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## Least Square and Gauss Jordan Methods applied to fit the Dielectric data Vs. Concentration of Ionic Liquids

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### ABSTRACT

Ionic liquids are not only prominent for life but also important in chemical and biological industry. Starting from Debye-Huckel theory of electrolytes, a rich progress in theoretical and experimental studies was made over the past hundred years. K.S.Pitzer developed a set of equations for six coefficients on the basis of virial theorem and Statistical thermodynamics, starting from the Debye-Huckel model. He adopted calculations of Guggenheim, with the modification of Scatchard, Hammer and Bronsted to incorporate specific interactions, for electrolytic state, in which terms related to short range forces between ions were partly accounted. However the very significant lowering of Dielectric constant of solvent continuum on addition of electrolyte, as modeled by Glueckauf was not considered in their work. We report a better & more general method of possible correction starting with the dielectric data of Brahmajirao, P.S.K.M.Rao and Sastry by using Least Square and Gauss Jordan Technique for the dielectric property is accounted in this presentation, because it is an essential characteristic that governs the ion-ion, ion-solvent interactions. It is now realized by several authors that this property forms the crux of explanation, in many interesting results, like Eigen and Tamm's mechanism. The details of the method, including the program in 'C' language used in our attempt are furnished in this paper. An attempt to interpret the nature of the involved coefficients is made.

**Keywords:** Dielectric constant, Ionic liquids, Electrolyte solution, Gauss Jordan Method, Curve fitting, Pitzer's model, Ion-Solvent-Ion interactions, Eigen's Mechanism.

### 1. INTRODUCTION

Kohlrausch started the mathematical analysis of the state of an electrolyte way back in the early 19<sup>th</sup> century. In this celebrated work he was the first to establish the law for the conductivity as a function of the square root of concentration, which was later, justified theoretically by Debye and Hückel [1], and Onsager [5]. The departure from ideality of electrolyte solutions was estimated by Debye and Hückel with a linearized Poisson-Boltzmann equation. They assumed that in dilute solutions, ions could be regarded as point a charge (which is justified at very low concentrations). However it is invalid as the density of charge carriers increases. These charged ions are surrounded by an ionic atmosphere. They established the infinite dilution limiting law, called the Debye-Hückel limiting law. This important expression is therefore not applicable to electrolytes solutions at concentration above 0.01 M. Hence the Thermodynamic properties of the electrolytic solutions are not in a position to be explained on a firm theoretical ground even today, due to the complexity of the forces that prevail in these systems, at higher concentrations. Several new experimental findings

are getting added with time and pose a challenge, in terms of a satisfactory model for the electrolytic state.

Debye and Hückel used naïve fundamentals of Coulomb's law & the Poisson-Boltzmann equation. It was felt that the ions in the ion atmosphere could not approach the central ion by more than some distance, termed as closest approach distance to ions. This was explicit in the expression for ' $\kappa$ '. having dimensions of the reciprocal of length. This parameter, being the characteristic of the nature of the ion, governs the behaviour of the electrolytic system. This point forms the stem of the later problems. This work was carried forward by Fuoss and Accascina, Pitts, Fuoss and Onsager, Fuoss and Hsia.[3 to 12] and several others by trying to introduce several modifications to the original model. More recently Pitzer [2] impregnated the virial theorem and added several terms after the modifications suggested by Scatchard, Hammer and Bronsted to incorporate specific interactions between the ion-solvent-ion of the Ionic solution system. Still a gulf of disagreement persists between theory and experiment.

One of the main reasons for this is the fact that the electrostatic field in the vicinity of the central ion increases as the concentration of the solute increases. Glueckauf [13] developed a mathematical model treating the electrolytic solutions as a dielectric continuum and evaluated expressions for the lowering of dielectric constant of the electrolytic solution, on addition of the solute. P.S.Sastry [14] and P.S.K.M.Rao [15], V.Brahmajirao [16] in their doctoral theses reported dielectric data (both theoretical & experimental) of several electrolytic solutions. applied Glueckauf model to several physical characteristics of several electrolytic solutions and established discrete evidences for the Nobel prize winning hypothesis of ion pair formation mechanism proposed by Eigen and De Mayer and Tamm [17], extending the basic ion association hypothesis of Bjerrum[30]. However a detailed mathematical model incorporating the variation of dielectric constant of the electrolyte as a function of concentration of the solute in the solvent is still to be developed.

Using the statistical mechanics in order to obtain thermodynamic quantities for ionic solutions, a different way of investigation has also been explored. The Ornstein-Zernike (OZ) equation [18] expressing the total correlation function as a function of the direct correlation function describing only the two-body interactions, is used in these attempts. Many approximations have been proposed which can be obtained with the help of mathematical techniques of functional derivatives [20, 21].

Other semi-empirical models that have been developed, are (1) the Bromley model, (2) the Davis model or the Pitzer model, (3) the MSA NRTL model, (4) the UNIQUAC model (5) the COSMOS RS model. The MSA model that has been utilized in our work is adequate to the description of charged hard spheres in a continuum, and has the main advantage of giving simple analytical expressions.

The binary solvent-solvent parameters required in the NRTL model are already available from previous fits of experimental data for solvent mixtures. A previous version of NRTL, called the e-NRTL model, extended to electrolyte solutions with the help of a Debye- Hückel term had already been studied by C. C. Chen and L. B. Evans [22]. This enables the NRTL to be applied to electrolyte solutions. The electrostatic term that has to be added to the NRTL model is important at low concentrations. At higher concentrations, it reaches a low asymptotic value. In this case, the interactions between ions are short ranged. Thus, the substitution of the PDH term in the e-NRTL by a MSA term will not affect the precision of the e-NRTL for high concentrations. A modification of the NRTL term, dominant at high concentrations, is then required. In the original e-NRTL model, assumptions on ions interacting with their neighbourhood had been made in the NRTL model. Some of these have been relaxed in the new model. These modifications of NRTL combined with a MSA term resulted in the MSA-NRTL model.

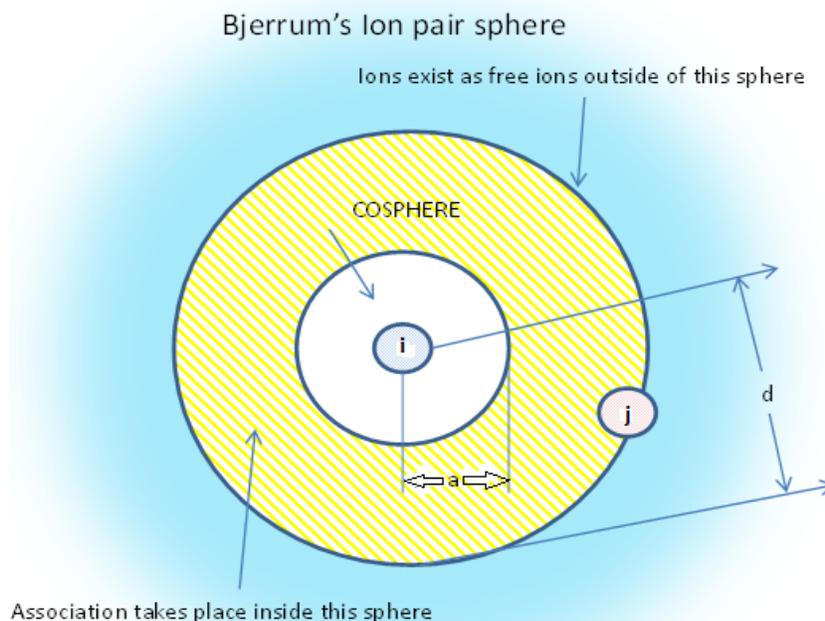


Fig 1: Structure of Ionic Atmosphere as per the D-H theory, used by Bjerrum in the explanation of ion association

The MSA-NRTL model was developed for the description of the thermodynamic properties of electrolyte solutions by N. Papaiconomou et.al.[23] The mean spherical approximation (MSA) approach for electrolyte solutions is combined with a modified non-random two-liquid (NRTL) approach. The resulting model is suitable for a description of the thermodynamic properties of electrolyte-multi solvent systems. The ability of this MSA-NRTL model is investigated by examining activity and osmotic coefficients of binary and ternary electrolyte solutions. Especially for non-aqueous solutions, the model is superior to standard semi-empirical calculations. The work of Watanasiri et al.[24] concentration dependence has been introduced in the NRTL parameters. Since that time, other semi-empirical models have been developed, such as the Bromley model [26], the Davis model [27] or the Pitzer model [28]. The parameters of the Pitzer equations are linear combinations of parameters, of a virial expansion of the excess Gibbs free energy, which characterise interactions amongst ions and solvent. This model took the expressions of the osmotic coefficient obtained from the extended Debye-Hückel law and applied a virial expansion in molality, as recommended by other theories (Guggenheim).

## 2. PITZER'S MODEL

Since the year 1961, K. S. Pitzer [28] has chosen the best available system proposed by Guggenheim[29], developed in a series of papers, detailed mathematical equations for activity coefficient, osmotic coefficient and other thermodynamic parameters. Still the permittivity parameter of the dielectric continuum, is being left unaccounted in all the above attempts by several workers in the field. This parameter is essential to account for the short range as well as long range interactions, since it governs the electrostatic interactions.

V.Brahmajirao et.al, [19] applied Glueckauf's model in his studies of acoustic, thermodynamic, conductance, compressibility, activity coefficient of electrolytic solutions and concluded that a systematic model incorporating lowering of dielectric property is necessary for proper understanding of their behavior.

The residual  $d_i$  is given by

$$d_i = \delta\epsilon_i - (\lambda_0 + \lambda_1 c_i + \lambda_2 c_i^2 + \lambda_3 c_i^3 + \lambda_4 c_i^4 + \lambda_5 c_i^5 + \lambda_6 c_i^6)$$

$$\therefore \sum d_i^2 = \sum (\delta\epsilon_i - \lambda_0 - \lambda_1 c_i - \lambda_2 c_i^2 - \lambda_3 c_i^3 - \lambda_4 c_i^4 - \lambda_5 c_i^5 - \lambda_6 c_i^6)^2 = R \text{ (Say)} \quad (3)$$

The principle of least squares states that the sum of the squares of the residuals is minimum. Therefore, by the principle of least squares we have to determine the parameters  $\lambda_0, \lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5, \lambda_6$  so that R is minimum. To minimize the equation (2), take the

The present paper is an attempt to develop a set of curve fit equations to have a preliminary insight into the coefficients of a polynomial for the dielectric constant as a function of concentration of solute in a solvent.

## 3. METHOD OF CURVE FITTING ADOPTED

We attempted and proved that the dependence of the dielectric constant was found to depend non-linearly on the salt concentration 'c' for molar concentrations are ranging between zero and 1.5 M by using our experimental data and curve fitting simulations.

We attempt to use our dielectric data for curve fitting in to an equation is of the form

$$\delta\epsilon = \epsilon_0 - \epsilon(c) \quad (1)$$

Where 'c' is the concentration of an electrolyte,  $\delta\epsilon$  is the decrement in dielectric constant of an electrolyte,  $\epsilon(c)$  is the dielectric constant of the ionic solution,  $\epsilon_0$  is the static dielectric constant of the solvent (Double distilled water) = 78.57 at temperature 298.17K.

We have  $(c_i, \delta\epsilon_i)$ , where  $i = 1, 2, 3 \dots 15$  are the observed experimental values of  $(c, \delta\epsilon)$ . Let  $\delta\epsilon = f(c)$  be a functional relationship sought between the variables  $(c, \delta\epsilon)$ . The difference between the observed experimental value of  $\delta\epsilon$  and the value of  $\delta\epsilon$  determined by the functional relation is called residual.

$$\therefore d_i = \delta\epsilon_i - f(c_i), \text{ where } d_i \text{ is the residual.}$$

Now consider the polynomial curve fitting of order 6 as below.

$$\delta\epsilon = \lambda_0 + \lambda_1 c + \lambda_2 c^2 + \lambda_3 c^3 + \lambda_4 c^4 + \lambda_5 c^5 + \lambda_6 c^6 \quad (2)$$

derivative w.r.t each coefficient  $\lambda_0, \lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5, \lambda_6$  and set each to zero.

Derivative w.r.t  $\lambda_0$ , we get

$$\frac{\partial R}{\partial \lambda_0} = 0$$

$$\Rightarrow -2 \sum (\delta \varepsilon_i - \lambda_0 - \lambda_1 c_i - \lambda_2 c_i^2 - \lambda_3 c_i^3 - \lambda_4 c_i^4 - \lambda_5 c_i^5 - \lambda_6 c_i^6) = 0$$

$$\Rightarrow \sum \delta \varepsilon_i - 15 \lambda_0 - \lambda_1 \sum c_i - \lambda_2 \sum c_i^2 - \lambda_3 \sum c_i^3 - \lambda_4 \sum c_i^4 - \lambda_5 \sum c_i^5 - \lambda_6 \sum c_i^6 = 0$$

$$\therefore 15 \lambda_0 + \lambda_1 \sum c_i + \lambda_2 \sum c_i^2 + \lambda_3 \sum c_i^3 + \lambda_4 \sum c_i^4 + \lambda_5 \sum c_i^5 + \lambda_6 \sum c_i^6 = \sum \delta \varepsilon_i \quad (4)$$

Similarly, derivative w.r.t  $\lambda_1$ , we get

$$\frac{\partial R}{\partial \lambda_1} = 0 \Rightarrow \lambda_0 \sum c_i + \lambda_1 \sum c_i^2 + \lambda_2 \sum c_i^3 + \lambda_3 \sum c_i^4 + \lambda_4 \sum c_i^5 + \lambda_5 \sum c_i^6 + \lambda_6 \sum c_i^7 = \sum c_i \delta \varepsilon_i \quad (5)$$

Derivative w.r.t  $\lambda_2$ , we get

$$\frac{\partial R}{\partial \lambda_2} = 0 \Rightarrow \lambda_0 \sum c_i^2 + \lambda_1 \sum c_i^3 + \lambda_2 \sum c_i^4 + \lambda_3 \sum c_i^5 + \lambda_4 \sum c_i^6 + \lambda_5 \sum c_i^7 + \lambda_6 \sum c_i^8 = \sum c_i^2 \delta \varepsilon_i \quad (6)$$

Derivative w.r.t  $\lambda_3$ , we get

$$\frac{\partial R}{\partial \lambda_3} = 0 \Rightarrow \lambda_0 \sum c_i^3 + \lambda_1 \sum c_i^4 + \lambda_2 \sum c_i^5 + \lambda_3 \sum c_i^6 + \lambda_4 \sum c_i^7 + \lambda_5 \sum c_i^8 + \lambda_6 \sum c_i^9 = \sum c_i^3 \delta \varepsilon_i \quad (7)$$

Derivative w.r.t  $\lambda_4$ , we get

$$\frac{\partial R}{\partial \lambda_4} = 0 \Rightarrow \lambda_0 \sum c_i^4 + \lambda_1 \sum c_i^5 + \lambda_2 \sum c_i^6 + \lambda_3 \sum c_i^7 + \lambda_4 \sum c_i^8 + \lambda_5 \sum c_i^9 + \lambda_6 \sum c_i^{10} = \sum c_i^4 \delta \varepsilon_i \quad (8)$$

Derivative w.r.t  $\lambda_5$ , we get

$$\frac{\partial R}{\partial \lambda_5} = 0 \Rightarrow \lambda_0 \sum c_i^5 + \lambda_1 \sum c_i^6 + \lambda_2 \sum c_i^7 + \lambda_3 \sum c_i^8 + \lambda_4 \sum c_i^9 + \lambda_5 \sum c_i^{10} + \lambda_6 \sum c_i^{11} = \sum c_i^5 \delta \varepsilon_i \quad (9)$$

Derivative w.r.t  $\lambda_6$ , we get

$$\frac{\partial R}{\partial \lambda_6} = 0 \Rightarrow \lambda_0 \sum c_i^6 + \lambda_1 \sum c_i^7 + \lambda_2 \sum c_i^8 + \lambda_3 \sum c_i^9 + \lambda_4 \sum c_i^{10} + \lambda_5 \sum c_i^{11} + \lambda_6 \sum c_i^{12} = \sum c_i^6 \delta \varepsilon_i \quad (10)$$

Equations (4) to (10) are called normal equations from which  $\lambda_0, \lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5, \lambda_6$  can be found.

Rewrite the above equations and put into matrix form i, e  $AX = B$

$$\begin{pmatrix}
 15 & \sum c_i & \sum c_i^2 & \sum c_i^3 & \sum c_i^4 & \sum c_i^5 & \sum c_i^6 \\
 \sum c_i & \sum c_i^2 & \sum c_i^3 & \sum c_i^4 & \sum c_i^5 & \sum c_i^6 & \sum c_i^7 \\
 \sum c_i^2 & \sum c_i^3 & \sum c_i^4 & \sum c_i^5 & \sum c_i^6 & \sum c_i^7 & \sum c_i^8 \\
 \sum c_i^3 & \sum c_i^4 & \sum c_i^5 & \sum c_i^6 & \sum c_i^7 & \sum c_i^8 & \sum c_i^9 \\
 \sum c_i^4 & \sum c_i^5 & \sum c_i^6 & \sum c_i^7 & \sum c_i^8 & \sum c_i^9 & \sum c_i^{10} \\
 \sum c_i^5 & \sum c_i^6 & \sum c_i^7 & \sum c_i^8 & \sum c_i^9 & \sum c_i^{10} & \sum c_i^{11} \\
 \sum c_i^6 & \sum c_i^7 & \sum c_i^8 & \sum c_i^9 & \sum c_i^{10} & \sum c_i^{11} & \sum c_i^{12}
 \end{pmatrix}
 \begin{pmatrix}
 \lambda_0 \\
 \lambda_1 \\
 \lambda_2 \\
 \lambda_3 \\
 \lambda_4 \\
 \lambda_5
 \end{pmatrix}
 =
 \begin{pmatrix}
 \sum \delta \varepsilon_i \\
 \sum c_i \delta \varepsilon_i \\
 \sum c_i^2 \delta \varepsilon_i \\
 \sum c_i^3 \delta \varepsilon_i \\
 \sum c_i^4 \delta \varepsilon_i \\
 \sum c_i^5 \delta \varepsilon_i \\
 \sum c_i^6 \delta \varepsilon_i
 \end{pmatrix}$$

A
X
B

All summations above are over  $i = 1, 2, 3 \dots 15$ . We have data points  $(c_i, \delta \varepsilon_i)$  for  $i = 1, 2, 3 \dots 15$ . Using Gauss Jordan method, we can solve the above problem. But due

to large number of data points and huge number of system of linear equations, we developed the code in 'C' programming.

#### 4. DEVELOPED CODE IN 'C' PROGRAMMING

```

#include<stdio.h>
#include<math.h>
void main()
{
float augm[7][8]={ {0,0,0,0,0,0,0,0},{0,0,0,0,0,0,0,0},{0,0,0,0,0,0,0,0},{0,0,0,0,0,0,0,0},
{0,0,0,0,0,0,0,0},{0,0,0,0,0,0,0,0},{0,0,0,0,0,0,0,0}};
float a,b,c,d,e,f,g,x,y,t;
int i,j,k,n;
clrscr();
printf("Enter the no of pairs of observed value:");
scanf("%d",&n);
augm[0][0]=n;
for(i=0;i<n;i++)
{
printf("pair no:%d\n",i+1);
scanf("%f %f",&x,&y);
augm[0][1]+=x;
augm[0][2]+=pow(x,2);
augm[0][3]+=pow(x,3);
augm[0][4]+=pow(x,4);
augm[0][5]+=pow(x,5);
augm[0][6]+=pow(x,6);
augm[0][7]+=y;
}
}

```

```

augm[1][7]+=x*y;
augm[2][7]+=pow(x,2)*y;
augm[3][7]+=pow(x,3)*y;
augm[4][7]+=pow(x,4)*y;
augm[5][7]+=pow(x,5)*y;
augm[6][7]+=pow(x,6)*y;
augm[1][6]+=pow(x,7);
augm[2][6]+=pow(x,8);
augm[3][6]+=pow(x,9);
augm[4][6]+=pow(x,10);
augm[5][6]+=pow(x,11);
augm[6][6]+=pow(x,12);
}

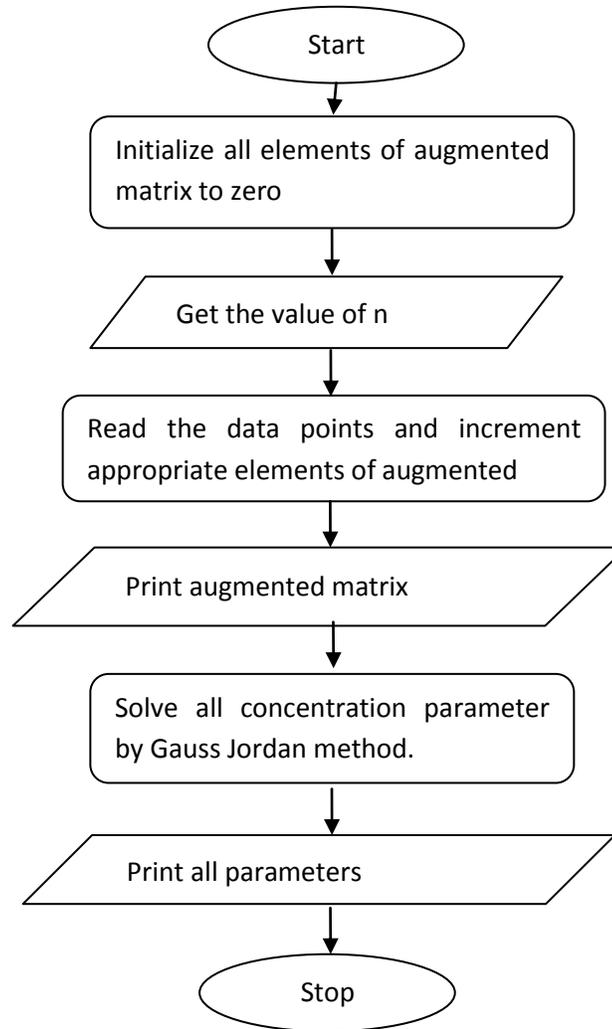
augm[1][0]=augm[0][1];
augm[1][1]=augm[0][2];
augm[1][2]=augm[0][3];
augm[1][3]=augm[0][4];
augm[1][4]=augm[0][5];
augm[1][5]=augm[0][6];
augm[2][0]=augm[0][2];
augm[2][1]=augm[0][3];
augm[2][2]=augm[0][4];
augm[2][3]=augm[0][5];
augm[2][4]=augm[0][6];
augm[2][5]=augm[1][6];
augm[3][0]=augm[0][3];
augm[3][1]=augm[0][4];
augm[3][2]=augm[0][5];
augm[3][3]=augm[0][6];
augm[3][4]=augm[1][6];
augm[3][5]=augm[2][6];
augm[4][0]=augm[0][4];
augm[4][1]=augm[0][5];
augm[4][2]=augm[0][6];
augm[4][3]=augm[1][6];
augm[4][4]=augm[2][6];
augm[4][5]=augm[3][6];
augm[5][0]=augm[0][5];
augm[5][1]=augm[0][6];
augm[5][2]=augm[1][6];
augm[5][3]=augm[2][6];
augm[5][4]=augm[3][6];
augm[5][5]=augm[4][6];
augm[6][0]=augm[0][6];
augm[6][1]=augm[1][6];
augm[6][2]=augm[2][6];
augm[6][3]=augm[3][6];
augm[6][4]=augm[4][6];
augm[6][5]=augm[5][6];
printf("The Augmented matrix is :\n");
for(i=0;i<7;i++)
{
for (j=0;j<8;j++)
printf("%9.2f",augm[i][j]);
printf("\n");
}

```

```
/* Solving a,b,c,d,e,f,g by Gauss Jordan Method */
for(j=0;j<7;j++)
for(i=0;i<7;i++)
if(i!=j)
{
t=augm[i][j]/augm[j][j];
for(k=0;k<8;k++)
augm[i][k]-=augm[j][k]*t;
}
a=augm[0][7]/augm[0][0];
b=augm[1][7]/augm[1][1];
c=augm[2][7]/augm[2][2];
d=augm[3][7]/augm[3][3];
e=augm[4][7]/augm[4][4];
f=augm[5][7]/augm[5][5];
g=augm[6][7]/augm[6][6];
printf("a=%5.4f b=%5.4f c=%5.4f d=%5.4f e=%5.4f f=%5.4f g=%5.4f",a,b,c,d,e,f,g);
getch();
}
```

**Solving the concentration parameters in the best fit curve by using least square and Gauss Jordan method in c programming**

### FLOW CHART



The above set of equations has been applied to the dielectric data of V. Brahmajirao [19] four chosen nitrates dissolved in water (Aqueous solutions). The values of the coefficients  $\lambda_0, \lambda_1, \lambda_2, \lambda_3, \lambda_4, \lambda_5, \lambda_6$  used in the curve fitting have been evaluated using the above computer program and are tabulated in below table.

## 5. RESULTS AND DISCUSSIONS

Table

Electrolyte	$\lambda_0$	$\lambda_1$	$\lambda_2$	$\lambda_3$	$\lambda_4$	$\lambda_5$	$\lambda_6$
Cadmium Nitrate	-52.65	-45.60	102.01	-155.88	141.14	-67.32	12.96
Copper Nitrate	-53.54	-25.40	24.28	-34.29	41.31	-25.39	5.88
Cobalt Nitrate	-0.27	-33.47	-77.20	278.26	-338.73	187.73	-39.89
Chromium Nitrate	0.44	-76.47	94.12	-41.60	-32.43	43.78	-14.05

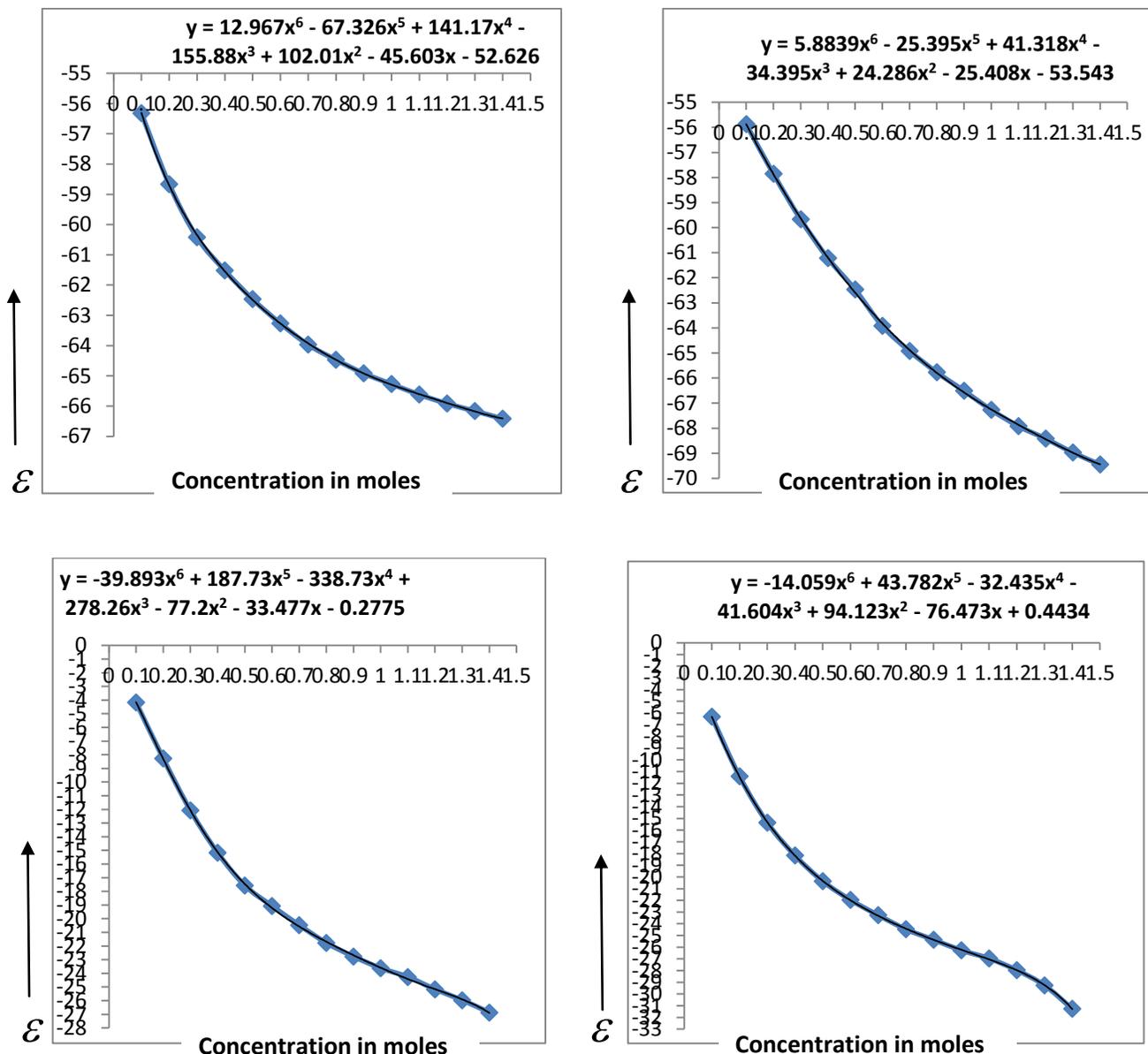


Fig1 to 4 : Concentration (abscissa) vs Variation in Dielectric constant of the chosen electrolytic solutions

About the plots:

The following information is implied in the presented plots

- (1) The plot for each electrolyte consists of two elements of information. One element is the dielectric data obtained experimentally (shown with square dots). The second element is the line forming the curve after curve fitting is implemented.
- (2) Also each of the coefficients evaluated correspond to a particular exponent of concentration (obvious from the process of curve fitting). This facilitates

understanding of the relation between the dielectric constant and concentration with the help of literature, which will be useful in coining the necessary terms for future development of the model

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