



Thermodynamic Effect of Bulk and Nano-CuCl₂ Salts on Tenoxicam Using a Variety of Different Techniques

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Abstract

Nanoparticles are very important for medicine and environment, because of their increased behaviours. The increasing in the physical and chemical properties of nanomaterials are due to theirs high surface area and small volume, makes them very reactive , catalytic and able to pass through cell membranes. Characterization of nano-CuCl₂ is done by using a variety of different techniques, transmission electron microscopy (TEM), infra red spectroscopy (IR) and determination of its thermodynamic parameters using conductometric measurements. The association parameters of both bulk and nano-CuCl₂ salts in DMF were easily calculated using Fuoss-Shedlovsky method from temperatures, 298.15K (degree Kelvin) to 313.15K. In order to have a better understanding of thermodynamics of the complexation reactions between (bulk, nano-CuCl₂) salts and tenoxicam in DMF, it is useful to determine the contribution of enthalpy and entropy of the reactions. The thermodynamic parameters were calculated from the temperatures dependence of the complexation constants (Van't Hoff plot). The formation constants were measured as a function of temperature and increased by increasing temperature. Also, different volumes of tenoxicam in mixed (DMF+H₂O) were determined from density measurement.

Keyword: CuCl₂, Tenoxicam, Transmission electron microscopy (TEM), Fuoss –Shedlovsky method, Association and formation constants, Thermodynamic parameters.



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1. Introduction

Nanostructural materials becomes attractive than the bulk materials due to their small size and surface activity. So, there has been considerable interest in fabrication of low-dimensional nano-sized materials such as nano-wires, nano-rods and nano-tubes because they possess distinctive geometries, novel physical , chemical properties and have potential applications in nanotechnology [1-8]. Many of the applications of new nano materials that have different properties from the bulk large sizes.

Rheumatoid arthritis is one of the common disease caused by muscle and articulations inflammation [7-9]. Treatment with tenoxicam can be used for this case. Complexation with metal ions improved the efficiency of drugs [10-15].

Transmission electron microscopy (TEM) is good tool for measuring the nano materials sizes. It is a vital characterization tool for directly imaging nanomaterials to obtain quantitative measures of particle and/or grain size, size distribution, and morphology. TEM images are very sensitive. By using (TEM) , we can investigate the size and the shape of ceftazidime antibiotic which had been found under nanoscale range.

The study of the interactions involved in the complexation of different cations with ligand in solvent mixtures is important for a better understanding of the mechanism of biological transport, molecular recognition, and other analytical applications. Recently, there has been much research on complex formation. There are a number of physico-chemical techniques that can be used in the study of these complexation reactions, for example, spectrophotometry, polarography, NMR spectrometry, calorimetry, potentiometry and conductometry [16]. Conductometric measurements are good tool for studying solution complexation. This is because conductometric techniques are highly sensitive and inexpensive, with a simple design of experimental arrangement for such investigations [17]. Therefore, it offers useful data than other methods.

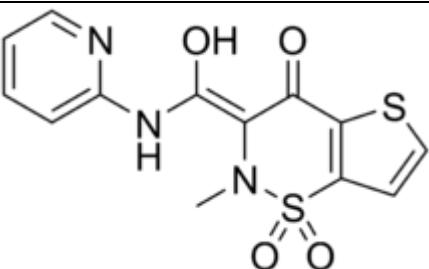
Among numerous thermodynamic properties, partial and apparent molar volumes of ions in solution are particularly useful in understanding the solvation as well as the complexes formation processes. They can be estimated accurately and they provide important information about (solute–solvent) interactions in solution. A great effort has been made in past years to perform such research and collect the respective data.

2. Experimental

2.1. Chemicals and Ligand

- Copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) was provided from Merck Co. while nano- CuCl_2 salt was prepared by ball milling method using copper chloride salt. The ball milling was a Retsch MM 2000 Swing mill with 10 cm^3 stainless steel, double-walled tube. Two balls (stainless steel) with diameter of 12 mm were used. Ball milling was performed at 20225 Hz and shaking were used for 30 min, usually at room temperature without circulating liquid and the temperature did not rise above 30 °C.

- Tenoxicam (E.I.P.I.CO.) was used as purchased and investigated under transmission electron microscopy (TEM).

Tenoxicam	
	
Formula	$\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_4\text{S}_2$
Mol. Wt.	337.376g/mol

- Dimethylformamide solvent (DMF) was provided from El Nasr pharmaceutical chemicals co and used directly without purification.

2.2. Experimental

2.2.1. Transmission Electron Microscopy (TEM) Images

Transmission electron microscope is a special kind of electron microscope for imaging of different objects. In contrast to other microscopes the electrons in TEM pass through and interact with atoms of the sample. Due to this interaction the electrons are being scattered. The final image is very complicated interference pattern of incident and diffracted beams.

2.2.2. Conductometric Measurements

A solution of bulk and nano- CuCl_2 (10^{-4} M) was placed in a titration cell, thermostated at a given temperature and the conductance of the solution was measured. The ligand (10^{-3} M) (tenoxicam) was transferred step by step to the titration cell using a precalibrated micropipette and the conductance of the solution was measured after each transfer. The addition of the ligand solution was continued until the total concentration of the ligand was approximately four times higher than that of the metal ions. The conductance of the solution was measured by titration of ligand with metal salt. The complex formation constant K_f , and the molar conductance of the complex ML, were evaluated by computer fitting to the molar conductance mole ratio data. The temperatures used are (298.15, 303.15, 308.15 and 313.15K). The specific conductivity K_s was achieved by using a conductivity bridge of the type (OAKTON WD-35607-10,-20,-30) with platinum electrode and a cell constant equal (1). The solutions were put in ultra-thermostat of the type (Kottermann 4130) during measurements.

2.2.3. Density Measurement

Weighting bottle (1ml of pyknometric type) was used for measuring the density of mixed (DMF+ H_2O) at 298.15K, weighing using four digital weighing balance of the type Mettler AE 240.

Also, the density of the solution of tenoxicam in mixed (DMF+ H_2O) was measured at temperature 298.15K by the same method. The experiment was repeated at least three times and then the mean absolute density was taken. The maximal error was to be ± 0.001 gm.

3. Data Results and Discussion

3.1. Transmission Electron Microscopy (TEM) Images

The photographs from (TEM) are presented for nano- CuCl_2 salt and tenoxicam were shown in (Fig. 1 and Fig. 2) respectively. It was observed from TEM images that:-

- Nano- CuCl_2 particles appear as sheets in scale range 100 nanometers.
- Tenoxicam particles appear with size range between (37.14: 43.40) nm in scale range 200 nanometers.

3.2. Conductometric Results

The stability of a transition metal complex with a polydentate chelate ligand depends on a range of factors including the number and the type of the donor atoms presented, the number and the size of chelate rings formed on

the complexation [18]. In addition, the stability and the selectivity of the complexities are strongly depend on the donor ability and the dielectric constant of the solvent [19], the shape, the size of the solvent molecules [20].

Tenoxicam, [4-hydroxy - 2 - methyl - N-2- pyridinyl - 2H - thieno -[2,3e]1,2-thiazine-3-carboxamide-1,1-dioxide] is a non-steroidal anti-inflammatory drug (NSAID). It is very effective as analgesic and anti-inflammatory drug for the systemic treatment of rheumatoid arthritis, osteoarthritis and other joint diseases. However, being a lipophilic drug, tenoxicam is sparingly soluble in water, so that its dissolution may be the rate determining step in the absorption process.

A- Calculation of Thermodynamic Parameters of Association for Bulk and Nano-CuCl₂ in DMF.

The specific conductance values (K_s) of different concentrations for bulk and nano-CuCl₂ in DMF were measured experimentally in absence of ligand at different temperatures (298.15, 303.15, 308.15 and 313.15K). The molar conductance (Λ_m) values were calculated [21, 22] using equation (1):

$$\Lambda_m = \frac{(K_s - K_{solv})K_{cell} \times 1000}{C} \quad (1)$$

Where K_s and K_{solv} are the specific conductance of the solution and the solvent, respectively; K_{cell} is the cell constant and C is the molar concentration of the bulk and nano-CuCl₂ solutions.

The limiting molar conductances (Λ_0) at infinite dilutions were estimated for bulk and nano-CuCl₂ in DMF in absence of ligand at different temperatures by extrapolating the relation between Λ_m and $C_m^{1/2}$ to zero concentration as shown in Fig.(3).

The experimental data for conductance measurements were analyzed using Fuoss – Shedlovsky [23] extrapolation techniques which follows equations :

$$\frac{1}{\Lambda S(Z)} = \frac{1}{\Lambda_0} + \left(\frac{K_A}{\Lambda_0^2} \right) (C \Lambda \gamma_{\pm}^2 S(Z)) \quad (2)$$

Where, $S(Z) = 1 + Z + Z^2/2 + Z^3/8 + \dots$ etc.

$$\text{and } Z = \frac{S(\Lambda C)^{1/2}}{\Lambda_0^{3/2}} \quad (3)$$

he value of (Λ_0) was used to calculate the Onsager slope (S) from the equation (4):

$$S = a\Lambda_0 + b \quad (4)$$

$$\text{Where, } a = 8.2 \times 10^5 / (\epsilon T)^{3/2} \quad (5)$$

$$b = 82.4 / \eta ((\epsilon T)^{1/2}) \quad (6)$$

Where (ϵ) is the dielectric constant of the solvent, (η_0) is the viscosity of the solvent and (T) is the temperature. Using the values of (ϵ) and (η_0), the value of (S) were easily estimated. Using the data of (Λ), $S_{(z)}$ and (Λ_0), the values of degree of dissociation (α) were calculated by using the following equation (7):

$$(\alpha) = \Lambda S_{(z)} / \Lambda_0 \quad (7)$$

Using these (α) and (ϵ) values, the mean activity coefficients (γ_{\pm}) were evaluated by means of equation (8) :

$$\log \gamma_{\pm} = - z_- z_+ A (\alpha C)^{1/2} / [1 + B r^0 (\alpha C)^{1/2}] \quad (8)$$

Where (z_- , z_+) are the charges of ions in solutions A, B are the Debye-Hückel constant.

$A = 1.824 \times 10^6 (\epsilon T)^{-3/2}$; $B = 50.29 \times 10^8 (\epsilon T)^{-1/2}$ and (r^0) is the solvated radius.

The association constant (K_A) is evaluated from equation (2).

Using the values of association constant (K_A), the values of the dissociation constant (K_D) were easily calculated by means of the following equation (9):

$$K_D = 1/K_A \quad (9)$$

The values of the triple ion association constant (K_3) were calculated [24, 25] by using the equation (10):

$$\frac{\Lambda C^{1/2}}{(1 - \frac{\Lambda}{\Lambda_0})^{1/2}} = \frac{\Lambda_0}{(K_A)^{1/2}} + \frac{\lambda_3^0 C}{K_3 (K_A)^{1/2}} (1 - \frac{\Lambda}{\Lambda_0}) \quad (10)$$

Equation (11) was derived by Fuoss [25] and using Walden approximation ($\Lambda_0 = 3\lambda_0$).

The values of free energy of association (ΔG_A) for bulk and nano-CuCl₂ in DMF at different temperatures (298.15, 303.15, 308.15 and 313.15 K) were calculated [26, 27] from the association constant (K_A) values by using equation (11).

$$\Delta G_A = - 2.303 RT \log K_A \quad (11)$$

Where R is the gas constant ($8.314 \text{ J.mol}^{-1} \text{ degree}^{-1}$) and T is the absolute temperature. The calculated values of η_0 , Λ_0 , Λ , C, S, Z, $S_{(z)}$, γ_{\pm} , K_A , K_D , α , K_3 and Gibbs free energies for the solutions of bulk and nano-CuCl₂ in DMF at different temperatures (298.15, 303.15, 308.15 and 313.15K) were calculated and reported in Table.1 (a,b).

The enthalpy (ΔH_A) for bulk and nano-CuCl₂ in DMF at different temperatures were calculated by using Van't Hoff equation [28, 29].

Where R is the gas constant(8.314 J.mol⁻¹ degree⁻¹) and T is the absolute temperature.

By drawing the relation between log K_A and 1/T, ΔH_A can be calculated from the slope of each line which equal (- $\Delta H_A/2.303R$) as shown in Fig.(4) .The entropy (ΔS_A) for bulk and nano-CuCl₂were calculated by using equation (12) [27-104]:

$$\Delta G_A = \Delta H_A - T\Delta S_A \quad (12)$$

Where (S) is the entropy of system.

The calculated values of (ΔH_A) and (ΔS_A) for bulk and nano-CuCl₂are presented in Table(2).

B- Calculation of Thermodynamic Parameters of Complex Formation for Bulk and Nano-CuCl₂ with tenoxicam in DMF.

The specific conductance values (K_s) of different concentrations of bulk and nano-CuCl₂ in DMF were measured experimentally in the presence of ligand at different temperatures (298.15, 303.15, 308.15 and 313.15 K). The molar conductance (Λ_m) values were calculated [21, 22] using equation (1).

By drawing the relation between molar conductance (Λ_m) for bulk and nano-CuCl₂in presence of ligand at different temperatures and the molar ratio of metal to ligand [M]/[L] concentrations, Fig.(5) different lines are obtained with breaks indicating the formation of 1:2 and 1:1 (M:L) stoichiometric complexes ,as done in previous works [59, 84-91].

The formation constants (K_f) for bulk and nano-CuCl₂complexes were calculated for each type of complexes (1:2) and (1:1) (M:L) by using equation (13) [30, 31]:

$$K_f = \frac{[ML]}{[M][L]} = \frac{\Lambda_M - \Lambda_{obs}}{(\Lambda_{obs} - \Lambda_{ML})[L]} \text{ and } [L] = C_L - \left\{ C_M + \frac{\Lambda_M - \Lambda_{obs}}{(\Lambda_M - \Lambda_{ML})} \right\} \quad (13)$$

Where Λ_M is the limiting molar conductance of the bulk and nano-CuCl₂alone, Λ_{obs} is the molar conductance of solution during titration , Λ_{ML} is the molar conductance of the complex and [L] is the ligand concentration.

The Gibbs free energies of formation for each stoichiometric complex (ΔG_f) were calculated by using the equation (14) [45-104]:

$$\Delta G_f = -2.303 RT \log K_f \quad (14)$$

The obtained values (K_f) for bulk and nano-CuCl₂stoichiometric complexes and their calculated ΔG_f values are presented in Tables.3 (a,b).

By drawing the relation between log K_f and 1/T, different lines are obtained indicating the formation of 1:2 and 1:1 (M:L) stoichiometric complexes Fig.(6) as explaines in previous works [58-86].

From the relation between log K_f and 1/T, ΔH_f can be calculated for each type of complexes, from the slope of each line which equal (- $\Delta H_f/2.303R$). The entropy (ΔS_f) for bulk and nano-CuCl₂stoichiometric complexes were calculated [32, 33] for each type of complexes (1:2) and (1:1) (M:L) by using by using Gibbs-Helmholtz equation (15) [44-104]:

$$\Delta G_f = \Delta H_f - T\Delta S_f \quad (15)$$

The calculated values of (ΔH_f) and (ΔS_f) for bulk and nano-CuCl₂stoichiometric complexes are presented in Table.4 (a,b).

3.3. Determination of Different Volumes of Tenoxicamin Mixed (DMF+H₂O) at 298.15 K.

The densities of different concentrations of tenoxicam ranging from 6×10^{-4} to 1×10^{-3} M were measured in mixed (DMF+H₂O) at 298.15K then the molar volumes (V_m) of tenoxicam were obtained by dividing the molar mass of tenoxicam by the experimental densities as shown in equation (16).

$$V_m = \frac{M}{d} \quad (16)$$

Where: M is the molecular weight of tenoxicam and (d) is the density of the used solutions

- The packing density (P) for electrolytes as reported by Kim and Gomaa [34-44] and [59-84] , i.e. the relation between Van der Waals volume (V_w) and the molar volume (V_m) of relatively large molecules (M.Wt > 35) was found to be a constant value equals 0.661 as in equation (17).

$$\text{Packing density (P) for electrolytes} = \frac{V_w}{V_m} = 0.661 \pm 0.017 \quad (17)$$

The electrostriction volumes [45-51] (V_e) is the volume of solute which impressed by the solvent were calculated by using equation (18) [52] after Kim [53] and King [54].

$$V_e = V_w - V_m \quad (18)$$

The apparent molar volumes V_Φ[47, 55] were calculated by using equation (19) [56]:

$$V_\Phi = \frac{M}{d_o} - \left[\left(\frac{d - d_o}{dd_o} \right) \cdot \frac{1000}{C_m} \right] \quad (19)$$

Where M is the molar mass of tenoxicam and C_m is the molar concentration, d and d_o are the densities of tenoxicam and the solvent used, respectively.

The values of the V_m , V_w , V_e and V_Φ for tenoxicam in mixed (DMF+H₂O) are presented in Table (5-8) respectively.

The partial molar volume (V_Φ^0) was obtained by linear extrapolation of (V_Φ) against C_m to zero concentration as shown in Fig (7). The intercept of Masson relation [57], equation (20) gives (V_Φ^0) Table (9).

$$V_\Phi = V_\Phi^0 + S_v \cdot C_m \quad (20)$$

Where V_Φ^0 is the limiting value of the apparent molar volume which equals to the partial molar volumes.

The proportionality constant S_v (the slopes of V_Φ^0 vs. C_m relations), obtained from equation (20) are given in Table (10).

4. Conclusion

The association constants of both bulk and nano-CuCl₂ salts in DMF were easily calculated using Fuoss-Shedlovsky method. Also, the effect of temperature can be noticed from increasing in the negative values of the associating free energy (ΔG_A) as the temperature increased from 298.15 to 313.15 K. This indicates that ion-pair association is favored with lowering of dielectric constant of medium. Also, the negative value of (ΔH_A) indicates that ion association processes are exothermic in nature. A positive entropy change (ΔS_A) is explained on the assumption that iceberg structure around the cation is broken when association takes place leading to an increase in the degree of disorderliness. Positive ΔS values attributed to desolvation of both ions are also supported by the positive enthalpy values indicating a lack of covalent bonds.

In order to have a better understanding of thermodynamics of the complexation reactions between (bulk, nano-CuCl₂) salts and tenoxicam in DMF, it is useful to determine the contribution of enthalpy and entropy of the reactions. The thermodynamic parameters were calculated from the temperatures dependence of the complexation constants (Van't Hoff plot). The formation constants were measured as a function of temperature and increased by increasing temperature. The formation constants and Gibbs free energies of different complexes in DMF at different temperatures follow the order: K_f (1:1) > K_f (1:2) for (M:L), and ΔG_f (1:1) > ΔG_f (1:2) for (M:L). Also, high positive values of (ΔH_f) and (ΔS_f) for (1:1) complex indicated that the stability of (1:1) complex is higher than (1:2) and more favor complex.

Also, different volumes of tenoxicam in mixed (DMF+H₂O) were determined to conclude that Van der Waals values (V_w) show the following order:

$$(100\% > 80\% > 60\% > 40\% > 20\%) \text{ DMF}$$

This indicated that the electronic cloud of the used compound is bigger in case of 100% DMF than the other percentages, due to more electrostatic interaction.

All the partial molar volume (V_Φ^0) values are negative showing high solvation effect of DMF on tenoxicam. All the evaluated S_v values for solutions are positive in their values indicating the association behaviour in the used solvent. Consequently, these data can be used to facilitate their estimations.

References

- [1] J. N. Park, B. Koo, and K. Y. Yoon, *J Am Chem Soc.*, vol. 127, p. 8433, 2005.
- [2] D. E. Zhang, X. J. Zhang, X. M. Ni, H. G. Zheng, and D. D. Yang, *J Magn Mater*, vol. 292, p. 79, 2005.
- [3] B. Y. Xia, P. D. Yang, and Y. G. Sun, *Adv Mater*, vol. 15, p. 353, 2003.
- [4] X. Duan, Y. Huang, Y. Cui, J. Wang, and C. M. Lieber, *Nature*, vol. 409, p. 66, 2001.
- [5] Y. H. Li, V. P. Kotzeva, and D. J. Fray, *Mater Lett.*, vol. 60, p. 2743, 2006.
- [6] W. J. Liu, W. D. He, and Z. C. Zhang, *J Cryst Growth 2006*; 290: 592. *Yizahak Marcus*, vol. 62, pp. 2069-2076, 1990.
- [7] Z. Guo, P. J. Sadler, and Angew, *Chem. Int. Ed.*, vol. 38, pp. 1512-1531, 1999.
- [8] A. Sayah and J. C. English, *J. Am. Acad. Dermatol*, vol. 53, pp. 191-209, 2005.
- [9] S. Defazio, R. Cini, and J. Chem., *Dalton Trans.*, pp. 1888-1897, 2002.
- [10] E. Dubler, *Biochemical and pharmaceutical aspects of metal complexation by drugs*, in: *Metal ions in biological systems* vol. 32. New York: Marcel Dekker, 1996.
- [11] G. E. Jackson, P. M. May, and D. H. Williams, *J. Inorg. Nucl. Chem.*, vol. 40, pp. 1189-1194, 1978.
- [12] A. M. Fiabane and D. R. Williams, *J. Inorg. Nucl. Chem.*, vol. 40, pp. 1195-1200, 1978.
- [13] M. Micheloni, P. M. May, and D. R. Williams, *J. Inorg. Nucl. Chem.*, vol. 40, pp. 1209-1219, 1978.
- [14] G. Arena, G. Kavu, and D. R. Williams, *J. Inorg. Nucl. Chem.*, vol. 40, pp. 1221-1226, 1978.
- [15] G. E. Jackson, P. M. May, and D. R. William, *J. Inorg. Nucl. Chem.*, vol. 40, pp. 1227-1234, 1978.
- [16] N. Jose, S. Sengupta, and J. K. Basu, *J Mol Catal A-Chem.*, vol. 309, pp. 153-158, 2009.
- [17] M. Rezayi, S. Ahmadzadeh, A. Kassim, and Y. H. Lee, *Int J Electrochem Sci.*, pp. 6350-6359.
- [18] A. I. Popov and J. M. Lehn, *Coordination chemistry of macrocyclic compounds*. New York: Plenum Press, 1985.
- [19] B. O. Strasser and A. I. Popov, *J. Am. Chem. Soc.*, vol. 107, pp. 7921-7924, 1985.
- [20] A. I. Popov, *Pure Appl. Chem.*, vol. 51, pp. 101-105, 1979.
- [21] W. Gryzykowski and R. Pastewski, *Electrochimica Acta*, vol. 25, p. 279, 1980.
- [22] A. A. El-Khouly, E. A. Gomaa, and S. E. Salem, *South. Braz. J. Chem.*, vol. 20, 2012.
- [23] T. Shdlovsky and R. L. Kay, *J. Phys. Chem.*, vol. 60, p. 151, 1956.
- [24] E. Hirsch and R. M. Fuoss, *J. Amer. Chem. Phys.*, vol. 25, p. 1199, 1956.
- [25] R. M. Fuoss and F. Accascina, *Electrolytic conductance*. New York: Interscience, 1959.
- [26] O. Popvych, A. Gibofsky, and D. H. Berne, *Analytic. Chem.*, vol. 44, p. 811, 1972.
- [27] M. S. Isabel, L. Lampreia, and A. V. Ferreira, *J. Chem. Soc. Faraday Trans. T.*, vol. 92, p. 1487, 1996.
- [28] P. W. Atkins, *Physical chemistry*: Oxford University Press, 1978.
- [29] D. J. G. Ives, *Chemical thermodynamics*. London: University Chemistry, Macdonald Technical and Scientific, 1971.
- [30] Y. Takeda, *Bull. Chem. Soc. Jpn.*, vol. 56, p. 3600, 1983.
- [31] D. P. Zollinger, E. Bulten, A. Christenhuse, M. Bos, and W. E. Van Der Linden, *Anal. Chim. Acta*, vol. 198, pp. 207-222, 1987.
- [32] P. Debye and H. Hückel, *Phys. Z.*, vol. 24, p. 305, 1923.
- [33] E. A. Gomaa, *Analele Uni. Din Bucuresti-Chimie*, vol. 19, pp. 45-48, 2010.
- [34] J. I. Kim, *J. Physic. Chem.*, vol. 82, p. 191, 1978.
- [35] J. Padova and I. Abrahame, *J. Phys. Chem.*, vol. 71, p. 2112, 1967.
- [36] G. Schwitzgebel and Z. Barthel, *Physic. Chem., N.F.*, vol. 68, p. 79, 1967.

- [37] R. E. Verwall and B. E. Conway, *J. Phys. Chem.*, vol. 70, p. 3961, 1966.
- [38] F. J. Millero, *J. Phys. Chem.*, vol. 72, p. 4589, 1968.
- [39] J. I. Kim, A. Cecal, H. J. Born, E. A. Gomaa, and Z. Physik Chemic, *Neue Folge*, vol. 110, p. 209, 1978.
- [40] J. I. Kim and E. A. Gomaa, *Bull.Soci.Chim.Belg.*, vol. 90, p. 391, 1981.
- [41] E. J. King, *J. Phys. Chem.*, vol. 73, p. 1220, 1969.
- [42] A. A. El-Khouly, E. A. Gomaa, and S. A. Abou El-Leef, *Bulletin of Electrchemistry*, vol. 19, pp. 153 - 164, 2003.
- [43] F. I. El-Dossoki and E. A. Gomaa, *Indian Chemi.Soc.*, vol. 82, pp. 219 -224, 2005.
- [44] E. A. Gomaa and F. I. El-Dossoki, *Indian Journal of Chem. A.*, vol. 44, p. 1594, 2005.
- [45] F. C. Schmidt, W. E. Hoffmann, and S. Proc, *Indiana, Acta, Sci.*, vol. 72, p. 127, 1962.
- [46] R. Gopal and M. A. Siddiqui, *J. Phys. Chem.*, vol. 73, p. 3390, 1969.
- [47] Y. Marcus, *The properties of solvents*. London: Wiley, 1998.
- [48] E. A. Gomaa, M. A. Hamada, and R. Galal, *Avances En Quimica*, vol. 5, pp. 117-121, 2010.
- [49] N. A. El-Shishtawi, M. A. Hamada, and E. A. Gomaa, *Physical Chemistry*, vol. 1, pp. 14-16, 2011.
- [50] E. A. Gomaa and B. A. M. Al Jahdali, *American Journal of Condensed Matter Physics*, vol. 2, pp. 16-21, 2012.
- [51] A. J. Bondi, *Phy. Chem.*, vol. 68, p. 441, 1964.
- [52] J. I. Kim, *Phys. Chem. Neue Folge*, vol. 113, p. 129, 1978.
- [53] E. J. King, *J. Phys. Chem.*, vol. 73, p. 1228, 1969.
- [54] S. L. Oswal, J. S. Desai, S. P. Ijardar, and D. H. Jain, *Jounal of Molecular Liquids*, vol. 144, 2009.
- [55] D. Bohicz, W. Grzybkowski, and A. Lwandowski, *Journal of Molecular Liquids*, vol. 105, pp. 93-104, 2003.
- [56] A. K. Covington and Dickinson, *Physical chemistry of organic solvent systems*: Plenum Press London, 1973.
- [57] E. A. Gomaa and R. M. Galal, *Basic Sciences of Medicine*, vol. 1, pp. 1-5, 2012.
- [58] H. M. Abu El-Nader and E. A. Gomaa, *Mansoura Science Bulletin. (A Chem.)*, vol. 23, 1996.
- [59] A. A. El-Khouly, E. A. Gomaa, and S. E. Salem, *Southern Brazilian Journal of Chemistry*, vol. 20, pp. 43-50, 2012.
- [60] E. A. Gomaa, *Thermochimica Acta*, vol. 91, p. 235, 1985.
- [61] E. A. Gomaa, *Indian J.of Tech.*, vol. 24, p. 725, 1986.
- [62] E. A. Gomaa, *Thermochimica Acta*, vol. 128, p. 99, 1988.
- [63] E. A. Gomaa, *Thermochimica Acta*, vol. 128, p. 287, 1988.
- [64] E. A. Gomaa, *Thermochimica Acta*, vol. 142, p. 19, 1989.
- [65] E. A. Gomaa, *Croatica Chimica Acta*, vol. 62, p. 475, 1989.
- [66] E. A. Gomaa, *Thermochimica Acta*, vol. 147, p. 313, 1989.
- [67] E. A. Gomaa, *Thermochimica Acta*, vol. 140, p. 7, 1989.
- [68] E. A. Gomaa, *Bull.Soc.Chim.Fr.*, vol. 5, p. 620, 1989.
- [69] E. A. Gomaa, *Bull.Soc.Chim.Fr.*, vol. 5, p. 623, 1989.
- [70] E. A. Gomaa, *Thermochimica Acta*, vol. 152, p. 371, 1989.
- [71] E. A. Gomaa, *Thermochimica Acta*, vol. 156, p. 91, 1989.
- [72] E. A. Gomaa, *Physics and Chemistry of Liquids*, vol. 50, pp. 279-283, 2012.
- [73] E. A. Gomaa, *International Journal of Materials and Chemistry*, vol. 2, pp. 16-18, 2012.
- [74] E. A. Gomaa, *American Journal of Environmental Engineering*, vol. 2, pp. 54-57, 2012.
- [75] E. A. Gomaa, *American Journal of Polymer Science*, vol. 2, pp. 35-38, 2012.
- [76] E. A. Gomaa, *Food and Public Health*, vol. 2, pp. 65-68, 2012.
- [77] E. A. Gomaa, *Global Advanced Research Journal of Chemistry and Material Science*, vol. 1, pp. 35-38, 2012.
- [78] E. A. Gomaa, *Frontiers in Science*, vol. 2, pp. 24-27, 2012.
- [79] E. A. Gomaa, *International Journal of Theoretical and Mathematical Physcics*, vol. 3, pp. 151-154, 2013.
- [80] E. A. Gomaa, *Science and Technology*, vol. 3, pp. 123-126, 2013.
- [81] E. A. Gomaa, *Eur. Chem. Bull.*, vol. 1, pp. 259-261, 2013
- [82] E. A. Gomaa, *Research and Reviews: Journal of Chemistry*, vol. 3, pp. 28-37, 2014.
- [83] E. A. Gomaa and M. G. Abdel Razek, *International Research Journal of Pure and Applied Chemistry*, vol. 3, pp. 320-329, 2013.
- [84] E. A. Gomaa and E. M. Abou Elleef, *American Chemical Science Journal*, vol. 3, pp. 489-499, 2013.
- [85] E. A. Gomaa and E. M. Abou Elleef, *Science and Technology*, vol. 3, pp. 118-122, 2013.
- [86] E. A. Gomaa and E. M. Abou Elleef, *Thermal and Power Engineering*, vol. 3, pp. 222-226, 2014.
- [87] E. A. Gomaa, E. M. Abou Elleef, and E. T. Helmy, *Research and reviews :Journal of Chemistry*, vol. 3, pp. 22-27, 2014.
- [88] E. A. Gomaa, E. M. Abou Elleef, E. T. Helmy, and S. M. Defrawy, *Southern Journal of Chemistry*, vol. 21, pp. 1-10, 2013.
- [89] E. A. Gomaa, H. M. Abu El-Nader, and S. E. Rashed, *The International Journal of Engineering and Science*, vol. 3, pp. 64-73, 2014.
- [90] E. A. Gomaa and B. A. Al Jahdali, *Education*, vol. 2, pp. 37-40, 2012.
- [91] E. A. Gomaa and B. A. M. Al -Jahdali, *American Journal of Environmentrnal Engineering*, vol. 2, pp. 6-12, 2012.
- [92] E. A. Gomaa and G. Begheit, *Asian Journal of Chemistry*, vol. 2, p. 444, 1990.
- [93] E. A. Gomaa, A. H. El-Askalany, and M. N. H. Moussa, *Rev.Roum. Chim.*, vol. 32, p. 243, 1987.
- [94] E. A. Gomaa, A. A. El-Khouly, and M. A. Mousa, *Indian Journal of Chemistry* vol. 23, p. 1033, 1984.
- [95] E. A. Gomaa, A. E. Elsayed, and E. A. Mahmoud, *Eur. Chem. Bull.*, vol. 2, pp. 732-735, 2013.
- [96] E. A. Gomaa, K. M. Ibrahim, and N. M. Hassan, *The International Journal of Engineering and Science*, vol. 3, pp. 44-51, 2014.
- [97] E. A. Gomaa, M. A. Mousa, and A. A. El-Khouly, *Thermochimica Acta*, vol. 86, p. 351, 1985.
- [98] E. A. Gomaa, M. A. Mousa, and A. A. El-Khouly, *Thermochimica Acta*, vol. 89, p. 133, 1985.
- [99] E. A. Gomaa, A. M. Shallapy, and M. N. H. Moussa, *J.Indian Chem.Soc.*, vol. 68, p. 339, 1991.
- [100] E. A. Gomaa, A. M. Shallapy, and M. N. H. Moussa, *Asian J.of Chem.*, vol. 4, p. 518, 1992.
- [101] M. A. Hamada, E. A. Gomaa, and N. A. El-Shishtawi, *International Journal of Optoelectronic Enegineering*, vol. 1, pp. 1-3, 2012.
- [102] M. R. Nasrabadi, F. Ahmadi, S. M. Pourmortazavi, M. R. Ganjali, and K. Alizadeh, *Journal of Molecular Liquids*, vol. 144, pp. 97-101, 2009.
- [103] I. S. Shehatta, A. H. El-Askalany, and E. A. Gomaa, *Thermochimica Acta*, vol. 219, p. 65, 1993.
- [104] Y. Takeda, *Bull. Chem. Soc. Jpn.*, vol. 56, pp. 3600-3602, 1983.

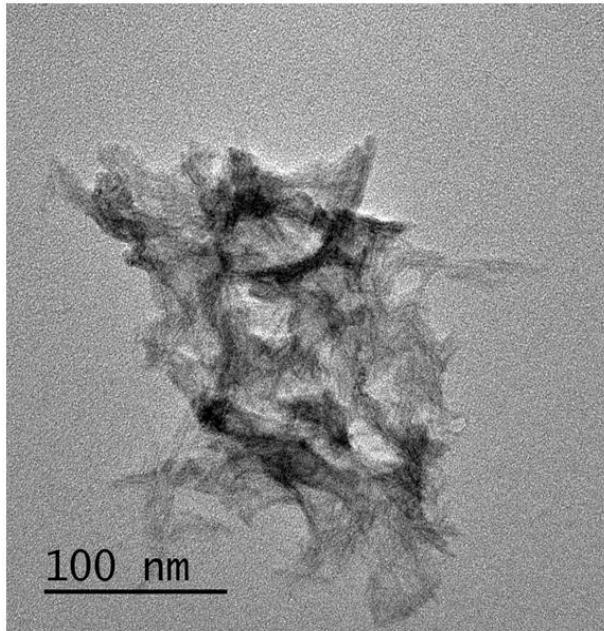


Fig-1. TEM photograph of Nano- CuCl_2

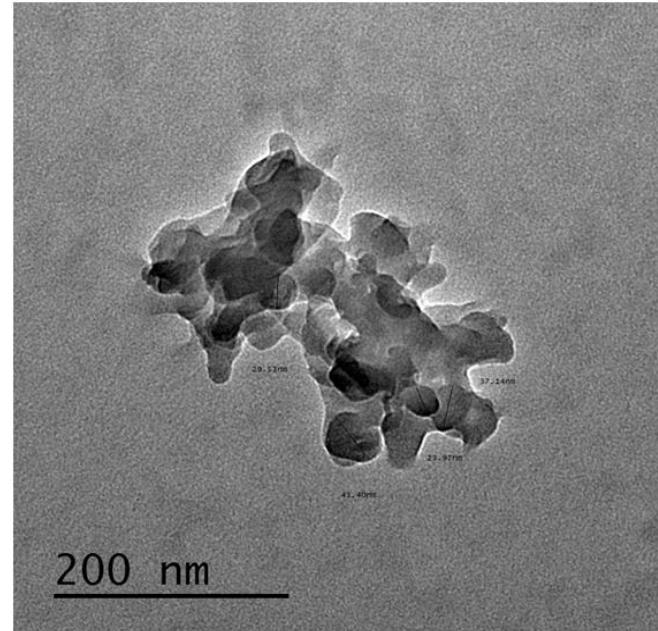


Fig-2. TEM photograph of Tenoxicam

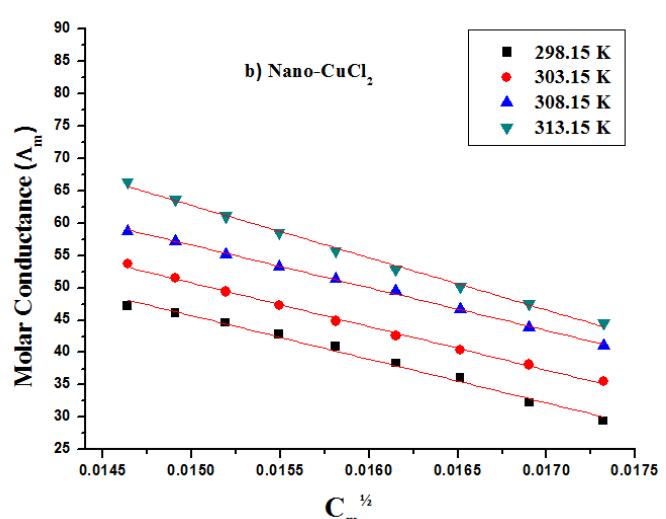
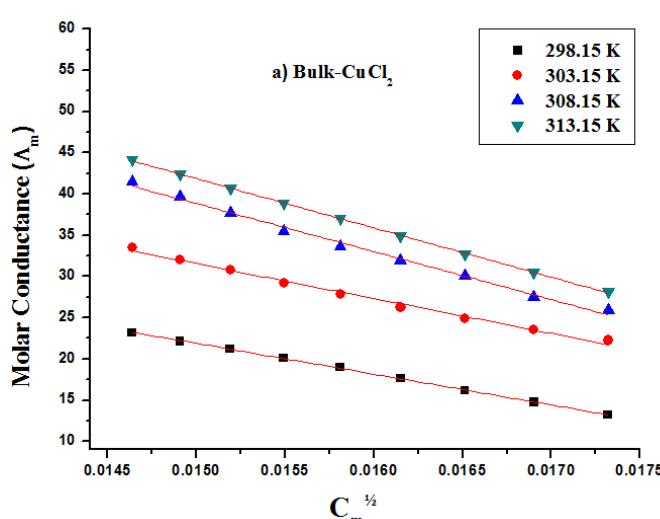


Fig-3. Variation of the molar conductance Λ_m ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) with $C_m^{1/2}$ for (a) bulk- CuCl_2 and (b) nano- CuCl_2 in DMF at (298.15, 303.15, 308.15 and 313.15 K).

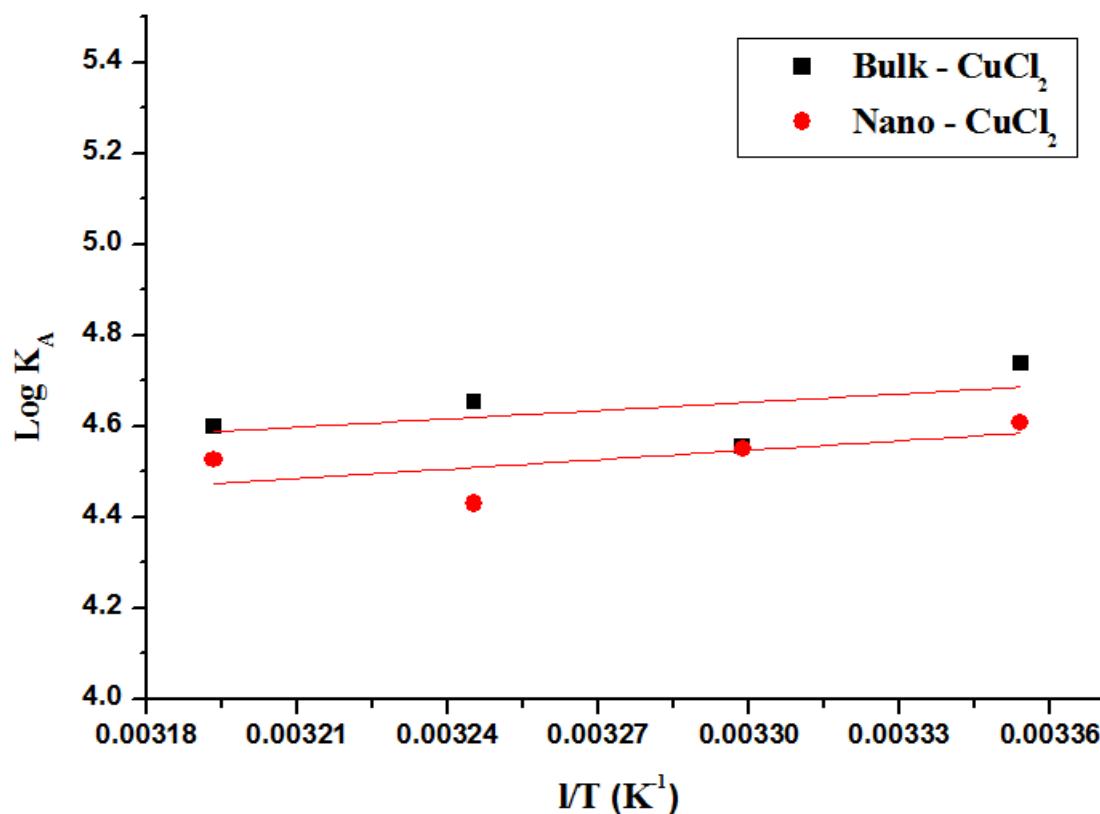


Fig-4. Variation of log K_A with $1/T$ (K^{-1}) of bulk- CuCl_2 and nano- CuCl_2 in DMF.

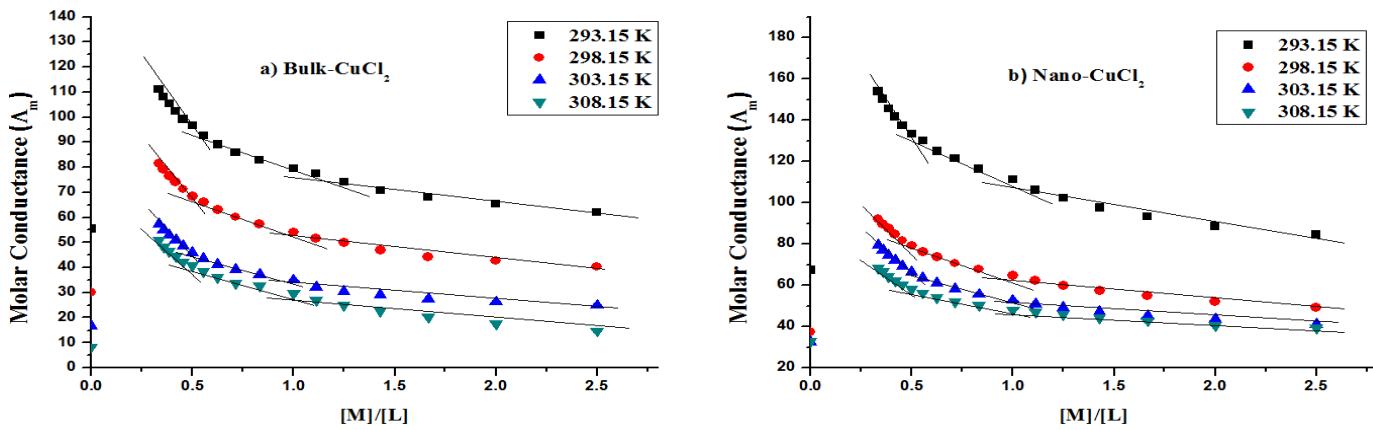


Fig-5. Variation of the molar conductance Λ_m ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) with $[M]/[L]$ for (a) bulk-CuCl₂ and (b) nano-CuCl₂ with tenoxicam in DMF at (298.15, 303.15, 308.15 and 313.15 K).

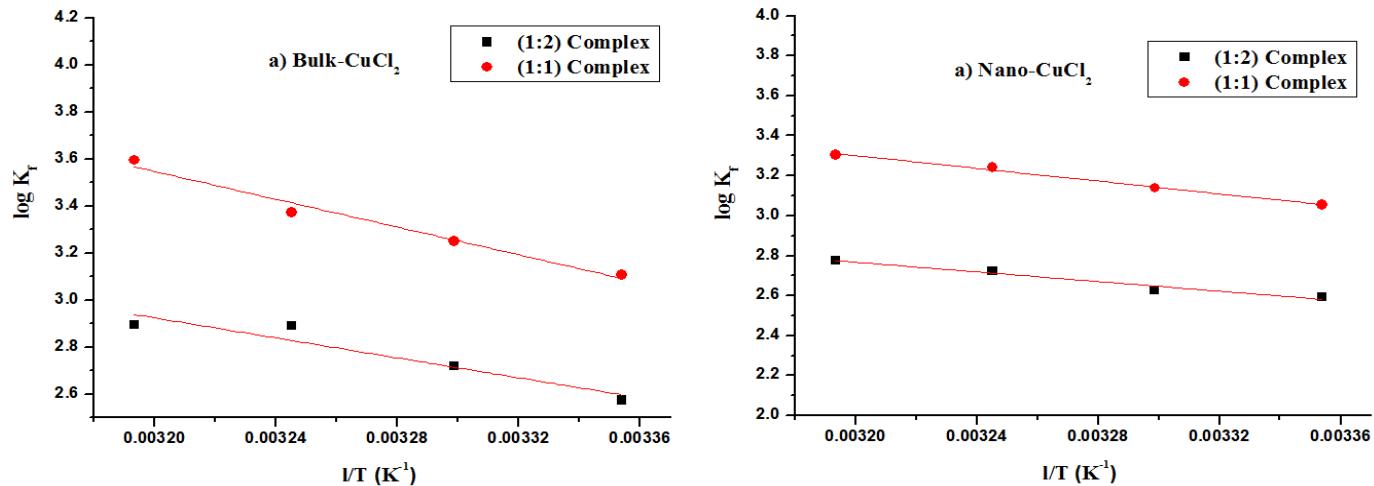


Fig-6. Variation of $\log K_f$ with $1/T$ (K⁻¹) of (a) bulk-CuCl₂ and (b) nano-CuCl₂ in presence of tenoxicamin DMF.

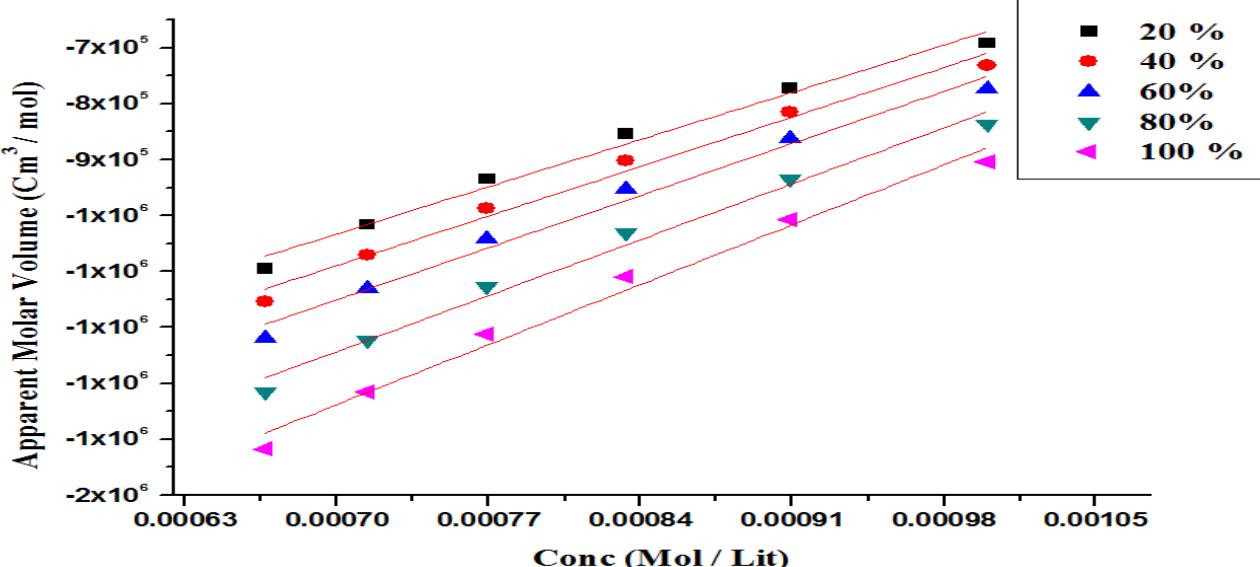


Fig-7. Variation of apparent molar volume (V_ϕ) with C_m of tenoxicam in mixed (DMF+H₂O) at 298.15K.

Table-1(a). The values of viscosity (η_0), limiting molar conductance (Λ_m), molar conductance (Λ), Fuoss-Shedlovsky parameters (S, Z and $S_{(z)}$), activity coefficient (γ_\pm), association constant ($\log K_A$), dissociation constant (K_D), degree of dissociation (α), triple ion association constant (K_3), Gibbs free energy of association (ΔG_A) for bulk-CuCl₂ in DMF at different temperatures.

Temp.	$10^2 \eta_0$ (poise)	Λ_m	Λ	S	Z	$S_{(z)}$	γ_\pm	α	$10^3 K_D$	$10^5 K_3$	$\log K_A$	ΔG_A
298.15 K	0.796	77.91	18.993	150.128	0.0150	1.0151	0.9467	0.2474	0.0182	8.049	4.739	-27.05
303.15 K	0.777	95.02	27.851	163.396	0.0147	1.0148	0.9421	0.2974	0.0279	6.462	4.553	-26.43
308.15 K	0.758	126.18	33.619	187.862	0.0121	1.0122	0.9444	0.2696	0.0222	7.211	4.653	-27.45
313.15 K	0.738	131.44	36.997	196.357	0.0125	1.0126	0.9419	0.2850	0.0252	6.740	4.598	-27.57

Λ_0 in ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$), Λ in ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) and ΔG_A in (kJ mol⁻¹).

Table-1(b). The values of viscosity (η_0), limiting molar conductance (Λ_m), molar conductance (Λ), Fuoss-Shedlovsky parameters (S , Z and $S_{(z)}$), activity coefficient (V_\pm), association constant ($\log K_A$), dissociation constant (K_D), degree of dissociation (α), triple ion association constant (K_3), Gibbs free energy of association (ΔG_A) for nano-CuCl₂ in DMF at different temperatures.

Temp.	$10^2 \eta_0$ (poise)	Λ_m	Λ	S	Z	$S_{(z)}$	γ_\pm	α	$10^3 K_D$	$10^5 K_3$	$\log K_A$	ΔG_A
298.15 K	0.796	146.83	40.952	196.936	0.0112	1.0112	0.9432	0.2820	0.0246	6.809	4.608	-26.30
303.15 K	0.777	151.92	44.866	201.751	0.0114	1.0114	0.9420	0.2987	0.0282	6.348	4.549	-26.40
308.15 K	0.758	155.56	51.458	207.829	0.0121	1.0122	0.9382	0.3348	0.0370	5.460	4.430	-26.14
313.15 K	0.738	184.01	55.661	232.704	0.0109	1.0110	0.9399	0.3058	0.0297	6.130	4.526	-27.13

Λ in ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$), Λ in ($\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$) and ΔG_A in (kJ mol⁻¹).

Table-2. Gibbs free energy of association (ΔG_A), enthalpy change (ΔH_A) and entropy change (ΔS_A) for bulk CuCl₂ and nano-CuCl₂ in DMF at different temperatures.

Temp(K)	ΔG_A (kJ mol ⁻¹)		ΔH_A (kJ mol ⁻¹)		ΔS_A (J mol ⁻¹ K ⁻¹)	
	Bulk CuCl ₂	Nano CuCl ₂	Bulk CuCl ₂	Nano CuCl ₂	Bulk CuCl ₂	Nano CuCl ₂
298.15	-27.05	-26.30			0.0516	0.0439
303.15	-26.43	-26.40	-11.65	-13.20	0.0487	0.0435
308.15	-27.45	-26.14			0.0512	0.0419
313.15	-27.57	-27.13			0.0508	0.0445

Table-3(a). Molar conductance of complex (Λ_{mL}), formation constants ($\log K_f$) and Gibbs free energies of formation (ΔG_f) for 1:2 and 1:1 (M/L) of bulk-CuCl₂ with tenoxicam in DMF at (298.15, 303.15, 308.15 and 313.15 K).

Complex ratio(M:L)	Temp. (K)	$\log K_f$	ΔG_f
(1:2)	298.15	2.5740	-14.694
	303.15	2.7173	-15.772
	308.15	2.8908	-17.056
	313.15	2.8940	-17.352
(1:1)	298.15	3.1075	-17.739
	303.15	3.2506	-18.868
	308.15	3.3730	-19.901
	313.15	3.5942	-21.550

Table-3(b). Molar conductance of complex (Λ_{mL}), formation constants ($\log K_f$) and Gibbs free energies of formation (ΔG_f) for 1:2 and 1:1 (M/L) of nano-CuCl₂ with tenoxicam in DMF at (298.15, 303.15, 308.15 and 313.15 K).

Complex ratio(M:L)	Temp. (K)	$\log K_f$	ΔG_f
(1:2)	298.15	2.5946	-14.811
	303.15	2.6248	-15.235
	308.15	2.7223	-16.062
	313.15	2.7772	-16.651
(1:1)	298.15	3.0534	-17.431
	303.15	3.1391	-18.221
	308.15	3.2433	-19.136
	313.15	3.3028	-19.803

Table-4(a). Gibbs free energy of association (ΔG_f), enthalpy change (ΔH_f) and entropy change (ΔS_f) for bulk-CuCl₂ with tenoxicam in DMF at different temperatures.

Temp. (K)	ΔG_f (kJ mol ⁻¹)		ΔH_f (kJ mol ⁻¹)		ΔS_f (J mol ⁻¹ K ⁻¹)	
	(1:2) Complex	(1:1) Complex	(1:2) Complex	(1:1) Complex	(1:2) Complex	(1:1) Complex
293.15	-14.694	-17.739			0.1857	0.2489
298.15	-15.772	-18.868	40.676	56.484	0.1862	0.2485
303.15	-17.056	-19.901			0.1873	0.2478
308.15	-17.352	-21.550			0.1853	0.2491

Table-4(b). Gibbs free energy of association (ΔG_f), enthalpy change (ΔH_f) and entropy change (ΔS_f) for nano-CuCl₂ with tenoxicam in DMF at different temperatures.

Temp. (K)	ΔG_f (kJ mol ⁻¹)		ΔH_f (kJ mol ⁻¹)		ΔS_f (J mol ⁻¹ K ⁻¹)	
	(1:2) Complex	(1:1) Complex	(1:2) Complex	(1:1) Complex	(1:2) Complex	(1:1) Complex
-14.811	-14.811	-17.431			0.1269	0.16076
-15.235	-15.235	-18.221	23.040	30.501	0.1262	0.16072
-16.062	-16.062	-19.136			0.1268	0.16108
-16.651	-16.651	-19.803			0.1267	0.16064

Table-5. The molar volumes (V_m) of tenoxicam in mixed (DMF+H₂O) at 298.15K.

Concentration	Molar Volume (V_m)				
	20 %	40 %	60 %	80 %	100 %
0.001	34.94676	35.00114	35.46473	36.09071	37.49039
0.000909	31.30519	31.3955	31.762	31.77397	33.49643
0.000833	28.1663	28.08658	28.59603	28.66406	30.4656
0.000769	25.61506	25.49312	26.09855	26.01403	27.7996
0.000714	23.44843	23.46311	23.98862	24.0245	25.54137
0.000667	21.86352	22.09693	22.07236	22.6093	23.60428

Table-6. The Van der Waal's volumes(V_w) of tenoxicam in mixed (DMF+H₂O) at 298.15K.

Concentration	Van der Waal's Volume (V_w)				
	20 %	40 %	60 %	80 %	100 %
0.001	23.09981	23.13575	23.44219	23.85596	24.78115
0.000909	20.69273	20.75242	20.99468	21.00259	22.14114
0.000833	18.61793	18.56523	18.90198	18.94694	20.13776
0.000769	16.93156	16.85095	17.25114	17.19528	18.37554
0.000714	15.49941	15.50911	15.85648	15.88019	16.88285
0.000667	14.45179	14.60607	14.58983	14.94475	15.60243

Table-7. The electrostatic volumes(V_e) of tenoxicam in mixed (DMF+H₂O) at 298.15K.

Concentration	Electrostatic Volume (V_e)				
	20 %	40 %	60 %	80 %	100 %
0.001	-11.847	-11.8654	-12.0225	-12.2348	-12.7092
0.000909	-10.6125	-10.6431	-10.7673	-10.7714	-11.3553
0.000833	-9.54838	-9.52135	-9.69406	-9.71712	-10.3278
0.000769	-8.68351	-8.64217	-8.84741	-8.81876	-9.42407
0.000714	-7.94902	-7.95399	-8.13214	-8.1443	-8.65853
0.000667	-7.41173	-7.49086	-7.48253	-7.66455	-8.00185

Table-8. The apparent molar volumes(V_a) of tenoxicam in mixed (DMF+H₂O) at 298.15K.

Concentration	Apparent Molar Volume (V_a)				
	20 %	40 %	60 %	80 %	100 %
0.001	-6.91E+05	-7.31E+05	-7.73E+05	-8.37E+05	-9.04E+05
0.000909	-7.72E+05	-8.16E+05	-8.63E+05	-9.35E+05	-1.01E+06
0.000833	-8.53E+05	-9.01E+05	-9.52E+05	-1.03E+06	-1.11E+06
0.000769	-9.34E+05	-9.87E+05	-1.04E+06	-1.13E+06	-1.21E+06
0.000714	-1.02E+06	-1.07E+06	-1.13E+06	-1.22E+06	-1.31E+06
0.000667	-1.09E+06	-1.15E+06	-1.22E+06	-1.32E+06	-1.42E+06

Table-9. The intercept of Masson relation (V_ϕ^0).

% (DMF+H ₂ O)	$V_\phi^0 (10^6)$
20 %	-1.877
40 %	-1.974
60 %	-2.082
80 %	-2.243
100 %	-2.409

Table-10. The proportionality constant S_v .

% (DMF+H ₂ O)	$S_v (10^9)$
20 %	1.206
40 %	1.264
60 %	1.331
80 %	1.428
100 %	1.531