

CATION CATALYTIC EFFECTS FOR THE IONIC REACTION BETWEEN 2, 3-DIBROMOSUCCINATE AND HYDROXIDE IONS

FAHIM UDDIN, SHAGUFTA AKBER AND SHAISTA JABEEN

Department of Chemistry, University of Karachi-75270, Karachi, Pakistan

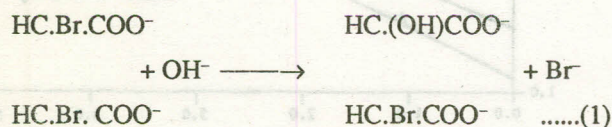
(Received July 21, 1991)

The second order reaction between 2, 3-dibromosuccinate and hydroxide ions was studied in the presence of inert electrolytes containing monovalent cations such as sodium nitrate and potassium nitrate. The kinetics of the reaction was studied at five different temperatures ranging from 25–45° and at various ionic strengths ranging from 1.4×10^{-2} – 51.4×10^{-2} mol. dm⁻³. Positive salt effect was observed. Cation catalytic effects on activation parameters as a function of ionic strength (μ) were studied. Temperature coefficients of the rate constants were also calculated and found to be unaffected due to the addition of electrolytes.

Key words: Ionic strength, Activation energy, Temperature coefficient.

Introduction

The kinetics of the reaction between 2, 3-dibromosuccinate and hydroxide ions was studied by Holomberg [1] at 25°. The reaction is a simple nucleophilic substitution reaction SN² at a saturated carbon atom. The substitution of one bromine by hydroxide ion takes place. The stoichiometric equation for reaction is:



The variation of the rate constant of the reaction between any two ionic species as a function of ionic strength of the medium was studied by several workers [2-13]. Fahim *et al.* [14-17] observed the effect of added electrolytes anion-anion reactions and evaluated activation parameters as a function of ionic strength.

The present paper reports the kinetic study of alkaline hydrolysis of dibromosuccinate ion at various temperatures in presence of different concentrations of electrolytes such as sodium nitrate and potassium nitrate respectively, and cation catalytic effect on activation parameters.

Experimental

All the chemicals (2, 3-dibromosuccinic acid, sodium hydroxide, hydrochloric acid, phenolphthalein, sodium nitrate and potassium nitrate) used were of E. Merk, A. R. quality. All the solutions were prepared in double distilled water.

Sodium salt of 2, 3-dibromosuccinic acid was prepared by adding equal volumes of dibromosuccinic acid and sodium hydroxide. pH of the neutral salt solution was observed by pH meter. The kinetics of the reaction between dibromosuccinate and hydroxide was studied at 25° by preparing various sets of reaction mixtures. The reactants were contained in closed

flasks, which were immersed in a constant thermostatic bath at the required temperature for about half an hour. Equal volumes of both reacting solutions were mixed and time of mixing was recorded.

Concentration of unreacted sodium hydroxide was determined by withdrawing from time to time 10 cc, of the reaction mixture and kept into ice cold water to freeze the reaction and then immediately titrating against standard hydrochloric acid solution using phenolphthalein solution as an indicator. The ionic strength of the reaction mixture was 1.4×10^{-2} mol. dm⁻³. By addition of different salts (NaNO₃, KNO₃) of five different concentrations ranging from 1.0×10^{-1} to 5.0×10^{-1} mol. dm⁻³, ionic strength was varied up to 51.4×10^{-2} mol. dm⁻³ in order to study the salt effect.

Results and Discussion

The influence of ionic strength and temperature on rate constant was studied for the reaction between disodium-dibromosuccinate and sodium hydroxide at various temperatures and ionic strengths in the presence of two alkali metal salts such as sodium nitrate and potassium nitrate respectively. Rate constants for two salts are given in Table 1. Results show that there is a regular increase in rate constant with the increase of ionic strength at constant temperature. This is in accordance with Debye-Huckel-Bronsted equation [18].

Kilpatrick [19] pointed out that ion-pair formation takes place between oppositely charged ions due to the interaction between ionic reactants and cation of electrolyte. These ion-pairs react faster than free ions, due to the decrease in electrostatic repulsion, therefore, rate constant increases with increase in salt concentration.

Our results follow this sequence of rate constants in the behaviour of alkali metal ion:



Reason for this behaviour lies in the size of the cations having same valency. Hydration sheaths are less around potassium ion as compared to sodium ion due to its large size. Ion pair formation tendency of potassium ion with reacting anion i.e. hydroxide ion is stronger as compared to sodium ion. The dissociation ability of ion pair is in following order:



Therefore rate constants are comparatively small in case of reactions in which sodium nitrate was used as an electrolyte. So less accelerating tendency was observed when sodium nitrate was used as an electrolyte.

In the Livingston's plots, i.e. plot of logarithm of rate constant (k) against square root of ionic strength (μ)^{1/2}, positive values of slopes of straight lines lead to the conclusion that the reaction is taking place between ions of similar charges.

From the Livingston plots the average value of $Z_A Z_B$ obtained by using sodium nitrate as electrolyte is 0.83 and by using potassium nitrate as electrolyte is 0.95. These results are not in agreement with Bronsted equation.

Kilpatrick [19] suggested that it might be advantageous to use $[(\mu)^{1/2}/1 + (\mu)^{1/2}]$ rather $(\mu)^{1/2}$ for calculating $Z_A Z_B$. The modified equation according to Kilpatrick is represented as:

$$\log k = \log k_0 + Z_A Z_B (\mu)^{1/2}/1 + (\mu)^{1/2} \dots \dots \dots (2)$$

TABLE 1. VARIATION OF RATE CONSTANT AT DIFFERENT IONIC STRENGTHS AND TEMPERATURES.

	Temperature (°C)				
$\mu \times 10^2$ mol. dm ⁻³	25	30	35	40	45
	Rate Constants ($k \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \cdot \text{s}^{-1}$) with NaNO ₃				
1.4	1.919	2.772	3.881	5.544	7.676
11.4	3.640	4.680	6.458	10.716	12.334
21.4	4.477	6.042	8.322	10.968	15.136
31.4	6.055	7.278	9.797	12.892	19.557
41.4	6.929	7.782	10.767	14.605	20.152
51.4	7.889	9.085	11.896	15.780	21.748
0.0	1.094	1.778	2.564	3.524	5.284
	Rate Constants ($k \times 10^2 \text{ mol}^{-1} \cdot \text{dm}^3 \cdot \text{s}^{-1}$) with KNO ₃				
1.4	1.919	2.772	3.881	5.544	7.676
11.4	4.009	5.544	7.676	10.982	14.454
21.4	5.800	6.930	9.595	14.600	17.037
31.4	6.930	8.318	10.982	17.165	20.151
41.4	8.316	9.595	12.687	20.257	22.177
51.4	9.958	10.982	14.606	21.750	23.669
0.0	1.164	1.845	2.636	4.111	5.420

Kilpatrick plots i.e. plot of logarithm of rate constant against $[(\mu)^{1/2}/1 + (\mu)^{1/2}]$ are shown in Fig. 1 and 2 respectively. These plots show that it is more convincing to calculate k_0 from equation (3).

The average value of $Z_A Z_B$ obtained by plotting logarithm of rate constant (k) vs $[(\mu)^{1/2}/1 + (\mu)^{1/2}]$ in presence of NaNO₃ comes out to be 1.58 and in presence of KNO₃ comes out to be 1.85. These values are in accordance with theoretical value ($Z_A Z_B = 2.0$). The values of $Z_A Z_B$ at different temperatures are also shown in Table 2.

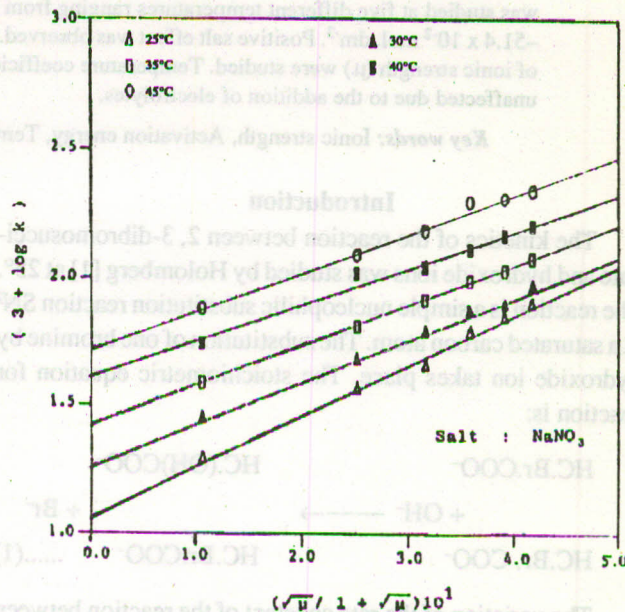


Fig. 1. Plots of log k vs $[\sqrt{\mu}/1 + \sqrt{\mu}]$ at various temperatures in presence of NaNO₃.

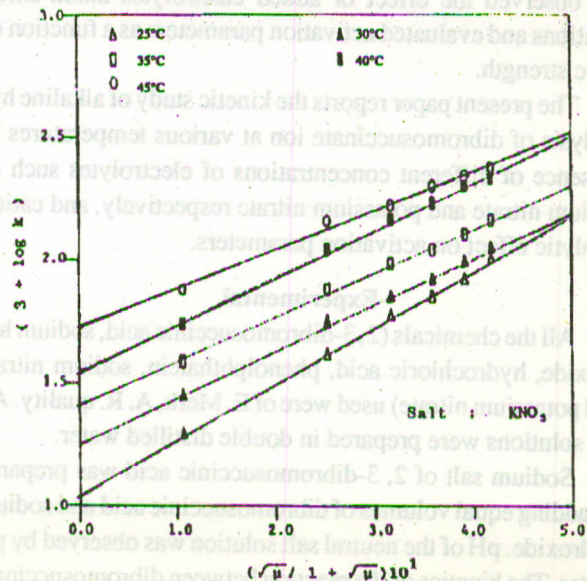


Fig. 2. Plots of log k vs $[\sqrt{\mu}/1 + \sqrt{\mu}]$ at various temperatures in presence of KNO₃.

From Arrhenius plot method, activation energy was determined. Linear relationship was obtained with negative slopes by plotting logarithm of rate constant against reciprocal of the absolute temperature (1/T). The results are presented in Table 3 and shown in Figs. 3 and 4 respectively.

It was observed that the apparent energy of activation decreases as the ionic strength of the medium increases by the addition of electrolyte. As ionic strength changes, the configuration of the transition state changes.

It was also observed that activation energy is affected by size of the cation of the added electrolyte at the same ionic strength (μ). That is why activation energy in presence of potassium nitrate was found to be smaller than in presence of sodium nitrate.

Plots of E vs $(\mu)^{1/2}$ are linear having negative slopes as shown in Figs. 5 and 6 respectively. The extrapolated value of

TABLE 2. EVALUATION OF Z_A, Z_B VALUES.

Plots	Temperature °C					Average
	25	30	35	40	45	
Z_A, Z_B Values in presence of NaNO_3						
Livingston	1.00	0.83	0.79	0.70	0.75	0.83
Kilpatrick	1.93	1.60	1.54	1.38	1.46	1.58
Z_A, Z_B Values in presence of KNO_3						
Livingston	1.15	0.95	0.90	0.97	0.78	0.95
Kilpatrick	2.22	1.84	1.76	1.88	1.53	1.85

TABLE 3. ACTIVATION PARAMETERS AT DIFFERENT IONIC STRENGTHS AT 25°.

$10^2 \mu$	E_a KJ/mol.	ΔH^\ddagger KJ/mol.	ΔS^\ddagger (J/mol.deg.)	ΔG^\ddagger KJ/mol.
In presence of NaNO_3 as electrolyte				
1.4	52.39	49.91	-101.70	80.22
11.4	49.50	47.02	-106.50	78.76
21.4	45.78	43.30	-117.00	78.17
31.4	43.94	41.47	-121.30	77.61
41.4	41.65	39.17	-127.90	77.28
51.4	38.89	36.41	-136.00	76.94
Zero	56.26	53.79	- 91.00	80.87
In presence of KNO_3 as electrolyte				
1.4	52.39	49.91	-101.70	80.22
11.4	49.11	46.63	-106.70	78.43
21.4	43.71	41.23	-122.20	77.65
31.4	43.25	40.77	-122.30	77.22
41.4	41.01	38.53	-128.40	76.80
51.4	36.53	34.05	-141.90	76.34
Zero	55.97	53.49	- 91.00	80.73

activation energy corresponding to zero ionic strength are also shown in Table 3.

The activation parameters i.e. change of enthalpy of activation (ΔH^\ddagger), change of entropy of activation (ΔS^\ddagger) and change of free energy of activation (ΔG^\ddagger), were calculated by using the following expressions:

$$\Delta H^\ddagger = E_a - RT \quad \dots \dots \dots (3)$$

$$A = (KT/h) \exp. (\Delta S^\ddagger/R) \dots \dots \dots (4)$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \dots \dots \dots (5)$$

where E_a , A and h are the energy of activation (determined

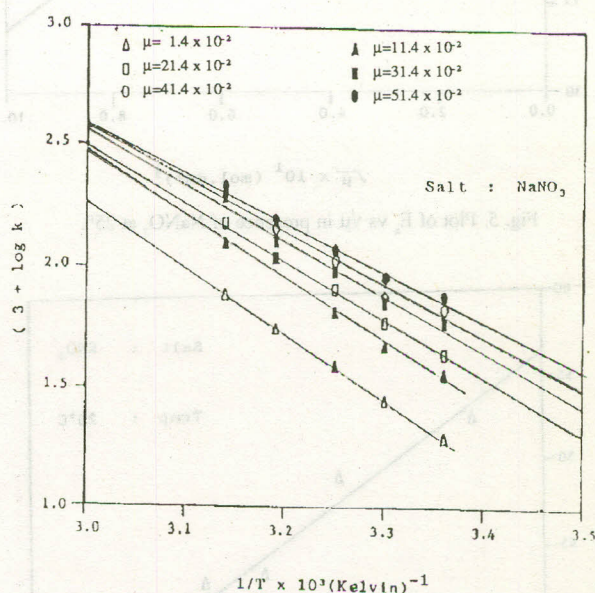


Fig. 3. Plots of $\log k$ vs $1/T$ at various ionic strengths in presence of NaNO_3 .

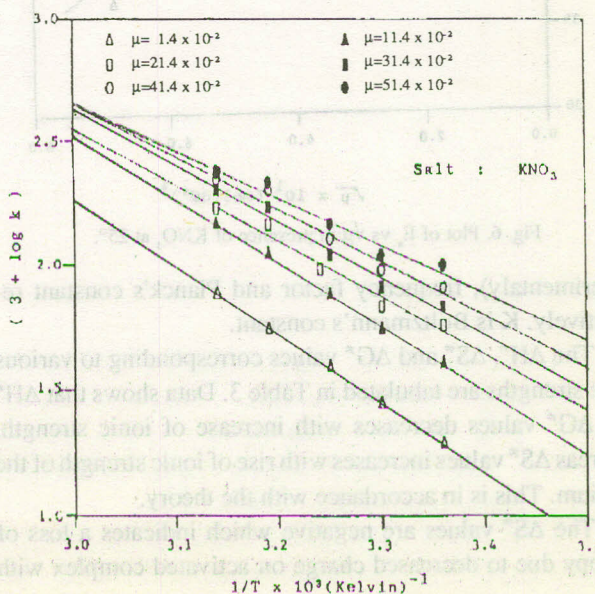
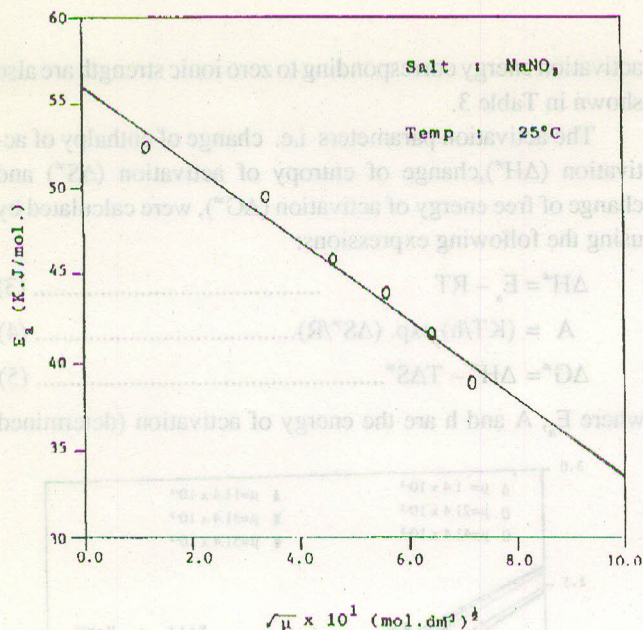
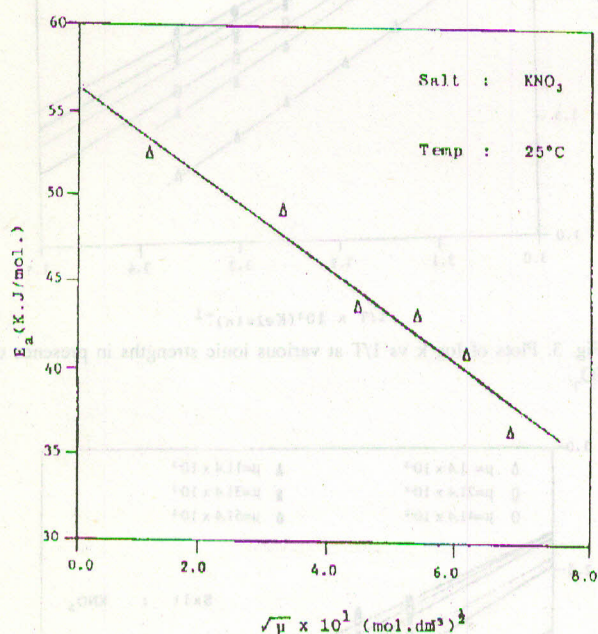


Fig. 4. Plots of $\log k$ vs $1/T$ at various ionic strengths in presence of KNO_3 .

Fig. 5. Plot of E_a vs $\sqrt{\mu}$ in presence of NaNO_3 at 25° .Fig. 6. Plot of E_a vs $\sqrt{\mu}$ in presence of KNO_3 at 25° .

experimentally), frequency factor and Planck's constant respectively. K is Boltzmann's constant.

The ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger values corresponding to various ionic strengths are tabulated in Table 3. Data shows that ΔH^\ddagger and ΔG^\ddagger values decreases with increase of ionic strength, whereas ΔS^\ddagger values increases with rise of ionic strength of the medium. This is in accordance with the theory.

The ΔS^\ddagger values are negative which indicates a loss of entropy due to decreased charge on activated complex with

TABLE 4. TEMPERATURE CO-EFFICIENTS OF RATE CONSTANTS.

$\mu \times 10^2$ (mol. dm ⁻³)	K_{30}/K_{25}	K_{35}/K_{30}	K_{40}/K_{35}	K_{45}/K_{40}	Average
In presence of NaNO_3 as electrolyte					
1.4	1.444	1.400	1.428	1.384	1.414
11.4	1.286	1.380	1.659	1.151	1.369
21.4	1.349	1.377	1.318	1.380	1.356
31.4	1.202	1.346	1.316	1.517	1.345
41.4	1.123	1.383	1.356	1.379	1.310
51.4	1.152	1.309	1.326	1.378	1.291
In presence of KNO_3 as electrolyte					
1.4	1.444	1.400	1.428	1.384	1.414
11.4	1.383	1.384	1.431	1.316	1.378
21.4	1.195	1.384	1.521	1.167	1.317
31.4	1.200	1.320	1.563	1.174	1.314
41.4	1.154	1.322	1.596	1.095	1.292
51.4	1.103	1.329	1.489	1.088	1.252

respect to charge of separated ions. Positive values of ΔS^\ddagger show that the formation of activated complex is a non-spontaneous process.

The values of temperature co-efficients of the rate constant per five degree rise in temperature are presented in Table 4 and found to be unaffected by the change of ionic strength of the medium. The average values of temperature coefficients of rate constants in presence of NaNO_3 and KNO_3 were found to be 1.347 and 1.328 respectively and are in agreement with those reported earlier [20].

References

1. B. Holmberg, Z. Physik. Chem., **97**, 134 (1921).
2. F. Secco, A. Indelli and P. L. Bonora, J. Am. Chem. Soc., **9**, 337 (1970).
3. A. Indelli, Israel. J. Chem., **9**, 301 (1971).
4. M. J. Blandamer, J. Burgers and S. H. Morris, J. Chem. Soc., Dalton Trans., 1717 (1974).
5. F. Uddin and M. G. Ahmed, Pak. j. sci. ind. res., **22**, 181 (1979).
6. F. Uddin and M. G. Ahmed, Gazz. Chim. Ital., **110**, 593 (1980).
7. M. B. Almeida, F. Ferranti, A. M. Alvarez and A. Indelli, Gazz. Chem. Ital., **110**, 129 (1980).
8. F. Uddin and M. G. Ahmed, Arab J. Sci. Engg., **6**, 105 (1981).
9. F. Uddin, J. Sci. Res., **14**, 13 (1985).
10. F. Uddin and M. G. Ahmed, Pak. j. sci. ind. res., **22**, 177 (1979).
11. K. C. Malhotra, A. Garg., T. D. Sherma and V. K. Syal, J. Ind. Chem. Soc., **64**, 551 (1987).

12. P. V. S. Rao, K. Ramakrishna and C. V. Saradamba, *J. Ind. Chem. Soc.*, **65**, 329 (1988).
13. B. Singh, A. K. Gupta, D. B. Pathek, V. K. Singh, Y. P. Singh, and R. T. Singh, *J. Ind. Chem. Soc.*, **66**, 377 (1989).
14. F. Uddin and I. Hussain, *Nig. J. Sci. Tech.*, **3** (2), 80 (1985).
15. F. Uddin, M. G. Ahmed and Q. Z. Hasnain, *Act. Cientif. Venez.*, **37**, 667 (1986).
16. F. Uddin and N. Shahid, *J. Pure. App. Sci.*, **8**, 27 (1989).
17. F. Uddin, R. Naheed and M. Mumtaz, *Sci. Int.*, **1**, 237 (1989).
18. K. J. Laidler, *Chemical Kinetics* (McGraw Hill Book Company, New York, 1965), pp. 53.
19. M. Kilpatrick, *J. Am. Chem. Soc.*, **56**, 2326 (1934).
20. F. Uddin and I. M. Adhami, *Phys. Chem.*, **9**, (1990).

Key words: Single drops, Vanadium(V) system, Mass transfer model.

Experimental

pH was measured with Orion Research pH meter, model 707A. The concentration of vanadium (IV) was determined spectrophotometrically by the peroxide method [8], any organic phase vanadium being initially stripped into the aqueous phase with 3M sulphuric acid. Vanadium (IV) sulphate (BDH) was assayed with standard potassium permanganate (KMnO₄) before use. Di-2 ethyl hexyl phosphate (BDH) was purified by the method described by Zito [9]. The diluent, n-hexane was used as supplied. The aqueous phase (0.1 M VO²⁺) was kept at 0.2 M sodium sulphate in order to keep the ionic strength constant. The organic phase was 0.2M D2EHPA in n-hexane. Temperature was maintained constant at 28±0.2, this value being within the range of temperature recommended for the extraction of vanadium (IV) from its ore [10].

The apparatus and experimental procedure for the single drop technique have been fully described elsewhere [4-6]. In this work single drops of di-2 ethyl hexyl phosphate were released from the tip of a hypodermic needle (33 gauge size) and many pressure from oxygen-free nitrogen, the drops were made to rise through a continuous phase of VO²⁺ in four Pyrex type jacketed columns of heights 37.5, 71.0, 132 and 163.2 cm and internal diameter of 24 mm. The four columns were used one at a time for a set of kinetic experiments during which the time it took for a drop to move through each column was measured. The amount of vanadium extracted per unit surface area was then calculated.

Results and Discussion

The data from only two experimental runs are given in the Table I. Other are not tabulated to save space.

If the overall rate of mass transfer was controlled by internal mass transfer of the extractant molecules to the reaction site, Miller [11] has shown that the fractional change in the extractant concentration with time could be theoretically predicted from the Newman [12] equation for stagnant drops:

Introduction

Several experimental techniques have been used in the investigation of the rate of metal extraction in liquid-liquid systems. Among others are the stirred tank [1], the static constant interfacial cell of the Lewis type [2], the static constant interfacial cell of the Hahn type [3] and the single drop [4,5]. Each method has its merits, shortcomings and limitations. Of the various methods, the single drop has been widely used by many authors [4-6]. The basic principle is to produce drops of one phase at the tip of a hypodermic needle or glass capillary and make the drop rise or fall through a vertical column filled with the other phase. The method has the advantage of simplicity and the capacity to yield information on the magnitude of the interfacial area for mass transfer. Moreover, it can be used to simulate a column extractor.

The hydrodynamics of the single drop is however, very complicated. Any attempt to treat single drops as moving spheres for the purpose of internal mass transfer has inherent short-comings because liquid drops, depending on their size, differ remarkably from solid spheres in being capable of deformation, oscillation and even fragmentation. Three aspects have been identified in a log-log plot of the terminal velocity of a rising drop against the drop diameter [7]. First there exists small drops which lack internal circulation and tend to behave like rigid spheres. In second case, the drops are bigger, with internal circulation to enhance mass transfer and in third case where drops have become so large that the flow pattern becomes a combination of eddy flow in circulation. In effect, mass transfer is not favoured, not only by small drops alone, but by very large drops as well that tend to drag a wake when moving.

The aim of this study is to generate mass transfer data with the single drop experimental technique and use the results to test the model equations for systems controlled by internal mass transfer.