Complexation studies of N,N′ -ethylene-bis(salicylideneimine)-cation complexation behavior in dioxane-water mixtures by conductometric studies

3 authors, including:

Hamdi Temel
Dicle University
119 PUBLICATIONS   1,516 CITATIONS

SEE PROFILE

H. Ibrahim Ugras
Duzce University
42 PUBLICATIONS   313 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Project   Catalytic Studies View project

Project   discovery of carbonic anhydrase inhibitors View project

Complexation Studies of *N*,*N*'-Ethylene-bis(salicylideneimine)-Cation Complexation Behavior in Dioxane–Water Mixtures by Conductometric Studies[1]

H. Temel*, Ü. Çakir**, and H. İ. Uğras**

* Dicle University, Faculty of Education, Chemistry Department, Diyarbakir, Turkey
** Balikesir University, Faculty of Arts and Sciences, Chemistry Department, Balikesir, Turkey
e-mail: htemel@dicle.edu.tr

Received March 12, 2004

Abstract—The tetradentate-ligand Schiff base derived from salicylaldehyde and 1,2-diaminoethane has been synthesized. The stability constants and thermodynamic values for the complexation between $ZnCl_2$, $Cu(NO_3)_2$, and $AgNO_3$ salts and the ligand in 80% dioxane–water were determined by conductance measurements. The order of the formation constant for complexes of the ligand with Cu(II), Zn(II), and Ag(I) ions was found to be: Ag(I) < Cu(II) < Zn(II). The magnitudes of these ion association constants are related to the nature of the solvation of the cation and the complexed cation.

Schiff bases derived from the reaction of salicylaldehyde with primary amines represent a versatile series of ligands. Schiff bases and the relevant transition-metal complexes are still found to be of great interest in inorganic chemistry, although this subject has been studied extensively [1–7]. Binary dioxane aqueous solvents are frequently employed in broad areas of chemistry. However, the physical properties of these aqueous binaries are only partly understood and 1,4-dioxane–water mixtures constitute a notable example [8, 9]. Conductance measurements of an electrolyte solution in the presence of a convenient ligand provide two valuable pieces of information. The first is the detection of complexation between the ligands and cations constituting the electrolyte. Furthermore, the stability constant of the ligand–cation complex can be determined from the conductance data. The second useful piece of information is related to the transport phenomena of the ligand–electrolyte complex in the solution. Studies recorded in the literature were related to conductometric measurement of some electrolytes in nonaqueous solvents [10–12].

In this study, we reported the stability constants and thermodynamic values for the complexation of Zn(II), Cu(II), and Ag(I) with ligands containing nitrogen and oxygen donor atoms in 80% dioxane–water as the solvent.

[1] The text was submitted by the authors in English.

EXPERIMENTAL

All the chemicals were obtained from Aldrich and used without further purification.

Synthesis. *N*,*N*'-ethylene-bis(salicylideneimine) is a common tetradentate ligand, which binds metal in a fascinating way and was prepared as in the literature [13–22].

Complexation studies and the determination of the stability constants (K_e). Anhydrous $ZnCl_2$, $Cu(NO_3)_2$, and $AgNO_3$ of the highest purity were used. The stability constants were measured by a conductometric method. The water used in the conductometric studies was redistilled from alkaline potassium permanganate. The dioxane was dried over sodium metal. The solutions were prepared at a constant 1 : 1 ratio of the metal salt to the ligand in an 80% dioxane–water mixture. All the solutions were prepared in a dry box and transferred to the dry conductivity cell. The conductances were measured at $25 \pm 0.05°C$. The measuring equipment consisted of a glass vessel (type in gold) with an external jacket. At the same time, the system was connected to a thermostatted water bath ($25 \pm 0.05°C$) and a conductivity cell (Cole Parmer 19050-66) with a conductometer (Suntex Model SC-170). The cell constant was determined as $0.769 \ cm^{-1}$ at 25°C for measuring the conductivity of the aqueous potassium chloride solutions of various concentrations [8]. The $\log K_e$ and $-\Delta G^0$ values for the reaction of the ligand with the cations were determined using the conductometric procedure that was outlined

previously. The results are reported as the average and standard deviation from the average of four to six independent experimental determinations.

RESULTS AND DISCUSSION

When the Schiff base ligand (L) forms a 1 : 1 complex with the metal ion (M^{m+}), the equilibrium equation may be written as in Eq. (1):

$$M^{m+} + L \rightleftharpoons ML^{m+}, \quad (1)$$
$$\alpha[M]_t \quad [L]_t - (1-\alpha)[M]_t \quad (1-\alpha)[M]_t$$
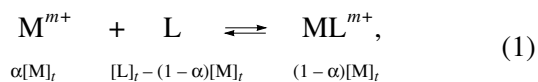
where M^{m+}, L, $[M]_t$, $[L]_t$, and α are the cation, the ligand, the total concentration of the metal salt, the Schiff base ligand, and the fraction of free cations, respectively. Thus, the complex formation constant (K_{ML}) is defined by

$$K_{ML} = [ML^{m+}]/[M^{m+}][L] = 1 - \alpha/\alpha[L]. \quad (2)$$

The apparent conductivity (κ_{app}) of the metal nitrate (MA_m) solution in the presence of ligand L is given by

$$\kappa_{app} = \kappa_{MAm} + \kappa_{MLAm}, \quad (3)$$

where A denotes an anion, and κ_{MAm} and κ_{MLAm} refer to the conductivities of the electrolyte and the ligand–electrolyte complex, respectively. The molar conductivities are

$$\Lambda_{MAm} = \kappa_{MAm}/[M^{m+}] = \kappa_{MAm}/\alpha[M]_t, \quad (4)$$

$$\Lambda_{MLAm} = \kappa_{MLAm}/[ML^{m+}] = \kappa_{MLAm}/(1-\alpha)[M]_t, \quad (5)$$

where Λ_{MAm} and Λ_{MLAm} designate the molar conductivities of the electrolyte and the ligand–electrolyte complex, respectively. The apparent molar conductivity of the metal salt is defined as

$$\Lambda_{app} = \kappa_{app}/[M]_t = \alpha\Lambda_{MAm} + (1-\alpha)\Lambda_{MLAm}. \quad (6)$$

As a consequence of Eq. (6), Eq. (2) may be transformed into

$$K_e = (\Lambda_{MAm} - \Lambda_{app})/(\Lambda_{app} - \Lambda_{MLAm})[L],$$

where

$$[L] = [L]_t - [M]_t = (\Lambda_{MAm} - \Lambda_{app})/(\Lambda_{app} - \Lambda_{MLAm}).$$

The differences in the complexing ability using the solvent (80% dioxane–water) between the Schiff base and metal ion can be determined based on the thermodynamic equation shown below:

$$\Delta G_c^0 = -2.303 RT \log K_e,$$

where ΔG_c^0 is the Gibbs free energy of complexation in these solvents. All the experimental studies were performed using a 1 : 1 ratio of the metal ion and the Schiff base ligand. The results show that the ligand forms a complex with the metal ion and that the complex is less mobile than the corresponding free metal ion. Our results suggest that a number of cation–ligand complexes undergo ion association and that this phenomenon is highly dependent on the nature of both the ion–solvent and ion–ligand interactions. It was observed that, for the metal complexes with the ligand in the dioxane–water mixture, the K_e values were dependent on the chemical characteristics of the ligand and solvent, indicating that the electrostatic ion–dipole forces, which depend on the macroscopic dielectric constant of the solvent and on the dipole moment of the ligands, are the strongest factors in the complexation processes in such a system. The formation constant of each complex was determined from the average value of four–six measurements; the $\log K_e$ of $Zn(L)^{2+}$, $Cu(L)^{2+}$, and $Ag(L)^+$ are 3.83 ± 0.07, 2.70 ± 0.02, and 2.32 ± 0.11, respectively. We observed that the ligand forms the most stable complex with Zn(II) ion in the dioxane–water binary system.

The stability constants ($\log K_e$) increase in 80% dioxane–water in the order Ag(I) < Cu(II) < Zn(II). We found that the stabilities of the complex ions are affected not only by the relative sizes of the cationic radii but also by the physical properties of the solvent. This was the case with $Zn(II)–LH_2$, and an essentially similar interpretation can be applied to the present chelating effect: a favorable orientation of the ligand before chelation due to the steric requirements and,

The $\log K_e$ and $-\Delta G°$ (kcal/mol) values for the interaction of the ligand with $ZnCl_2$, $Cu(NO_3)_2$, and $AgNO_3$ in an 80% dioxan–water mixture at 25°C by to the conductometric study

Ligand	Value	Zn^{2+}	Cu^{+2}	Ag^+
L	$\log K_e$	3.83 ± 0.07	2.70 ± 0.02	2.32 ± 0.11
	$-\Delta G°$	5221.90 ± 0.03	3681.23 ± 0.09	3163.14 ± 0.31

probably, decreased complex solvation in the outer sphere [23–26].

The stability constants and thermodynamic parameters for the complex formation between the ligand containing nitrogen and oxygen donor atoms and the Zn(II), Cu(II), and Ag(I) ions in the dioxane–water mixture are summarized in the table. No results from the literature are available for comparison. As indicated by the values of the reaction-free enthalpy, the simultaneous interactions of Zn(II) with nitrogen and oxygen donor atoms are responsible for the complex formation. Thus, the complex formation is favored by enthalpy contributions.

REFERENCES

1. H. Temel and H. Hosgoren, Trans. Met. Chem. **27** (6) (2002).
2. H. Temel, S. Ilhan, M. Sekerçi, and R. Ziyadanogullari, Spectrosc. Letters **35** (2), 219 (2002).
3. H. Temel and M. Sekerçi, Synth. React. Inorg. Met.-Org. Chem. **31** (5), 849 (2001).
4. H. Temel, *MBCAC: The 3rd Mediterranean Basin Conference on Analytical Chemistry, Antalya (Turkey), 2000* (Antalya (Turkey), 2000).
5. H. Temel, Ü. Çakir, B. Otludil, and I. H. Uğras, Synth. React. Inorg. Met.-Org. Chem **31** (8), 1323 (2001).
6. H. Temel, Ü. Çakir, and H. I. Uğras, Russ. J. Inorg. Chem. **46** (12), 2022 (2001).
7. H. Temel, S. Ilhan, and M. Sekerçi, Synth. React. Inorg. Met.-Org. Chem. **32** (9), 1625 (2002).
8. B. Cicek, Ü. Çakir, and C. Erk, Polym. Adv. Technol. **9**, 831 (1998).
9. G. Topal, H. Temel, Ü. Çakir, *et al.*, Synth. Commun. **32** (11), 1721 (2002).
10. Ü. Çakir, H. I. Uğras, H. Temel, and G. Topal, J. Appl. Polym. Sci. **91** (4), 2497 (2003).
11. M. D. Monica, A. Ceglie, and A. Agostiano, Electrochim. Acta **29**, 161 (1984).
12. H. P. Hopkins and A. B. Norman, J. Phys. Chem. **84**, 309 (1980).
13. H. Temel, T. Taskn, and M. Sekerçi, Russ. J. Inorg. Chem. **49** (3) (2004).
14. H. Holm, G. W. Everett, and Jr. A. Chakravorty, Prog. Inorg. Chem. **7**, 183 (1966).
15. D. A. Atwood, J. Benson, J. A. Jegier, *et al.*, Main Group Met. Chem. **1**, 99 (1995).
16. K. M. Carroll, J. Schwartz, and D. M. Ho, Inorg. Chem. **33**, 2707 (1994).
17. A. A. Isse, A. Gennaro, and E. Vianello, Electrochim. Acta **42** (13–14), 2065 (1997).
18. E. Spodine, S. Zolezzi, V. Calvo, and A. Decinti, Tetrahedron: Asymmetry **11** (16), 2277 (2000).
19. Y. Z. Shen, Y. Pan, L. Y. Wang, *et al.*, J. Organomet. Chem. **590** (2), 242 (1999).
20. A. Syamal, M. M. Singh, and D. Kumar, React. and Functional Polymers **39** (1), 27 (1999).
21. V. Subramanian, C. Shankaranarayanan, B. U. Nair, *et al.*, Chem. Phys. Lett. **274** (1–3), 275 (1997).
22. M. S. Singh and P. Narayan, Synth. React. Inorg., Met-Org. Chem. **30** (6), 1007 (2000).
23. J. E. Lind, J. J. Zwolnikand, and R. M. Fuoss, J. Am. Chem. Soc. **81**, 1557 (1959).
24. Y. Takeda, *Cation Binding by Macrocycles*, Ed. by Y. Inoue and G. W. Gokel (Marcel Dekker, New York, 1991).
25. M. Kodama and E. J. Kimura, Chem. Soc., Chem. Commun., 326 (1975).
26. M. Kodama and E. J. Kimura, Chem. Soc., Dalton Trans., 116 (1976).