ISSN : 0974-7419 Volume 16 Issue 6

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 16(6) 2016 [251-257]

Spectrophotometric and conductometric determination of propranolol as Mg(II), Pb(II), Fe(II), Mn(II) and Ni(II)-dithiocarbamate complexes

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ABSTRACT

A spectrophotometric method was developed for the determination of the beta adrenergic blocking drug propranolol. The method was based on the formation of Mg(II), Pb(II), Fe(II), Mn(II) and Ni(II)-dithiocarbamate complexes from the secondary amine group of propranolol with carbondisulfide (CS_2) and the acetate salts of the metals in ammonia medium. and The interaction of the Propranolol with $Pb(C_2H_3O_2)_2$, $Mg(CH_3COO)_2$, $Mn(CH_3COO)_2$, $C_{14}H_{27}Fe_3O_{18,}$ $C_4H_6NiO_4$ in methanol has been investigated by conductometric method under equilibrium conditions[1-6]. The stability constants of the complexes were determined using a GENPLOT computer program[7]. The conductance data and Absorbance–mole ratio plots show that in all solvent systems, the stochiometric of the complexes formed between Propranolol and Mg(II), Pb(II), Fe(II), Mn(II) and Ni(II) cations is 1:1 (M:L). The obtained results show that the stability of Mg(II)-Pr, Pb(II)-Pr, Fe(II)- Pr, Mn(II)-Pr and Ni(II)-Pr complexes is sensitive to the mixed solvents composition. The values of thermodynamic parameters (ΔG°, ΔH° and ΔS°) for formation of Mg(II)-Pr, Pb(II)-Pr, Fe(II)-Pr, Mn(II)-Pr and Ni(II)-Pr complexes were obtained from temperature dependence of the stability constant using the van't Hoff plots. The value of $logk_f$ calculated from the absorption spectra measurement for Mg(II)-Pr, Pb(II)-Pr, Fe(II)-Pr, Mn(II)-Pr and Ni(II)-Pr complexes at 25ÚC. The results show that the complexation formation is affected by the nature of solvents © 2016 Trade Science Inc. - INDIA

KEYWORDS

Spectrophotometric;
Conductometric;
Propranolol;
Metal cations.

INTRODUCTIONS

Propranolol ((RS)-1-(1-methylethylamino)-3-(1-naphthyloxy) propan-2-ol) (Pr) is a sympatholytic non-selective beta blocker. Sympatholytics are used to treat hypertension, anxiety and panic. It was the first successful beta blocker developed. The method is based on the reaction of its secondary amino group

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with CS_2 in the presence of ammonia to form the corresponding dithiocarbamate, which forms coloured complexes with of Mg(II), Pb(II), Fe(II), Mn(II) and Ni(II) ions.

EXPERIMENTAL

Spectrophotometric apparatus

A double beam spectrophotometer (Schimadzu 160 A) with a xed slitwidth was used. An MP 220 pH meter was used for the pH measurements.

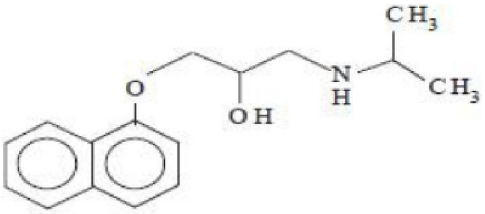

Figure 1 : Propranolol

Conductometric apparatus

The conductance measurements were performed on Methrohm conductivity apparatus, in a water bath thermostated with a constant temperature. The electrolytic conductance was measured using a cell consisting of two platinum electrodes to which an alternating potential was applied. A conductometric cell with a cell constant of 1.061 cm^{-1} was used throughout the study.

Material

The propranolol dihydrate used in this investigation was purchased from Sigma, inc and was used without further purification. The solvent Ethanol,MeOH and PrOH (Merck) and $Pb(C_2H_3O_2)_2$, $Mg(CH_3COO)_2$, $Mn(CH_3COO)_2$, $C_{14}H_{27}Fe_3O_{18}$, $C_4H_6NiO_4$ (Merck) were used with the highest purity.

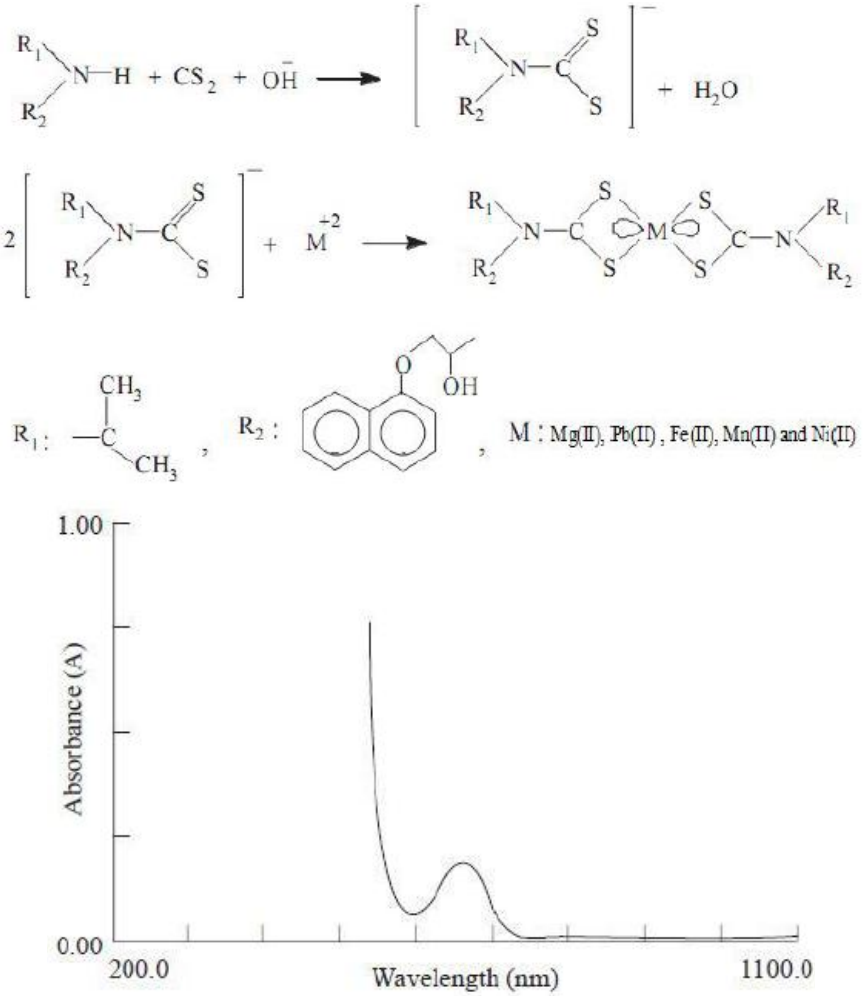

Figure 2 : The calculated absorption spectra of Mg(II)-Pr complex

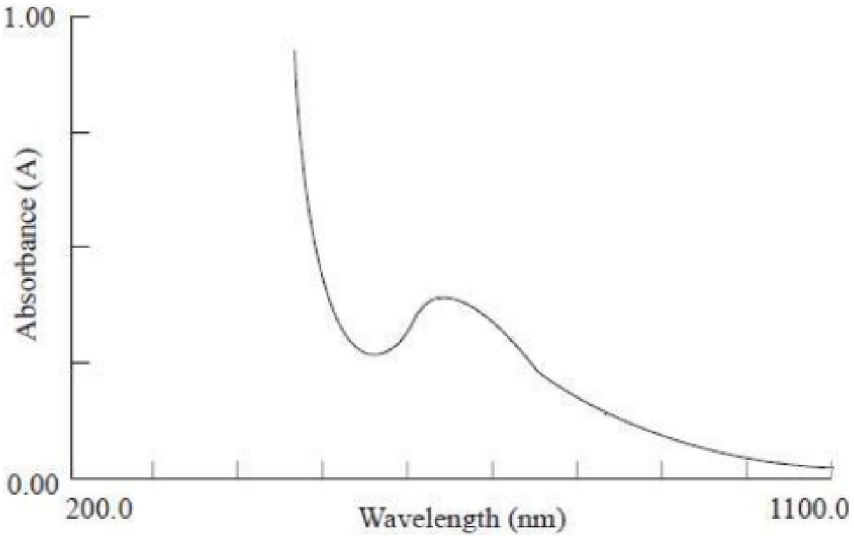

Figure 3 : The calculated absorption spectra Pb(II)- Pr complex

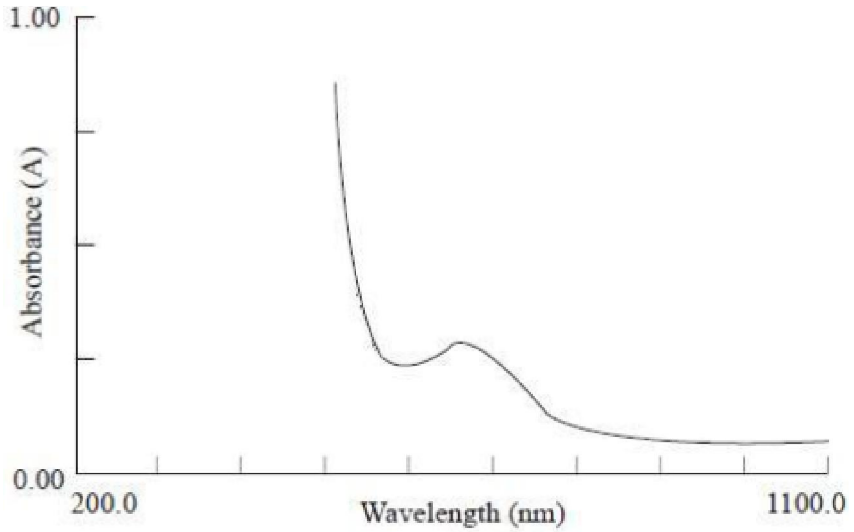

Figure 4 : The calculated absorption spectra of Fe(II)-Pr complex

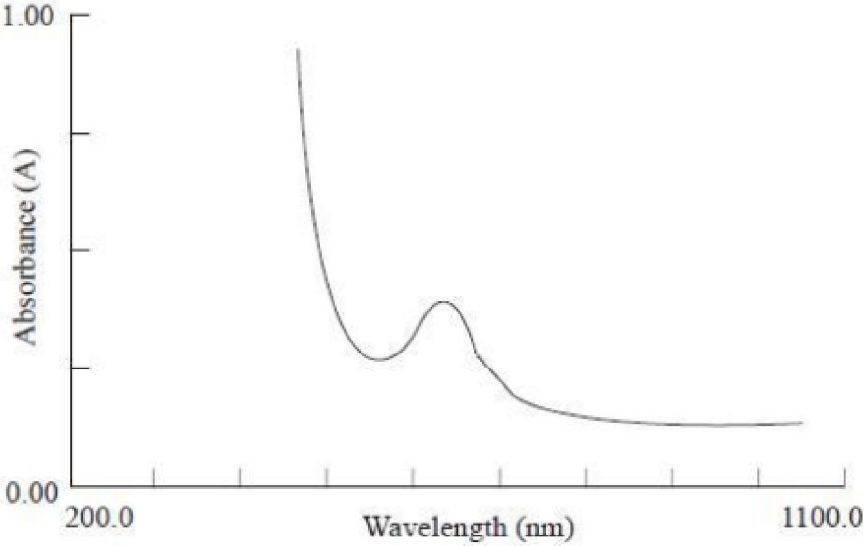

Figure 5 : The calculated absorption spectra of Mn(II)-Pr complex

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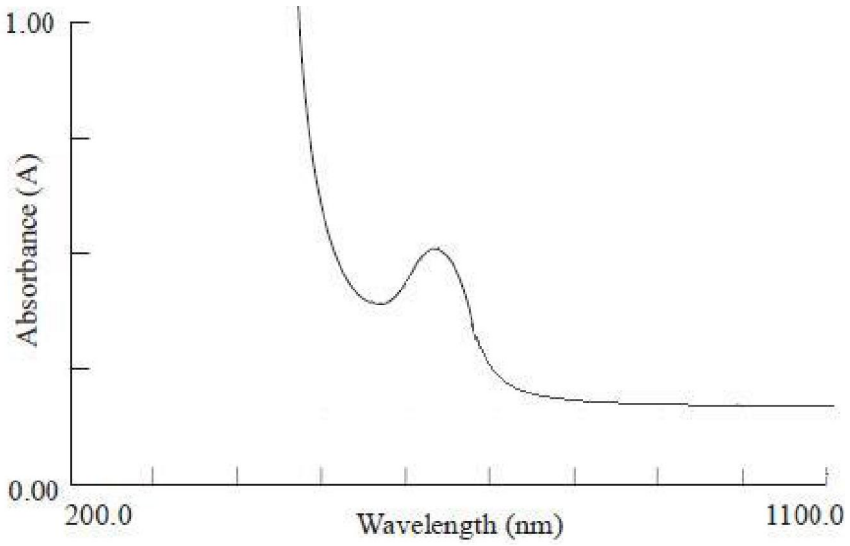

Figure 6 : The calculated absorption spectra of Ni(II)- Pr complex

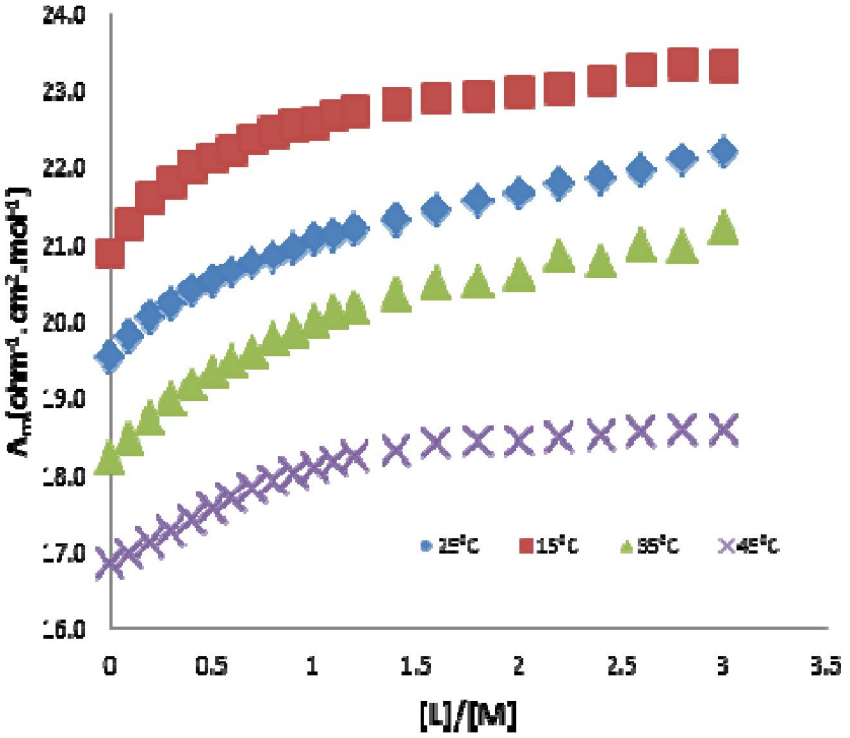

Figure 7 : Molar conductance–mole ratio plots for (Mg(II)- Pr) complex in EtOH at different temperatures

Metal solutions

9×10^{-4} M and 9×10^{-3} M metal solutions were prepared in methanol. Other Solutions 25% ammonia and 5% CS_2 solutions were prepared in ethanol (EtOH).

Stock solution of drug

Prepared by weighing accurately 25 mg of the drug into a 50 mL volumetric ûask, dissolving in absolute ethanol and diluting to volume with EtOH.

RESULT AND DISCUSSION

Spectrophotometric method

0.1-0.5 mg.mL-1 standard solution was transferred to test tubes. 1.0 mL 10% CS_2 solutions, 0.5 mL 25% ammonia solutions were added to each tube. All of the tubes were vortexed for 2 min and 1 mL metal solutions were added to each tube. The absorbance of the resulting solution was measured at

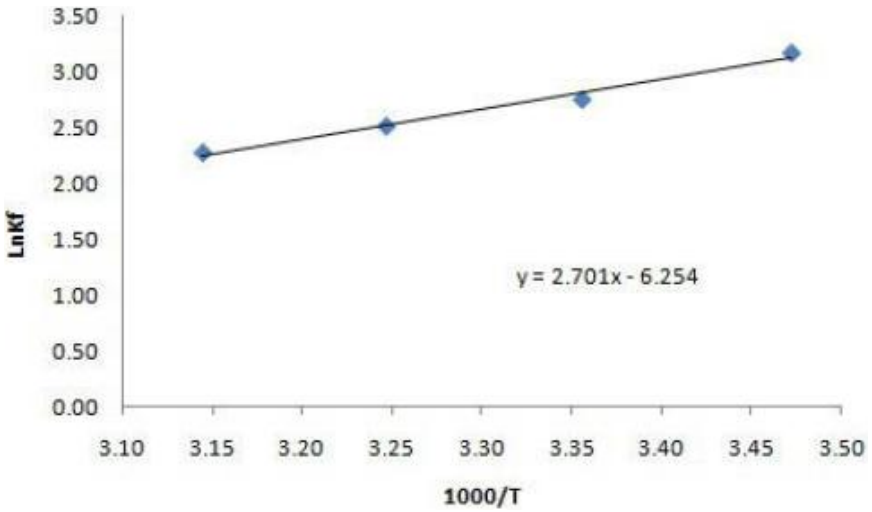

Figure 8 : Van't Hoff plots or (Mg(II)-Pr) complex

TABLE 1 : log K_f values of complex in binary mixtures at different temperatures

complex	Medium	$LogK_f \pm SD^a$			
		15 ?C	25?C	35?C	45?C
	Pure H_2O				
Mg(II)-Pr		2.3±0.12	1.82±0.14	1.53±0.4	1.28±0.06
Pb(II)-Pr		2.71±0.02	2.68±0.05	2.48±0.04	2.38±0.06
Fe(II)-Pr		2.96±0.04	2.71±0.07	2.52±0.09	2.12±0.11
Mn(II)-Pr		2.3±0.09	2.14±0.052	1.97±0.01	1.87±0.07
Ni(II)-Pr		1.98±0.07	1.84±0.05	1.79±0.11	1.7±0.07
	Pure PrOH				
Mg(II)-Pr		2.41±0.7	2.26±0.08	2.14±1.1	2.0±0.09
Pb(II)-Pr		2.85±0.07	2.62±0.15	2.5±0.13	2.29±0.04
Fe(II)-Pr		3.16±0.03	2.75±0.07	2.53±0.05	2.33±0.06
Mn(II)-Pr		2.37±0.12	2.3±0.11	2.1±0.08	1.87±0.09
Ni(II)-Pr		2.1±0.01	1.87±0.03	1.71±0.02	1.58±0.02
	Pure EtOH				
Mg(II)-Pr		2.51±0.78	2.22±0.12	2.19±0.41	2.07±012
Pb(II)-Pr		2.94±0.24	2.85±0.091	2.79±0.4	1.62±0.18
Fe(II)-Pr		3.17±0.1	2.75±0.1	2.51±0.1	2.27±0.5
Mn(II)-Pr		2.47±0.03	2.31±0.02	2.2±0.07	1.94±0.05
Ni(II)-Pr		2.3±0.02	2.14±0.09	2.03±0.04	1.92±0.07
	Pure MeOH				
Mg(II)-Pr		2.76±0.09	2.58±0.04	2.47±0.3	2.34±0.08
Pb(II)-Pr		3.1±0.04	2.85±0.4	2.64±0.03	2.3±0.06
Fe(II)-Pr		3.8±0.09	3.74±0.04	3.61±0.13	3.48±0.11
Mn(II)-Pr		2.74±0.07	2.62±0.06	2.53±0.11	2.39±0.04
Ni(II)-Pr		3.35±0.2	3.37±0.07	3.28±0.07	3.11±0.12

a SD = standard deviation
c With high uncertainty
d The data cannot be fitted in equations

653 nm Mg(II)-Pr,644 Pb(II)-Pr, 671 nm Fe(II)-Pr, 639 nm Mn(II)-Pr and 636 nm Ni(II)-Pr against re-

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TABLE 2 : Thermodynamic parameters

Scomplex	Medium	$-\Delta G_c^\circ \pm SD^a$ (25 °C) (kJ/mol)	$\Delta H_c^\circ \pm SD^a$ (kJ/mol)	ΔS_c° (kJ/mol)
	Pure H_2O			
Mg(II)-Pr		20.74±2.8	-25.2±2.8	69
Pb(II)-Pr		2.5±1.6	-8.9±1.6	8
Fe(II)-Pr		13.6±2.2	-20.4±2.2	45
Mn(II)-Pr		5.3±0.7	-10.6±6.6	17
Ni(II)-Pr		1.99±0.8	-6.6±0.9	6
	Pure PrOH			
Mg(II)-Pr		4.4±0.2	-10.14±0.2	14
Pb(II)-Pr		6.9±0.3	-13.5±1.08	23
Fe(II)-Pr		12.6±2.7	-19.7±2.8	42
Mn(II)-Pr		7.2±0.5	-12.8±1.9	24
Ni(II)-Pr		8.6±1.1	-12.9±1.1	29
	Pure EtOH			
Mg(II)-Pr		4.4±2.7	-10.1±2.7	14
Pb(II)-Pr		6.95±4.7	-14.05±4.8	23
Fe(II)-Pr		15.14±2.3	-22.2±2.3	50
Mn(II)-Pr		6.95±1.5	-12.08±1.5	23
Ni(II)-Pr		3.9±0.6	-9.3±6.4	13
	Pure MeOH			
Mg(II)-Pr		4.47±0.2	-10.1±0.2	14
Pb(II)-Pr		12.6±1.2	-19.1±1.3	42
Fe(II)-Pr		-0.9±0.8	-8.2±0.9	-3
Mn(II)-Pr		1.2±0.7	-7.6±0.7	4
Ni(II)-Pr		-2.08±2.2	-6.07±1.6	-6

SD standard deviation b With high uncertainty

agent blanks. Figure (2-6)

Conductometric method

The experimental procedure to determine the number of complexes formed by conductometric method is as follows: a solution of metal salt (9×10^{-4} M) was placed in a titration cell and the conductance of the solution was measured, then step by step increase in propranolol ligand concentration was performed by a rapid transfer from propranolol solution prepared in the same solvent (9×10^{-3} M) to the titration cell using a microburet and the conductance of the solution in the cell was measured after each transfer at the desired temperatures. The variations of molar conductance versus the ligand to the cation molar ratio for complexation of propranolol and Mg(II), Pb(II), Fe(II), Mn(II) and Ni(II) cations in Ethanol solvent were studiedat different temperatures and is shown in Figure 1. The value of Log k_f calculated from the Mg(II)-Pr, Pb(II)-Pr, Fe(II)-Pr, Mn(II)-Pr and Ni(II)-Pr complexes calculated from the conductivity measurements In non-aqueous solvent at different temperatures[8]. the value of thermodynamic parameters (ΔH°,ΔS°) for formations of Mg(II)-Pr, Pb(II)-Pr, Fe(II)-Pr, Mn(II)-Pr and Ni(II)-Pr complexes were obtained from temperature depended of stability constant.

CONCLUSION

Result from spectrophotometric method

The reaction between propranolol and metal (Scheme) is a simple condensation reaction with CS_2 in the presence of ammonia to form the corresponding dithiocarbamate, which forms a coloured complex with metal (II) ions[9].

In order to obtain the exact amount of reactive for optimal complex colour formation, 0.5, 1.0, 1.5, 2.0 mL of metal solutions were added to reaction media. The addition of 0.5 mL metal did not yield any complex as this was a low concentration for prporanolol-metal dithiocarbamate complex formation. The addition of 1.0, 1.5, 2.0 mL metal solutions gave high absorbance values and the relative standard deviations were close to each other. However, the addition of 1.5-2.0 mL of metal solution series yielded high absorbance blank solutions. Therefore it was decided to work with 1.0 mL metal solutions.

The effect of the percentage of CS_2 in ethanol was studied by changing it from 1 to 10%. The maximum absorbance was obtained with EtOH containing 5% of CS_2.

Effect of pH

Several previous experiences have shown that the complexes formations rates are rather high. In a series of solutions, the pH was changed from 7 to 11, maintaining the metals concentration of 9×10^{-3} M and legend concentration of 25 mgL^{-1}. The maximum absorbances showed maximum values with the minimum change in the pH range from 9.0 to 10.0. Hence pH 9.0 was chosen for further studies.

Result from conductometric method

It is shown that molar conductivity in methanol system increases with the molar ratio increase of the ligand to cation. The slope of molar conductance mole ratio curves change at the point (=1) which indicates the formation of complex 1:1 (ligand: cation) (Figure 7). The investigations of the curves show that raising prporanolol concentration will cause the increase of molar conductivity so the alterative slope will depend on solvent. The relevant curve slope can be a criterion of stable complex qualitatively. Raising temperature increases the curve slope and shows it is an endothermic reaction (Figure 8). In Ethanol with a relatively high Guttman Donor Number (DN= 20), the solvation of the Mg(II), Pb(II), Fe(II), Mn(II) and Ni(II) ions should be strong. Although the solvation of the cations are an important factor in complexation reactions, solvation of the ligand and resulting complex has also been documented to contribute to the overall free energy of complex formation[11,10]. The value of Log K_f calculated form the Mg(II)-Pr, Pb(II)-Pr, Fe(II)-Pr, Mn(II)-Pr and Ni(II)-Pr complexes calculated conductivity measurements in non-aqueous solvents methanol (MeOH), Propanol (PrOH), and etanol (EtOH) at different temperatures (TABLE 1). Enthalpy and entropy of complexation were determinated from temperature dependence of complextion constance (TABLE 2)

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of this research by Department of Chemistry, Mashhad Branch, Islamic Azad University, Mashhad, Islamic Republic of Iran & Department of pharmacutical Chemistry, Faculty of pharmacy, Zabol University of Medical Sciences, Zabol, and Zabol University of Medical Sciences, Zabol, Islamic Republic of Iran

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