Original Research Article

Thermodynamic studies of MnCl2 salt in aqueous medium by conductivity method

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Abstract The solubility product are measured for the salt $MnCl_2$ in ethanol solvent system at 299.15K, 306.15K and 311.15K by conductometric method. The thermodynamic parameters for the dissolution of $MnCl_2$ such as ΔG, ΔS and ΔH were calculated from conductivity values at different temperatures in aqueous medium. It was found that the solubility and solubility product of $MnCl_2$ significantly decreased linearly by decreasing concentration of salt in water solvent systems. The Gibbs free energy ΔG, enthalpy ΔH and entropy ΔS were also changed.
Key Word: Conductivity, Solubility, solubility product, Gibbs free energy ΔG, enthalpy ΔH and entropy ΔS, etc.

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INTRODUCTION

To study the solubility product of $MnCl_2$ in water solvent, conductometric method is widely used because of its various advantages such as low cost, eco-friendly, less time consuming, proper thermodynamic calculation with different parameters and most important easy to operate[1,2,3] Magnesium is a typical ionic halide, and is very soluble in water. Magnesium has a variety of biological roles in enzymology, cell membrane/wall structure, muscle cell physiology, and nucleic acid structure. Magnesium is an essential co-factor in many enzymes, including DNAse, some restriction enzymes, and Ribonuclease-H. Magnesium chloride is widely used to supply the magnesium ion in various molecular biology applications, including PCR reactions[1,2]. also Magnesium chloride (MnCl2) has been used as an anesthetic agent for cephalopods more than 75 years ago[1]. And its property are varied in water medium[2,3]. Using conductometric method, researcher can calculate all thermodynamic parameters for specific reactions and also investigate solubility product. By using conductometric method, basic research on thermodynamic studies like enthalpy, entropy, Gibbs free energy can also be determined[1,2]. The factors responsible for the stability of metal salt are charge and size of the metal ion, type of the metal ion, counter ion, nature of the temperature and physical properties of solvents. From conductometric method, the value of solubility product (Ksp) can be evaluated from the value of solubility of metal salt. In this paper we have reported the solubility product of MnCl2 in water solvent at 299.15K, 306.15K and 311.15K. This study is useful to understand the effect of ionic size, solvent, temperature and the nature of the solute-solvent interaction. Conductivity method is used for the study of the dissolution of compound in mixed and pure solvent system[1]. Also it is an important tool to measure degree of disassociation of weak electrolyte, to measure degree of hydrolysis and for the analysis of the physicochemical properties of electrolyte in solution[1].Conductometric measurement at different temperature gives idea of solubility product of salt. Which is useful to explain the thermodynamic properties $MnCl_2$ salt in aqueous medium. Molar solubility “S”, solubility product “Ksp” and Gibbs free energy "ΔG" is determined from the following equation[1].

$Ksp = [A+] [2Cl^-]^2 = S \times 4S^2 = 4S^3$ ..(1)

$\Delta G = -RT \ln (Ksp)$ ..(2)

Where "R" is the universal gas constant, 'T' is the absolute temperature and "ΔG" is Standard Gibbs free energy is related to "ΔH" and "ΔS" by following relation

$\Delta G = \Delta H - T\Delta S$ ..(3)

The value of thermodynamic parameters are calculated at two different temperature T_1=299.15K and T_2 = 305.15K by considering temperature range 299.15K to 311.15K

MATERIAL AND METHOD

In the present research work, conductivity method was used for the study of the influence of temperature on solute-solvent interaction in alcoholic medium. All reagents are used such as $MnCl_2$ (E. Merck), Ethanol (E. Merck) each of these analytical grade reagent. These stock solutions were prepared in double distilled water. Digital Conductivity meter ELICO (CM-180), JCE (LJ-101) magnetic stirrer, Thermostat (No.51633075, India) Pioneer Analytical Balance (SCPA64C) were used to carried out experiment. 0.01M $MnCl_2$ prepared by M/1000 molecular weight into 100ml of ethanol. Solution of different concentration (0.005M, 0.0025M, 0.00125M and 0.000625M) were prepared by considering 0.01M stock solution. And this solution was stirred for 30 minutes and then this solution was kept overnight to get maximum saturation. On next day the conductivity of different concentration solution were recorded at different temperature using digital conductivity meter. The solution was placed in water bath during the measurement of conductance and temperature was controlled by thermostat at a fixed temperature.

Calibration of Conductivity meter: At the given reading of the conductivity cell the knob of the conductivity meter was adjust and the conductivity cell was dipped in conductivity water so that the calibration was done.

Determination of cell constant: The 0.1 N KCl solution was prepared in 100 ml of distilled water then conductivity cell was immersed in a beaker which containing KCl solution and the conductance was recorded. that gives value specific conductance of KCl by considering following equation.

Cell Constant=Specific Conductance / Observed Conductance …(4)

Table 1: Cell constant (k) in cm^{-1} of conductivity cell at experimental temperature.

Temp in K	Equivalence conductance(λ) of 0.1M KCl in $x10^{-3}$ Scm^2eq^{-1}	Observed conductance(λ) of 0.1M KCl in $x10^{-3}$ Scm^2equ^{-1}	Cell Constant (k) in cm^{-1}
301.15	13.12	14.55	0.902
308.15	14.60	14.85	0.983
318.15	16.05	15.65	1.025

Determination Equivalent Conductance: It is defined as the conducting power of all the ions produced by dissolving one gram equivalent of an electrolyte in solution. It is expressed as Λ_e and is related to specific conductance as

$$\Lambda_e = \frac{\kappa \times 1000}{C} = \kappa \times \frac{1000}{M}$$ …(5)

where C is the concentration in gram equivalent per litre (or Normality). This term has earlier been quite frequently used. Now it is replaced by molar conductance. The units of equivalent conductance are $Ohm^{-1}\ cm^{1} (gm\ equiv)^{-1}$.

RESULT AND DISCUSSION

Solubility is the amount of substance dissolved into the solution. If the compound is soluble in major extent it means that its dissolution is in large amount, i.e form large numbers of ion in a solution. that's why solubility is directly related to conductance of solution. Solubility of compound can be calculated by equivalent conductance of solution at different temperature. Value of cell constant are mentioned in table-1 which is utilize to calculate equivalent conductance of solution by using equation[5]. The solubility and solubility product of the various solutions of $MnCl_2$ in aqueous medium were calculated at 299.15K, 306.15K and 311.15K shown in the table no[2,3,4] respectively. In general solubility of substance increases with temperature but from table[2,3,4] it is observed that solubility and solubility product decreases with temperature. This is because of association of $MnCl_2$ molecule takes place when temperature of solution increases. Figure-1 represent the plot between concentration of $MnCl_2$ and observed conductance, which tells that conductance decreases with decrease in concentration of solution this is because of less numbers of mobile ions present in a solution. Figure-2 represent the plot between concentration and log Ksp which shows that solubility product is low when concentration is less and it increases when concentration increases.

Table 2: Conductance measurement of $MnCl_2$ solution at different concentration and fixed Temperature 299.15K in water solvent

Concentration in Mole/lit	Observed conductance(λ) of $MnCl_2$ in $x10^{-3}$ Scm^2equ^{-1}	Specific conductance (k) of $MnCl_2$	Solubility (S)	Solubility Product (Ksp) x 10^6	logKsp
0.01	10.35	9.2746	717.295	1476.23	21.112
0.005	5.92	5.3049	410.279	2762.47	19.436
0.0025	3.39	3.0377	234.940	5187.19	17.764
0.00125	1.85	1.6577	128.212	8430.41	15.947
0.000625	1.15	1.0305	79.6995	2025.01	14.521

Table 3: Conductance measurement of $MnCl_2$ solution at different concentration and fixed Temperature 305.15K in water solvent

Concentration in Mole/lit	Observed conductance(λ) of $MnCl_2$ in $x10^{-3}$ Scm^2equ^{-1}	Specific conductance (k) of $MnCl_2$	Solubility (S)	Solubility Product (Ksp) x 10^6	logKsp
0.01	9.45	9.2799	711.648	1441.640	21.089
0.005	5.39	5.2929	405.903	2675.025	19.404
0.0025	3.05	2.9951	229.685	4846.868	17.696
0.00125	1.62	1.5908	121.996	7262.844	15.798
0.000625	0.89	0.8739	67.0230	1204.291	14.001

Table 4: Conductance measurement of $MnCl_2$ solution at different concentration and fixed Temperature 311.15K in water solvent

Concentration in Mole/lit	Observed conductance(λ) of $MnCl_2$ in $x10^{-3}$ Scm^2equ^{-1}	Specific conductance (k) of $MnCl_2$	Solubility (S)	Solubility Product (Ksp) x 10^6	logKsp
0.01	8.59	8.4800	643.891	1067.818	20.788
0.005	4.71	4.6497	353.053	1760.276	18.986
0.0025	2.55	2.5173	191.143	2793.435	17.145
0.00125	1.21	1.1945	90.6994	2984.518	14.908
0.000625	0.61	0.6021	45.7245	3823.900	12.854

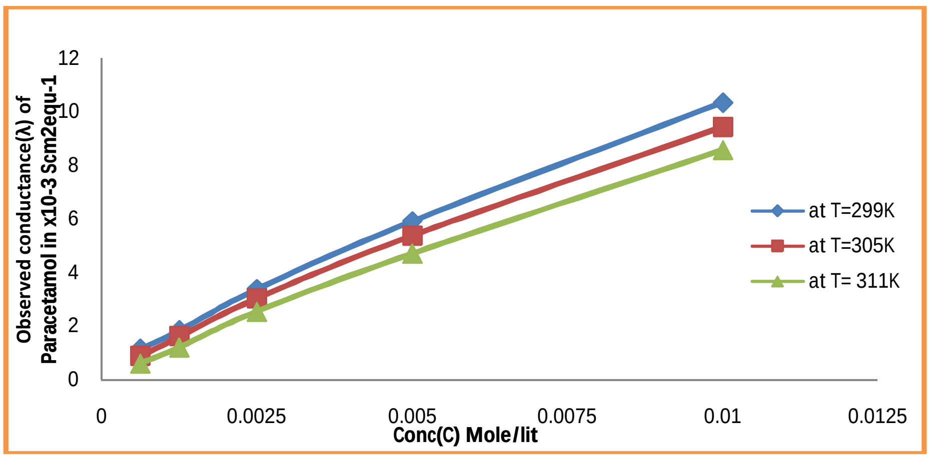

Figure 1: Plot of concentration Vs observed conductance at 299.15K, 306.15K & 311.15K

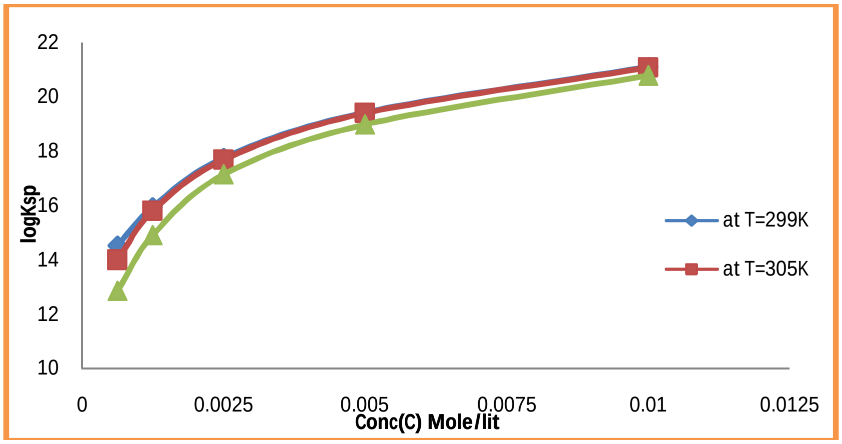

Figure 2: Plot of concentration Vs log Ksp at 299.15K, 306.15K & 311.15K

Table 5: Thermodynamic parameters of $MnCl_2$ at different concentration for temperature difference **299.15K-305.15K**

Concentration in Mole/lit	ΔG in Joule/mole	ΔH in Joule/mole	ΔS in Joule/mole
0.01	-52835.0	6012.88	155.555
0.005	-48640.9	8157.66	188.699
0.0025	-44455.4	17208.56	204.863
0.00125	-39908.5	37803.06	258.177
0.000625	-36339.2	131783.81	558.548

Table 6: Thermodynamic parameters of $MnCl_2$ at different concentration for temperature difference **305.15K-311.15K**

Concentration in Mole/lit	ΔG in Joule/mole	ΔH in Joule/mole	ΔS in Joule/mole
0.01	-54003.0	56291.16	358.097
0.005	-49689.7	78481.10	416.138
0.0025	-45315.5	103343.01	482.657
0.00125	-40454.9	166780.90	672.843
0.000625	-35853.6	215140.52	814.915

However the dissolution of $MnCl_2$ was decreased slightly and by increasing temperatures. The reversed trend in dissolution against temperature, in $MnCl_2$ was found due to its lattice energy. The solvation of ion was possibly influenced by temperature in two ways. For instance it has been reported that ions-ions interaction is usually decreased by increasing temperature that results in the solvation of ions which enhances by rise in temperature[1,2,3]. However, the solvation of ions may inversely be influenced by the rise in temperature, were a possible decrease in solvation occurs with the rise in temperature. The solubility of the salts in solutions in aqueous medium were calculated at 299.15K, 306.15K and 311.15K. But in this paper the solubility of $MnCl_2$ were studied in aqueous solvent systems notice able thing is that the solubility product of $MnCl_2$V/S different concentration of solvent systems is showed linear pattern which is shown in Figure-2. The Ksp values of $MnCl_2$ were decreased with the decrease in Concentration of systems. Form table no.5 and table no.6 it is observed that value of ΔG is negative in all cases which indicate process of dissolution of $MnCl_2$ in water is spontaneous and moving in forward direction. Spontaneity of reaction is depends upon magnitude of ΔG. If value of ΔG is higher greater is the spontaneity of reaction. ΔH is positive at high concentration and it increases with decrease in concentration. Positive value of ΔH indicate endothermic reaction and process of crystallization.ΔSi is the measure of disorder or randomness. System is stable when value of ΔS is high. At high temperature molecule associate with energy which increase randomness of molecule, hence ΔS has greater value at high temperature.

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