Viscosity Coefficients and Activation Parameters of Lanthanum Chloride in Pure and Mixed Solvents at Different Temperatures

Shaista Jabeen* and Shagufta Akber

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

The measurement of viscosities of various solutions of Lanthanum chloride in pure water, pure methanol and different percentages of water-methanol i.e. mixed solvents has been made at different temperatures 298, 303, 308 and 313°K. The viscosity coefficients have been determined by using the Jone-Dole equation and found to vary with temperature and solvent compositions. The activation parameters have been determined in pure water, pure methanol and in 54% aqueous methanol at 298, 303 and 313°K. The salt has been found to be a structure breaker.

Key words : Viscosity coefficients, Jone-Dole equation, Activation parameters.

Introduction

The work on viscosity coefficients and activation parameters of electrolytic solution has been carried out by many workers (Nightingale and Benck 1959; Ganapathy and Ramanu 1980; Varma and Jain 1981; Fahimuddin and Farooqi 1984; Fahimuddin *et al* 1989; Afzal and Ahmed 1991).

The present work involves the viscosity measurements of lanthanum chloride in pure and mixed solvents at 298,303,308 and 313°K. The viscosity data have been utilized to calculate viscosity coefficients of Jone-Dole equation (Jones and Dole 1929) and activation parameters.

The activation parameters such as energy of activation (E*) change of free energy of activation (ΔG^*) and entropy of activation (ΔS^*) have been determined in pure solvents and in 54% w/w aqueous methanol at 298, 303 and 313°K.

Energy of activation has been determined by the Andrade equation (Levitt 1972), given as:

$$n \quad = \quad A_{exp}(E_n^*/RT \dots\dots\dots\dots \quad (1)$$

where E* is the energy of activation, A is pre-exponential factor and R is the gas constant.

These measurement and calculations have been made to study the ion-solvent interaction and structure breaking or promoting effect of the solute.

Experimental

Lanthanum chloride of Analar grade was used in the work.

*Author for correspondence

Double distilled water and distilled methanol (E.Merk) was used for the preparation of solvents.

Density measuements were carried out by using the specific gravity bottle of 10 ml capacity. The Ostwald Viscometer was used for viscosity measurements and the data were calculated by taking the density and time of flow for different solutions which was noted between two marked positions on the capillary fitted in the Viscometer by using a stopwatch.

To maintain the constant temperature throughout the work, a sensitive thermostate "HAAKE" (Model RT-33) with an accuracy of ± 0.01 °C was used.

Each tabulated viscosity value is a mean of three readings.

Results and Discussion

The solutions were prepared in pure and mixed solvents. The concentrations were from 1.2×10^{-3} to 3.5×10^{-3} mol dm^{-3}. The measured viscosity data have been tabulated in Tables 1-4. The data shows an increase in viscosities with the increase of solute concentration and a decrease with the increase of tempeature.

The viscosities were found to increase with the increase of methanol content of the solvent upto 34% and therefore the viscosity decreased. This is due to the solvent structure. As the methanol content is increased further, the structure is distorted and viscosity decreases (Herskovit and Kelly 1973; Sandhu *et al* 1983). In some cases this has been noticed to be achieved earlier at lower temperature (Jabeen 1993,1994).

Table 1
Viscosities of lanthanum chloride in different solutions at 298°K

$10^3 \times C/$ mol dm^{-3}	3.5	2.7	2.2	1.8	1.5	1.2	Solvent composition %
$10^3 \times n/$ Kg m^{-1} s^{-1}	0.9753 ±0.004	0.9675 ±0.001	0.9478 ±0.000	0.9365 ±0.001	0.9259 ±0.003	0.9161 ±0.005	00.00
	1.1894 ±0.002	1.1765 ±0.001	1.1628 ±0.003	1.1489 ±0.001	1.1406 ±0.002	1.1326 ±0.004	08.02
	1.2368 ±0.001	1.2301 ±0.002	1.2265 ±0.003	1.2195 ±0.005	1.2112 ±0.003	1.2035 ±0.002	16.41
	1.2849 ±0.004	1.2764 ±0.001	1.2634 ±0.003	1.2446 ±0.005	1.2389 ±0.002	1.2264 ±0.004	25.17
	1.2868 ±0.001	1.2709 ±0.003	1.2679 ±0.005	1.2564 ±0.002	1.2413 ±0.004	1.2398 ±0.002	34.36
	1.2265 ±0.005	1.2114 ±0.003	1.1982 ±0.001	1.1905 ±0.002	1.1855 ±0.004	1.1763 ±0.003	54.08
	1.1364 ±0.002	1.1294 ±0.001	1.1185 ±0.005	1.1099 ±0.003	1.1087 ±0.002	1.1068 ±0.001	75.85
	0.6439 ±0.003	0.6305 ±0.005	0.6217 ±0.001	0.6027 ±0.003	0.5869 ±0.004	0.5698 ±0.001	100.00

Table 2
Viscosities of lanthanum chloride in different solutions at 303°K

$10^3 \times C/$ mol dm^{-3}	3.5	2.7	2.2	1.8	1.5	1.2	Solvent composition %
$10^3 \times n/$ Kg m^{-1} s^{-1}	0.8856 ±0.002	0.8721 ±0.004	0.8664 ±0.001	0.8521 ±0.005	0.8465 ±0.003	0.8299 ±0.004	00.00
	0.9264 ±0.001	0.9202 ±0.002	0.9169 ±0.003	0.9017 ±0.004	0.8987 ±0.005	0.8921 ±0.003	08.02
	1.0767 ±0.002	1.0643 ±0.004	1.0521 ±0.001	1.0436 ±0.003	1.0317 ±0.004	1.0128 ±0.005	16.41
	1.1862 ±0.004	1.1479 ±0.001	1.1368 ±0.003	1.1226 ±0.002	1.1171 ±0.005	1.0988 ±0.004	25.17
	1.2087 ±0.001	1.1962 ±0.003	1.8153 ±0.005	1.1768 ±0.002	1.1621 ±0.004	1.1569 ±0.002	34.36
	1.0886 ±0.002	1.0834 ±0.004	1.1769 ±0.003	1.0712 ±0.005	1.0645 ±0.001	1.0581 ±0.002	54.08
	0.9646 ±0.005	0.9539 ±0.003	0.9471 ±0.001	0.9321 ±0.002	0.9276 ±0.004	0.9116 ±0.001	75.85
	0.6646 ±0.002	0.6312 ±0.004	0.6122 ±0.003	0.5907 ±0.001	0.5721 ±0.002	0.5538 ±0.005	100.00

Table 3
Viscosities of lanthanum chloride in different solutions at 308°K

$10^3 \times C/$ mol dm^{-3}	3.5	2.7	2.2	1.8	1.5	1.2	Solvent composition %
$10^3 \times n/$ Kg m^{-1} s^{-1}	0.8231 ±0.000	0.7992 ±0.001	0.7864 ±0.002	0.7726 ±0.000	0.7631 ±0.003	0.7562 ±0.005	00.00
	0.8521 ±0.000	0.8466 ±0.000	0.8321 ±0.005	0.8261 ±0.001	0.8206 ±0.002	0.8176 ±0.003	08.02
	0.9551 ±0.004	0.9469 ±0.001	0.9303 ±0.005	0.9261 ±0.001	0.9112 ±0.005	0.8991 ±0.000	16.41
	0.9984 ±0.005	0.9826 ±0.001	0.9734 ±0.000	0.9582 ±0.001	0.9463 ±0.000	0.9383 ±0.004	25.17
	1.1367 ±0.001	1.1287 ±0.005	1.1092 ±0.001	1.0986 ±0.004	1.0903 ±0.000	1.0813 ±0.003	34.36
	1.0431 ±0.005	1.0281 ±0.001	1.0103 ±0.003	1.0089 ±0.001	1.0076 ±0.002	1.0058 ±0.000	54.08
	0.8936 ±0.005	0.8773 ±0.001	0.8621 ±0.004	0.8567 ±0.000	0.8402 ±0.002	0.8284 ±0.003	75.85
	0.5762 ±0.001	0.5598 ±0.005	0.5431 ±0.000	0.5362 ±0.000	0.5202 ±0.003	0.5192 ±0.001	100.00

The viscosity data have been fitted in Jone-Dole equation (Jone and Dole 1929).

$$n/n_0 = 1 + A \sqrt{C} + BC \dots \dots (2)$$

where C is the molar concentration, A and B are the coefficients representing ion-ion and ion-solvent interaction respectively.

The values of A and B were obtained from the intercept and slope of the linear plots of $n_{sp} / \sqrt{C}$ vs $\sqrt{C}$.

Least square method was used to obtain these coefficients and are tabulated in Table 5.

An irregular variation in the values of "A" coefficient has been observed which can be explained as:

a) Negative and positive values of "A" show an incomplete dissociation and ion association of electrolyte in aqueous methanol solvent. The oxygen of methanol has a tendency to hold water molecules as it happens in higher alcohols. This may be due to different degrees of hydration of ion instead of formation of three dimentional clusters (Fahimuddin and Farooqi 1984).

b) Variation of "A" values is due to the size of the ions which differs in their degree of hydration.

In the present wok a few values of "A" have been found nega-

tive which are meaningless (Seal and Chatterjee 1979; Blokhra and Kumar 1983).

With the rise of temperature, the values of "A" have been found to be decreasing with a few exceptions. This is due to greater thermal agitation and reduction of attractive forces between ions (Das and Das 1983). The increase in "A" values is due to the inter-penetration effect which brings the ions closer (Gopal and Singh 1970; Das et al 1976).

The B-coefficient can be discussed with the help of stokes equation (Stokes and Mills 1965) given as :

$$n^E + n^A + n^D = n^O B \dots \dots (3)$$

where n^E and n^A are the viscosity increments due to size and shape of the ions and orientation of the solvent molecules around the ions respectively, n^D is the decrement due to distortion of solvent structure by the ions. The tabulated results show a decrease in the B coefficients with the increase of temperature with the exception of some cases, this indicates that the solvent distortion is large and solvents are behaving as structure breakers (Misra and Das 1978).

In mixed solvents the n^D is of considerable magnitude due to the significant distortion in the solvent molecules present in the vicinity of ionic field (Iqbal et al 1976).

Table 4
Viscosities of lanthanum chloride in different solutions at 313°K

| $10^3 \times C/$ mol dm^{-3}	3.5	2.7	2.2	1.8	1.5	1.2	Solvent composition %
$10^3 \times n/$ Kg m^{-1} s^{-1}	0.7436 ±0.002	0.7245 ±0.005	0.7103 ±0.001	0.6987 ±0.003	0.6845 ±0.000	0.6784 ±0.000	00.00
	0.7684 ±0.003	0.7599 ±0.004	0.7506 ±0.001	0.7434 ±0.002	0.7367 ±0.005	0.7462 ±0.000	08.02
	0.8697 ±0.005	0.8648 ±0.001	0.8558 ±0.003	0.8498 ±0.000	0.8406 ±0.001	0.8319 ±0.000	16.41
	0.8995 ±0.001	0.8831 ±0.000	0.8767 ±0.005	0.8666 ±0.001	0.8602 ±0.003	0.8575 ±0.000	25.17
	0.9989 ±0.003	0.9912 ±0.001	0.9837 ±0.005	0.9773 ±0.001	0.9703 ±0.000	0.9608 ±0.002	34.36
	0.9347 ±0.002	0.9208 ±0.001	0.9039 ±0.005	0.8998 ±0.001	0.8903 ±0.003	0.8897 ±0.000	54.08
	0. 7992 ±0.002	0.7864 ±0.003	0.7704 ±0.000	0.7665 ±0.005	0.7601 ±0.001	0.7586 ±0.000	75.85
	0.5561 ±0.000	0.5282 ±0.002	0.5189 ±0.001	0.5076 ±0.005	0.4937 ±0.003	0.4851 ±0.001	100.00
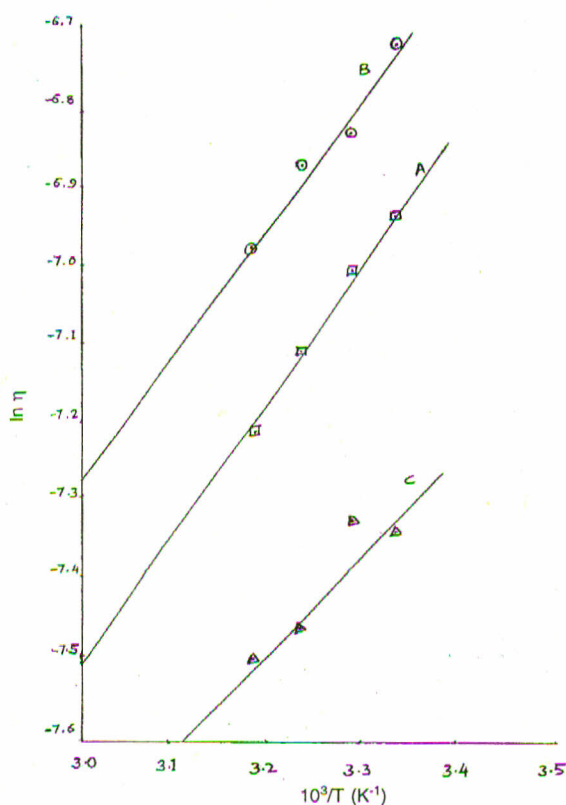
Fig 1. Plots of ln η vs 1/T (LaCl$_3$)C = 3.5 x 10^{-3} mol. dm^{-3}.
A; in pure water, B; in 54.08% methanol, C; in pure methanol.

A solute with a positive B coefficient possesses structure making effect and a less positive or negative value indicates structure breaking effect (Mandal and Sanyal 1982).

As the molecular mass of the salt is very large, it may show an obstructive effect which causes bending of the streamlines around a large solute particle. In such a case B coefficients will be always positive irrespective of how it interacts with the solvent (Mandal and Sanyal 1982).

As the methanol is generally considered less structured than water (Criss and Mastoianni 1971), the B coefficients have been found higher in pure methanol at each temperature indicating a much structure promoting effect on methanol. Activation parameters such as E^*_n, ΔG^* and ΔS^* have been determined at 298, 303 and 313°K

The concentration of the solution was 3.5 x 10^{-3} mol dm^{-3} in pure water, pure methanol and 54.08% methanol. The values of energy of activation have been obtained from the slope of the plots of 1n η vs 1/T given in Table 6. Plots are shown in Fig 1.

The values of change of free energy of activation (ΔG^*) have been calculated by the following equation (Nightinagle and Benck 1959).

$$\Delta G^* = \frac{RT (l_n n v)}{h.N} \qquad (4)$$

Table 5
'A' & 'B' coefficients of Jone-Dole equation for chloride at different temperature

Solvent Composition	298°K A/ $(dm^3mol^{-1})^{1/2}$	298°K B/ $(dm^3mol^{-1})^{1/2}$	303°K A/ $(dm^3mol^{-1})^{1/2}$	303°K B/ $(dm^3mol^{-1})^{1/2}$	308°K A/ $(dm^3mol^{-1})^{1/2}$	308°K B/ $(dm^3mol^{-1})^{1/2}$	313°K A/ $(dm^3mol^{-1})^{1/2}$	313°K B/ $(dm^3mol^{-1})^{1/2}$
00.00	-0.3125	32.8598	0.3518	26.2822	-0.1353	42.1122	-0.8577	54.1678
08.02	-0.1696	25.4541	1.4635	3.4002	1.9584	0.3455	2.9431	-14.5186
16.41	0.4835	7.5198	1.4973	8.9854	0.9716	19.2273	2.6111	-5.5536
25.17	-0.0425	23.3381	1.2719	9.3569	-0.5549	35.6323	2.0837	2.0762
34.36	0.2568	15.1344	2.1914	-1.4828	1.0945	13.4691	2.9485	-12.7472
54.08	-0.0169	19.0161	3.0122	-18.2815	3.2842	-18.1531	2.4028	-0.8979
75.85	-0.6196	19.3474	3.6847	-11.3264	3.7801	-15.0372	2.1578	2.7833
100.00	-0.9002	71.6012	-0.9970	106.0772	-0.0216	54.4135	-0.6772	73.7174

Table 6
Viscosites of lanthanum chlorides in different solvents at different temperatures
$C = 3.5 \times 10^{-3}$. mol.dm^{-3}

Temperature(K°)	Solvent ΔG^*/ K.J.mol^{-1}	Solvent ΔS^*/ J.K^{-1}.mol^{-1}	Lanthanum Chloride (In pure water) ΔG^*/ K.J.mol^{-1}	Lanthanum Chloride (In pure water) ΔS^*/ J.K.mol^{-1}
298	9.1662	25.0000	9.3856	19.6560
303	9.0467	25.0000	9.3035	19.6026
313	8.8355	24.0000	8.9232	20.1913
E^*_n / K.J.mol^{-1}	16.6288			15.2431
[In 54.06% methanol]				
298	10.9135	26.1000	11.0721	7.4862
303	10.7139	26.4000	10.9875	7.6419
313	10.6266	25.8000	10.9757	7.4354
E^*_n / K.J.mol^{-1}	1 8.7074			13.3030
[In pure methanol]				
298	9.9654	0.400	10.3706	-4.1107
303	9.9757	0.0053	10.6417	-4.9369
313	10.0395	-0.1987	10.5556	-4.5041
E^*_n / K.J.mol^{-1}	9,9773			9.1458

where 'h' is the Plank constant, 'V' is molar volume (Nightinagle and Benck 1959) and 'N' is the Avogadro number.
The change of entropy of activation (ΔS^*) is given :

$$\Delta S^* = \Delta H^* - \Delta G^* / T \qquad (5)$$

The E^*_n does not differ appreciably from activation enthalpy change (ΔH^*) (Varma and Jain 1981). Thus

$$\Delta S^* = \Delta E^*_n - \Delta G^* / T \qquad (6)$$

From Table 6, it is apparent that the values of E^*_n and ΔS^* are lesser than that of the pure solvent indicating that the solvent structure is broken by th presence of the solute (Jabeen 1998).

References

Afzal M, Ahmed H, Ali Z 1991 Measurements of excess thermodynamic function from viscosity data. *J Chem Soc Pak* **13** (1) 4-10.

Blokhra R L, Kumar S 1983 Solute-solvent interactions in multicomponents electrolyte solutions. *J Ind Chem Soc* **60** 27-29.

Criss C M, Mastolanni M J 1971 Viscosity coefficients of ions in various solvents. *J Phys Chem* **75** (16) 2532-2534.

Das B K, Singh K C, Das P K 1976 Viscosity of solutions of sodium bromate and potassium iodate at 30°,35° 40°, calcium chloride at 35°, 40° and 45° and barium chloride at 30°, 40° and 45°. *J Ind Chem Soc* **53** 112-113.

Das P K, Das P B 1983 Viscosity of Sr $(NO_3)_2$ and Cd $(NO_3)_2$ in mixed solvent at different temperatures. *J Ind Chem Soc* **60** 501-502.

Fahimuddin, Farooqi A N 1984 The influence of salt concentration and temperature on the activation energy of aqueous solution by viscosity method. *Pak J Sci Ind Res* **27** 271-274.

Fahimuddin, Adhami I M, Zahid M 1989 Viscosity of sodium citrate solutions in acidic aqueous method. *Kim Ve Sanay* **32** 108-111.

Ganapathy K, Ramanu J 1980 Solute solvent interactions. Part I: Viscosity of sodium acetate in acidic aqueous ethanol. *J Ind Chem Soc* **57** 613-616.

Gopal R, Singh K 1970 Study of the applications of the Debye-Huckel theory in dilute tetraalkyl ammonium salt solutions in formamide from apparent molal volume data. *Z Phys Chem Frank Ausg.* **69** 81-87.

Herskovit T T, Kelly T M 1973 Viscosity studies of aqueous solutions of alcohol, ureas and amides. *J Phys Chem* **77** (3) 381-388.

Iqbal M J, Saleem M, Afzal M 1976 Viscosity and ion-solvent interactions. *J Sci* **3** (1) 21-24.

Jabeen S 1993 viscometric study and determination of activation parameters of D Tungsto silica and D-Tungsto phosphoric acids in pure and mixed solvents at different temperatures. *J Bangladesh Ac Sc* **17** 247-255.

Jabeen S 1994 Study of ion solvent interaction by viscosity measurements of ascorbic and sulfanitic acids. *Physical Chemistry* **13** 7-21.

Jabeen S 1998 Viscosity and activation parameters of D-Molybdo Phosphoric acid in pure and mixed solvents at different temperatures. *J Bangladesh Ac Sci* **22** (1) 21-27.

Jones G, Dole M 1929 The visocity of aqueous solutions of strong electrolytes with special reference to barium chloride. *J Am Chem Soc* **51** (10) 2950-2968.

Levitt BP 1972 *Findlay's Practical Physical Chemistry.*

Longman, Landon 89-90.

Mandal SK, Sanyal S K 1982 Viscosity Bcoefficient of phenols and benzyl alcohol. *J Ind Chem* **59** 803-804.

Misra P P, Das P B 1978 Ion solvent viscosity of branates, iodates and sulphates of potassium and sodium in dioxane-water mixtures al-different temperatures. *J Ind Chem Soc* **55** 137-140.

Nightingale ER, Benck R F 1959 viscosity of aqueous flouride and sodium per iodate solutions, ionic energies and entropies of activation for viscous flow. *J Phys Chem* **63** 1777-1781.

Sandhu J S, Wadi R K, Kashyap U 1983 Viscosity of glycine in alcohol water mixtures at 308.15 K . *J Ind Chem Soc* **60** 192-194.

Seal B K, Chatterjee D K 1979 Viscosity behaviour of O-amino benzoic acid and O-amino benzoate ion in aqueous solution. *J Ind Chem Soc* **56** 1196-1198.

Stokes R H, Mills R 1965 *The Stokes equation International Encyclopedia of Phy. Chem and Chem-Phys.* Pergamon press, New York.

Varma R P, Jain P K 1981 Studies on the behaviour of cobalt and calcium soaps. Part-VII: Viscosity and surface tension studies in benzene and carbotetrachloride. *J Ind Chem Soc* **58** 959-962.