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Thermodynamic studies on metal complexes of Cd^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+} with pyridine-2,6-dicarboxylic acid in water, methanol and water-methanol binary solvent systems at 298.15, 308.15 and 318.15 K by conductometric method

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ABSTRACT

Stability constants are measured for complexes of Cd^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+} with pyridine-2,6-dicarboxylic acid(PDA) in water, methanol and water-methanol binary solvent systems at 298.15, 308.15 and 318.15 K by conductometric method. The result shows that the stoichiometry of the complexes of PDA with all metals in all binary solvent systems is 1:2 [ML_2]. The logK_f values of PDA-M^{2+} complexes in H_2O-MeOH binary solvent systems increase with increasing % of MeOH and temperature. The ΔH^0 and ΔS^0 of the complexation reaction in the different H_2O-MeOH binary solvent systems were evaluated by the temperature dependence of the formation constants using a linear least square analysis according to van't Hoff equation.

Capsule Summary: Stability of Cd^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+} complexes with pyridine-2,6-dicarboxylic acid (PDA) in water, methanol and water-methanol binary solvent systems at was measured at different temperature and both solvent and temperature affected the stability of PDA complexes with Cd^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+}.

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INTRODUCTION

Conductometric method is very simple and easy technique for metal complex studies. To study the effect of charge, size and type of the metal ion, nature of ligand, physical and chemical properties of solvent, temperature on the stabilities of the complexes. Researcher can also calculate thermodynamic parameters like enthalpy, entropy and Gibb's free energy (G. A. Lawrance, 2010; N. Matsuura et al., 1976; Francis and Shrivastav, 2011). From conductometric method, the value of formation constant(logK_f) can be evaluated by GENPLOT computer program. The enthalpy change(ΔH) and entropy change (ΔS) of the complexation reactions in the different binary solvent systems can be calculated by temperature dependence of the formation constant using a linear least square analysis according to van't Hoff equation (Ravi and Maisuria, 2013; Dhruvi et al., 2014). Pyridine 2,6-dicarboxylic acid (PDA) and its derivatives occupy a uniquely important place in analytical chemistry. Complexes of PDA with some transition metals are helpful in normalizing elevated blood glucose levels in diabetic rats, therefore, fundamental information regarding solution chemistry of metal complexes of PDA as ligand is important (Eugenijus Norkus et al., 2005). In this paper we have reported the formation constants of PDA with Cd^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+} in water, methanol and H_2O-MeOH binary solvent systems at 298.15, 308.15 and 318.15 K. This study is useful to understand the effect of ionic size, solvent composition, temperature and the nature of the complexing agent.

MATERIAL AND METHODS

The reagents used were of analytical reagent grade and used without further purification. Nickel nitrate($Ni(NO_3)_2.6H_2O$), cobalt nitrate($Co(NO_3)_2.6H_2O$) and potassium chloride(KCl) from Merck limited Mumbai, cupric nitrate($Cu(NO_3)_2.3H_2O$), cadmium nitrate($Cd(NO_3)_2.4H_2O$) were purchased from ACS chemicals, Ahmedabad. Pyridine 2,6-dicarboxylic acid(PDA) was purchased from Fluka. Methanol extra pure was purchased from Finar Chemicals limited Ahmedabad. Conductivity water with conductivity less than 2.0 x 10^{-6} was used for preparation of all the solutions. Glassware used were thoroughly cleaned with freshly prepared aqua - regia and rinsed thoroughly with deionized water.

The conductance measurements were performed using model EQ-665, a digital Equiptronics conductivity apparatus, at a constant temperature maintained within ±0.3 °C using WENSAR thermostat, model WMS 300. The conductance of the solutions was measured using a conductivity cell consisting of two platinum electrodes with a cell constant of 1.02 cm^{-1} throughout the studies. The cell constant was determined using 0.1N and 0.01 N analytical grade KCl in deionized water and the mean value was used. The specific conductance of this solution at various temperatures has been reported in the literature (H. J. Bushmann, 1989).

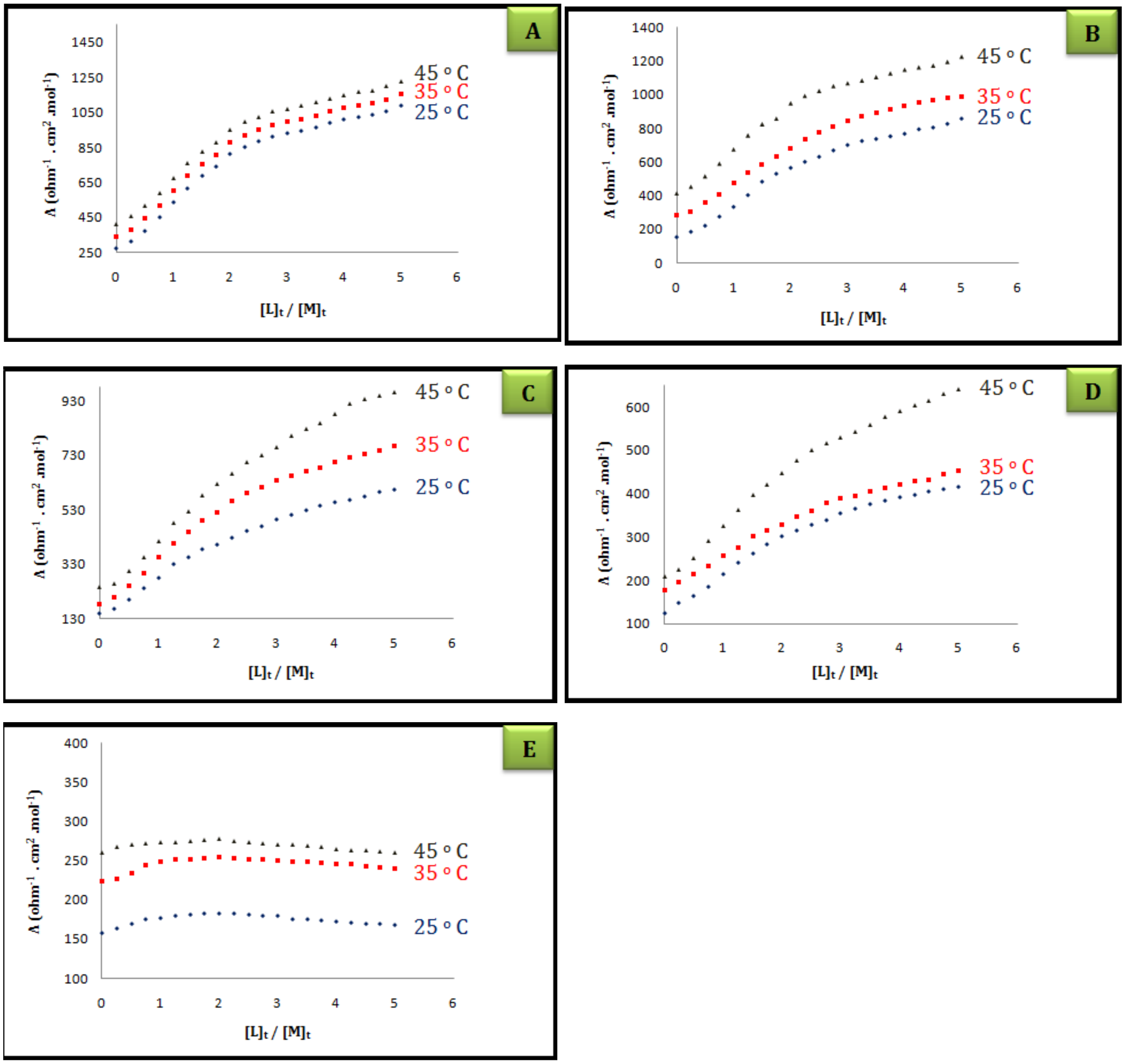


Fig. 1: Molar conductance (ohm^{-1} cm^2 mol^{-1}) *vs.* PDA/[Cd^{2+}] plots in pure H_2O, pure MeOH and H_2O–MeOH binary solvent systems at various temperatures. v/v % of MeOH in the binary solvent systems is: (A) 0% (B) 20 % (C) 40%, (D) 60% and (E) 100%.

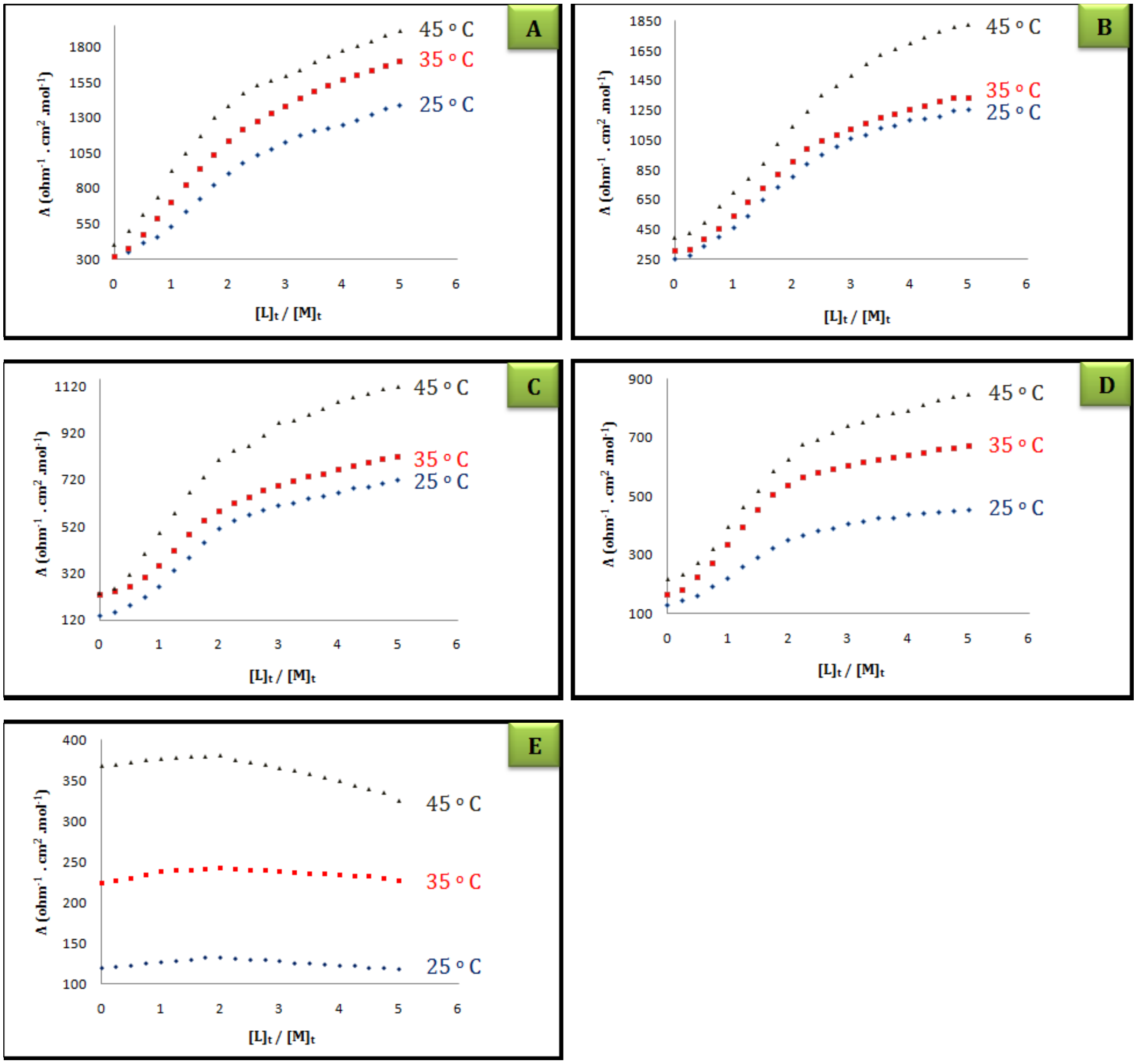


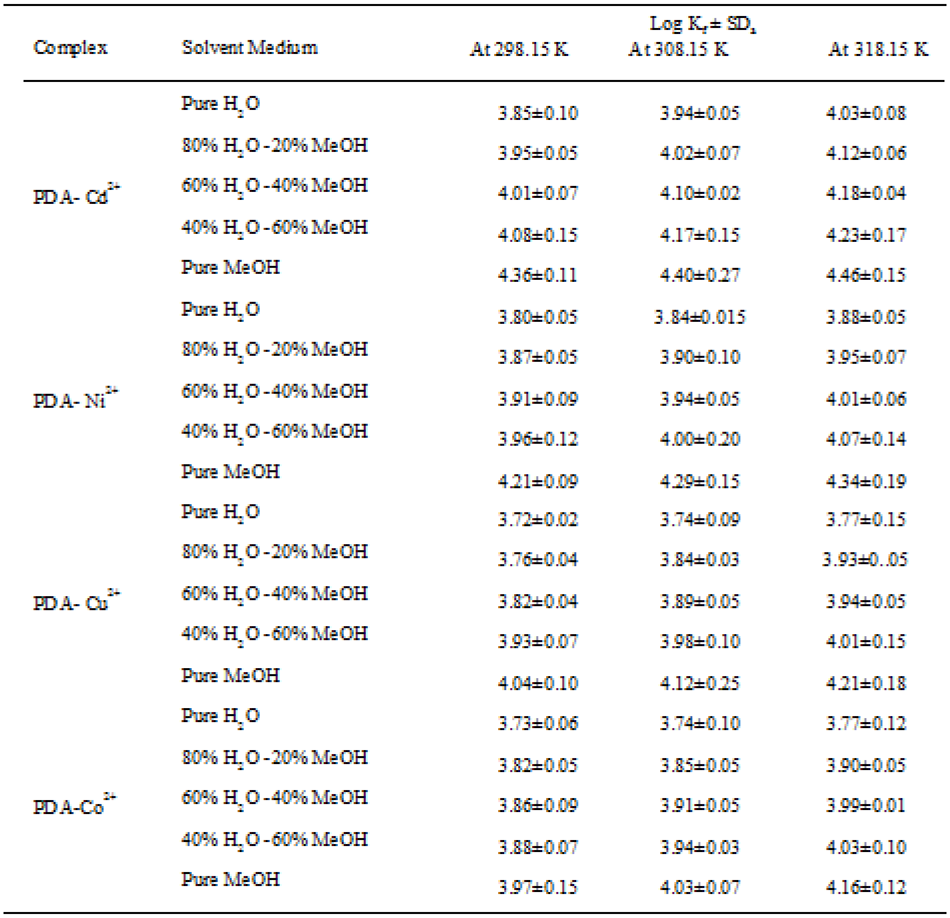
Fig. 2: Molar conductance ($ohm^{-1}\ cm^2\ mol^{-1}$) *vs.* PDA/[Ni^{2+}] plots in pure H_2O, pure MeOH and H_2O–MeOH binary solvent system at various temperatures. v/v % of MeOH in the binary solvent systems is: (A) 0% (B) 20 % (C) 40%, (D) 60% and (E) 100%.

Measurement of conductance and evaluation of formation constant (K_F)

The change in conductance is measured when a metal salt solution to which ligand solution is added, this provide valuable information about metal ligand interactions. Conductance measurement gives information about the affinity of the ligand and the stoichiometry of the complexation reaction. The measurement of conductance is generally carried out by titrating the metal salt solution with ligand solution in a suitable solvent system. The titration may give rise to two different conductometric effects. In the case when ligand titrated to the metal salt solution in which the metal salt is not fully dissociated, the opposite conductometric effect is observed. In the case when the metal salt is completely dissociated in the solvent, the complexation by a ligand leads to a large cationic complex of the metal ion and the ligand. In this case the complex has less mobility in the solution than the uncomplexed metal cation, resulting in the diminished capacity of charge transfer and hence the conductivity of the solution decreased. Since the ligand coordinates to the metal ion, leaving the anion undisturbed, dissociation of the metal salt increases and hence the conductivity of the solution is increased (Bushmann, 1989). In some cases, inspiteof increase in the ligand concentration the change in conductance is negligible; consequently, determination of the formation constant by conductometric method becomes difficult.

There are two factors responsible for a very small change in conductance in spite of an increase in the

Table 1: LogK_f values of PDA-M^{2+} complex in pure H_2O, pure MeOH and H_2O-MeOH binary solvent systems at different temperatures



Complex	Solvent Medium	Log K_f ± SD		
		At 298.15 K	At 308.15 K	At 318.15 K
PDA- Cd^{2+}	Pure H_2O	3.85±0.10	3.94±0.05	4.03±0.08
	80% H_2O -20% MeOH	3.95±0.05	4.02±0.07	4.12±0.06
	60% H_2O -40% MeOH	4.01±0.07	4.10±0.02	4.18±0.04
	40% H_2O -60% MeOH	4.08±0.15	4.17±0.15	4.23±0.17
	Pure MeOH	4.36±0.11	4.40±0.27	4.46±0.15
PDA- Ni^{2+}	Pure H_2O	3.80±0.05	3.84±0.015	3.88±0.05
	80% H_2O -20% MeOH	3.87±0.05	3.90±0.10	3.95±0.07
	60% H_2O -40% MeOH	3.91±0.09	3.94±0.05	4.01±0.06
	40% H_2O -60% MeOH	3.96±0.12	4.00±0.20	4.07±0.14
	Pure MeOH	4.21±0.09	4.29±0.15	4.34±0.19
PDA- Cu^{2+}	Pure H_2O	3.72±0.02	3.74±0.09	3.77±0.15
	80% H_2O -20% MeOH	3.76±0.04	3.84±0.03	3.93±0..05
	60% H_2O -40% MeOH	3.82±0.04	3.89±0.05	3.94±0.05
	40% H_2O -60% MeOH	3.93±0.07	3.98±0.10	4.01±0.15
	Pure MeOH	4.04±0.10	4.12±0.25	4.21±0.18
PDA-Co^{2+}	Pure H_2O	3.73±0.06	3.74±0.10	3.77±0.12
	80% H_2O -20% MeOH	3.82±0.05	3.85±0.05	3.90±0.05
	60% H_2O -40% MeOH	3.86±0.09	3.91±0.05	3.99±0.01
	40% H_2O -60% MeOH	3.88±0.07	3.94±0.03	4.03±0.10
	Pure MeOH	3.97±0.15	4.03±0.07	4.16±0.12

concentration of ligand: (1) when there is no complexation occurs between metal ion and ligand and (2) mobilities of a resulting metal-ligand complex and the corresponding metal ion are both equal at the same concentration. The first factor is responsible in the most of the cases. When the dielectric constant of the solvent is very high and conductance measurements are made at low concentration, the correction for viscosity changes and association between the metal ion i.e. an uncomplexed metal ion, an anion and the ligand metal complex are neglected. The equilibrium can be described for a 1:1 metal-ligand binding is as follows;

$$M^+ + L = ML^+ \quad (1)$$

Where, M^+, L, and ML^+ represent the free solvated cation, the free ligand, and the complex respectively. The thermodynamic equilibrium constant K_f for the association is given by

$$K_f = \frac{[ML^{n+}] \cdot f_{(ML)}{}^{n+}}{[M^{n+}][L] \cdot f_{(M)}{}^{n+} \cdot f_{(L)}} \quad (2)$$

Where, $[ML^+]$, $[M^+]$, [L], and f represent the equilibrium molar concentrations of the complex, the free cation, the free ligand, and the activity coefficients of the species indicated, respectively. Under the dilute conditions used, where the ionic strength is less than 0.001 M, the activity coefficient of the uncharged ligand $f_{(L)}$ can be reasonably assumed to be unity. The use of the Debye-Huckel limiting law of electrolytes leads to the conclusion that $f_{(ML^+)} \approx f_{(M^+)}$; thus, Equation (6) reduces to

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \quad (3)$$

If α is the fraction of total metal cation that is uncomplexed with the ligand, then the following equations result:

$$[M^+] = \alpha\, [M]_t \quad (4)$$

$$[ML^+] = (1 - \alpha)\, [M]_t \quad (5)$$

$$[L] = [L]_t - (1 - \alpha)\, [M]_t \quad (6)$$

Where, $[M]_t$, $[L]_t$, $[M^+]$, $[ML^+]$ and [L] represent the concentration (in molarity) of total cation, total ligand, free uncomplexed cation, and the complex and free solvated ligand respectively.

The dilute conditions used make it possible to neglect ion aggregation and corrections for viscosity changes. The molar conductivities Λ can be calculated by using the following equation.

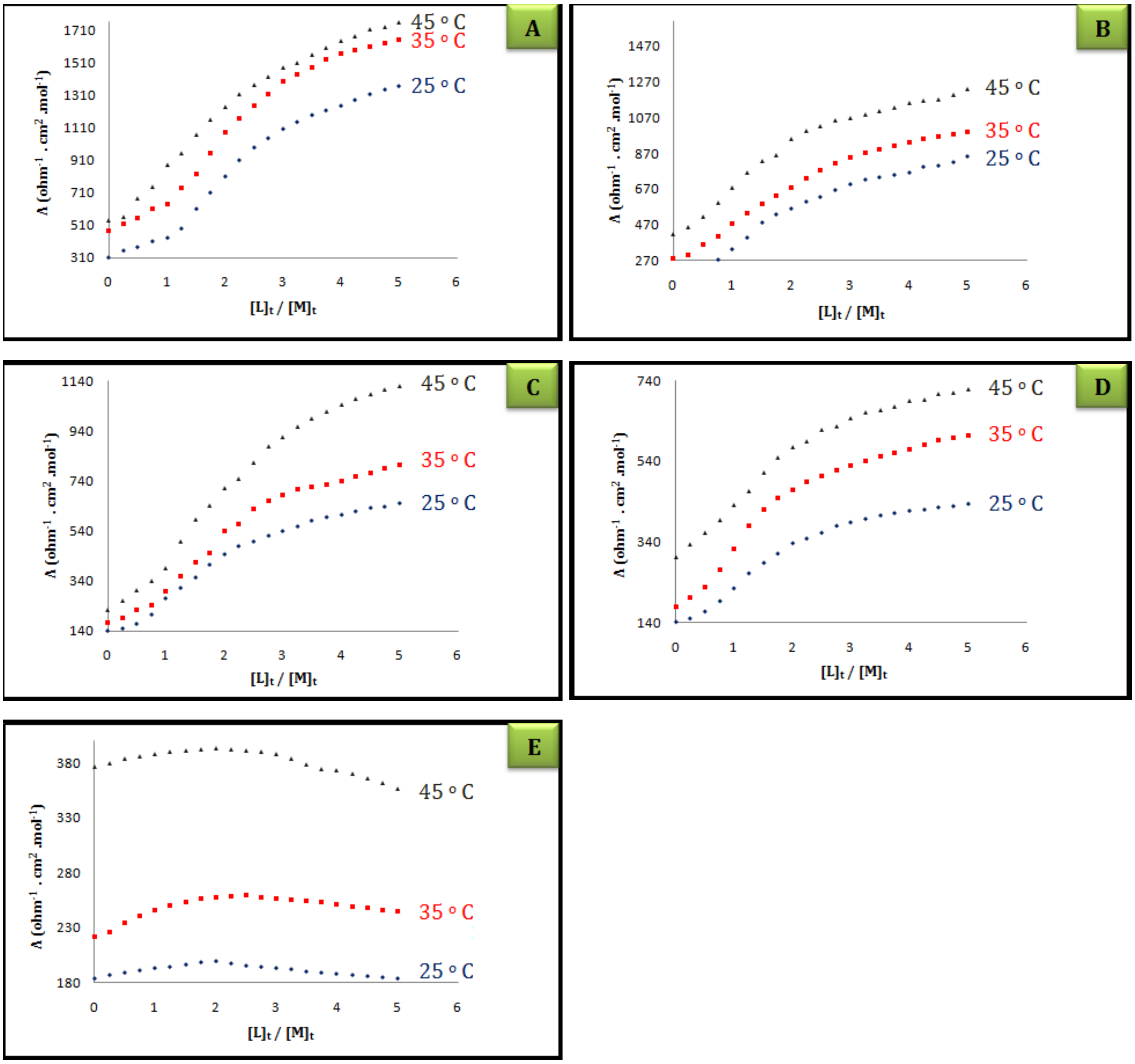


Fig. 3: Molar conductance (ohm^{-1} cm^2 mol^{-1}) *vs.* PDA/Cu^{2+}] plots in pure H_2O, pure MeOH and H_2O–MeOH binary solvent systems at various temperatures. v/v % of MeOH in the binary solvent systems is: (A) 0% (B) 20 % (C) 40%, (D) 60% and (E) 100%.

$$\Lambda = \frac{1000\ \kappa}{[M]_t} \tag{7}$$

Where, κ is the conductivity of the test solution in Siemens.cm^{-1}.

On the other hand, Λ can be related to α by the following equation,

$$\Lambda = \alpha\, \Lambda_{M+} + (1 - \alpha)\, \Lambda_{ML} \tag{8}$$

Where, Λ_{M^+} and Λ_{ML} represent the molar conductivities of the ligand free metal salt solution and the complexed cation solution at the same concentration, respectively.

Rearranging Equation (8) gives an expression for α as;

$$\alpha = \frac{\Lambda - \Lambda_{ML}}{\Lambda_{M^+} - \Lambda_{ML}} \tag{9}$$

Substituting Equations (8) and (9) into Equation (7) gives the following equation:

$$K_{ML^+} = (1 - \alpha)/\alpha\, [L] \tag{10}$$

Substituting the value of *α* from Equation (9) in (10):

$$K_{ML^+} = \frac{\Lambda_{M^+} - \Lambda}{\Lambda - \Lambda_{ML}\, [L]} \tag{11}$$

Further, substitution of Equation (9) into Equation (6) gives (12)

$$[L] = [L]_t - \left(\frac{\Lambda_{M^+} - \Lambda}{\Lambda_{M^+} - \Lambda_{ML}}\right) [M]_t \tag{12}$$

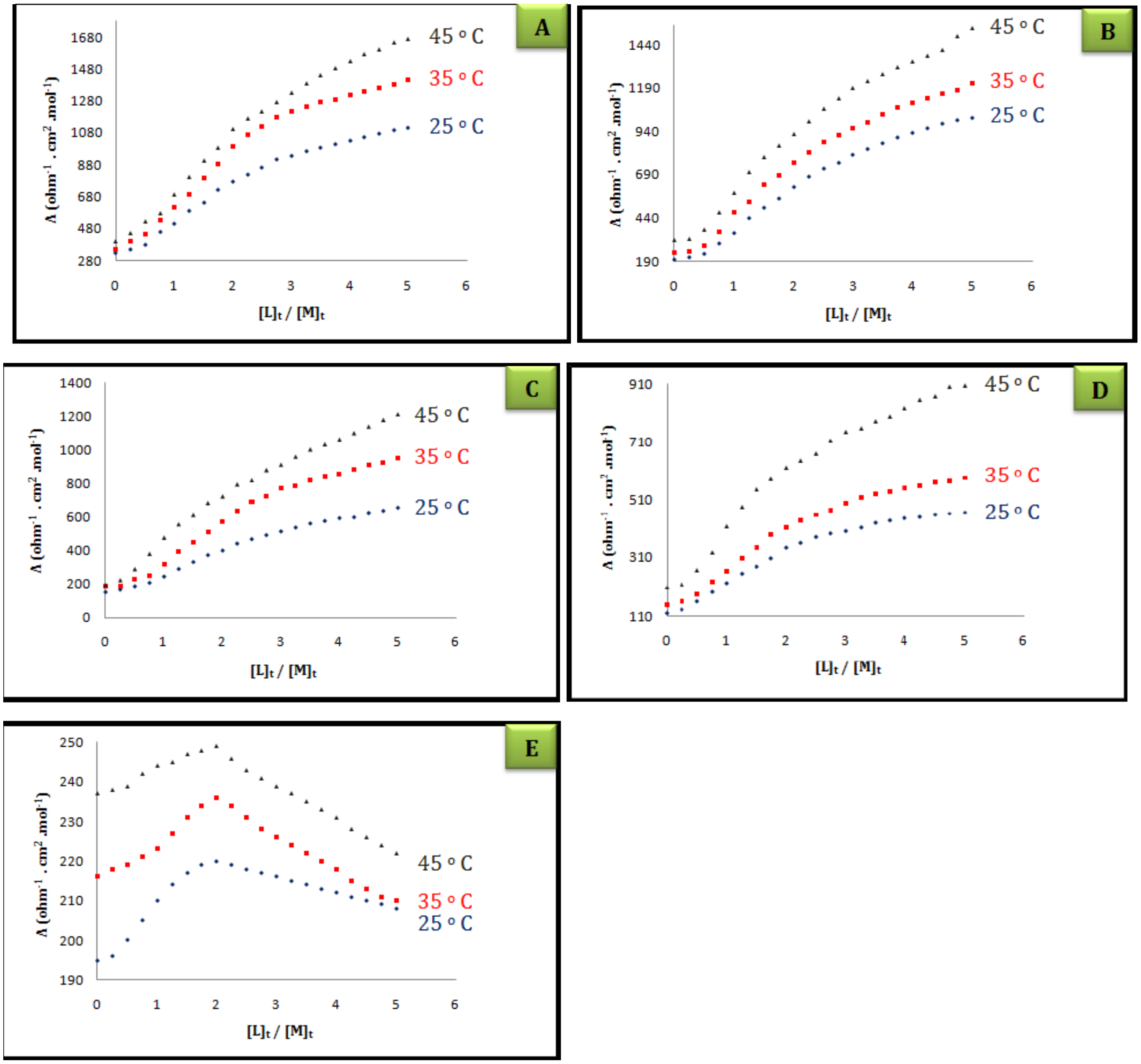


Fig. 4: Molar conductance (ohm^{-1} cm^2 mol^{-1}) *vs.* PDA [Co^{2+}] plots in pure H_2O, pure MeOH and H_2O–MeOH binary solvent systems at various temperatures. v/v % of MeOH in the binary solvent system is: (A) 0% (B) 20 % (C) 40%, (D) 60% and (E) 100%.

Substitution of Equation (12) into Equation (11) gives the expression for K_{ML^+}:

$$K_{ML^+} = \frac{\Lambda_{M^+} - \Lambda}{\Lambda - \Lambda_{ML} \left\{ L]_t - \left(\frac{\Lambda_{M^+} - \Lambda}{\Lambda_{M^+} - \Lambda_{ML}} \right) [M]_t \right\}} \qquad (13)$$

The above equation can be simplified as

$$K_{ML^+} = \frac{a_1\, a_2}{a_3\, a_2 [L]_t \text{ - } a_3\, a_1 [M]_t} \qquad (14)$$

Where, $a_1 = \Lambda_{M^+} - \Lambda$, $a_2 = \Lambda_{M^+} - \Lambda_{ML}$, $a_3 = \Lambda - \Lambda_{ML}$.

Here, Equation (18) can be rearranged to form a quadratic equation in terms of Λ as:

$$a\Lambda^2 + b\Lambda + c = 0 \qquad (15)$$

Where

$a = K_{ML^+} [M]_t$

$b = (K_{ML}+ [L]_t + 1) - [M]_t K_{ML^+} (\Lambda + \Lambda_{ML})$ and

$c = [M]_t K_{ML^+} \Lambda\Lambda_{ML} - a_2 ([L]_t K_{ML^+}\Lambda + \Lambda_{ML})$.

RESULTS AND DISCUSSION

The variation of molar conductance(Λ) versus the ligand$[L]_t$ to cation$[M]_t$ molar ratio ($[L]_t$ / $[M]_t$) for complexation of PDA with Cd^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+} in water, methanol and H_2O-MeOH binary solvents were studied at various temperatures. Typical series of molar conductance values as a function of-

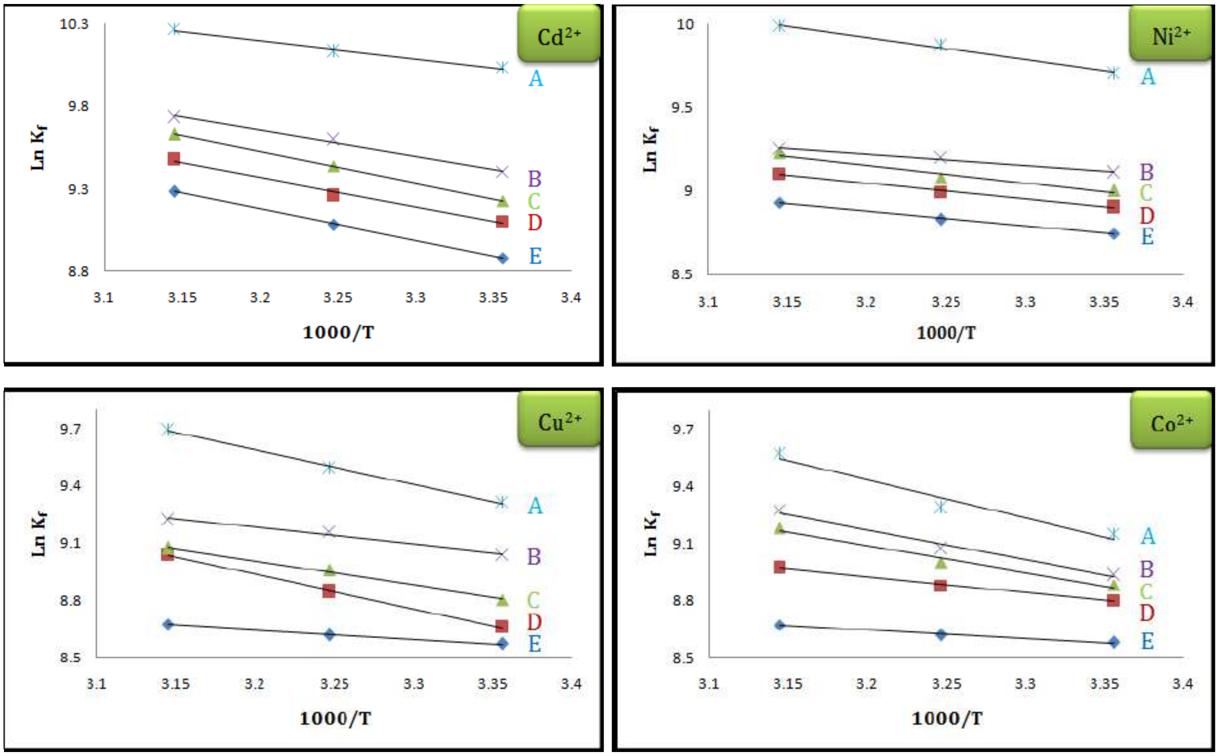


Fig. 5: LnK$_f$ *vs.* 1000/T plots for the complexation of Cd^{2+}, Ni^{2+}, Cu^{2+}and Co^{2+} ions with PDA in binary solvent systems: (A = Pure MeOH, B = 60% MeOH, C = 40% MeOH, D = 20% MeOH, E = Pure H$_2$O)

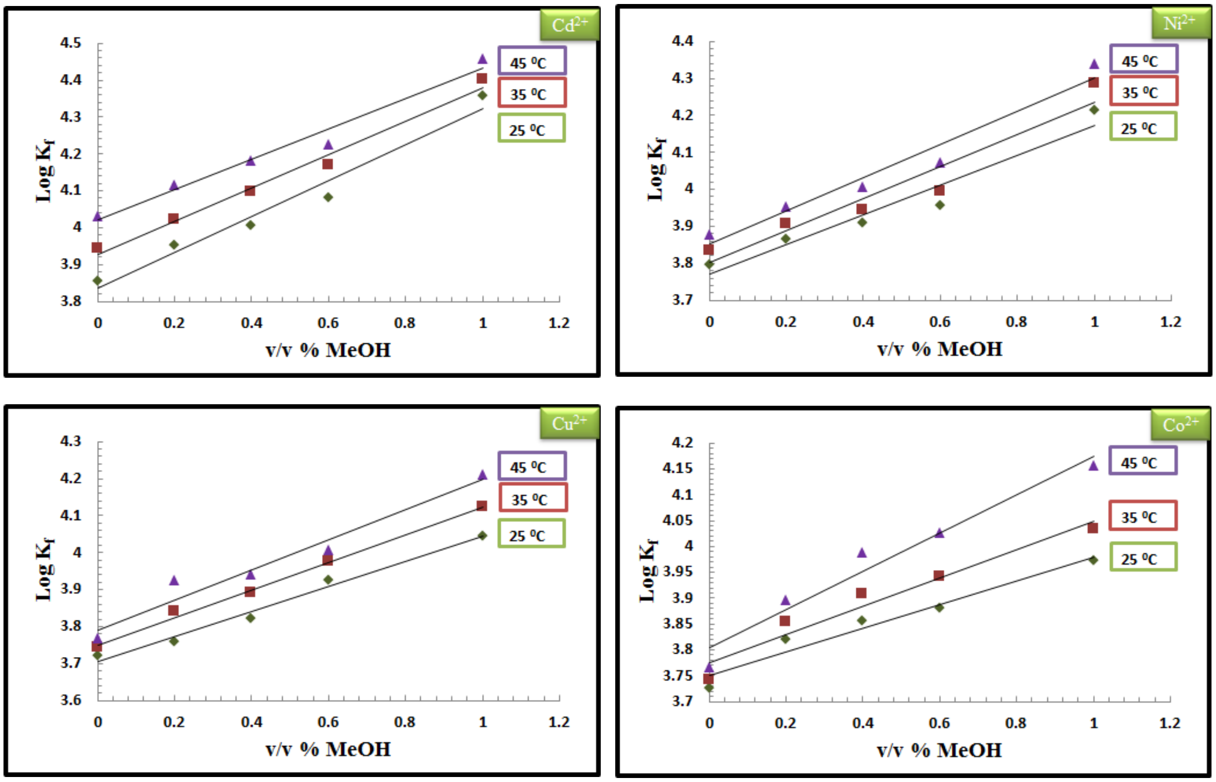


Fig. 6: Changes of the stability constant (logK$_f$) of PDA-Cd^{2+}, PDA-Ni^{2+}, PDA-Cu^{2+} and PDA-Co^{2+} complex with the

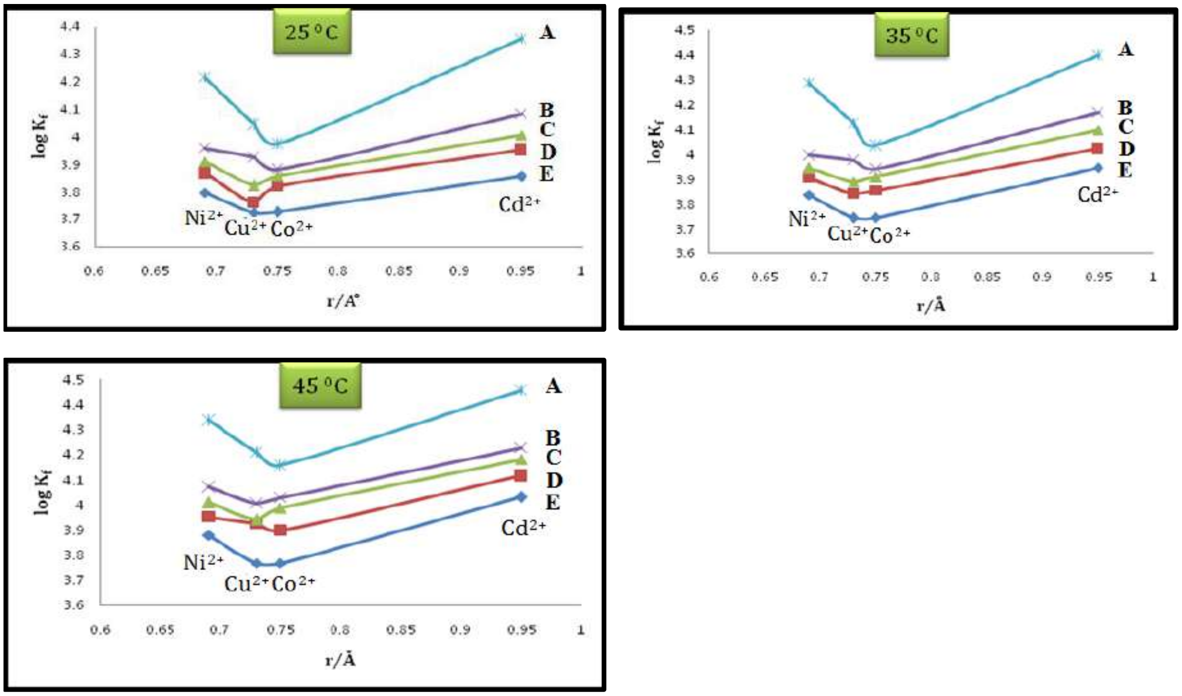


Fig. 7: Variation of logK_f for PDA-Cd^{2+}, PDA-Ni^{2+}, PDA-Cu^{2+} and PDA-Co^{2+} complexes versus cationic radius in H_2O–MeOH binary solvent systems (A = Pure MeOH, B = 60% MeOH, C = 40% MeOH, D = 20% MeOH, E = Pure H_2O) at various temperatures.

$[L]_t/[M]_t$ mole ratios in pure H_2O, pure MeOH and H_2O-MeOH (v/v % MeOH =20/40/60) binary solvent systems are shown in Figure1-4. From figure 1–4, it is observed that, addition of PDA to metal ions (Cd^{2+}, Ni^{2+}, Cu^{2+} and Co^{2+}) in pure H_2O , pure MeOH and H_2O - MeOH (v/v % MeOH = 20/40/60) binary solvent systems at different temperatures resulted in an increase in molar conductance by increasing the ligand concentration.

It is observed that addition of PDA to cadmium ion solution at different temperatures results in an increase in molar conductance. Thus indicates that (Cd^{2+} - PDA) complex is more mobile than free solvated cadmium cations. Similar behavior was observed for Cu^{2+}, Co^{2+} and Ni^{2+} cations in various binary solvent systems.

The formation constant of the PDA at each temperature were calculated from the variation of the molar conductance as a function of $[L]_t/[M]_t$ mole ratios using GENPLOT computer programme. The values of the formation constant [LogK_f] for the PDA-M^{2+} (M^{2+} = Cd^{2+}, Ni^{2+}, $Cu^{2+}$and Co^{2+}) complexes in various binary solvent systems listed in Table-1.

It is evident that the formation constant values increases with increases in temperature. This indicates that the complexation reactions for PDA and metal ions (Cd^{2+}, Ni^{2+}, $Cu^{2+}$and Co^{2+}) in pure H_2O, pure MeOH and H_2O-MeOH binary solvent systems are endothermic.

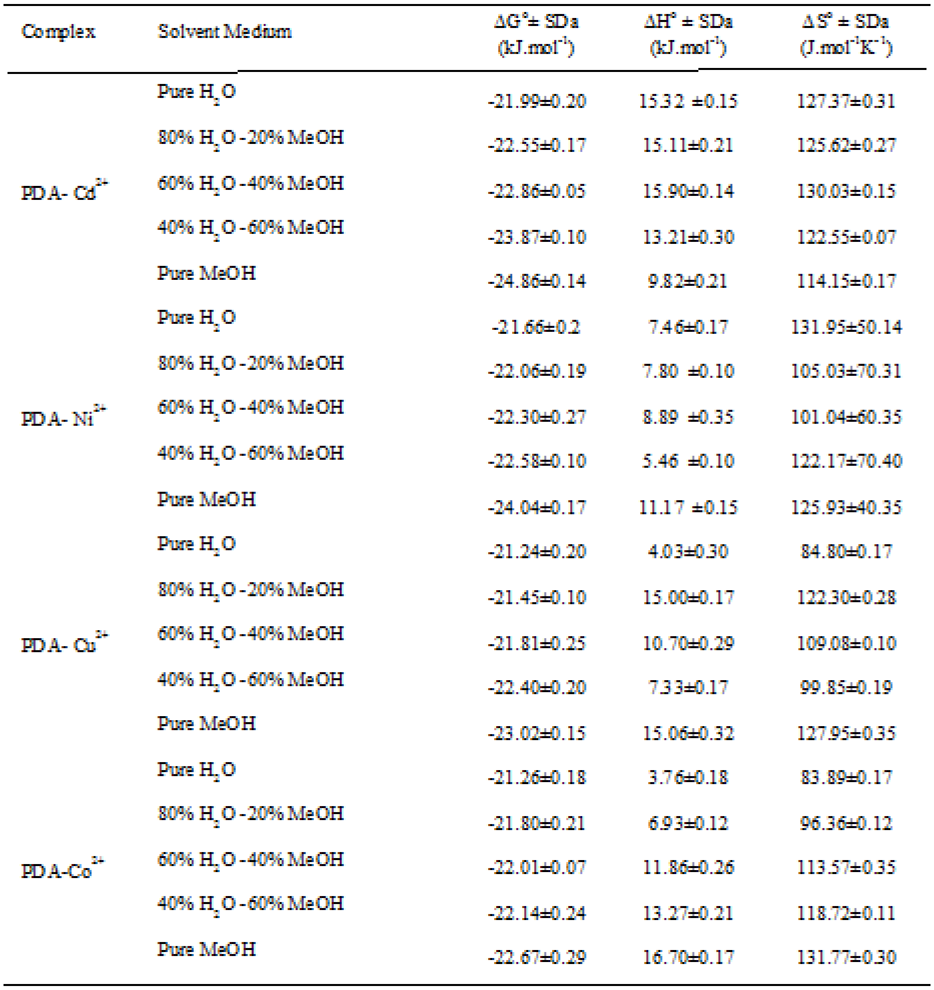
Van't Hoff plot for complexation

For better understanding of the thermodynamics of complexation reactions of Cd^{2+}, Ni^{2+}, $Cu^{2+}$and Co^{2+} ions with PDA, it is useful to investigate the enthalpic and entropic contributions in these reactions. The ΔH^o and ΔS^o of the complexation reactions in different H_2O–MeOH binary solvent systems were evaluated by the temperature dependence of the formation constants using a linear least squares analysis according to the van't Hoff equation (M. Shamsipur et al., 2000).

Comparison of the stability constant values given in the Table-1 provides information that the stability constant increase by increase in the concentration of MeOH with smaller Gutmann donor number (DN: MeOH=19.0) in binary solvent systems. However the formation constant decreases with increases H_2O concentration with relatively equal donor number(Dn: H_2O>19.0) which is in accordance with the reverse order of the solvating ability according to Gutmann donor number. As donor number of MeOH(19.0) and H_2O(≥ 19.0) are approximately equal and if we ignore very small difference in donor number of solvents it seems to dielectric constant(ε) of solvents play an important role in the formation of complexes.

The result which are summarized in Table-2 show that in all the cases, the complexation reactions between PDA and the studied metal cations in H_2O–MeOH binary solvent systems are entropy stabilized and enthalpy destabilized. According to the data in the table indicates that the thermodynamic quantities are very sensitive to the composition and the nature of the mixed solvent and non-

Table 2: Thermodynamic parameters for PDA-M^{2+} complexes in pure H_2O, pure MeOH and H_2O–MeOH binary solvent systems at 298.15 K.



Complex	Solvent Medium	$\Delta G^\circ \pm$ SDa (kJ.mol^{-1})	$\Delta H^\circ \pm$ SDa (kJ.mol^{-1})	$\Delta S^\circ \pm$ SDa (J.mol^{-1}K^{-1})
PDA- Cd^{2+}	Pure H_2O	-21.99±0.20	15.32 ±0.15	127.37±0.31
	80% H_2O -20% MeOH	-22.55±0.17	15.11±0.21	125.62±0.27
	60% H_2O -40% MeOH	-22.86±0.05	15.90±0.14	130.03±0.15
	40% H_2O -60% MeOH	-23.87±0.10	13.21±0.30	122.55±0.07
	Pure MeOH	-24.86±0.14	9.82±0.21	114.15±0.17
PDA- Ni^{2+}	Pure H_2O	-21.66±0.2	7.46±0.17	131.95±50.14
	80% H_2O -20% MeOH	-22.06±0.19	7.80 ±0.10	105.03±70.31
	60% H_2O -40% MeOH	-22.30±0.27	8.89 ±0.35	101.04±60.35
	40% H_2O -60% MeOH	-22.58±0.10	5.46 ±0.10	122.17±70.40
	Pure MeOH	-24.04±0.17	11.17 ±0.15	125.93±40.35
PDA- Cu^{2+}	Pure H_2O	-21.24±0.20	4.03±0.30	84.80±0.17
	80% H_2O -20% MeOH	-21.45±0.10	15.00±0.17	122.30±0.28
	60% H_2O -40% MeOH	-21.81±0.25	10.70±0.29	109.08±0.10
	40% H_2O -60% MeOH	-22.40±0.20	7.33±0.17	99.85±0.19
	Pure MeOH	-23.02±0.15	15.06±0.32	127.95±0.35
PDA-Co^{2+}	Pure H_2O	-21.26±0.18	3.76±0.18	83.89±0.17
	80% H_2O -20% MeOH	-21.80±0.21	6.93±0.12	96.36±0.12
	60% H_2O -40% MeOH	-22.01±0.07	11.86±0.26	113.57±0.35
	40% H_2O -60% MeOH	-22.14±0.24	13.27±0.21	118.72±0.11
	Pure MeOH	-22.67±0.29	16.70±0.17	131.77±0.30

monotonic behavior is observed for the variation of enthalpy and entropy changes versus the composition of the water-methanol binary solvent systems (Hakimi et al., 2008).

Effect of solvent on complexation

From Figure 6, the changes of the stability constant (logK_f) of PDA-Cd^{2+}, PDA-Ni^{2+}, PDA-Cu^{2+} and PDA-Co^{2+} complexes versus the composition of H_2O-MeOH binary solvent systems at various temperatures were observed. It is interesting to note that the formation constants of PDA-M^{2+} (M = Cd, Ni, Cu, Co) complexes increase, with increases concentration of methanol in H_2O–MeOH binary solvent systems.

Effect of ionic size on complexation

The variation of logK_f for formation of PDA-Cd^{2+}, PDA-Ni^{2+}, PDA-Cu^{2+} and PDA-Co^{2+} complexes *vs.* the ionic radius in H_2O–MeOH binary mixtures is shown in Figure 7. It is evident in these figures that the order of selectivity of logK_f of these complexes at 298.15, 308.15 and 318.15 K is PDA-Cd^{2+} > PDA-Ni^{2+} > PDA-Cu^{2+} > PDA-Co^{2+}. Further, it is observed that no particular selectivity order is observed for all compositions of binary solvent systems as well as in pure water as the radius of Cu^{2+} and Co^{2+} is very close to each other.

CONCLUSIONS

According to the results obtained in the present work, complexes formed between the ligand and the metal cation, it indicates the probability of changes in the stabilities and stoichiometry of the complex. In most of the cases PDA formed 1:2 [ML_2] complex. The results obtained in our studies suggest that stability of the complexes of PDA with the metal cations in solutions undergoes the chemical and physical properties of each solvent molecule such as donor number and polarity and with increasing methanol percent when mixed one another and therefore changing their solvating ability towards the ligand, metal cation and the resulting complex .The negative values of ΔG shows the ability of the studied ligand to form stable complexes and process trends to be spontaneously. However, the obtained positive value of ΔH indicates that enthalpy is not driving force for the formation of the complexes. Furthermore, the positive value of ΔS indicates that entropy is a driving force for the complexation reaction.

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