Dilution Effect on the Thermodynamic Parameters of some Transition Metal Salt by Viscosity Method

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ABSTRACT

The physical properties such as densities, specific viscosities of CaCl2, MnCl2 and NiCl2 at different concentration in the range (1x10-2 M to 6x10-4 M) in aqueous medium at temperature 299K, 305K and 311K are reported. The experimental data shows, the effect of concentration of solute on viscosity in aqueous medium which gives idea about the molecular interactions present in different solutions. Appreciable molecular interactions have been observed between the Chloride salt of Ca2+, Mn2+ & Ni2+ and water. The thermodynamic parameters ΔG, ΔS and ΔH for the dissolution of CaCl2, MnCl2 and NiCl2 were calculated from values of viscosity and densities at different temperatures such as 299K, 305K and 311K in aqueous medium. The experimental data gives the idea about effect of temperature on the molecular interaction and structural changes in solute.

Keywords : Specific Viscosity, Density, Thermodynamic Parameters, Thermodynamic Parameters ΔG, ΔS and ΔH, Chloride Salt of Ca2+, Mn2+ & Ni2+.

I. INTRODUCTION

Physicochemical and thermodynamic investigations play an important role in understanding the nature and the extent of the patterns of molecular aggregation that exist in liquid mixtures and their sensitivities to variations in composition and the molecular structure of the pure components[1] .Since most of the biochemical processes occur in aqueous media, the studies on the thermodynamic and transport properties of drugs in the aqueous phase provide useful information in pharmaceutical and medicinal chemistry[2].

The solute-solvent molecular interaction and their temperature dependence play an important role in the understanding of nature of solute. Viscometric properties provide valuable clues for solute–solvent interactions in the solution phase. Such results can be helpful in predicting the absorption of metal salt and transport of metal across the biological membranes.

Therefore, it may be interesting to investigate variation of their properties with temperature for understanding the mechanism of some transition metal salt such as CaCl$_2$, MnCl$_2$ and NiCl$_2$. The detailed literature survey reveals that thermodynamic and transport properties of the above mentioned chloride salt of metal in aqueous medium are scarce. This prompted us to investigate the thermodynamic and transport properties of three significant metal salt in aqueous solutions at different temperature.

Ca^{2+}, Mn^{2+} & Ni^{2+} has a variety of biological roles in enzymology, cell membrane/wall structure, muscle cell physiology, and nucleic acid structure. Ca^{2+}, Mn^{2+} & Ni^{2+} are an essential co-factor in many enzymes, including DNAse, some restriction enzymes, and Ribonuclease-H. CaCl$_2$, MnCl$_2$ and NiCl$_2$ are widely used to supply the Ca^{2+}, Mn^{2+} & Ni^{2+} ion in various molecular biology applications, including PCR reactions[3,4].

The present work represents the continuation of a systematic investigation of the viscometric properties of some transition metal salt of chloride in aqueous medium at various temperatures. Viscosity is one of the important physical property owned by the liquid. Shearing effect in the liquid is responsible for the viscous nature of the liquid which is nothing but the movement of liquid layers over each other.

The study of molecular interaction of an electrolyte in aqueous medium by viscometrically plays an important role[1,2]. Many researcher study the biologically important $CaCl_2$, $MnCl_2$ and $NiCl_2$ at different temperature[1,2,3] . The Jones-Doles equation [1] helps to evaluate the observed viscosity concentration dependence of dilute electrolyte solutions.

II. Material and Method

The chemicals $CaCl_2$, $MnCl_2$ and $NiCl_2$ of AR grade were used. The densities of pure solvent and solutions of various concentrations were measured at different temperature using a precalibrated bicapilary pycnometer. All the weighings were made on one pan digital balance (petit balance AD_50B) with an accuracy of (±0.001)gm. Viscosities of the solutions were determined with the help of calibrated Ostwald viscometer (± 0.1% $Kgm^{-1}s^{-1}$). The flow time of solutions were measured by using digital clock of racer company having error (±0.01sec).

III. Result and Discussion

In the present investigation, the relative viscosity of $CaCl_2$, $MnCl_2$ and $NiCl_2$ solutions decreases with decrease in concentration of solutions. The increase in viscosity with increase in concentration may be ascribed to the increase in the interactions of solute-solvent. The increasing order of relative viscosity for a solution of $CaCl_2$, $MnCl_2$ and $NiCl_2$ is $Ni^{2+}>Ca^{2+}>Mn^{2+}$ at all temperature which are consider for study. The relation between viscosity ($\eta_{sp}/\sqrt{C}$) and concentration of solution ($\sqrt{C}$) represented by plotting the graph (Figure1-3). The plotted graphs prove the validity of Jones-Dole equation for all systems by giving linear straight line. The values of Jones-Dole coefficients especially β -coefficients are the slope of graph ($\eta_{sp}/\sqrt{C}$) Vs ($\sqrt{C}$) while the values of Falkenhagen coefficient i.e. A-Coefficient are the intercept of graph of ($\eta_{sp}/\sqrt{C}$) Vs ($\sqrt{C}$). The order or disorder introduced by solute in solvent is measured by the values of β coefficient which shows either positive or negative values. β coefficient is in turn measures the effective hydrodynamic volume of solute, which accounts for the ion-solvent interaction.

In this work, the values of β -coefficients for all systems are negative at all temperature. It is apparent from table-4 that, β -coefficient is found to be negative for all system and is measure the effective thermodynamic volume of solute which accounts for solute-solvent interaction. It is known as a measure of disorder introduced by a solute in to the solvent. From data of table-4, it is conclude that, the order of Falkenhagen coefficient (A) are $Ni^{2+}>Ca^{2+}>Mn^{2+}$.

From Table 1, 2 & 3 the value of relative viscosity and density decreases for all system as the concentration of solution decreases. Polar nature of metal ion is depend upon its electropositivity and size of ion. Hence, metal ion having more polar character shows high value of relative viscosity. The order of decreasing the relative viscosity all metal ion at all temperature (299K, 305K & 311K) are as $Ni^{2+}>Ca^{2+}>Mn^{2+}$ and density of solution change in the order of $Ni^{2+}>Mn^{2+}>Ca^{2+}$.

As the temperature increases the value of relative viscosity and density decreases shown in table-1, 2 & 3. Due to increase in temperature the interaction between solute-solute and solute-solvent decreases. The thermodynamic parameter such as free energy change(ΔG), enthalpy change(ΔH) and entropy change (ΔS) of different $CaCl_2$, $MnCl_2$ and $NiCl_2$ metal salt are calculated by plotting graph between 1/T Vrs $log\eta_r$ for a concentration of 0.01M at three temperature are shown in (Figure4-6). Thermodynamic parameters are mentioned in table-4, indicate variation of metal ion with water. The negative value free energy change (ΔG) shows interaction is feasible in all cases. Enthalpy change (ΔH) interpreted that interaction of metal ion and water solvent are spontaneous and exothermic and positive value of entropy change (ΔS) interpreted that, randomness of solute molecule in solvent increases i.e. there is dissociation of solute molecule in aqueous medium.

IV. Calculation

To determine the relative and specific viscosity, in the different concentration of $CaCl_2$, $MnCl_2$ and $NiCl_2$ solutions were prepared and there viscosities are measured with help of the following mathematical relation

(η_r)=(ds ×ts/dw ×tw)× η_w 1

Where η_r = Relative viscosity,

η_w = Viscosity of water

ds = Density of solution,

dw = Density of water

ts = Flow time for solution,

tw = Flow time for water.

From the calculated values of relative viscosities (η_r) and the temperature (T), the graph between log (η_r) vs 1/T are plotted.

The relative viscosities of $CaCl_2$, $MnCl_2$ and $NiCl_2$ solutions at different concentration at 299K, 305K & 311K are presented in table no. 1, 2, & 3 respectively. The viscosity data have been analyzed by Jones –Dole equation.

$$(\eta_r -1)/\sqrt{C} = \eta_{sp}/\sqrt{C} = A + B \sqrt{C} \text{------------ 3}$$

Where A = Falkenhagen coefficient

B = Jones-Dole coefficient

C = concentration of solutions

The Falkenhagen coefficient (A) measures the solute-solute interation while Jones-Dole coefficient (B) measures the solute-solvent interaction.

The thermodynamic parameters i.e. free energy change(ΔG), enthalpy change(ΔH) and entropy change (ΔS) are determined by using following relation,

$$\Delta G = -2.303 \times R \times slope \qquad …4$$
$$\log \eta_{r1} - \log \eta_{r2} = (\Delta H/2.303) \times (1/T1 - 1/T2) …5$$
$$\Delta S = (\Delta G - \Delta H)/T \qquad …6$$

Table 1. Densities (d) gm/cc and relative viscosities (η_r) of Chloride salt of Ca^{2+}, Mn^{2+} & Ni^{2+} at different concentration in aqueous solvent at 299K.

Conc. mole/lit	CaCl₂		MnCl₂		NiCl₂	
	Density (d) (Kgm⁻³)	Rel. Viscosity η_r	Density (d) (Kgm⁻³)	Rel. Viscosity η_r	Density (d) (Kgm⁻³)	Rel. Viscosity η_r
0.01	0.9974	2.5223	0.9998	1.7552	1.0052	2.6786
0.005	0.9927	2.1992	0.9964	1.6139	0.9998	2.4234
0.0025	0.9877	1.9094	0.9925	1.4727	0.9965	2.1347
0.00125	0.9848	1.6774	0.9902	1.3555	0.9931	1.8576
0.000625	0.9837	1.4905	0.9805	1.2602	0.9908	1.6359

Table 2. Densities (d) gm/cc and relative viscosities (η_r) of Chloride salt of Ca^{2+}, Mn^{2+} & Ni^{2+} at different concentration in aqueous solvent at 306K.

Conc. mole/lit	CaCl₂		MnCl₂		NiCl₂	
	Density (d) (Kgm⁻³)	Rel. Viscosity η_r	Density (d) (Kgm⁻³)	Rel. Viscosity η_r	Density (d) (Kgm⁻³)	Rel. Viscosity η_r
0.01	0.9937	2.3837	0.9937	1.5247	1.0002	2.4966
0.005	0.9855	2.1404	0.9902	1.4016	0.9985	2.3305
0.0025	0.9815	1.9408	0.9886	1.3032	0.9962	2.1421
0.00125	0.9795	1.7463	0.9856	1.2247	0.9925	1.9197
0.000625	0.9771	1.5626	0.9815	1.1666	0.9885	1.7090

Table 3. Densities (d) gm/cc and relative viscosities (η_r) of Chloride salt of Ca^{2+}, Mn^{2+} & Ni^{2+} at different concentration in aqueous solvent at 311K.

Conc. mole/lit	CaCl₂		MnCl₂		NiCl₂	
	Density (d) (Kgm⁻³)	Rel. Viscosity η_r	Density (d) (Kgm⁻³)	Rel. Viscosity η_r	Density (d) (Kgm⁻³)	Rel. Viscosity η_r
0.01	0.9899	2.2706	0.9905	1.3410	0.9985	2.3462
0.005	0.9839	2.0367	0.9882	1.2937	0.9954	2.1719
0.0025	0.9812	1.8115	0.9861	1.2357	0.9923	1.9652
0.00125	0.9796	1.6222	0.9835	1.1775	0.9911	1.7521
0.000625	0.9762	1.4636	0.9812	1.1308	0.9895	1.5722

The value of A = Falkenhagen coefficient, B= Jones-Dole coefficient is calculated by ploting the graph between of $\sqrt{C}$ V/S $\eta_{sp}/\sqrt{C}$ of Chloride salt of Ca^{2+}, Mn^{2+} & Ni^{2+} at 299K, 306K & 311K.

Table-4

Temp in K	CaCl₂		MnCl₂		NiCl₂	
	A	B (Lit/mol)	A	B (Lit/mol)	A	B (Lit/mol)
299	6.6964	-5.9494	3.600	-3.829	8.972	-11.579
305	7.9317	-11.746	2.227	-1.851	10.210	-17.946
311	6.4256	-7.7740	1.861	-2.456	8.143	-12.541

Figure 1. Plot of $\sqrt{C}$ Vs $\eta_{sp}/\sqrt{C}$ for CaCl₂, MnCl₂ and NiCl₂ at 26°C
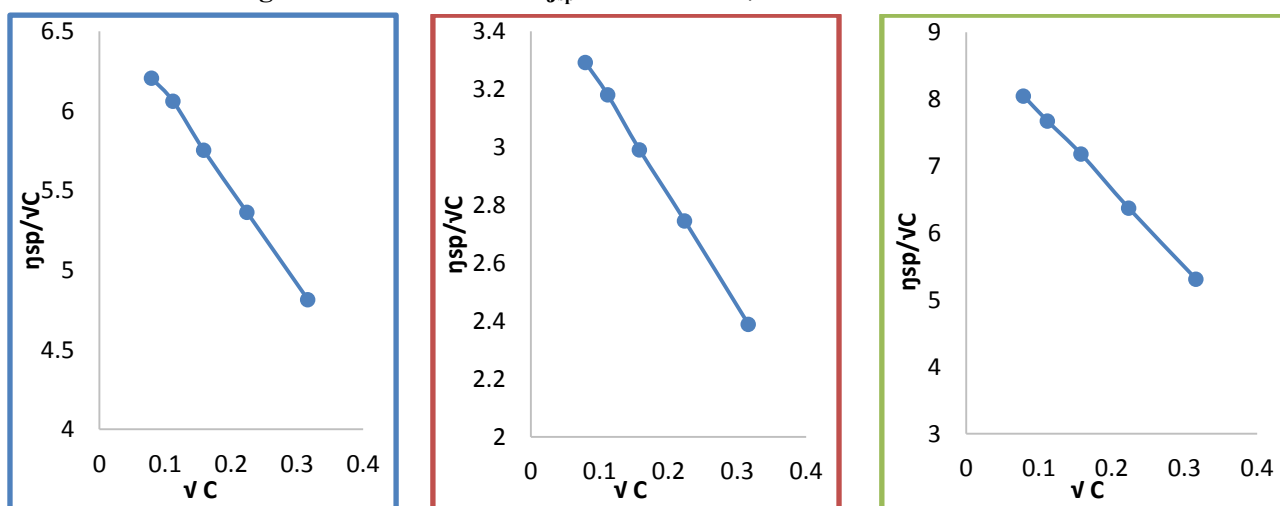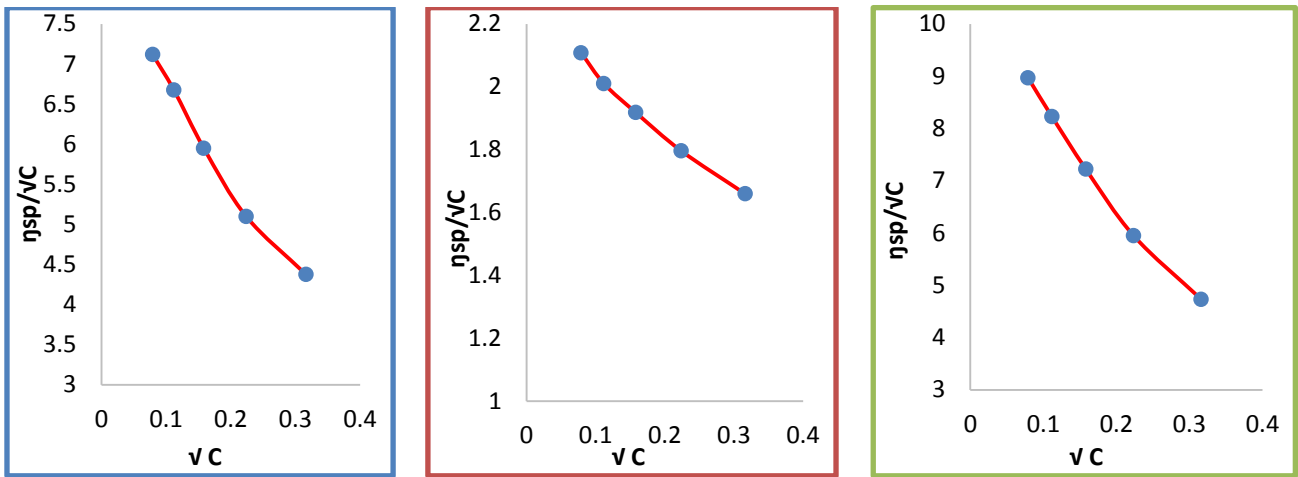

Figure 2. Plot of $\sqrt{C}$ Vs $\eta_{sp}/\sqrt{C}$ for CaCl₂, MnCl₂ and NiCl₂ at 32°C

Figure 3. Plot of $\sqrt{C}$ Vs $\eta_{sp}/\sqrt{C}$ for CaCl$_2$, MnCl$_2$ and NiCl$_2$ at 38°C
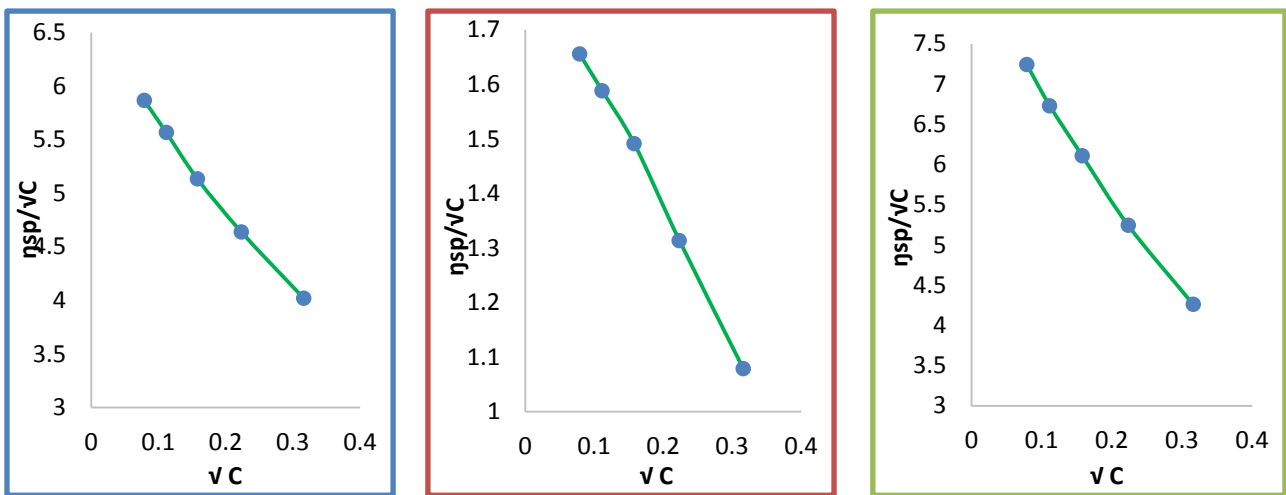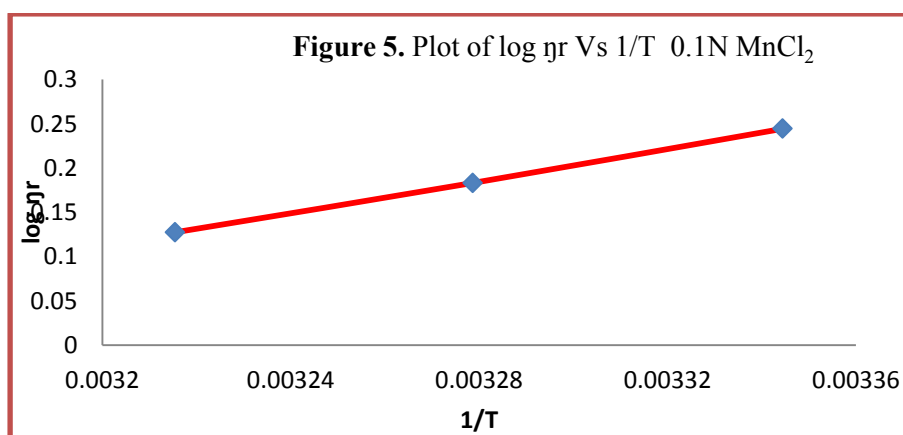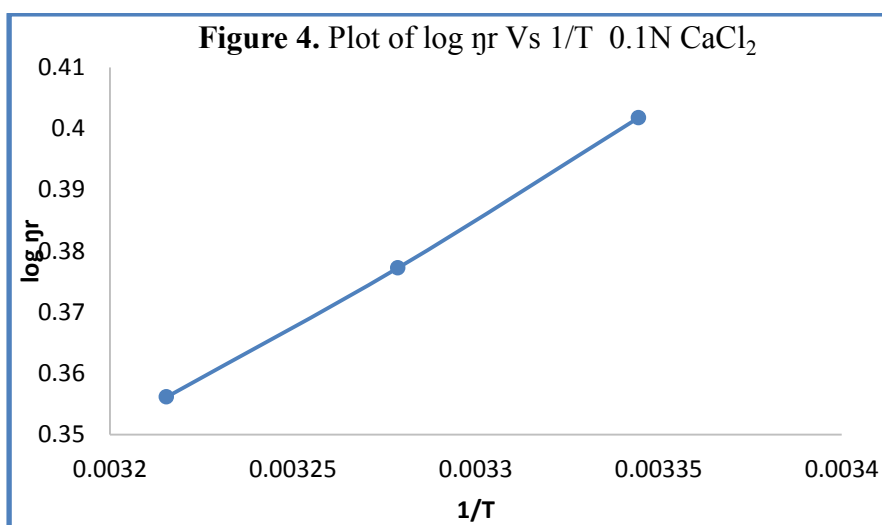
Table 5. Densities (d) gm/cc Relative and relative viscosities (ŋr) of Chloride salt of Ca^{2+}, Mn^{2+} & Ni^{2+} 0.01M concentration in aqueous medium at 299K, 306K & 311K.

Temp. in K	CaCl$_2$		MnCl$_2$		NiCl$_2$	
	Density (d) (Kgm^{-3})	Rel. Viscosity ŋ$_r$	Density (d) (Kgm^{-3})	Rel. Viscosity ŋ$_r$	Density (d) (Kgm^{-3})	Rel. Viscosity ŋ$_r$
299	0.9974	2.5223	0.9998	1.7552	1.0052	2.6786
306	0.9937	2.3837	0.9937	1.5247	1.0002	2.4966
311	0.9899	2.2706	0.9905	1.3410	0.9985	2.3462

Figure 4. Plot of log ŋr Vs 1/T 0.1N CaCl$_2$

Figure 5. Plot of log ŋr Vs 1/T 0.1N MnCl$_2$

Figure 6. Plot of log ŋr Vs 1/T 0.1N NiCl$_2$
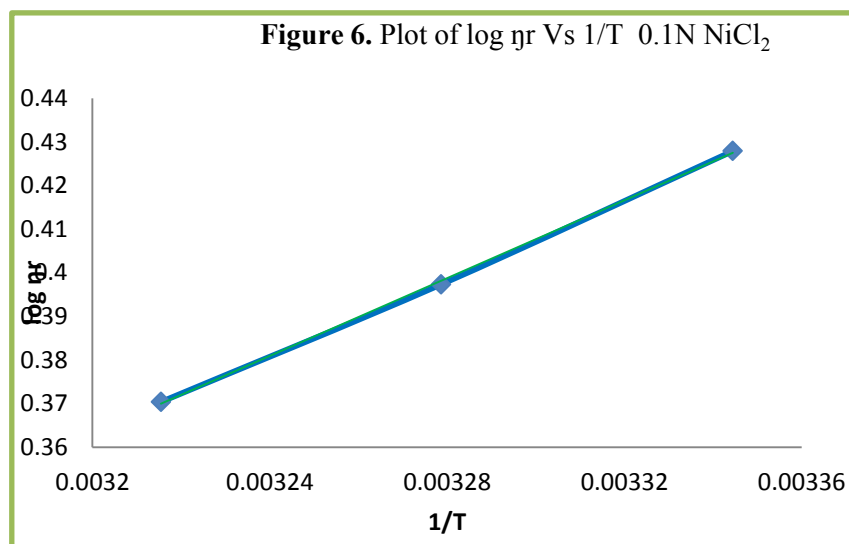
Table 4. Values of Thermodynamic Parameters for temperature difference **299K – 306K**

System	ΔG (J mol^{-1} K^{-1})	ΔH (J mol^{-1} K^{-1})	ΔS (J mol^{-1} K^{-1})
CaCl$_2$	-6676712	-6774.69	21446.74
MnCl$_2$	-5397550	-17343.30	17299.70
NiCl$_2$	-2657042	-8535.87	8516.09

V. References

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