 – glass plates forming the measuring cell of the Fizeau interferometer, 3 – diffusion cell, 5 – CCD camera.

The duration of the experiment was defined by two factors. On the one hand, the interference fringes should be resolvable by a camera sensor. On the other hand, the diffusion front should be far enough from the upper and lower boundaries of the cell to have the liquid areas with initial concentration. On average, a typical experiment run lasted approximately one hour. The same factors defined the upper limit of the concentration difference between the layers, which can be applied in the experiments under fixed cell’s thickness. For all substances considered in this paper, the concentration range up to 3.0 mol/L interested for us was available, except the cesium hydroxide the aqueous solution of which has the maximal refractive index. For this substance, measurements were made for two concentration ranges: (0-1.50) mol/L and (1.50-3.00) mol/L.

2.2. Image processing
To extract information on the refractive index distribution caused by concentration inhomogeneities, the spatial phase-shifting method was applied. The glass plates of the measuring cell were positioned at a small (near 0.3 degree) angle in such a way that the interference pattern was observed on the fringes of constant thickness. All image processing steps were realized with the help of IntelliWave software (Mahr GmbH, Germany). An example of interference patterns obtained for cesium hydroxide at the beginning of the experiment (Fig. 2a) and at two different moments of time after the experiment run starts (Figure 2a and 2b) is presented in Figure 2. It is clearly visible that the initially sharp transition zone between the layers widens with time. The next three pictures in Fig. 2 demonstrate the wrapped phase difference at the same time moments as in the interferograms. It is seen that the constant phase fringes are not horizontal oriented as it would be expected. This can be attributed to small deviations of the diffusion cell shape from the ideal plane-parallel geometry. Modern digital interferometry techniques are able to take into account these distortions. To this end, the interference pattern corresponding to the cell completely filled with water and containing information only about the inhomogeneities of the cell thickness was used as a reference image.

Figure 3 illustrates the main steps of image processing by the example of the analysis of the interferogram obtained for nitric acid. The first two frames (Fig. 3a and 3b) demonstrate the interference pattern and the wrapped phase difference for a certain experiment. The third frame (Fig. 3c) is the wrapped phase difference for the reference image. The fourth frame (Fig. 3d) demonstrates the optical path difference (OPD) field obtained after subtracting the OPD corresponding to the reference image. It is seen that there is almost no dependence on the transverse coordinate that allows using any vertical cross-section of this 2D dependence for calculation of the refractive index distribution \( n(y) \) and then the concentration-distance curve \( C(y) \) using the dependence of the refractive index on the concentration \( n(C) \). The dependencies for NaOH,
KOH, and HNO₃ were taken from [13]. The data for LiOH and CsOH were measured by us using a refractometer IRF-454B (Kazan Optical-Mechanical Plant, Russia). The obtained data was approximated by a quadratic polynomial \( n(C) = n_0 + AC + BC^2 \), where \( n_0 \) is the refractive index of water. The values of coefficients \( A \) and \( B \) are given in Table 2. For the nitric acid, the refractive index of which linearly depends on the concentration with good accuracy, the \( n(y) \) dependence can be easily converted into \( C(y) \) as:

\[
C(y) = \frac{C_{\text{max}}}{\Delta n_{\text{max}}} n(y),
\]

where \( \Delta n_{\text{max}} \) is the maximal refractive index difference corresponding to the maximal concentration difference \( C_{\text{max}} \) in the experiment. For other substances, the nonlinearity of the \( n(C) \) dependence was taken into account (see Table 2), although it is worth to note that the correction in the diffusion coefficient value caused by taking into account the quadratic term in the \( n(C) \) dependence is rather small. The exclusion is the cesium hydroxide, where the nonlinearity is larger, but because the measurements with this substance were made in two concentration ranges, as noted above, the correction in the diffusion coefficient value also turns out to be small.

**Figure 2.** Interference patterns and wrapped phase difference obtained for CsOH at different moments of time after the experiment run starts \( t \), min: (a) and (d) 0, (b) and (e) 47 min, (c) and (f) 77 min. The width of each image is 0.2 cm.

**Figure 3.** Main steps of image processing by the example of the analysis of the interferogram obtained for HNO₃ at \( t = 70 \) min: (a) interference pattern, (b) wrapped phase difference, (c) wrapped phase difference for the reference image, obtained for the cell filled with water, (d) OPD field obtained after subtracting the OPD corresponding to the reference image, (e) OPD field after approximation by a tenth-degree polynomial. The image width is 0.35 cm.
Table 1. Parameters for approximation of the dependence of the refractive index on the concentration by the quadratic polynomial \( n(C) = n_0 + AC + BC^2 \). The refractive index of water is \( n_0 = 1.333 \).

| Chemical | A, L/mol | B, L^2/mol^2 |
|----------|----------|--------------|
| HNO\(_3\) | 0.00801  | -            |
| LiOH     | 0.01042  | -0.00048     |
| NaOH     | 0.01065  | -0.00037     |
| KOH      | 0.01049  | -0.00036     |
| CsOH     | 0.01715  | -0.00134     |

\( ^1 \) Data taken from [13]. \(^2 \) Our measurements.

The example of the \( C(y) \) dependency for nitric acid which was calculated from the OPD map shown in Figure 3 is presented in Figure 4a. The parts of the dependency located near the upper and lower boundaries of the cell where the concentration remained constant and equal to the initial one in the layers are not shown in the graph. Although the interferometric method is a good tool for accurate concentration measurement, a certain data scatter is clearly visible, which becomes still more evident for the concentration derivative dependence (Fig. 4b). This is mainly caused by local inhomogeneities in the light beam intensity, which results in the data scatter on the OPD map, clearly visible in Figure 3d. Since the MB method suggests numerical differentiation and integration of the concentration-distance dependence, the experimental data scatter may cause a great error to occur in the concentration dependence of the diffusion \( D(C) \). To avoid this, the OPD maps obtained experimentally were approximated by a tenth-degree polynomial (Fig. 3e and the corresponding inset). A cross-section of the two-dimensional function obtained in such a way (red solid lines in Fig. 4) was used to calculate the \( D(C) \) dependency. The experiment with each substance was repeated 5 times to estimate an experimental error.

![Figure 4](image)

**Figure 4.** Concentration-distance curve (a) and its derivative (b) for the aqueous solution of nitric acid calculated from the OPD map shown in Fig. 3d. Red lines indicate the results calculated from the OPD map obtained after the approximation of the experimental results by a tenth-degree polynomial (see Fig. 3e and the corresponding inset). A cross-section of the two-dimensional function obtained in such a way (red solid lines in Fig. 4) was used to calculate the \( D(C) \) dependency. The experiment with each substance was repeated 5 times to estimate an experimental error.

2.3. Data processing

To calculate the concentration dependence of the diffusion coefficient from the concentration-distance curve \( C(y) \) obtained experimentally, the MB analysis [14] was used. In case of one-dimensional diffusion, the diffusion coefficient at any concentration \( C_i \) can be found as follows:
where $t$ is the diffusion time. In Eq. (1), the coordinate $y$ is counted from the Matano interface whose position is chosen so that the mass fluxes passing through it to the left and the right are equal. Graphically it means that the areas under the curve $C(y)$, which are located to the left and to the right from the Matano interface, are equal. Since the diffusion coefficient is a concentration function, the position of the Matano interface does not coincide with the position of the initial contact line between the liquid layers, and it should be calculated from the following condition:

$$
\int_0^{C_c} y \, dC = 0,
$$

where $C_c$ is the initial concentration of a studied substance. Since the calculation of the diffusion coefficient by this method suggests numerical differentiation and integration of the experimentally obtained concentration-distance dependence, the resulting accuracy turns out to be very sensitive to the experimental data scatter. The accuracy can be enhanced through the replacement of the experimental data on the approximation function during calculations.

Figure 5. Concentration dependence of the diffusion coefficient of (a) nitric acid in water at 25°C. Black symbols present our result, with error bars representing the uncertainty; White squares and triangles represent results of [15] and [8] respectively; (b) alkali metal hydroxides in water at 25 °C. Symbols: diamonds, squares, circles, triangles represent results for LiOH, NaOH, KOH, and CsOH, respectively. Open symbols with black borders and error bars represent our measurements; black symbols indicate values for diluted solutions [13]; all other symbols are results obtained for concentrated solutions by other researchers.
3. Results and Discussion

To verify the efficiency of the developed experimental techniques and data processing methods, the diffusion of nitric acid in aqueous solution in the concentration range 0 to 3.0 mol/L was measured and the obtained data were compared with those available in the literature. The results are presented in Fig. 5a. It is seen that the error in measuring the diffusion coefficient grows as we approach the boundaries of the concentration range, which is due to an increase in the noise-signal ratio, as well as an increase in the error in approximating the data near the limiting concentration values. The measurements demonstrate good agreement with the results obtained by other researchers [8, 15]: the discrepancies do not exceed 2% within the concentration range studied.

The concentration dependence of the diffusion coefficient for the aqueous solutions of lithium, sodium, potassium, and cesium hydroxides in the concentration range 0 to 3.0 mol/L is given in Fig. 5b. Additionally, the data obtained by other researchers are shown in Fig. 5b for comparison. For lithium hydroxide solutions, the diffusion coefficient was previously measured only in the range of low concentrations [4], and these data cohere well with our results in this region. For sodium hydroxide, there is more data to compare [4, 7]. In the region of low concentrations, the results of all measurements are in good agreement with our results. As the concentration increases, there is a little divergence with our measurements, but the maximum difference at a concentration of 2.0 mol/L does not exceed 2%. The largest amount of data for comparison is available for potassium hydroxide solutions [4, 6, 9]. The difference between our results and those of other authors does not exceed 1% in the entire comparison range. As regards to the cesium hydroxide solution, there are no available data in the literature. The only point for comparison is the diffusion coefficient which can be calculated for the infinite diluted solution [13]. It is seen from Fig. 5b that the data obtained by us are well extrapolated to this value in the range of small concentrations. It is interesting here to note the differences in concentration dependencies obtained for different alkali metals. In the region of low concentrations, up to approximately 0.1 mol/L, the diffusion coefficient sharply decreases with the increase of concentration for all solutions studied. At higher concentrations, a rate of curves becomes differing: from descending dependence specific for lithium and sodium hydroxides to ascending one for potassium and cesium hydroxides. In this concentration range, all the dependencies can be well described by a linear dependence, but with a different sign of the coefficient in the linear term.

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References

1. Turner J S 1979 Buoyancy Effects in Fluids (Cambridge university press, New York) p 368
2. Almarcha C, Trevelyan P M J, Grosfils P, and De Wit A 2010 Chemically driven hydrodynamic instabilities Phys. Rev. Lett. 104 044501
3. Bratsun D, Kostarev K, Mizev A, and Mosheva E 2015 Concentration-dependent diffusion instability in reactive miscible fluids Phys. Rev. E 92 011003
4. Noulty R A and Leaist D G 1984 Activity coefficients and diffusion coefficients of dilute aqueous solutions of lithium, sodium, and potassium hydroxides J. Solution Chem. 13 767–778
5. Cooper J F, Hosmer P K and Homsy R V 1978 The anodic behavior of lithium in aqueous lithium hydroxide solutions J. Electrochem. Soc. 125 1–7
6. Bhatia R N, Gubbins K E, and Walker R D 1968 Mutual diffusion in concentrated aqueous potassium hydroxide solutions Trans. Faraday Soc. 64 2091–2099
7. Fary D A 1966 The Diffusional Properties of Sodium Hydroxide, Ph. d thesis (The Institute of Paper Chemistry, Appleton, Wisconsin)
8. Chapman T W 1967 *The Transport Properties of Concentrated Electrolytic Solutions* Ph. d. thesis (University of California)

9. See D M and White R E, 1998 Diaphragm cell measurement of mutual diffusion coefficients for potassium hydroxide in water from 1 °C to 25 °C *J. Chem. Eng. Data* **43** 986–988

10. Nikolsky B N 1965 *Spravochnik Khimika (Chemist's Handbook)* Vol. 3 2nd ed. (Khimiya Publishing House, Moscow)

11. Pringle S E, Glass R J and Cooper C A 2002 Double-diffusive finger convection in a Hele–Shaw cell: an experiment exploring the evolution of concentration fields, length scales and mass transfer *Transp. Porous Media* **47** 195–214

12. Komiya A and Maruyama S 2006 Precise and short-time measurement method of mass diffusion coefficients *Exp. Therm. Fluid Sci.* **30** 535–543

13. Haynes W M 2005 *Handbook of Chemistry and Physics. Internet Version* (CRC press)

14. Crank J 1979 *The Mathematics of Diffusion* (Oxford university press) p 414

15. Nisancioglu K and Newman J 1973 Diffusion in aqueous nitric acid solutions *AIChe J.* **19** 797–801