# The Electrical Conductivity Of Barium Perchlorate In Different Solvents At 298K

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## ABSTRACT

The electrical conductivities of barium perchlorate $[Ba(ClO_4)_2]$ in methanol, ethanol, n-propanol and n-butanol are measured at 298K and the conductivity parameters ($\Lambda_o$, $K_A$ and R) are calculated. Values of $\Lambda_o$ are found to be in the order: MeOH > EtOH > n-Propanol > n-Butanol, but the order is reversed for the values of $K_A$ and R. This indicate the increase of ion-solvent interaction and formation of solvent separated ion-pair in the above order.

**298**

–　　　　　　　　　　　298

$\Lambda_o$　　　　( R　$K_A$ ,　$\Lambda_o$)

$\Lambda_o$　　　　　　.　　　　　　　R　　　　　　　$K_A$

R　$K_A$　　　　　　　MeOH > EtOH > n-PrOH > n-BuOH

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## INTRODUDTION

Measurements of conductivity of electrolytes has been made nearly century ago, and from the earliest times interest has been restricted to aqueous solutions and very little on non-aqueous solutions or mixed electrolytes. However interpretation has been only made on the conductance of single symmetrical electrolytes and much less attention, either practical or theoretical, has been paid to unsymmetrical electrolytes (especially associated ones) or to the mixture of the electrolytes.

Some studies of unsymmetrical electrolyte solutions have been made in the past few decades. Das and Patriak (1961) have been studied sthe conductance of the solutions of barium chloride and bromide in dioxane-water mixtures at 35°C, the spectroscopic and conductance studies of $CoCl_2$ in dimethylsulfoxide have been determined by (Libus et al., 1982), Akrawi (1981) has measured the conductivities of unsymm- etrical (alkaline earth

and transition metal halides) salts in methanol at 25°C over a wide range of concentration and the results were analyzed by using LW equation. The conductometry and potentiometric measurements of alkali earth chloride in methanol at different temperatures (5-45°C) have been studied by (Doe et al., 1987) and the results were determined by using Fuoss and Edelson equation, the ionic association constant of $M(ClO_4)_2$ where (M = Co, Ni, Zn, Cu) were determined conductometrically in methanol-ethylene glycol mixtures at 5-45°C. Yokoyoma and Ohta (1989) have measured the association constants of $K_2SO_4$ in water and the results were analyzed by Jenkin and Monk method at 0-50°C.

The conductance behaviour of alkaline earth perchlorate in methanol-ethlyene glycol mixtures at different temperatures were also studied and data were analyzed by an improved Fuoss and Edelson method; the $K_A$, $\Delta G°$, $\Delta H°$ and $\Delta S°$ parametrs with $\Lambda_o$ have been determined (Doe et al., 1990).

Conductance measurements were emloyed (Kumar, 1988-1989) to determine the limitting conductances, the degree of dissociation of butyrates of strontium and barium in 70% methanol at 30% nitrobenzene (v/v) at different temperatures. These results show that the salts behave as weak electrolytes at higher concentrations.

(Jauher et al., 1988) had measured the conductances of $Et_4NBr$ and $Et_4NClO_4$ in dimethyl sulphoxide-water mixtures  at 25 °C at different percentages.The data were analysed by Fuoss-Hsia equation to calculate the conductivity data. The same authors (Jauher et al., 1988) had measured also the conductances of Li,Na, and K perchlorates in different percentages of dimethyl formamide-water mixtures at 25 °C and the conductivity parameters were determined by Fuoss-Onsager-Skinner equation and Fuoss-Hsia equation .

Conductance measurements had been made on solutions of $NaClO_4$ and $C_6H_5COONa$ in acetonitrile + water at 298.15 K . $\Lambda_o$, $K_a$ and R were obtained by Lee-Wheaton equation (Niazi  et al., 1993).

Precise conductance measurements of $LiClO_4$ in N,N-dimethylacetamide at 25 °C were reported by using 1978 Fuoss conductance equation (Das et al., 2002). The electrolytic conductances of $LiClO_4$ in propylene carbonate-Toluene mixtures at 25,30 and 35 °C had been measured by (Moumouzia et al.,1998) $\Lambda_o$, $K_a$ and R were calculated by means of Lee-Wheaton equation .

We have measured the electrical conductivities of $Ba(ClO_4)_2$ in methanol, ethanol, n-propanol and n-butanol at 298K and conductivity parameters were calculated using LW equation.

## EXPERIMENTAL

Methanol and ethanol were purified and dried using the same procedure as before (Akrawi, 1981). n-propanol and n-butanol were refluxed over calcium oxide for 2 days and fractionally distilled. The salt barium perchlorate was recrystallised three times from conductivity water, then dried at 110°C for 14 hours.

A 427 multi-frequency LCR meter (Hewlett-Packard) was used for measuring the resistance of the solution from which the conductance obtained with accuracy 0.05% at 1KHz frequency. A thermostat of type Hakke $G_3$with a thermo bath $D_3$ was used for controlling the temperature of the conductance cell with ±0.1°C sensitivity. The nitrogen line was used to ensure complete isolation of the system.

The conductivity cell used in this work has two platinized platinum electrodes with cell constant of 0.05582 cm$^{-1}$. This cell was designed to maintain an  isolation during the

several additions of stock solution. A plastic syringe (1 ml) was used for injection the stock solution into the conductivity cell. All stock solutions were generally prepared by weighing using freshly prepared solvents. For conductivity measurements a known amount of the solvent was added to a dry, clean and weighed conductivity cell, and the cell reweighed again then the cell was placed in a thermostated water bath at the required temperature. The resistance of the solvent was measured then a small amount of the stock solution was injected by a plastic syringe (which was weighed before and after each addition) into the cell. Nitrogen gas was passed for about 2-3 minutes for mixing the solution, and then the resistance of the solution was measured. This procedure was repeated for 10-12 times for each run.

After the completion of all additions, the cell was dried, reweighed again to calculate the change in the weight which was found that the loss not be more than 0.02%.

## RESULT AND DISCUSSION

According to Lee-Wheaton theory and in the case of unsymmetrical electrolyte $MX_2$ (i.e. 2:1), it will ionize to $M^{+2}$ and $X^{-1}$. The possible association equilibria are:

$$M^{+2} + X^{-1} \quad \xrightleftharpoons{K_A^{(1)}} \quad MX^{+1}$$

$$MX^{+1} + X^{-1} \quad \xrightleftharpoons{K_A^{(2)}} \quad MX_2$$

This means that there are three ionic species present in the solutions which are $M^{+2}$, $X^{-1}$ and $MX^{+1}$, since $MX^{+1}$ is an ion-pair conducting species.
In this case:
$$\Lambda_{equiv.} = f(K_A^m \ldots K_A, C, R, \lambda_\circ, \lambda_{\circ\,s}).$$
$$i$$

Using this expression in least –square curve fitting procedure (Unsym.) which was described by Lee and Wheaton (1978), all the terms above can be determined at the minimum value of $\sigma_s(\Lambda)$, where $\sigma_s(\Lambda) = [\ \sum(\Lambda_{equiv.} \text{ calculated} - \Lambda_{equiv.} \text{ (exptly)}^2/\text{ Np}]^{1/2}$ where Np is the number of points of measurements .
In the case of $MX_2$ where s (no. of ions) = 3, $\Lambda_{equiv.}$ is given by:

$$\Lambda_{equiv.} = f(M^{+2}, MX^{+1}, X^{-1}, K_A^{(1)}, K_A^{(2)}, R).$$
Where $\lambda_{MX}^{+1} = \lambda_{BaClO4}^-$, $\lambda_M^{+2} = \lambda_{Ba}^{2+}$, $\lambda_X^{-1} = \lambda_{Cl}^-$

The input data to computer program are:
T, D, $\eta$, $Z_i$ and $\lambda_i°$ for each ionic species, $K_A^{(1)}$, $K_A^{(2)}$, $\lambda_{MX}^{+1}$, $\lambda_M^{\circ+2}$, $\lambda_X^{-1}$, and°R, all in the form $K_{(min)}^{(1)}$, $K_{(max)}^{(2)}$, and $\Delta K_A^{(1)}$ ….etc., then the experimental data which are the molar concentration and the equivalent conductance,. The multi parameter procedure calculate the minimum $\sigma_s(\Lambda)$ as mentioned before.

Experimentally, we have measured the conductance of barium perchlorate in methanol, ethanol, n-propanol and n-butanol at 25°C. The equivalent conductance of 10-1concentrations of $Ba(ClO_4)_2$ solution covering the range $1\times10^{-4} – 17\times10^{-4}$ mol. /l in the four alcohols have been calculated and the plot of $\Lambda_{equiv.}$ Against $C^{1/2}$ for them are shown in Figure (1). The results of analysis of the concentration-conductance data are given in Table (1). The results of the analysis shows that both of the values of $(\lambda°Ba^{+2})$ and $(\lambda_oBaClO^{+1})$ decreases in the order: MeOH > EtOH > n-PrOH > n-BuOH, due to the increase of viscosity of the medium in the same order (Doe et al., 1999). The plot of

Walden product of the ionic species $Ba^{+2}$ and $BaClO_4^{+1}$ against 1/D is shown in Figure (2). It is clear that $\lambda_\circ \eta$ decrease with decreasing D. The increase of D of the solvent will increase the solvating power of that solvent, this causes that the ion will move with only the primary solvation shell in the solvent and the effect of the secondary solvation appears to be very small (Doe and Kitagaw, 1985). Thus the size of the primary solvated ion is expected to be smaller in the order: MeOH < EtOH < n-PrOH < n-BuOH. The ion association constant $K_A^{(1)}$ increase with decreasing D of the solvent due to the multiple-step association process with solvation and desolvation of $ClO_4^-$ by the alcohol molecules (Evans and Gardam, 1968; Evans et al., 1971).

$$Ba^{+2} + ClO_4^-\,(ROH)_n \rightleftharpoons Ba(ROH)_nClO_4 \rightleftharpoons Ba(ROH)_n-ClO_4 + ROH$$
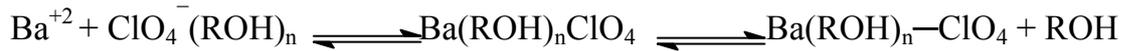
The increasing effect of $K_A^1$ due to this multiple-step association process increases in the order: MetOH, EtOH, PrOH and BuOH (Matesich et al., 1970).

The values of R obtained (Table 1) varied with the variation of the solvent. The order of R is in MeOH < EtOH < n-PrOH < n-BuOH which can be explained by the formation of solvent separated ion-pair which increases with the decrease of D. This is in accord with the result of the multiple-step association of $ClO_4^{-1}$ by the alcohol which had been found by Evans (Evans et al., 1971) and also in agreement with the results found by (Lind and Fuoss, 1961: Fabry and Fuoss, 1964) for symmetrical electrolyte in dioxane-water mixtures.

Here again, LW equation is applied also to the unsymmetrical electrolyte at different solvents (17.49 < D < 32.62) in a good extent. It is a first equation which can calculate $\lambda^\circ$ theoretically for the conductor ion-pair $(MX^{-1})$ formed in the solution.

Table 1: The conductance parameters ($K_A$, $\lambda^\circ Ba^{+2}$, $\lambda^\circ BaClO^{+1}$, $\lambda^\circ ClO_4^-$ R, $\sigma_s(\Lambda)$) for $Ba(ClO_4)_2$ electrolyte in MeOH, EtOH, PrOH and BuOH at 25°C, with the Walden product for $Ba^{+2}$ and $BaClO_4^{+1}$.

| Parameters | MeOH | EtOH | PrOH | BuOH |
|---|---|---|---|---|
| R(A°) | 6.60 | 8.5 | 9.8 | 10.4 |
| $K_A$ | 410 | 1050 | 1634 | 1956 |
| $\lambda^\circ BaClO^{+1}$ | 47.64 | 20.87 | 11.18 | 7.59 |
| $\lambda^\circ Ba^{+2}$ | 59.80 | 27.34 | 13.97 | 9.45 |
| $\lambda^\circ ClO_4$ | 70.00 | 32.04 | 16.42 | 11.22 |
| $\sigma_s(\Lambda)$ | 0.062 | 0.066 | 0.056 | 0.049 |
| $\lambda^\circ BaClO^{+1}\eta$ | 0.2594 | 0.2258 | 0.2178 | 0.1965 |
| $\lambda^\circ Ba^{+2}\eta$ | 0.3256 | 0.2958 | 0.2721 | 0.2447 |
| D | 32.62 | 24.33 | 18.3 | 16.2 |

Comparing $\lambda^\circ ClO_4^-$ in water at $25^\circ C$ with our data in different alcohols ,(Jauher et al., 1988), in a series of papers ,pointed out that $\lambda^\circ ClO_4^-$ in water at 25 $^\circ$C is 68.00 which is almost equal or little less than our $\lambda^\circ ClO_4^-$ value in methanol (Table(1)) This may be understand as discussed by Lee and Wheaton (1978) that in water (D~79) and in presence of hydrogen bonding, the salvation will be higher and then both the relaxation and electrophoretic effects will become larger which reduce ionic mobility slightly .
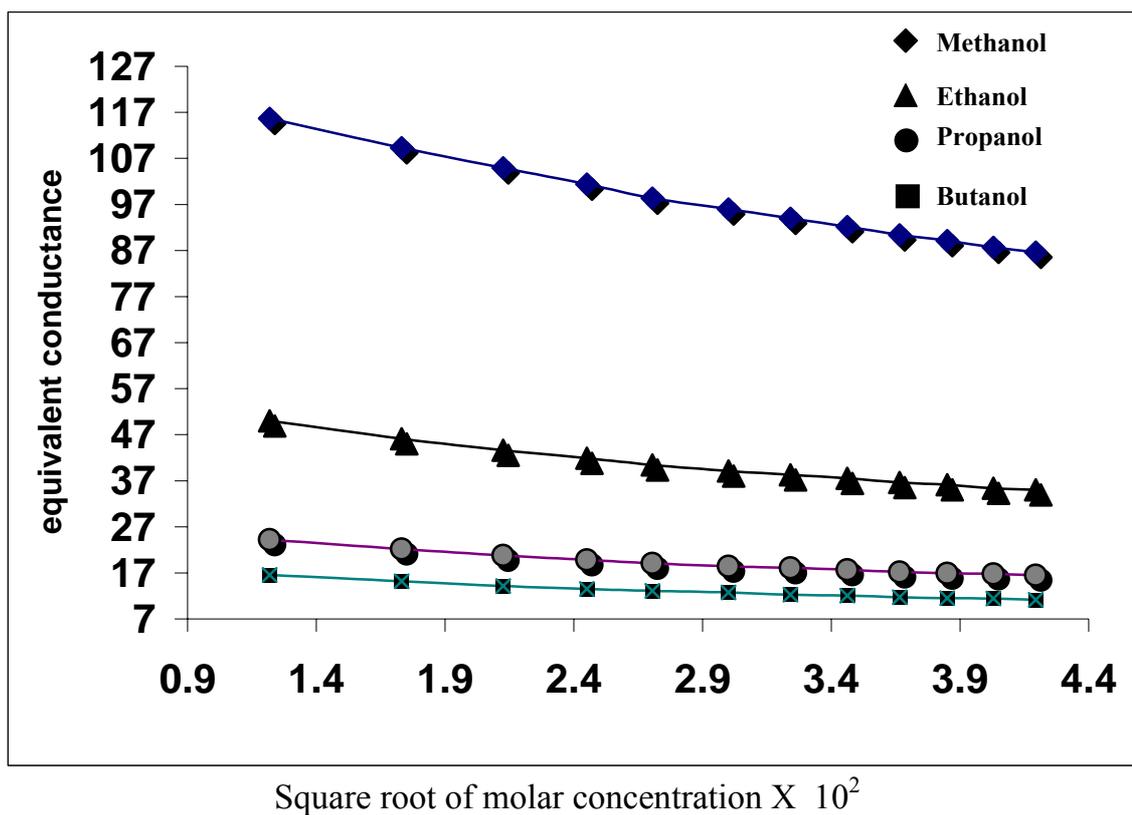
Fig. 1: The plot of equivalent conductance against the square root of molar $BaClO_4^+$ concentration for $Ba(ClO_4)_2$ in different solvents at 25 °C
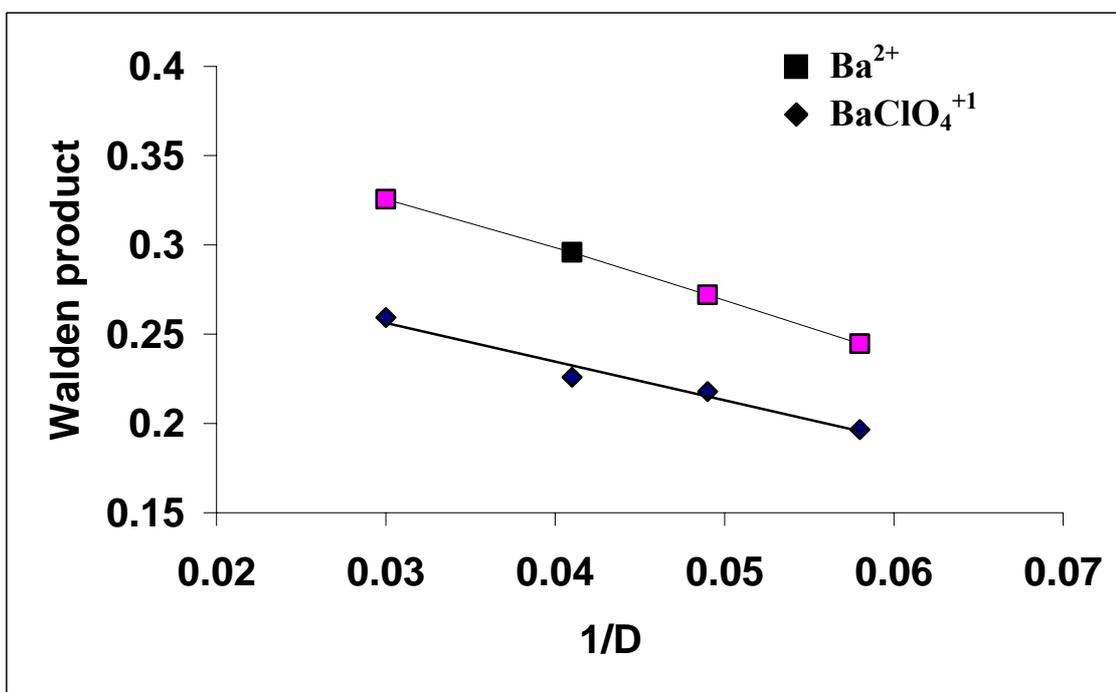


Fig 2: The plot of Walden product of both the barium ion and $BaClO_4^{+1}$ ion pair against 1/D at 25

**RFERENCES**

Akrawi, B.A., 1981. Ph. D. Thesis, Surrey University, Guildford, Surrey.

Das, D., Das, B.J. and Hazra, D.K., 2002. Conductance of some 1:1 Electrolytes in N,N-dimethylformamide at 25 $^{o}$C, Solution Chemistry, 31(5), pp.425-431.

Das, P.B. and Patraik, D., 1961. Conductance of Barium Chloride and Bromide in Dioxane-water Mixtures at 35°C, J. Indian Chem. Soc., 38, No. 5, pp. 410-413.

Doe, H. and Kitagawa, T., 1985. Conductometric Study of Co(II), Ni(II), Cu(II) and Zn(II) Perchlorates in Methanol-Ethylene Glycol Mixtures, Bull. Chem. Soc. Jpn., 58, pp.2975-2980.

Doe, H., Wakamiya, K. and Kitagawa, T., 1987. Comparison of Stability Constants of Alkaline Earth Chlorides Between Condutometric and Potentiometric Studies, Bull. Chem. Soc. Jpn., 60, pp.2231-2235.

Doe, H., Ohe, H., Matoba, H., Ichimura, A. and Kitagawa, T., 1990. Conductometric Study of Ca(II) , Sr(II) and Ba(II) Perchlorates in Methanol-Ethylene Glycol Mixtures, Bull. Chem. Soc. Jpn., 63, pp.2785-2789.

Evans, D.F. and Gardam, P., 1968. Transport Process in Hydrogen- Bonding Solvents. The Conductance of Tetraalkyl-Ammonium Salts in Ethanol and Propanol at 25°C, J. Phys. Chem., 72, pp.3281-3286.

Evans, D.F., Thomas, J., Nadas, J.A. and Matesich, S.M.A., 1971. The Conductance of Electrolytes in Acetone and in 1-Propanol-Acetone Mixtures at 25°C, J. Phys. Chem., 75, pp.1714-1722.

Fabry, T.L. and Fuoss, R.M., 1964. Conductivity of Alkali Halides (LiCl and RbI) in Dioxane-Water Mixtures, J. Phys. Chem., 68, pp.971-974.

Jauher, S.P., Guraya, P.S. and Narula, S.P., 1998. Condactances of Lithium,Sodium and Potassium Perchlorates in Diethyl-formmide–Water Mixtures, Indian J.Chem., Vol. 27A., pp.629-631.

Jauher, S.P., Guraya, P.S. and Narula, S.P., 1998. Conductance Behaviour of Tetraethyl-ammonium Bromide and Perchlorate in Dimethylsulphoxide-Water Mixtures at 25$^{o}$C, Indian J.Chem., Vol.27A., pp.727-729.

Kumar, A., 1988-1989. Conductometric Studies of Strontium and Barium Butyrates in Methanol and Nitrobenzene, Colloids and Surface, 34, pp.87-90.

Lee, W.H. and Wheaton, R.H., 1978. Conductance of Symmetrical, Unsymmetrical and Mixed Electrolytes, J. Chem. Soc. Faraday II, 74, pp.743-765.

Libus, W., Pilarczky, M., Pastewski, R. and Szuchnicks, T., 1982. Conductance of CoCl$_2$ in Dimethylsulfoxide, Electrochimica Acta, 27, pp.573-577.

Lind, J.E. and Fuoss, R.M., 1961. Electrolytic Conductance of Salts of Several Cyanocarbon Acids, J. Phys. Chem., 65, pp.1414-1418.

Matesich, S.M.A., Nadas, J.A. and Evan, D.F., 1970. Transport Process in Hydrogen-Bonding Solvents. The Conductance of Tetraalkyl-Ammonium Salts in 2-propanol, J. Phys. Chem., 74, pp.4568-4573.

Moumouzias, G. and Ritzoulis, G., 1998. Conductometric study of LiClO$_4$ in Propylene carbonate-Toulene Mixtures,Ber.Bunsen-Ges.Phys. Chem. Chem. phys.102(5), pp. 786 -791.

Niazi, M.S.K. and Khan, A., 1993. Conductometric Studies on Sodium Perchlorate and Sodium Benzoate Solutions in Binary Mixtures of Acetonitrile with Water at 298.15 K , J.Chem. Eng, Data, 38(1), pp.98-100.

Yokoyama, H. and Ohta, T., 1989. Conductivity Measurements of Potassium Sulfate in Water at Different Temperatures, Bull. Chem. Soc. Jpn., 62, pp.345-348.