

TABLE 3 — VALUES OF  $\Lambda_0$ ,  $\Lambda_0\eta$  AND  $a$  (Å) AT DIFFERENT TEMPERATURES FOR LITHIUM ACETATE IN WATER AND AQUEOUS METHYL ACETATE OBTAINED FROM THE TEST OF THE FUOSS-ONSAGER-SKINNER EQUATION

Temp. (°C)	$\Lambda_0$ (ohm <sup>-1</sup> cm <sup>2</sup> ) Water	$\Lambda_0$ (ohm <sup>-1</sup> cm <sup>2</sup> ) Aq.-methyl acetate	$\Lambda_0\eta$		$a$ (Å)	
			Water	Aq.-methyl acetate	Water	Aq.-methyl acetate
40	121.9	128.4	0.80	1.06	1.4	1.7
45	130.2	135.5	0.78	0.99	1.6	1.9
50	133.2	143.6	0.73	0.95	2.2	2.0

The data in Table 3 reveal that the limiting equivalent conductances obtained by Onsager extrapolation method and Fuoss-Onsager-Skinner equation differ slightly for solution in water, but for solutions in aq.-methyl acetate, there is large difference in  $\Lambda_0$  values. This large difference may be due to the fact that (a) the Fuoss-Onsager-Skinner conductance equation takes into account the points at higher concentrations also whereas these points show deviations from simple Onsager plots and (b) manual extrapolation in Onsager plots may be the source of error.

The structural effects on the conductance of ions in aqueous solutions are derived by a comparison of their Walden-products in aqueous and non-aqueous solutions at different temperatures<sup>14,15</sup>. From the Table 3, it is clear that as the temperature increases the Walden-product goes on decreasing. The  $\Lambda_0\eta$  versus  $t$  plots are almost linear for both the solutions and have negative temperature coefficient. The negative temperature coefficient<sup>7</sup> suggests that the lithium acetate acts as a structure-breaker both in water and in aq.-methyl acetate. The slight increase in the ion size parameter  $a$  (Å) with temperature for lithium acetate in water and aqueous methyl acetate may be interpreted<sup>7</sup> as an indication of the structure-breaking tendency of the electrolyte in a solvent.

The structure-breaking capacity of lithium acetate in water and aqueous methyl acetate is also supported from the viscosity measurements<sup>16</sup>.

One of the authors (P.C.V.) is thankful to CSIR, New Delhi, for the award of a junior research fellowship.

#### References

1. MACINNES, D. A., *The principles of electrochemistry* (Dover, New York), 1967, 327; 360.
2. FUOSS, R. M., ONSAGER, L. & SKINNER, J. F., *J. phys. Chem. Ithaca*, **69** (1965), 2581.
3. TIMMERMANS, J., *Physico-chemical constants of pure organic compounds*, Vol. I (Elsevier, New York), 1950, 413.
4. LANGE, N. A., *Handbook of chemistry* (McGraw-Hill, New York), 1967, 1221.
5. SHOEMAKER, D. P. & GARLAND, C. W., *Experiments in physical chemistry* (McGraw-Hill, New York), 1967, 131.
6. BLOKHRA, R. L. & SEHGAL, Y. P., *Indian J. Chem.*, **14A** (1976), 162.
7. BLOKHRA, R. L. & PARMAR, M. L., *J. electroanal. Chem.*, **57** (1974), 117.
8. BLOKHRA, R. L. & SEHGAL, Y. P., *J. electroanal. Chem.*, **62** (1975), 381.
9. BLOKHRA, R. L. & SEHGAL, Y. P., *Z. phys. Chem.*, **93** (1974), 155.

10. FUOSS, R. M. & KRAUSS, C. A., *J. Am. chem. Soc.*, **55** (1933), 1019; 2387.
11. BJERRUM, N., *Det. Kgl. Danske Vidensk. Selsk. Medd.*, **9** (1926), 2.
12. BLOKHRA, R. L. & SEHGAL, Y. P., *Indian J. Chem.*, **12** (1974), 998.
13. BLOKHRA, R. L. & PARMAR, M. L., *J. electroanal. Chem.*, **59** (1975), 226.
14. KAY, R. L. & EVANS, D. F., *J. phys. Chem. Ithaca*, **70** (1966), 366; 2325.
15. KAY, R. L., CUNNINGHAM, G. P. & EVANS, D. F., *Hydrogen bonded solvent systems*, edited by A. K. Govington & J. Jones (Taylor & Francis, London), 1968, 249.
16. BLOKHRA, R. L. & VERMA, P. C., *Electrochim. Acta*, (in press).

#### Study of Hydrolysis Kinetics & Lactone-Acid-Salt Equilibria of $\gamma$ -D-Mannonolactone

S. K. DUTTA\* & SUVA BRATO ROY†

Department of Pharmacy, Jadavpur University  
Calcutta 700032

Received 2 August 1975; accepted 31 January 1976

Specific rate constant ( $k_H$ ) for the hydrolysis of  $\gamma$ -D-mannonolactone in aqueous solution has been determined conductometrically, the values at 25° and 37° are 2.04 and  $5.37 \times 10^{-5} \text{ sec}^{-1}$  respectively. Activation energy ( $E_a = 14.73 \text{ kcal mole}^{-1}$ ) has been found from the Arrhenius plot. The overall equilibrium constant ( $K_{eq}$ ) for the hydrolysis of the lactone,  $k_A$  for mannonic acid and the equilibrium constant  $k_L$  for the hydrolysis of the lactone have been determined from pH and optical rotation measurements and are found to be  $2.48 \pm 0.10 \times 10^{-5}$ ,  $1.60 \pm 0.16 \times 10^{-4}$  and 0.18 respectively. Lactonization constants  $k_1$  for mannonic acid at 25° and 37° are  $1.34$  and  $2.98 \times 10^{-5} \text{ sec}^{-1}$  respectively.

THE hydrolysis kinetics of industrially important aldonolactones, viz. D-glucono- $\delta$ -lactone<sup>1</sup>, lactobiono- $\delta$ -lactone<sup>2</sup>, maltobiono- $\delta$ -lactone<sup>3</sup>, cellobiono- $\delta$ -lactone<sup>4</sup> and  $\gamma$ -D-galactonolactone<sup>5</sup> have been reported earlier, but such data on  $\gamma$ -D-mannonolactone are wanting. A systematic study of the hydrolysis kinetics of this lactone and lactone-acid-salt equilibria are reported in this note.

$\gamma$ -D-Mannonolactone — D-Mannose (45 g) was electrolytically oxidized in the presence of  $\text{NaHCO}_3$  (25 g) and 1% sodium bromide in 800 ml water

\*To whom correspondences are to be directed.

†Abstracted from a dissertation submitted by Suva Brato Roy, Department of Pharmacy, Jadavpur University, Calcutta 32, in part fulfilment of Masters degree of Pharmacy requirements.

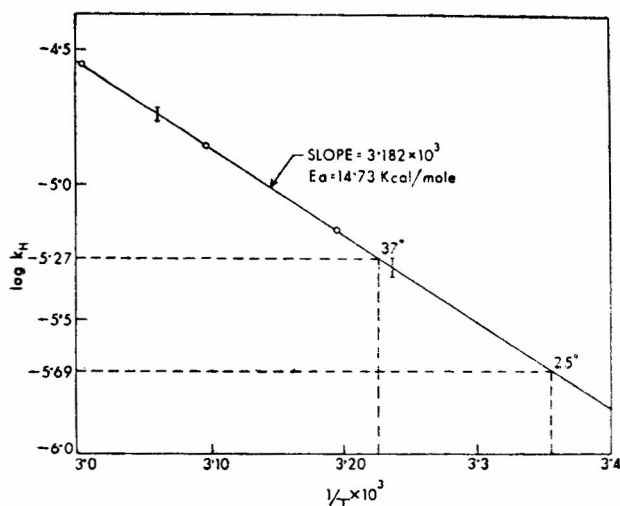


Fig. 1 — Arrhenius plot for determination of  $E_a$  for extrapolated values of  $k_H$  at 25° and 37°

by passing 1 amp current for 14 hr (percentage of oxidation of the sugar, approximately 90%). The volume of water was reduced to 50 ml by evaporating on a water-bath and sodium mannonate crystallized out by addition of methanol. The salt was filtered off, dissolved in minimum volume of water and recrystallized by the addition of methanol, which was finally purified by recrystallization from aq. methanol; m.p. 170°.

The salt was dissolved in minimum volume of water and passed through cation exchange resin (Amberlite IR 120) to give mannonic acid. The acid was concentrated to a syrup on a water-bath, dissolved in 95% ethanol by little warming and kept at room temperature to give white needle-shaped crystals of  $\gamma$ -D-mannonolactone; m.p. 150-51°.

Purity was checked by paper chromatography (solvent-pyridine-ethyl acetate-water, 2:8:1 v/v/v) which gave single spots.  $R_F$  0.11 and 0.12 for sodium mannonate and  $\gamma$ -D-mannonolactone respectively.

Conductance was measured using a Philips conductivity bridge model PR 9500. The pH measurements were made on a Beckman pH meter model H2. Optical rotations were measured on a Hilger micro-optic photoelectric polarimeter of precision 0.005°. A 2 dm polarimeter tube was used for all measurements.

Kinetics of hydrolysis of  $\gamma$ -D-mannonolactone in water was studied conductometrically. A known amount of lactone was placed in a fixed volume of water equilibrated at 40°, 50° and 60° respectively and changes in conductance with time measured. The  $k_H$  values at 40°, 50° and 60° were calculated from the relation  $k_H = 2.303/t \log (C_a - C_0)/(C_a - C_t)$  (where  $C_0$ ,  $C_t$  and  $C_a$  are the conductances at times 0,  $t$  and  $\infty$  respectively) and found to be 0.675, 1.38 and  $2.77 \times 10^{-5}$  respectively. Arrhenius plot of  $\log k_H$  versus  $1/T$  was linear (Fig. 1) which when extrapolated to 25° and 37° gave  $k_H$  values of 2.04 and  $5.37 \times 10^{-6}$  respectively. Also the value of energy of activation  $E_a$  has been calculated from the slope of Arrhenius plot and found to be 14.73 kcal mole<sup>-1</sup>.

TABLE 1 — VALUES FOR LACTONE-ACID-SALT EQUILIBRIUM CONSTANT ( $K_{eq}$ ) AND DISSOCIATION CONSTANT ( $k_A$ ) OF MANNONIC ACID

[Lactone] (M)	pH	$K_{eq} \times 10^5$	Optical rotation	$K_A \times 10^4$
0.0995	2.80	2.56	1.765°	1.74
0.0999	2.80	2.55	1.770°	1.51
0.0999	2.80	2.55	1.770°	1.51
0.0998	2.82	2.28	1.770°	1.46
0.1004	2.81	2.40	1.780°	1.43
0.0998	2.80	2.56	1.770°	1.92
		Mean $2.48 \pm 0.10$		Mean $1.60 \pm 0.16$

The hydrolysis of  $\gamma$ -D-mannonolactone (M) in water can be expressed by relation (1)



mannonic acid                  mannonate ion

The equilibrium constant ( $K_{eq}$ ) is given by Eq. (2)

$$K_{eq} = \frac{[H^+][MH_4^-]}{[HMH_4] + [M]} = \frac{[H^+][MH_4^-]}{C_i - [H^+]} \quad \dots(2)$$

where  $[M]$  = equilibrium concentration of unhydrolysed lactone and  $[HMH_4]$  = equilibrium concentration of undissociated mannonic acid and  $C_i$  = [initial lactone].

The values of  $K_{eq}$  determined pH-metrically are given in Table 1.

The dissociation constant is given by Eq. (3)

$$k_A = \frac{[H^+][MH_4^-]}{[HMH_4]} \quad \dots(3)$$

The  $k_A$  values for mannonic acid at different pH and optical rotation are given in Table 2. The specific rotation  $[\alpha]_D^{25}$  for  $\gamma$ -D-mannonolactone, mannonic acid and sodium mannonate have been found to be  $+51^\circ \pm 0.5^\circ$ ,  $+44.85^\circ \pm 0.05^\circ$  and  $-8.0^\circ \pm 0.5^\circ$  respectively and molar rotations (2 dm-tube) are  $+18.16^\circ$ ,  $+17.58^\circ$  and  $-3.49^\circ$  respectively.

Dividing Eq. (3) by Eq. (2) and rearranging the equilibrium expression for hydrolysis of lactone is

$$k_L = \frac{[HMH_4]}{[M]} = \frac{K_{eq}}{K_A - K_{eq}} = 0.18 \quad \dots(4)$$

which is in good agreement with the observation of Carter *et al.*<sup>6</sup>

Lactonization constant  $k_L$  of mannonic acid is given by the expression

$$k_1 = \frac{k_H}{k_L} = 1.34 \times 10^{-5} \text{ sec}^{-1} \text{ at } 25^\circ \text{ and } 2.98 \times 10^{-5} \text{ sec}^{-1} \text{ at } 37^\circ \quad \dots(5)$$

## References

1. SAWYER, D. T. & BAGGER, J. B., *J. Am. chem. Soc.*, **81** (1959), 5303.
2. DUTTA, S. K. & MUKHERJEE, S. K., *Indian J. Chem.*, **9** (1971), 229.
3. DUTTA, S. K., *Indian J. Chem.*, **11** (1973), 240.
4. DUTTA, S. K., *Indian J. Chem.*, **13** (1975), 192.
5. DUTTA, S. K., *Indian J. Chem.*, **13** (1975), 980.
6. CARTER, S. R., HAWORTH, W. N. & ROBINSON, R. A., *J. chem. Soc.*, (1930), 2125.