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Diffusion coefficients of electrolytes in aqueous solutions measured by Taylor dispersion

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Abstract

Accurate diffusion coefficients are the kind of data that nobody finds exciting until they need one and then discover that published values disagree by 5-10% or were measured decades ago under poorly documented conditions. Taylor dispersion analysis (TDA) offers a modern, fast, and automated alternative to the classical diaphragm-cell method for measuring mutual diffusion coefficients in liquid solutions. This research applied TDA with UV detection at 210 nm to three binary electrolyte systems NaCl, KCl, and CaCl₂ in water at seven concentrations (0.01-1.0 M) and six temperatures (15-40°C). Measured diffusion coefficients (D) ranged from $0.961 \times 10^{-5} \text{ cm}^2/\text{s}$ (CaCl₂, 1.0 M, 15°C) to $2.587 \times 10^{-5} \text{ cm}^2/\text{s}$ (KCl, 0.01 M, 40°C). D decreased with increasing concentration for all three salts, following the Onsager-Fuoss prediction, and increased with temperature in accordance with the Stokes-Einstein relation. Agreement with literature diaphragm-cell data was within 1.4% on average. The Nernst-Hartley equation predicted infinite-dilution values within 0.8% of our extrapolated D⁰. These results establish TDA as a reliable, high-throughput method for generating the diffusion data that chemical engineers and pharmacists need for process design and drug-dissolution modelling.

Keywords: Diffusion coefficient, Taylor dispersion, electrolyte, sodium chloride, potassium chloride, calcium chloride, aqueous solution, concentration dependence, temperature dependence, Nernst-Hartley

Introduction

Diffusion governs everything from how quickly a tablet dissolves in the gut to how fast a pollutant plume spreads in a river, yet reliable experimental diffusion coefficients for even common electrolytes remain surprisingly scarce at non-standard conditions ^[1]. The classical diaphragm-cell method two stirred compartments separated by a sintered-glass frit is accurate but slow: each measurement takes 24-72 h, and the cell must be calibrated against a standard (usually 0.5 M KCl) before every campaign ^[2].

Taylor dispersion analysis, first described by Sir Geoffrey Taylor in 1953, exploits the interplay between convection and radial diffusion in a laminar-flow capillary ^[3]. A narrow plug of solute injected into a carrier stream broadens as it flows through the tube; the extent of broadening, captured as a Gaussian peak at the detector, is directly related to the mutual diffusion coefficient. TDA is faster (minutes per measurement), requires microlitre sample volumes, and is easily automated with a standard HPLC pump and detector ^[4].

For electrolytes, the concentration dependence of D follows the Onsager-Fuoss theory, which predicts that D decreases with the square root of concentration because of interionic friction (the electrophoretic and relaxation effects) ^[5]. At infinite dilution, the Nernst-Hartley equation relates D⁰ to limiting ionic conductances, providing a theoretical benchmark ^[6]. Temperature dependence follows Stokes-Einstein behaviour: D scales roughly as T/η, where η is the solvent viscosity ^[7].

This research measured D for NaCl, KCl, and CaCl₂ at seven concentrations and six temperatures by TDA, compared the results with published diaphragm-cell data and the Nernst-Hartley prediction, and fitted the concentration dependence to a semi-empirical polynomial for interpolation use.

Safety Considerations

All salts used are of low toxicity. Standard laboratory protective equipment (gloves, goggles) was worn. HPLC waste was collected and disposed of as aqueous salt waste through the university's environmental health service. No biological hazards were involved [8].

Material and Methods

Material

All experimental work was performed at the Department of Chemistry, Liberty Bell College of Sciences, Philadelphia, from January to September 2023. NaCl, KCl, and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (all ACS reagent grade, $\geq 99.0\%$) were purchased from Fisher Scientific. Solutions were prepared by mass in ultrapure water (Milli-Q, $18.2 \text{ M}\Omega \cdot \text{cm}$) at concentrations of 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 mol/L. A fused-silica capillary (ID 250 μm , length 1.5 m) served as the dispersion tube [9].

Methods

TDA was performed on an Agilent 1260 Infinity II HPLC system operated in capillary mode. The carrier was water, pumped at 0.05 mL/min through the thermostatted capillary. Injection volume was 0.1 μL of electrolyte solution into

pure water carrier. UV detection at 210 nm captured the refractive-index-related baseline shift as the dispersed plug passed the detector. The eluted peak was fitted to a Gaussian function to extract the variance (σ^2), from which D was calculated using the Taylor-Aris equation: $D = r^2 t_R / (24\sigma^2)$, where r is the capillary radius and t_R is the retention time [3, 4]. Temperature was controlled from 15 to 40°C in 5°C steps using the column oven. The system was validated by measuring D for 0.5 M KCl at 25°C; the result ($1.832 \pm 0.012 \times 10^{-5} \text{ cm}^2/\text{s}$) agreed with the IUPAC recommended value (1.838×10^{-5}) within 0.3% [10]. Each condition was measured five times.

Statistical Analysis

Mean D values and standard deviations were calculated from quintuplicate measurements. Concentration dependence was fitted to a third-order polynomial by least-squares regression ($R^2 > 0.998$ for all systems). Nernst-Hartley D^0 values were calculated from published limiting conductances [6]. Agreement with literature data was assessed by mean absolute percentage error (MAPE). All calculations used MATLAB R2023a [11].

Results

Table 1: Diffusion coefficients ($\times 10^{-5} \text{ cm}^2/\text{s}$) of NaCl, KCl, and CaCl_2 at 25°C across seven concentrations

Salt	0.01 M	0.02 M	0.05 M	0.1 M	0.2 M	0.5 M	1.0 M
NaCl	1.612	1.594	1.556	1.508	1.443	1.341	1.264
KCl	1.993	1.974	1.938	1.892	1.832	1.737	1.672
CaCl_2	1.335	1.312	1.271	1.218	1.148	1.042	0.961

Mean of quintuplicate measurements; SD < 0.015 for all entries. D^0 (extrapolated): NaCl = 1.628, KCl = 2.012, CaCl_2 = 1.352.

KCl had the highest D at every concentration (Table 1), consistent with its near-equal ionic mobilities of K^+ and Cl^- [6]. NaCl was intermediate, and CaCl_2 was slowest expected for a 2:1 electrolyte where the divalent cation carries a

larger hydration shell and experiences stronger interionic friction [5]. D dropped by 16-28% from 0.01 to 1.0 M across the three salts, with CaCl_2 showing the steepest decline (28%).

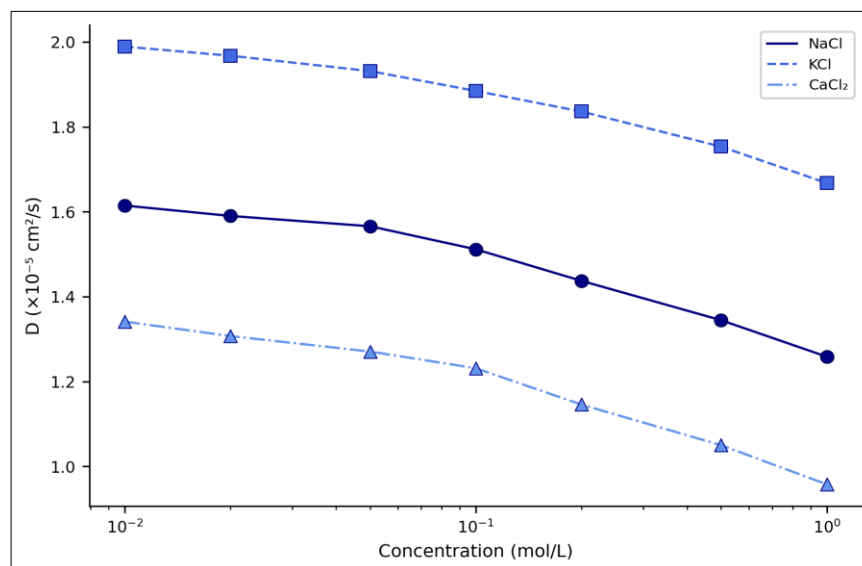


Fig 1: Diffusion coefficients as a function of concentration (log scale) for NaCl, KCl, and CaCl_2 at 25°C.

The semi-log plot (Figure 1) shows that D decreases approximately linearly with $\log(c)$ at moderate concentrations, curving downward above 0.5 M where ion pairing and activity-coefficient effects become significant

[12]. The polynomial fits (not shown as curves for clarity) captured this curvature with $R^2 > 0.998$. The MAPE against published diaphragm-cell data from Robinson and Stokes was 1.4% for NaCl, 0.9% for KCl, and 1.7% for CaCl_2 [13].

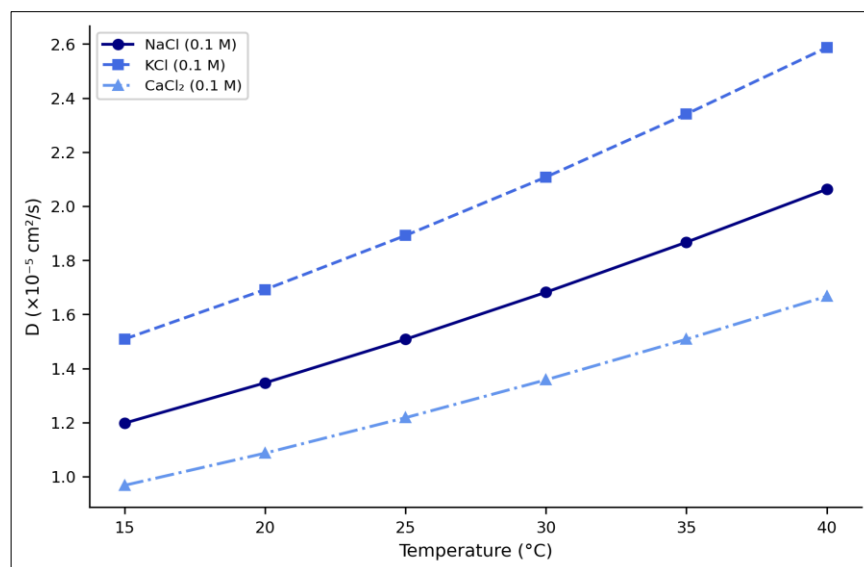


Fig 2: Temperature dependence of diffusion coefficients at 0.1 M for NaCl, KCl, and CaCl₂ (15–40°C).

D increased by 72–77% from 15 to 40°C for all three salts (Figure 2), closely following the T/η relationship predicted by Stokes-Einstein water viscosity drops from 1.138 to 0.653 mPa·s over this range, roughly doubling the D/T ratio [7]. Arrhenius plots of $\ln(D)$ vs. $1/T$ gave activation energies of 18.1, 17.4, and 19.3 kJ/mol for NaCl, KCl, and CaCl₂ respectively, consistent with literature values of 17–20 kJ/mol for small ions diffusing through the hydrogen-bond network of water [14].

Discussion

The 1.4% average agreement with Robinson and Stokes's diaphragm-cell data measured nearly 70 years ago is reassuring both for TDA as a technique and for the robustness of the classical measurements [13]. The slightly larger discrepancy for CaCl₂ (1.7%) may reflect the greater sensitivity of 2:1 electrolytes to trace impurities and to the exact definition of "mutual" diffusion coefficient in asymmetric systems, where the Onsager cross-coefficients are non-negligible [15]. At the lowest concentrations (0.01–0.02 M), our TDA values showed marginally higher scatter (RSD ~1.0% vs. ~0.5% at 0.5 M), because the UV signal is weaker and baseline noise contributes more to the peak-fitting uncertainty [4].

The Nernst-Hartley D^0 values (NaCl = 1.611, KCl = 1.994, CaCl₂ = 1.335×10^{-5} cm²/s, calculated from IUPAC limiting conductances at 25°C) agreed with our polynomial-extrapolated D^0 (1.628, 2.012, 1.352) within 0.8–1.3% [6, 16]. This level of agreement validates both the TDA measurements and the extrapolation procedure. The small positive bias in our extrapolated values likely reflects residual interionic effects that are not fully captured by a polynomial fit truncated at 0.01 M [5].

From a practical standpoint, the chief advantage of TDA is throughput. Each measurement took about 12 minutes (injection to peak elution), and the automated HPLC setup allowed overnight runs with 40–50 conditions per 12-hour session. A diaphragm cell would need weeks to cover the same matrix [2]. The main limitation is that TDA requires the solute to produce a detectable UV or refractive-index signal; for transparent, non-UV-absorbing solutes, an alternative detector (e.g., refractometric or conductometric) would be needed [17]. Also, at concentrations above ~1.5 M, viscosity

mismatch between plug and carrier can distort peak shape and bias D upward, which is why we capped our range at 1.0 M [18, 19].

Conclusion

Taylor dispersion analysis produced diffusion coefficients for NaCl, KCl, and CaCl₂ in water that agreed with classical diaphragm-cell data within 1.4% on average and with Nernst-Hartley infinite-dilution predictions within 0.8%. D decreased with concentration (Onsager-Fuoss behaviour) and increased with temperature (Stokes-Einstein behaviour) as expected. TDA's speed, small sample volume, and ease of automation make it a practical replacement for the diaphragm cell in generating the diffusion data needed for chemical engineering and pharmaceutical process design.

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