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Effect of Temperature on the Formation of Quaternary Complexes of Substituted Imidazoles

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The formation constants have been measured for the mixed ligand complexes MABL, where M = Cu(II), A = 2,2′-bipyridyl or *o*-phenanthroline, B = malonic acid and L = imidazole, 1-methyl-imidazole, 2-methyl-imidazole, 2-ethyl-imidazole at 25°, 35° and 45°C. The thermodynamic parameters have also been evaluated.

INTRODUCTION

In continuation of our earlier studies[1,2] on the coordinating tendencies of substituted imidazoles, we report herein the results of potentiometric studies on the Cu(II)-A-B-L mixed ligand system where A = 2,2′-bipyridyl (bipy), *o*-phenanthroline (phen), B = malonic acid (Malo) L = imidazole (imid), 1-methyl imidazole (1-Me-imid), 2-methyl imidazole (2-Me-imid), 2-ethyl imidazole (2-Et-imid).

EXPERIMENTAL

All the reagents used were of AR grade. Potentiometric measurements were carried out at 25°, 35° and 45°C with 0.1 M (KNO_3) as background electrolyte in aqueous medium using control dynamic pH meter. Calculations were made with the help of BEST Computer Program[3].

RESULTS AND DISCUSSION

A sharp inflection at m = 4 is observed for all these systems indicating the complete formation of ternary complexes (bipy + malonic) or (bipy + phen) or (phen + malo) in simultaneous fashion. A feeble inflection at m = 5 is due to the formation of quaternary complex. The formation constants computed from Computer Program were converted into step-wise constants by the method of Sigel[4] and are presented in Table 1 along with the σ fit (standard deviation) in parentheses. Quaternary complex having (bipyridyl, malonic) or (phen, malonic) as primary ligands are more stable than the quaternary complexes involving (bipy, phen) as primary ligands. This may be due to $d\pi$-$p\pi$ interaction between malo

TABLE 1

LOGARITHMS OF STEPWISE STABILITY CONSTANTS (log K^{CuAB}_{CuABL}) OF QUATERNARY COMPLEXES OF SUBSTITUTED IMIDAZOLES

μ = 0.1 M (KNO_3); aqueous medium

Ligand (L)	(Phen + Bipy)			(Phen + Mal)			(Bipy + Mal)		
	25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C
Imidazole	3.25 (0.00)	3.18 (0.09)	3.12 (0.03)	3.40 (0.01)	3.34 (0.03)	3.29 (0.05)	3.85 (0.00)	3.80 (0.05)	3.73 (0.06)
2-Me-imidazole	3.70 (0.01)	3.64 (0.08)	3.61 (0.07)	3.65 (0.02)	3.58 (0.05)	3.54 (0.06)	3.91 (0.00)	3.86 (0.01)	3.81 (0.05)
2-Et-imidazole	3.69 (0.00)	3.62 (0.05)	3.57 (0.03)	3.75 (0.05)	3.71 (0.05)	3.64 (0.00)	3.89 (0.01)	3.82 (0.02)	3.76 (0.05)
1-Me-imidazole	3.21 (0.04)	3.13 (0.03)	3.06 (0.05)	3.43 (0.06)	3.38 (0.07)	3.31 (0.03)	3.84 (0.04)	3.78 (0.05)	3.70 (0.04)

TABLE 2.

THERMODYNAMIC PARAMETERS ASSOCIATED WITH FORMATION OF MIXED LIGAND COMPLEXES

Ligand (L)	(Phen + Bipy)			(Phen + Mal)			(Bipy + Mal)		
	(−ΔG)	(−ΔH)	(ΔS)	(−ΔG)	(−ΔH)	(ΔS)	(−ΔG)	(−ΔH)	(ΔS)
Imidazole	18.53	12.29	20.26	19.39	10.53	28.76	21.95	8.78	42.75
2-Me-Imidazole	21.10	10.53	34.32	20.81	12.29	27.66	22.29	8.78	43.86
2-Et-Imidazole	21.04	12.29	28.40	21.38	7.02	46.60	22.18	10.54	37.79
1-Me-Imidazole	18.30	14.05	13.79	19.56	8.78	35.00	21.89	14.05	25.45

(−ΔG) = kJ mol^{-1} at 298 K; (−ΔH) = kJ mol^{-1} between 298–308 K; (ΔS) = J deg^{-1} mol^{-1} at 308 K.

and imidazole or substituted imidazoles which are lacking in Cu(II)-phen-bipy-imida/substituted imidazoles system. The calculated values of free energy of formation (ΔG), change in enthalpy (ΔH) and change in entropy (ΔS) are given in Table 2. The reactions are exothermic in nature as suggested by the negative value of enthalpy change. The negative values of free energy change indicate that all the reactions are spontaneous in nature. The formation of mixed ligand species is favoured due to the positive entropy values in all the cases.

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