*Research Journal of Chemical Sciences* _____ E-ISSN 2231-606X
Vol. **6(7),** 1-11, July **(2016)** *Res. J. Chem. Sci.*

# Conductometric and pH Metric Investigations on Thiosemicarbazone-Mn (II) Systems

**Rathore U., Gupta R., Joshi G. and Bhojak N.***
GCRC, P.G. Department of Chemistry, Govt Dungar College (NAAC –A Grade) Bikaner, India
drbhojak@rediffmail.com

**Available online at: www.isca.in, www.isca.me**
Received 27th February 2016, revised 1st July 2016, accepted 5th July 2016

## Abstract

*In current study thiosemicarbazone has been selected due to great therapeutic importance. Prepration, characterization, solution and antimicrobial study of Mn(II) thiosemicarbazone has been carried out. Solution studies on the complexes have also been carried out in different micellar systems at 25℃ and data have been compared with ethanol water mixture. Formation constants and molar ions in 60% ethanol were determined. Stability constants have been calculated from pH metric study.The conductivity of ligand and metal ligand complexes have been obtained in Triton X- 100 and polyoxethylene (23) lauryether. Association constants and formation constants have been calculated by molar conductance.*

**Keywords:** Thiosemicarbazone, Antimicrobial, Stability constants, Polyoxethylene (23)lauryether and Triton X-100.

## Introduction

Thiosemicarbazone ligands and its transition metal complexes are very important due to the pharmacological properties[1-3]. Thiosemicarbazone and their metal complexes are recently appreciable as they are showing beneficiary various biological activities[4-8]. The antiviral activity of Pt (II) complexes with various antiviral agents have been reported. In general thiosemicarbazones are better chelators for transition metals, this potential of chelation with metal is very interesting criteria in developing drugs, as anticancer, because of increasing demand of neoplastic cells for essential metals which requires in growth[9]. First row of transition metal and vitamin $K_3$ are very important for human life cycle. First transition metal elements and complexes of thiosemicarbazone derived from vitamin $K_3$ have good biological active effect[10].

In this paper we are reporting the synthesis, stability constant, association constant and Gibbs Free energies of Mn(II) complexes with thiosemicarbazide based ligand: 2,6-dihydroxyacetophenonethiosemicarbazone [2,6-DHAT] .

## Materials and Methods

Himedia and E. Merck procured chemicals (A.R .GRADE) have been used. Standard/spectroscopic grade solvents have been used during experimental work.

*Preparation of* 2,6-dihydroxyacetophenone thiosemicarbazone: 2,6-dihydroxyacetophenone thiosemicarbazone[11] was synthesized by condensation of thiosemicarbazid and 2,6-di acetophenone.

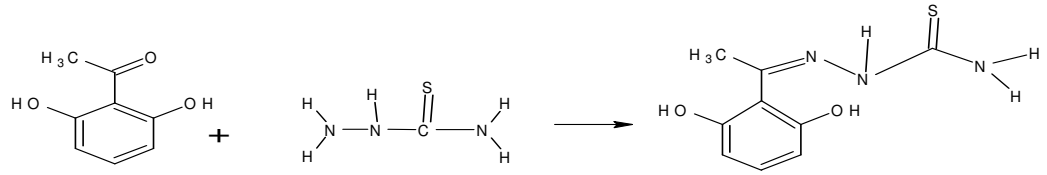
Metal ligand complexes were formed by potentiometric and conductometric titrations. Ligands and metal complexes were analyzed by TLC method.

**Procedure: Potentiometric titration:** pH metric studies have been done with the help of pH meter (pH meter 802). Calibration has been done with aqueous standard solution of pH 4.0, 7.0, 9.0 prepared from buffer tablets. The experiment procedure involved the titration of Solution (i): 1.00 ml $HNO_3$ (0.004 M) + 5 ml $KNO_3$ (0.1 M), Solution (ii): Solution (i) + 1.25 ml of ligand (0.0005M) and Solution (iii): Solution (ii) + 0.625 ml of $MnCl_2$. $nH_2O$ (0.00025 M).

Volume of all these reaction mixtures was made up to 25 ml using 60% ethanol. pH metric studies have performed using different miceller system as Triton X 100, SDS, HTAB. The reaction mixtures of ethanol and water – ethanol (1:1) solutions were also prepared. Titration of titrant have been done individually verses standard 0.05 M KOH. After each addition of a certain amount of alkali to the the reaction mixture the change in the pH of the solution is measured. The graphs were plotted against values of pH and volume of alkali added. To determine formation constants for metal ligand complexes Irving and Rossotti method has been used[12].

**Conductometric titration:** Conductivity TDS Meter 307 is emloyed in present study. The values of conductivity have been obtained by the reaction of ligand and metal ion solution in Water, Tx-100 and Brij-35 (polyoxethylene (23) lauryether system)[13-15]. Calibration was done with standard KCl solution[16].

The conductometric measurements have been carried out in water, brij-35 and TX-100 medium.



2,6-Dihydroxyacetophenone Thiosemicarbazide 2,6-Dihydroxyacetophenonethiosemicarbazone

Synthesis of ligands

**Scheme-1**

**Synthesis of 2,6-Dihydroxyacetophenonethiosemicarbazone**

## Results and Discussion

**Potentiometric titration:** Proton-ligand stability constants (pK). In current experiment ligand 2,6-DHAT provides a single free hydrogen ion. proton–ligand formation constant were estimated by plotting graphs between the values ($-n_A$) Vs pH readings. Proton-ligand stability constants are values of pH where ($-n_A$) has ½ and 1.5 values. Proton-ligand stability constants were evaluated according to literature survey[12].

$$\bar{n}_A = Y - \frac{(V_1 - V_2)(N^0 + E^0)}{(V^0 + V_1)T^0_{CL}} \quad (1)$$

Where, $V^0$ = 25 ml, $E^0$ = molarity of acid, Y= Number of free hydrogen given by ligand, $T_{CL}^0$ is concerntration of ligand in solution, ($V_1 - V_2$) = Difference of vol. of KOH used by $HNO_3$ and 2,6-DHAT to attain the similar value of pH [17].

**Metal ligand stability constant (logK):** Association of metal ions with 2,6-DHAT was estimated by plotting a graph between n- and pH. Metal ligand stability constant (logK) were obtained by curvature.

$$\bar{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V^0 + V_1)(\bar{n}_A)(T^0_{CM})} \quad (2)$$

$$pL = \log_{10} \frac{\sum_{n=0}^{n} \beta_n^H \cdot \frac{1}{(anti\log B)^n}}{T^0_{CL} - \bar{n}T^0_{CM}} \times \frac{V^0 + V_3}{V^0} \quad (3)$$

$V_3$= consumed amount of KOH (mL) with metal ions (titration to achieve mentioned pH) and $T_{CM}^0$ total concentration of metal present in solution. log K1and logK2 were calculated from the formation curve by the known value of pL at which n- =0.5 and n- =1.5 corresponding to the values of logK1 and logK2, respectively[18].

**Conductometric titration:** The values of molar conductance (Λm) for $MnCl_2$ were calculated[19] in water, Brij-35and TX-100 medium at 298.15 K temperature.

$$\Lambda m = (Ks - Ksolv.)Kcell \times 1000/C \quad (4)$$

Here, Ks = specific conductance of the solution, Ksolv = specific conductance of the solvent, Kcell = cell constant, C = molar concentration of the metal ion solution.

The stoichiometric of complexes were decided by association and formation constants. The association constants (Table -2) of complexes were calculated by using equation (5) [20, 21] in water, TX-100 and Brij-35 medium.

$$KA = [\Lambda_0^2 ( \Lambda_0 - \Lambda m )] / [4Cm^2 + \Lambda^3 S(z)] \quad (5)$$

KA = association constants, Λm =molar conductance, $\Lambda_0$ = limiting molar conductance of metal ion solution, γ± = activity coefficient, S(Z) = Fuoss-Shedlovsky factor [22]

The Gibbs free energies (Table-2) were obtained by employing equation (6) [22,23]

$$\Delta GA = - R T \ln KA \quad (6)$$

here, R = gas constant (8.314 J), T = $25^0$C

$$Kf = [\square M - \square\square obs]/[( \square\square obs- \square\square ML)[L]] \quad (7)$$

The formation constants (Kf)[24,25] of complexes were calculated by. applying above equation. Tables (3-9)
here, ΛM = molar conductance of the metal ion solution alone, Λobs = observed molar conductance of solution, ΛML= molar conductance of Mn(II) complexes.

Also the Gibbs free energies of complex formation constant were obtained using equation (8) and exhibited in tables(3-9).

$$\Delta G_f = - RT \ln K_f \quad (8)$$

## Conclusion

log K value greater than zero directs complex preparation by potentiometrically. Observations (conductometric methods) of negative ΔG value directs the formation of complexes (spontaneously).

## Acknowledgements

The author, Uma Rathore gratefully thanks the University Grant Commission (UGC) CRO Bhopal for awarding Minor Research Project (MRP) for experimental purpose at GCRC, Government Dungar College (A-Grade), Bikaner.

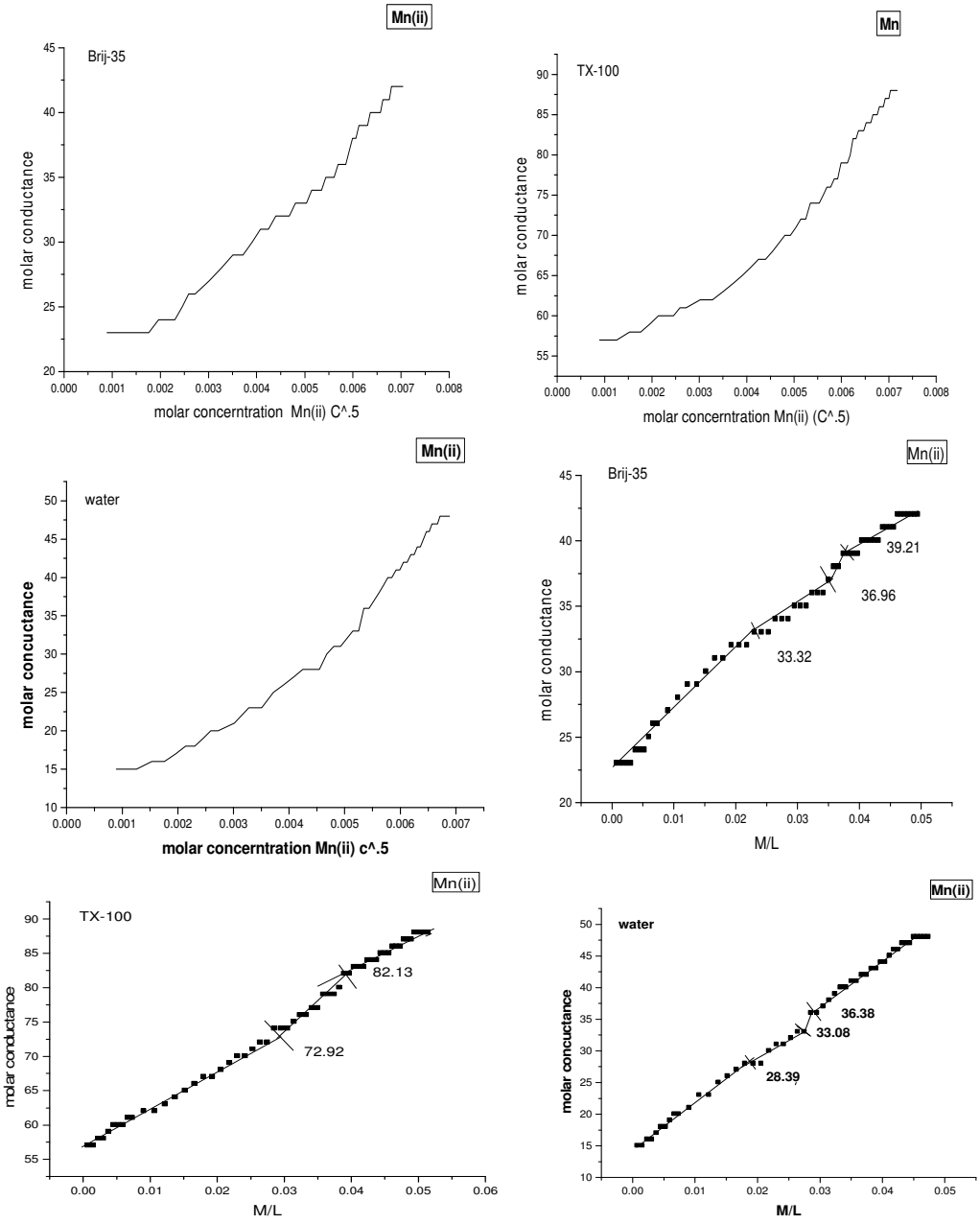



**Table-1**
**pK and logK**

| S.No. | System(ligand) | Medium | half integral method pK | log K1 | logK2 |
|---|---|---|---|---|---|
| 1 | 2,6-DHAT | Alc+Water | 10.26 | 0.481 | |
| 2 | 2,6-DHAT | Alc. | 11.4 | 2.1 | |
| 3 | 2,6-DHAT | CTAB | 10.15 | 1.573 | |
| 4 | 2,6-DHAT | SDS | 11.15 | 2.034 | |
| 5 | 2,6-DHAT | TX-100 | 10.4 | 4.22 | 4.08 |

**Table-2**
**Association constant ($K_A$) of $MnCl_2$ with 2,6-DHAT in different medium**

| | | $K_A$ | $K_A$ | $K_A$ | Δ GA | Δ GA | Δ GA |
|---|---|---|---|---|---|---|---|
| $C_{[ligand]}$ | $C_{m[MnCl2]}$ | Water | TX-100 | Brij-35 | Water | TX-100 | Brij-35 |
| 0.000992063 | 7.93651E-07 | 7.91E+11 | 1.44E+10 | 3.07E+10 | -4.5E+12 | -57.9651 | -59.836 |
| 0.000984252 | 1.5748E-06 | 2.01E+11 | 3.66E+09 | 7.79E+09 | -1.1E+12 | -54.569 | -56.44 |
| 0.000976563 | 2.34375E-06 | 7.23E+10 | 1.52E+09 | 3.52E+09 | -4.1E+11 | -52.3883 | -54.4693 |
| 0.000968992 | 3.10078E-06 | 4.13E+10 | 8.68E+08 | 2.01E+09 | -2.4E+11 | -51.0011 | -53.0821 |
| 0.000961538 | 3.84615E-06 | 2.17E+10 | 5.18E+08 | 1.09E+09 | -1.2E+11 | -49.7228 | -51.5649 |
| 0.000954198 | 4.58015E-06 | 1.24E+10 | 3.35E+08 | 7.68E+08 | -7.1E+10 | -48.6458 | -50.6992 |
| 0.00094697 | 5.30303E-06 | 9.27E+09 | 2.5E+08 | 5.73E+08 | -5.3E+10 | -47.9195 | -49.973 |
| 0.00093985 | 6.01504E-06 | 6.12E+09 | 1.94E+08 | 3.72E+08 | -3.5E+10 | -47.2951 | -48.9043 |
| 0.000932836 | 6.71642E-06 | 4.06E+09 | 1.43E+08 | 2.5E+08 | -2.3E+10 | -46.536 | -47.9168 |
| 0.000925926 | 7.40741E-06 | 3.34E+09 | 1.18E+08 | 2.05E+08 | -1.9E+10 | -46.0507 | -47.4314 |
| 0.000909091 | 9.09091E-06 | 1.84E+09 | 71685070 | 1.14E+08 | -1.1E+10 | -44.8219 | -45.977 |
| 0.000892857 | 1.07143E-05 | 1.01E+09 | 51607984 | 68868444 | -5.8E+09 | -44.0076 | -44.7226 |
| 0.000877193 | 1.22807E-05 | 7.4E+08 | 36010014 | 43836173 | -4.2E+09 | -43.1158 | -43.6031 |
| 0.000862069 | 1.37931E-05 | 4.39E+08 | 26146508 | 34750016 | -2.5E+09 | -42.3226 | -43.0275 |
| 0.000847458 | 1.52542E-05 | 3.06E+08 | 19561320 | 23705128 | -1.7E+09 | -41.6036 | -42.0797 |
| 0.000833333 | 1.66667E-05 | 2.19E+08 | 14976872 | 16509811 | -1.2E+09 | -40.9419 | -41.1833 |
| 0.000819672 | 1.80328E-05 | 1.6E+08 | 11677402 | 14103078 | -9.1E+08 | -40.3252 | -40.7929 |
| 0.000806452 | 1.93548E-05 | 1.39E+08 | 10136612 | 10127308 | -7.9E+08 | -39.9746 | -39.9723 |
| 0.000793651 | 2.06349E-05 | 1.16E+08 | 8127161 | 8909791 | -6.6E+08 | -39.4271 | -39.6549 |
| 0.00078125 | 0.000021875 | 80041697 | 6578589 | 7928244 | -4.6E+08 | -38.9032 | -39.3657 |
| 0.000769231 | 2.30769E-05 | 61781099 | 5365950 | 5852555 | -3.5E+08 | -38.3983 | -38.6134 |
| 0.000757576 | 2.42424E-05 | 55983409 | 4862396 | 5303336 | -3.2E+08 | -38.1542 | -38.3693 |
| 0.000746269 | 2.53731E-05 | 43903565 | 4019524 | 4841200 | -2.5E+08 | -37.6824 | -38.1433 |
| 0.000735294 | 2.64706E-05 | 34638017 | 3335012 | 3620118 | -2E+08 | -37.2198 | -37.4231 |
| 0.000724638 | 2.75362E-05 | 32008932 | 3081879 | 3345345 | -1.8E+08 | -37.0242 | -37.2275 |
| 0.000714286 | 2.85714E-05 | 20066541 | 2310388 | 3107321 | -1.1E+08 | -36.3102 | -37.0446 |
| 0.000704225 | 2.95775E-05 | 18724685 | 2155891 | 2329883 | -1.1E+08 | -36.1387 | -36.331 |
| 0.000694444 | 3.05556E-05 | 16160634 | 2020079 | 2183110 | -9.2E+07 | -35.9775 | -36.1698 |
| 0.000684932 | 3.15068E-05 | 13039947 | 1696066 | 2053270 | -7.4E+07 | -35.5443 | -36.0179 |

| | | $K_A$ | $K_A$ | $K_A$ | Δ GA | Δ GA | Δ GA |
|---|---|---|---|---|---|---|---|
| $C_{[ligand]}$ | $C_{m[MnCl2]}$ | Water | TX-100 | Brij-35 | Water | TX-100 | Brij-35 |
| 0.000675676 | 3.24324E-05 | 10518683 | 1421394 | 1529907 | -6E+07 | -35.1065 | -35.2888 |
| 0.000666667 | 3.33333E-05 | 9229470 | 1345600 | 1448327 | -5.3E+07 | -34.9707 | -35.153 |
| 0.000657895 | 3.42105E-05 | 8041654 | 1127335 | 1375006 | -4.6E+07 | -34.5321 | -35.0242 |
| 0.000649351 | 3.50649E-05 | 7107997 | 1073066 | 1007907 | -4.1E+07 | -34.4098 | -34.2546 |
| 0.000641026 | 3.58974E-05 | 5566699 | 778158.4 | 713687.2 | -3.2E+07 | -33.6135 | -33.3992 |
| 0.000632911 | 3.67089E-05 | 4952066 | 744137.3 | 682484.8 | -2.8E+07 | -33.5028 | -33.2884 |
| 0.000625 | 0.0000375 | 4745323 | 713070.3 | 457411.5 | -2.7E+07 | -33.3971 | -32.2969 |
| 0.000617284 | 3.82716E-05 | 3781918 | 587283.1 | 439153.4 | -2.2E+07 | -32.9162 | -32.1959 |
| 0.000609756 | 3.90244E-05 | 2745894 | 395956.6 | 422374.1 | -1.6E+07 | -31.9393 | -32.0994 |
| 0.00060241 | 3.9759E-05 | 2469060 | 381459.2 | 406909.5 | -1.4E+07 | -31.8469 | -32.0069 |
| 0.000595238 | 4.04762E-05 | 1995598 | 297301.3 | 246514.1 | -1.1E+07 | -31.2292 | -30.765 |
| 0.000588235 | 4.11765E-05 | 1802580 | 287275 | 238200.6 | -1E+07 | -31.1442 | -30.68 |
| 0.000581395 | 4.18605E-05 | 1632859 | 277963.6 | 230479.8 | -9316848 | -31.0626 | -30.5984 |
| 0.000574713 | 4.25287E-05 | 1275368 | 209445.6 | 223293.5 | -7277057 | -30.3612 | -30.5199 |
| 0.000568182 | 4.31818E-05 | 1159788 | 203158.2 | 216590.4 | -6617574 | -30.2857 | -30.4443 |
| 0.000561798 | 4.38202E-05 | 1126241 | 197281.8 | 102304.2 | -6426159 | -30.213 | -28.5857 |
| 0.000555556 | 4.44444E-05 | 831647.4 | 140597 | 99450.7 | -4745254 | -29.3736 | -28.5156 |
| 0.000549451 | 4.50549E-05 | 759729.7 | 136812.6 | 96773.82 | -4334903 | -29.306 | -28.448 |
| 0.000543478 | 4.56522E-05 | 739981.9 | 133256.4 | 94258.36 | -4222225 | -29.2407 | -28.3827 |
| 0.000537634 | 4.62366E-05 | 493105.3 | 85736.95 | 7771.106 | -2813584 | -28.1479 | -22.1985 |
| 0.000531915 | 4.68085E-05 | 481128.5 | 83654.52 | 7582.356 | -2745246 | -28.087 | -22.1376 |
| 0.000526316 | 4.73684E-05 | 469821.5 | 81688.56 | 7404.164 | -2680730 | -28.028 | -22.0786 |
| 0.000520833 | 4.79167E-05 | | 41410.24 | 7235.701 | -236281 | -26.3445 | -22.0216 |
| 0.000515464 | 4.84536E-05 | | 40497.54 | 7076.224 | -231073 | -26.2893 | -21.9664 |
| 0.000510204 | 4.89796E-05 | | 39632.42 | 6925.059 | -226137 | -26.2358 | -21.9129 |
| 0.000505051 | 4.94949E-05 | | 5172.862 | 6781.598 | -29515.6 | -21.19 | -21.861 |
| 0.0005 | 0.00005 | | 5068.887 | | -28922.3 | -21.1397 | |
| 0.00049505 | 5.0495E-05 | | 4969.984 | | -28358 | -21.0908 | |
| 0.000490196 | 5.09804E-05 | | 4875.805 | | -27820.6 | -21.0434 | |
| 0.000485437 | 5.14563E-05 | | 4786.029 | | -27308.4 | -20.9974 | |

**Table-3**
**Formation constants and Gibbs free energies of formation for 1:2 (M/L) complexes in water medium**

| Λobs | [L] | ($Λ_M$-$Λ_{obs}$) | (Λobs-$Λ_{ML}$)[L] | $K_f$ | Δ $G_f$ (k J/ mol) |
|---|---|---|---|---|---|
| 37 | 0.000694444 | 34 | 0.000430556 | 78967.74 | -27.94410524 |
| 38 | 0.000684932 | 33 | 0.001109589 | 29740.74 | -25.52426673 |
| 39 | 0.000675676 | 32 | 0.00177027 | 18076.34 | -24.29042622 |
| 40 | 0.000666667 | 31 | 0.002413333 | 12845.3 | -23.44387221 |
| 40 | 0.000657895 | 31 | 0.002381579 | 13016.57 | -23.47669413 |
| 41 | 0.000649351 | 30 | 0.003 | 10000 | -22.82339326 |
| 41 | 0.000641026 | 30 | 0.002961538 | 10129.87 | -22.85536814 |
| 42 | 0.000632911 | 29 | 0.003556962 | 8153.025 | -22.31739161 |
| 42 | 0.000625 | 29 | 0.0035125 | 8256.228 | -22.34856207 |
| 43 | 0.000617284 | 28 | 0.00408642 | 6851.964 | -21.88657888 |
| 43 | 0.000609756 | 28 | 0.004036585 | 6936.556 | -21.9169844 |
| 44 | 0.00060241 | 27 | 0.004590361 | 5881.89 | -21.50829155 |
| 44 | 0.000595238 | 27 | 0.004535714 | 5952.756 | -21.53796877 |
| 45 | 0.000588235 | 26 | 0.005070588 | 5127.61 | -21.16821228 |
| 46 | 0.000581395 | 25 | 0.005593023 | 4469.854 | -20.82802036 |
| 46 | 0.000574713 | 25 | 0.005528736 | 4521.83 | -20.85666829 |
| 47 | 0.000568182 | 24 | 0.006034091 | 3977.401 | -20.53876813 |
| 47 | 0.000561798 | 24 | 0.005966292 | 4022.599 | -20.56676864 |
| 47 | 0.000555556 | 24 | 0.0059 | 4067.797 | -20.59445628 |
| 48 | 0.000549451 | 23 | 0.006384615 | 3602.41 | -20.29338073 |
| 48 | 0.000543478 | 23 | 0.006315217 | 3641.997 | -20.32046317 |
| 48 | 0.000537634 | 23 | 0.006247312 | 3681.583 | -20.34725281 |
| 48 | 0.000531915 | 23 | 0.006180851 | 3721.17 | -20.37375594 |
| 48 | 0.000526316 | 23 | 0.006115789 | 3760.757 | -20.3999786 |

$Λ_{ML}$ = 36.38 $Cm^2Ohm^{-1}mol^{-1}$

**Table-4**
**Formation constants and Gibbs free energies of formation for 1:4 (M/L) complexes in water medium**

| Λobs | [L] | ($Λ_M$-$Λ_{obs}$) | (Λobs-$Λ_{ML}$)[L] | $K_f$ | Δ $G_f$ (k J/mol) |
|---|---|---|---|---|---|
| 30 | 0.00078125 | 41 | 0.001257813 | 32596.27 | -25.75145175 |
| 31 | 0.000769231 | 40 | 0.002007692 | 19923.37 | -24.5315122 |
| 31 | 0.000757576 | 40 | 0.001977273 | 20229.89 | -24.56934528 |
| 32 | 0.000746269 | 39 | 0.00269403 | 14476.45 | -23.74010743 |
| 33 | 0.000735294 | 38 | 0.003389706 | 11210.41 | -23.10652647 |
| 33 | 0.000724638 | 38 | 0.00334058 | 11375.27 | -23.14270256 |

$Λ_{ML}$ = 28.39 $Cm^2Ohm^{-1}mol^{-1}$

**Table-5**
**Formation constants and Gibbs free energies of formation for 1:2 (M/L) complexes in TX-100 medium**

| Λobs | [L] | ($Λ_M$-$Λ_{obs}$) | (Λobs-$Λ_{ML}$)[L] | $K_f$ | Δ $G_f$ (k J/mol) |
|---|---|---|---|---|---|
| 83 | 0.000595238 | 16 | 0.000517857 | 30896.55 | -25.58871048 |
| 83 | 0.000588235 | 16 | 0.000511765 | 31264.37 | -25.6180021 |
| 83 | 0.000581395 | 16 | 0.000505814 | 31632.18 | -25.64695112 |
| 84 | 0.000574713 | 15 | 0.001074713 | 13957.22 | -23.62186743 |
| 84 | 0.000568182 | 15 | 0.0010625 | 14117.65 | -23.65015474 |
| 84 | 0.000561798 | 15 | 0.001050562 | 14278.07 | -23.67812242 |
| 85 | 0.000555556 | 14 | 0.001594444 | 8780.488 | -22.47473927 |
| 85 | 0.000549451 | 14 | 0.001576923 | 8878.049 | -22.50208886 |
| 85 | 0.000543478 | 14 | 0.001559783 | 8975.61 | -22.52913955 |
| 86 | 0.000537634 | 13 | 0.002080645 | 6248.062 | -21.63255568 |
| 86 | 0.000531915 | 13 | 0.002058511 | 6315.245 | -21.65902773 |
| 86 | 0.000526316 | 13 | 0.002036842 | 6382.429 | -21.68521965 |
| 87 | 0.000520833 | 12 | 0.002536458 | 4731.006 | -20.94414392 |
| 87 | 0.000515464 | 12 | 0.002510309 | 4780.287 | -20.96979299 |
| 87 | 0.000510204 | 12 | 0.002484694 | 4829.569 | -20.99517899 |
| 88 | 0.000505051 | 11 | 0.002964646 | 3710.392 | -20.34269037 |
| 88 | 0.0005 | 11 | 0.002935 | 3747.871 | -20.36756609 |
| 88 | 0.00049505 | 11 | 0.002905941 | 3785.349 | -20.39219429 |
| 88 | 0.000490196 | 11 | 0.002877451 | 3822.828 | -20.41657984 |
| 88 | 0.000485437 | 11 | 0.002849515 | 3860.307 | -20.44072747 |

$Λ_{ML}$ = 82.13 $Cm^2Ohm^{-1}mol^{-1}$

**Table-6**
**Formation constants and Gibbs free energies of formation for 1:3 (M/L) complexes in TX-100 medium**

| Λobs | [L] | ($\Lambda_M$-$\Lambda_{obs}$) | (Λobs-$\Lambda_{ML}$)[L] | $K_f$ | Δ $G_f$ (k J/mol) |
|---|---|---|---|---|---|
| 74 | 0.000714286 | 25 | 0.000771429 | 32407.41 | -25.70687842 |
| 74 | 0.000704225 | 25 | 0.000760563 | 32870.37 | -25.74198699 |
| 74 | 0.000694444 | 25 | 0.00075 | 33333.33 | -25.77660453 |
| 75 | 0.000684932 | 24 | 0.001424658 | 16846.15 | -24.08749932 |
| 76 | 0.000675676 | 23 | 0.002081081 | 11051.95 | -23.04420031 |
| 76 | 0.000666667 | 23 | 0.002053333 | 11201.3 | -23.0774238 |
| 77 | 0.000657895 | 22 | 0.002684211 | 8196.078 | -22.30426296 |
| 77 | 0.000649351 | 22 | 0.002649351 | 8303.922 | -22.33661784 |
| 79 | 0.000641026 | 20 | 0.003897436 | 5131.579 | -21.14530999 |
| 79 | 0.000632911 | 20 | 0.003848101 | 5197.368 | -21.17684052 |
| 79 | 0.000625 | 20 | 0.0038 | 5263.158 | -21.20797443 |
| 80 | 0.000617284 | 19 | 0.00437037 | 4347.458 | -20.73488132 |
| 82 | 0.000609756 | 17 | 0.005536585 | 3070.485 | -19.87414626 |
| 82 | 0.00060241 | 17 | 0.00546988 | 3107.93 | -19.904148 |

$\Lambda_{ML}$ = 72.92 $Cm^2Ohm^{-1}mol^{-1}$

**Table-7**
**Formation constants and Gibbs free energies of formation for 1:3 (M/L) complexes in Brij-35 medium**

| Λobs | [L] | ($\Lambda_M$-$\Lambda_{obs}$) | (Λobs-$\Lambda_{ML}$)[L] | $K_f$ | Δ $G_f$ (k J/mol) |
|---|---|---|---|---|---|
| 40 | 0.000595 | 25 | 0.000470238 | 53165 | -26.93207168 |
| 40 | 0.000588 | 25 | 0.000464706 | 53797 | -26.9613633 |
| 40 | 0.000581 | 25 | 0.000459302 | 54430 | -26.99031233 |
| 40 | 0.000575 | 25 | 0.000454023 | 55063 | -27.01892667 |
| 40 | 0.000568 | 25 | 0.000448864 | 55696 | -27.04721399 |
| 41 | 0.000562 | 24 | 0.001005618 | 23866 | -24.94965354 |
| 41 | 0.000556 | 24 | 0.000994444 | 24134 | -24.97730873 |
| 41 | 0.000549 | 24 | 0.000983516 | 24402 | -25.00465832 |
| 41 | 0.000543 | 24 | 0.000972826 | 24670 | -25.03170901 |
| 42 | 0.000538 | 23 | 0.0015 | 15333 | -23.85460783 |

| Λobs | [L] | ($\Lambda_M$-$\Lambda_{obs}$) | ($\Lambda_{obs}$-$\Lambda_{ML}$)[L] | $K_f$ | Δ $G_f$ (k J/mol) |
|---|---|---|---|---|---|
| 42 | 0.000532 | 23 | 0.001484043 | 15498 | -23.88107988 |
| 42 | 0.000526 | 23 | 0.001468421 | 15663 | -23.9072718 |
| 42 | 0.000521 | 23 | 0.001453125 | 15828 | -23.93318945 |
| 42 | 0.000515 | 23 | 0.001438144 | 15993 | -23.95883853 |
| 42 | 0.00051 | 23 | 0.001423469 | 16158 | -23.98422453 |
| 42 | 0.000505 | 23 | 0.001409091 | 16323 | -24.00935279 |

$\Lambda_{ML}$ = 39.21 $Cm^2Ohm^{-1}mol^{-1}$

**Table-8**
**Formation constants and Gibbs free energies of formation for 1:4 (M/L) complexes in Brij-35 medium**

| Λobs | [L] | ($\Lambda_M$-$\Lambda_{obs}$) | ($\Lambda_{obs}$-$\Lambda_{ML}$)[L] | $K_f$ | Δ $G_f$ (k J/mol) |
|---|---|---|---|---|---|
| 38 | 0.000641 | 27 | 0.000666667 | 40500 | -26.25861817 |
| 38 | 0.000633 | 27 | 0.000658228 | 41019 | -26.2901487 |
| 39 | 0.000625 | 26 | 0.001275 | 20392 | -24.56031522 |
| 39 | 0.000617 | 26 | 0.001259259 | 20647 | -24.59106236 |
| 39 | 0.00061 | 26 | 0.001243902 | 20902 | -24.62143223 |
| 39 | 0.000602 | 26 | 0.001228916 | 21157 | -24.65143397 |

$\Lambda_{ML}$ = 36.96 $Cm^2Ohm^{-1}mol^{-1}$

**Table-9**
**Formation constants and Gibbs free energies of formation for 1:5 (M/L) complexes in Brij-35 medium**

| Λobs | [L] | ($\Lambda_M$-$\Lambda_{obs}$) | ($\Lambda_{obs}$-$\Lambda_{ML}$)[L] | $K_f$ | Δ $G_f$ (k J/mol) |
|---|---|---|---|---|---|
| 35 | 0.000704 | 30 | 0.001183099 | 25357 | -25.0996674 |
| 35 | 0.000694 | 30 | 0.001166667 | 25714 | -25.13428493 |
| 35 | 0.000685 | 30 | 0.001150685 | 26071 | -25.16842496 |
| 36 | 0.000676 | 29 | 0.001810811 | 16015 | -23.96225549 |
| 36 | 0.000667 | 29 | 0.001786667 | 16231 | -23.99547899 |
| 36 | 0.000658 | 29 | 0.001763158 | 16448 | -24.02826243 |
| 37 | 0.000649 | 28 | 0.00238961 | 11717 | -23.18891391 |

$\Lambda_{ML}$ = 33.32 $Cm^2Ohm^{-1}mol^{-1}$

## References

**1.** Kovala-Demertzi D., Boccarelli A., Demertzis M.A. and Coluccia M. (2007). In vitro antitumor activity of 2-acetyl pyridine 4N-ethyl thiosemicarbazone and its platinum (II) and palladium(II) complexes. *Chemotherapy*, 53(2), 148-152.

**2.** Kovala-Demertzi D., Varadinova T., Genova P., Souza P. and Demertzis M.A. (2007). Platinum (II) and palladium(II) complexes of pyridine-2-carbaldehyde thiosemicarbazone as alternative antiherpes simplex virus agents. *Bioinorganic Chemistry and Applications*, 2007.

**3.** Scovill J.P., Klayman D.L. and Franchino C.F. (1982). 2-acetylpyridine thiosemicarbazones. 4. Complexes with transition metals as antimalarial and antileukemic agents. *Journal of Medicinal Chemistry*, 25(10), 1261–1264.

**4.** Quiroga A.G., Perez J.M. and Lopez-Solera I. (1998). Novel tetranuclear orthometalated complexes of Pd(II) and Pt(II) derived from *p*-isopropylbenzaldehyde thiosemicarbazone with cytotoxic activity in *cis*-DDP resistant tumor cell lines Interaction of these complexes with DNA. *Journal of Medicinal Chemistry*, 41(9), 1399-1408.

**5.** Costa R.F.F., Rebolledo A.P. and Matencio T. (2005). Metal complexes of 2-benzoylpyridine-derived thiosemicarbazones: structural, electrochemical and biological studies. *Journal of Coordination Chemistry*, 58(15), 1307–1319.

**6.** Agarwal R.K., Singh L. and Sharma D.K. (2006). Synthesis, spectral, and biological properties of copper (II) complexes of thiosemicarbazones of Schiff bases derived from 4-aminoantipyrine and aromatic aldehydes. *Bioinorganic Chemistry and Applications*, 2006.

**7.** Pandey O.P., Sengupta S.K., Mishra M.K. and Tripathi C.M. (2003). Synthesis, spectral and antibacterial studies of binuclear titanium(IV)/zirconium(IV) complexes of piperazine dithiosemicarbazones. *Bioinorganic Chemistry and Applications,* 1(1), 35–44.

**8.** Shipman J.C., Smith S.H., Drach J.C. and Klayman D.L. (1986). Thiosemicarbazones of 2-acetylpyridine, 2-acetylquinoline, 1- acetylisoquinoline, and related compounds as inhibitors of herpes simplex virus in vitro and in a cutaneous herpes guinea pig model. *Antiviral Research*, 6(4), 197–222.

**9.** Gujarathi J.R., Pawar N.S. and Bendrea R.S. (2013). Synthesis, physicochemical and biological evaluation of Co (II) complexes derived from 5-chloro-2-hydroxy acetophenone *N*(4) methyl thiosemicarbazone. *Journal of Chemical and Pharmaceutical Research,* 5(7), 161-168.

**10.** Tang H.A., Wang L.F. and Yang R.D. (2003). Synthesis, characterization and antibacterial activities of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes with soluble Vitamin $K_3$ thiosemicarbazone. *Transition metal chemistry,* (28), 395-398.

**11.** Lobana T.S., Sanchez A. and Casas J.S. (1997). Synthesis, characterization, and in vitro cytotoxic activities of benzaldehyde thiosemicarbazone derivatives and their palladium (II) and platinum (II) complexes against various human tumor cell lines. *Bioinorganic Chemistry and Applications,* Article ID 690952, 9 pages.

**12.** Irving H.M. and Rosstti H.S. (1954). The calculation of formation curves in mixed solvents. *J. chem. Soc.*, 2904-2910.

**13.** Gomaa E.A. and Jahdali B.M.A. (2011). Association of Cu $(NO_3)_2$ with Kryptofix-221 in mixed (MeOH-DMF) solvents at different temperatures. *American Journal of Fluid Dynamics*, 1(1), 4-8.

**14.** Shishtawi N.E., Hamada M.A. and Gomaa E.A. (2011). Inflence of Permanent magnet on the association constants of $FeCl_3$+10% PVA(Polyvinylalcohol) in 50% ethanol-water solutions conductometrically at 298.25K using new equation for 1:3 asymmetric electrolytes. *Physical Chemistry*, 1(1), 14-16.

**15.** Gomaa E. A. (2010). Solvation parameters of lead acetate in mixed N, N-dimethylformamide-water mixtures at 298.15K. *Analele Universitatii din Bucuresti-Chimie*, (19), 45-48.

**16.** Biswas R. and Brahman D. (2009). Thermodynamics of the complexation between salicylaldehyde thiosemicarbazone with Cu(II) ions in methanol–1,4-dioxane binary solutions. *Indian J. Chem.,* (A 48), 1145.

**17.** Pund D.A., Bhagwatkar R.A., Tavade D.T. and Rathod D.B. (2010). Studies on interaction between La (ii), and Nd (iii) metal ions and 1-(4-Hydroxy-6-methyl pyrimidino)-3-substituted thicarbamide at 0.1 m ionic strength pH metrically. *Rasayan J. Chem*., 2(3), 246-249.

**18.** Janrao D.M., Pathan J., Kayande D.D. and Mulla J.J. (2014). An over view of potentiometric determination of stability constants of metal complexes. *Sci. Revs. Chem. Commun.,* 4(1), 11-24.

**19.** Gryzybkowski W. and Pilarczyk M. (1989). Electrical conductance and apparent molar volumes of $Al(ClO_4)_2$, $Be(ClO_4)_2$ and $Cu(ClO_4)_2$ in N,N-dimethylformamide solutions at 25$^o$C. *Electrochimica Acta*, (32), 1601-1605.

**20.** Shishtawi N.A.E., Hamada M.A. and Gomaa E.A. (2010). Influence of permanent magnet on the association constants of $FeCl_3$ in 50% ethanol-$H_2O$ solutions (conductometrically) at 298.15 K using a new equation for 1:3 asymmetric electrolytes. *Journal Chemical engineering data*, (55), 5422-5424.

**21.** Hamada M.A., Shishtawiand N.A.E. and Gomaa E.A. (2009). Conductometric evaluation of association constants for aqueous solutions of $CoCl_2$ in the absence and presence

of a magnetic field. *Southern Brazilian journal of chemistry*, 17, 33-40.

**22.** Gomaa E.A. (1987). Solute-solvent interactions of some univalent-univalent salts with various organic solvents at 25$^{o}$C. *Thermochimica Acta*, (120), 183-189.

**23.** Gomaa E.A. (1988). Theoretical contribution of salvation of AgBr in some organic solvents at 25$^{o}$. *Thermochimica Acta*, (128), 99-120.

**24.** Dossoki F.I.E. (2008). Electric conductance and semi-emperical studies on two thiophene derivatives/metal cation complexation. *Journal of Molecular Liquids*, 142, 53-56.

**25.** Nasrabadi M.R., Ahmedi F., Tazari S.M.P., Ganjal M.P. and Alizadeh K. (2009). Conductometric study of complex formation between some substituted pyrimidines and some metal ions in acetonitrile and the determination of thermodynamic parameters. *Journal of Molecular Liquids*, (144), 97-101.