

Novel Diffusimeter for Turbulent Super Diffusion of Electrolytes with Relative Rates Proportional to Respective Molar Mass Square Root

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ABSTRACT: The U-tube like diffusimeter with straightway stopcock at each end lets MCl(aq) (M = H, Li, Na, K, and Rb) and AgNO₃(aq) reactant pairs diffuse towards each other through water to produce white AgCl(s) as indicator at the intersection. High concentration gradient at each solution-solvent interface of the diffusimeter generates mild, turbulent diffusion-convection that gives rise to super diffusion with rates about 10² times higher than normal liquid diffusion and an apparent rate law, $V_{\infty} \sqrt{M}$ contradicting $V_{\infty} \sqrt{\frac{1}{M}}$ for gases. The heavier electrolyte in the diffusimeter travels faster. Distance travelled ratio (DTR) of a reactant pair and their molar mass ratio square root (MMRSR) taken in order are closely equal. Rate versus concentration plots for MCl-AgNO₃ pairs follow Fickian trend. The MCl or AgNO₃ do not show to carry any coordinated H₂O.

Keywords: Convection, Turbulent diffusion, Mass transfer, Diffusimeter

INTRODUCTION

Diffusion processes being collision hindered are very slow having rates of the order of 5, 0.05, and 10⁻⁵ cm min⁻¹ for gases, liquids, and solids respectively. Translational velocities of gases are in the range of hundred of meters per second. Diffusion of electrolytes is a case of mass transfer. Maxwell stated, “Mass transfer is due partly to the motion of translation and partly to that of agitation” [1]. We have developed a glass apparatus we termed Diffusimeter to determine relative diffusion rates of electrolytes in liquids. Diffusion of solutes in the confine of the diffusimeter generated reverse solvent convection. In the experimental setup high rates of diffusion as the consequence of big concentration gradient at the stopcock positions generated mild turbulence above and below those and the mass transport process turned exceedingly fast.

Gases follow the diffusion law, $V_{\infty} \sqrt{\frac{1}{M}}$ in which M is the molar mass. Fick’s First Law [2] states, $dm = -DA \frac{dc}{dx} dt$, where D (cm²s⁻¹) is the diffusion coefficient, dm is the amount of solute diffusing in the x direction across an area A in a time dt and is proportional to the concentration gradient $\frac{dc}{dx}$. Fick’s Second Law [2] states how diffusion causes with time the concentration field to change as in $\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$. Diffusion coefficient D_{AB} of solute A in solvent B can be computed using Equation 1 below [3]:

$$D_{AB} = \frac{7.4 \times 10^{-8} \times (\Phi \times M_B)^{0.5} \times T}{\mu \times V_A^{0.6}}$$

where D_{AB} = Diffusion Coefficient of Liquid Phase (Diffusion Coefficient of Solute A in Solvent B);

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M_B = Molecular Weight of B; Φ = Association Factor of Solvent B; T = Absolute Temperature; μ = Viscosity of Solvent B; V_A = Molal Volume of Solute A.

Often liquid diffusion is described by $\sigma_r^2 \sim Dt^\alpha$, where σ_r^2 is the mean squared displacement (MSD) and t is the time elapsed. For normal diffusion $\alpha = 1$; for anomalous diffusion $\alpha > 1$, the process is super diffusion (enhanced diffusion) and when $\alpha < 1$, the process is sub diffusion [4] (Fig. 1).

EXPERIMENTAL

Diffusimeter manufacturing, measuring its different arms, solution preparation, and diffusion tracking constitute the main organization and

techniques of this experiment. Four students in pairs can complete the work in three hours. The diffusimeter (Fig. 2) is manufactured as per specifications (Table 1). Arbitrary points X and Y closer to the curvatures are marked using waterproof marker. Measurement of BC, GF, CF as also CX and FY are taken with accuracy and precision using, say, thin paper strips and steel scale. The latter two measurements are required to avoid repeated scoring of the diffusimeter's curved sections. The last three arms are measured on the observer side.

MCl and AgNO_3 solutions of molarity 0.1M, 0.2M, 0.3M, 0.4M, 0.5M, 0.6M, and 0.7M are prepared using AR grade reagents. 2mL each of

Table 1
Diffusimeter Dimensions, cm

$DPL^{\S} = BG = BC + CF + GF$	CF range	BC & GF bore length	DC & FE	AB & GH	Stopcock bore diameter	Stopcock stem & DE outer diameter	Diameter at flared A & H
1	2	3	4	5	6	7	8
$1.2 + 33 + 1.2 = 35.4$	~32-34	1.2 each	~4-5 each	~7 each	0.4	1.0	~1.3

[§]Increasing DPL decreases diffusion rate. $DPL = BG = 19.3$ and 26.7 cm etc. were also used where V_d changed but $V_A \propto \sqrt{M}$ relation REMAIN remained unchanged.

MCl and AgNO_3 of corresponding concentration are taken in the left and right arms of the diffusimeter. Concurrent opening of the stopcocks

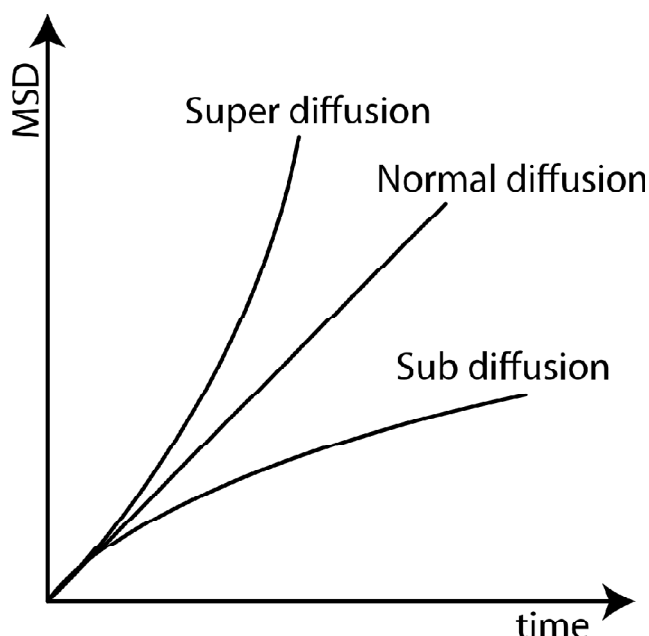


Figure 1: Normal and anomalous diffusion

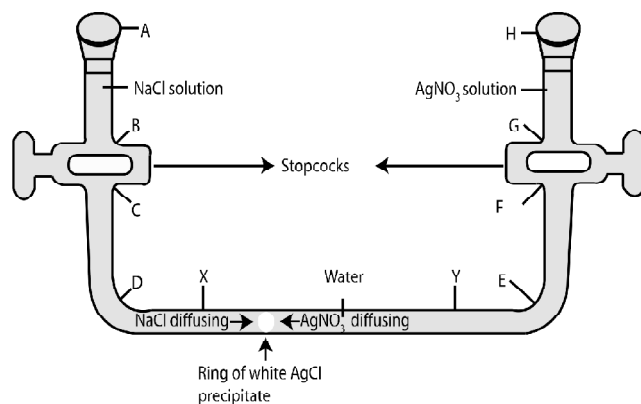


Figure 2: A typical Diffusimeter

(making the sound 'start' for the time keeper) marks the beginning of a run. MCl(aq) and $\text{AgNO}_3(\text{aq})$ (Reaction 1) approach each other through water. The reactants meet after a time (stopwatch reading) to produce AgCl(s) as the indicator at a point (marking with a fine marker making the sound 'stop'). Distance travelled (DT) by the slow reactant is measured making use of the known CX or FY. If the indicator mark is ahead

of X, DT will be CX + x, if it is behind, DT will be CX - x; adding the stopcock bore length is imperative. DT for the other reagent is obtained by subtraction from BG the Diffusion Path Length (DPL). Same technique is followed for the FY side.

Normal run follows 180° rotation of the diffusimeter and redoing the experiment pouring MCl(aq) and AgNO₃(aq) in the left and right arms. The averages of all parameters are taken. Opening the stopcocks generates turbulence above and below those as the consequence of solute's downward diffusion and solvent's upward convection at the B and G interfaces where concentration gradients are big. Turbulence appears as brisk movement of tiny wave like segments (consequence of changing refractive index) yielding place to steady states. Mock runs with covalent compounds like sugar, D-Mannitol, and D-Glucose showed turbulence, but the rates could not be determined for lack of suitable indicators.

The DTR = $\frac{DT_{MCl}}{DT_{AgNO_3}}$ and the Molar Mass Ratio

Square Root, MMRSR = $\sqrt{\frac{M_{MCl}}{M_{AgNO_3}}}$ are calculated.

MCl(aq) + AgNO₃(aq) = AgCl(s) + MNO₃(aq), M = H, Li, Na, K, Rb (**Reaction 1**)

Lithium chloride affects central nervous system and causes cardiac disturbance including severe irritation and possible burns of eyes and skin. Silver nitrate solutions are kept in carbon paper wrapped-shade to prevent decomposition

and their handling requires gloves for they produce dark spots on the skin. Dipping the diffusimeter overnight in baths of 25% sodium hydroxide and then in 1M nitric acid is essential particularly for cleaning the inside. Any AgCl grit can be removed by 10% ammonia.

RESULTS AND DISCUSSION

High diffusion rate ranks this process as stable super diffusive characterized by "accumulation of power-law jumps" (long jumps) (Fig. 3) rather than transient super diffusion that shows "super diffusive early-time to diffusive late-time behavior" [6]. The former is dominated by translational motion of the solute particles. Notionally turbulent diffusion sweeps the solute particles and enhances their rates [7]. Big concentration gradient triggers the particles to take power-law jumps through the stopcock holes (Fig. 3). The larger the hole diameter, the higher the diffusion rate [5].

The DTR for each MCl-AgNO₃ reactant pair is found nearly equal to the respective MMRSR =

$\sqrt{\frac{M_{MCl}}{M_{AgNO_3}}}$ (Table 2) conforming the relation,

$V_{\infty} \sqrt{M}$. Thirty electrolytes in pairs of MCl_x-AgNO₃, M_x(SO₄)_y-BaCl₂, Fe³⁺-MSCN with AgCl, BaSO₄, and Fe(SCN)₃ as indicators respectively were studied in water. The diffusion rates demonstrate one and the same relation, $V_{\infty} \sqrt{M}$ [5].

The V_{dHCl} shows sudden fall (Fig. 5) from those of V_{dLiCl} due partly to the low mobility of heavily

Table 2
DTR and MMRSR for MCl-AgNO₃ reactant pairs, T: 303-304K, DPL = BG = 35.4cm
FW: AgNO₃ = 169.87gmol⁻¹

MCl	FW, gmol ⁻¹	$DTR = \frac{DT_{MCl}}{DT_{AgNO_3}}$							Average DTR	$MMRSR = \sqrt{\frac{M_{MCl}}{M_{AgNO_3}}}$
		0.1 M	0.2 M	0.3 M	0.4 M	0.5 M	0.6 M	0.7 M		
1	2	3	4	5	6	7	8	9	10	11
HCl	36.5	0.40	0.43	0.43	0.44	0.44	0.44	0.44	0.43	0.46
LiCl.H ₂ O	60.41	0.49	0.48	0.49	0.51	0.51	0.51	0.53	0.50	0.50
NaCl	58.44	0.64	0.62	0.64	0.65	0.65	0.66	0.65	0.64	0.59
KCl	74.55	0.68	0.65	0.66	0.64	0.63	0.64	0.69	0.66	0.66
RbCl	120.92	0.86	0.83	0.78	0.85	0.86	0.85	0.83	0.84	0.84

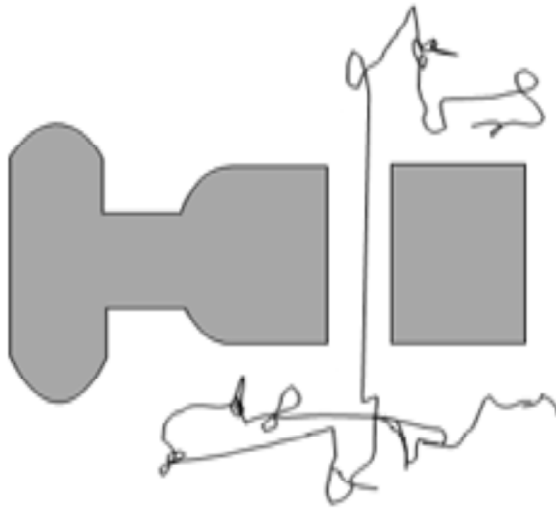


Figure 3: Power-law jump through stopcock hole

hydrated H^+ ion (high charge to size ratio) and partly to the high percent atomic number drop from Li to H. The rising of V_{dMCl} vs $[MCl]$ plots (Fig. 4) with rising M is a Fickian trend. Comparatively in the present cases the rates are 10^2 times higher. The NaCl and KCl plots are closer to each other (Fig. 4) for their low mass per cent difference. The narrowly differing V_{dAg^+-MCl} lines (Fig. 6) look twined at points due possibly to experimental flaws. Calculations suggests that the diffusing MCl holds no H_2O although for Na^+ and K^+ holding of four H_2O tetrahedrally is speculated [8].

A host of species in dilute solutions in different solvents show increasing D_{AB} (Equation 1) with decreasing molar masses; D_{AB} values being cited as multiple of 10^{-5} [9]. On the other hand Harned determined conductometrically the D of MCl ($M =$ alkali metals), KNO_3 , and $AgNO_3$ [10] in

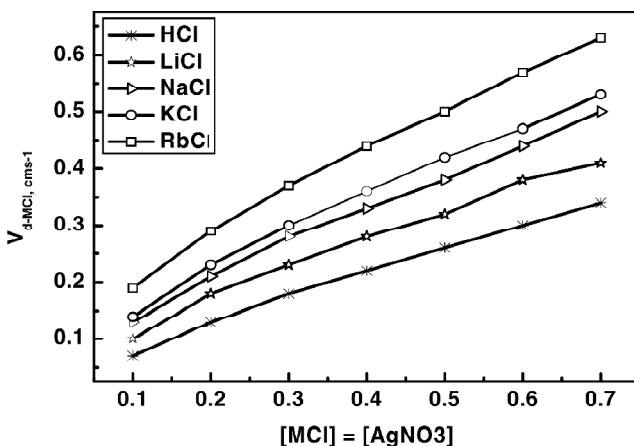


Figure 4: V_{dMCl} ($cm s^{-1}$) vs $[MCl]$ plots for MCl- $AgNO_3$ diffusion

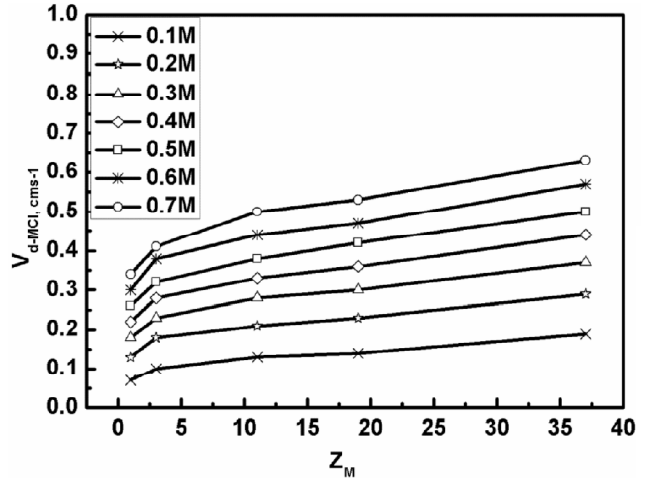


Figure 5: V_{dMCl} ($cm s^{-1}$) vs Z_M plots for MCl- $AgNO_3$ diffusion

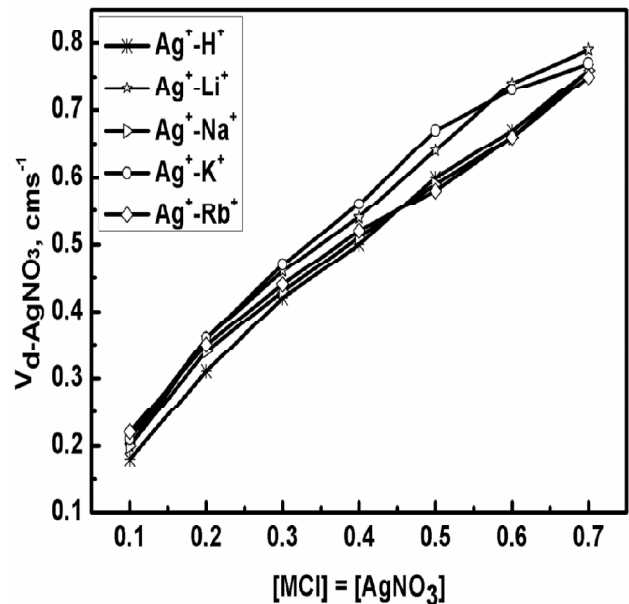


Figure 6: ($cm s^{-1}$) vs $[AgNO_3]$ plots for MCl- $AgNO_3$ diffusion

dilute solutions at $25^\circ C$ where values (averages) for LiCl-RbCl increase with increasing molar mass but thereafter D for the more massive CsCl and $AgNO_3$ drops in succession. Our computed D_{AB} for NaCl at 300K ($V_A = 27 cm^3 mol^{-1}$) shows to be $2.36 \times 10^{-5} cm^2 s^{-1}$.

The present process using the diffusimeter apparently is a “super diffusion in ordinary turbulence” [7]. Usually in such case the mean square displacement Δ^2 holds the nonlinear relation $\Delta^2 \propto T^{6/5}$ [7] being the same as equation $\sigma_r^2 \sim Dt^\alpha$ reflected in Fig. 1. Taylor predicted that “A single particle diffuses on large time scales, while at shorter times it might be ballistic” [11]. Ballistic motion requires initial trigger (in this

case big concentration gradient) to maximize velocities and accelerations over a very short period of time.

“There is a very close relation between quantum mechanics and gravity. Without gravity, quantum mechanics is ambiguous” [12]. Indeed microscopic particles like ion-pairs prevail under gravitational domain. “A heavier body falls faster than a lighter one of the same shape in a denser medium like water.” The power-law jumps as shown in Fig. 3 are actually falls in dense water medium where the DT and rate are enhanced by the FW of the solute and affected by steric grounds, water association, electrical interaction of ions at the closest approach etc. AgNO_3 being the heaviest electrolyte has the fastest rate. A related observation shows that in pressure diffusion gravitational segregation lets the heavier components of a hydrocarbon mixture move towards the bottom of a reservoir [13]. In effect this is a kind of qualitative version of the quantitative observation obtained in this experiment. Gravitation attracts an ion-pair as it does an apple. A particle in solution like an immersed pollen grain or a kite in the sky is acted upon by forces to counter gravity which endures overwhelming in falling bodies.

We conclude that the work presents a novel diffusimeter capable of carrying out turbulent, super diffusion experiments on chemical species in liquids. Diffusimetry with this tool can be used to determine relative, diffusion rates of solutes including their molar masses, molecular polarity, and hydration number. The rates are about 10^2 times higher than normal liquid diffusion. The art of diffusimetry is straightforward, interesting, and thought generating and can be introduced to all levels of chemical education. Although much to be seen yet, it appears that diffusion in liquid is pro-gravitation with the rate law, $V_{\infty}\sqrt{M}$ which

contradicts the law, $V_{\infty}\sqrt{\frac{1}{M}}$ for gases.

Diffusimetry can contribute to quick mass transfer, mass separation, biophysical sciences, diffusion controlled reactions, and environmental sciences.

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