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Studies on Reversed Micelles: Interpretation of Conductivity and Solubility Data of Copper Oleate in Organic Solvents

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The solution behaviour of copper oleate in cyclohexane, cyclohexanol and aniline has been interpreted on the basis of observations made on conductivity and solubility of the solutions. The values of critical micelle concentration, dissociation constant (K_d), Kraft temperature (T_K), heat of solution (Q), standard free energy of micellization (ΔG_m^0) and variation of entropy (ΔS) in the process of micellization in all the solvents has been reported. Smaller molecular aggregates are proposed to exist in premicellar solutions.

Key Words: Conductivity, Solubility, Critical micelle concentration, Copper oleate, Cyclo-hexane, Aniline, Cyclohexanol, Kraft Temperature.

INTRODUCTION

The micellar behaviour of some of the important colloidal systems in aqueous medium has been reported by different workers from time to time. However, some of the most important industrial colloidal systems are non aqueous in nature. Asphalts, lubricating greases, coal tar, rubber, paints, resins, plastics and many more petroleum products constitute non-ionic colloidal systems. Comparatively less study has been carried out on the non aqueous colloidal systems. Metallic soaps are becoming increasingly important in technological uses as well as in academic studies. The heavy metal soaps are not water soluble and are used as dryers for unsaturated fatty oils in paints, varnishes and printing inks[1]. The commercially available metallic soaps are derived from stearic, palmitic acid, lauric acid, oleic acid, linoleic acid and naphthenic acid[2-4]. The common metals used are Al, Cd, Li, Mn, Pb, Zn, Co, Ni, Mg, and Cu. The Cu and Cd oleates have been used for hydrogenation of unsaturated fatty acids. The Cu and Cd oleates have been used for hydrogenation of unsaturated fatty acids into unsaturated fatty alcohols[5,6].

A soap may sometimes be a costly material and its quantitative use may be regulated by knowing the value of its critical micelle concentration (CMC) along with other physico-chemical properties. Every worker carrying out studies on soap solutions essentially determines critical micelle concentration values. The critical micelle concentration happens to be the gateway to other important conclusions that may be drawn from the physico-chemical data of a soap solution. The micellar solutions have been found to play important role in catalysis[7,8].

A proper selection of a surfactant can increase the rate of a reaction 5 to 100 fold as compared to that in absence of the surfactant. This is observed not only in aqueous phase but reverse micelles are also reported to control kinetics of reactions[9-11]. At present reverse micelles have opened a new and important dimension of studies. These include synthesis of nano rods and nano particles[12], modeling of various biochemical reactions[13], extraction and purification of bio-molecules[14-16] and novel drug delivery systems[17], *etc*.

One of the greatest differences between heavy metal soaps and alkali soaps is solubility and swelling of the soaps in organic solvents. Alkali soaps are soluble in water or alcohols and generally insoluble in organic solvents, whereas, the heavy metal soaps of higher fatty acids containing more than six carbon atoms are rather soluble in organic solvents and insoluble in water. The solubility of metal soaps of saturated fatty acids in organic solvents has been studied by many researchers. However, not much work is reported on the solubility of heavy metal soaps of unsaturated long chain fatty acids. In present investigations, solubility and conductivity data of copper oleate solutions in cyclohexane, cyclohaxanol and aniline have been reported. The complex behaviour of reverse micelles of copper oleates in the solvents has been interpreted in the light of simple measurements on solubility and conductivity.

EXPERIMENTAL

The organic solvents namely cyclohexane, cyclohexanol and aniline were obtained from BDH, England and further

purified by repeated distillation. The purity of a solvent was checked by determing its boiling point. All other chemicals like oleic acid, perchloric acid, sulphuric acid, sodium hydroxide, copper sulphate and ethylenediamine tetra acetic acid (EDTA) were of AnalaR grade BDH or E. Merk reagents and used as such.

Metal soap: Copper oleate was prepared by direct metathesis of the corresponding sodium soap with slight excess than the required amount, of copper sulphate at 50-55 ºC[4]. The prepared sample was subjected to elemental analysis and assigned the molecular formula $(C_{17}H_{33}COO)_2Cu$[18].

Solubility: Since the boiling points of cyclohaxanol and aniline are relatively higher, the method of weighing the residue after evaporating the saturated solution was not preferred. Instead, copper contents of a saturated solution were estimated volumetrically by EDTA titration using copper pan indicator.

Conductivity: The conductivity of soap solutions was measured on a Philips conductivity meter model PR-9500.

RESULTS AND DISCUSSION

The variation of specific conductance (K) of copper oleate solutions with soap concentration (C) in different non aqueous solvents namely cyclohexane, cyclohexanol and aniline is shown in Fig. 1.
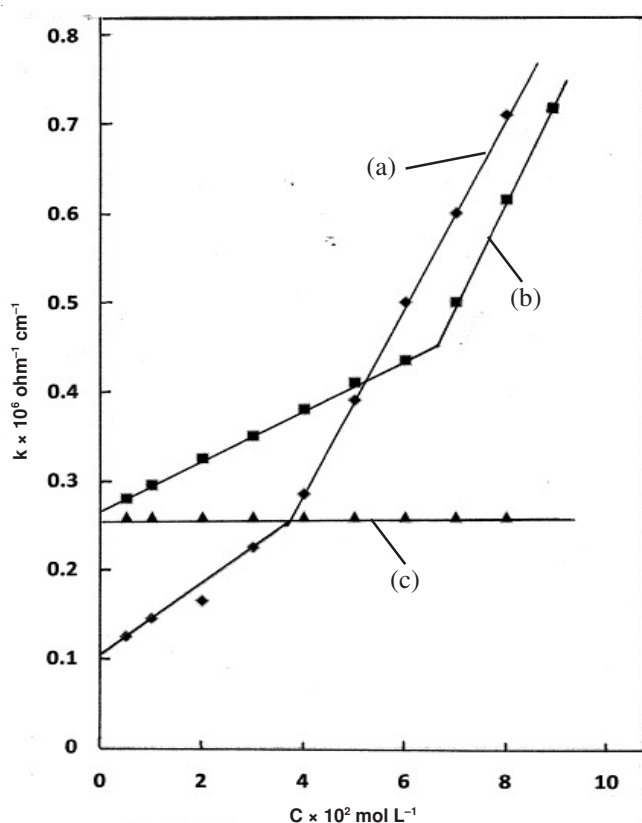

Fig. 1.   Variation of specific conductance (K) of copper oleate solutions with soap concentration (C) in different non aqueous solvents: (a) cycloheanol; (b) aniline; (c) cyclohexane; Temp. = 31 ºC

An increase in specific conductance with increase in soap concentration is observed in cyclohexanol and aniline. This may be due to dissociation of copper oleate into simple metal cations Cu^{2+} and fatty acid anions $(C_{17}H_{33}COO)^{2-}$. These plots

of K *versus* C in cyclohexanol and aniline are characterized by an intersection of two straight lines at a definite soap concentration. This nature of plots is indicative of formation of micellar aggregates in both these solvents. The values of critical micelle concentration in cyclohexanol and aniline at 31 ºC are observed at 3.7×10^{-2} mol L^{-1} and 6.5×10^{-2} mol L^{-1} respectively. However, such a behaviour is not observed in cyclohexane. This observation may be attributed to the polarity of the solvents. Cyclohexane being non-polar, does not facilitate ionization of copper oleate in it and consequently the specific conductivity of the soap solution does not vary with the soap concentration.

Considering dipole moment, cyclohexanol is more polar than aniline and ionization of copper oleate is likely to be more in former than in the later. But Fig. 1 shows that in premicellar concentration range, the specific conductivity of a soap solution in cyclohexanol is lower than that in aniline. This is contrary to what would be expected on the basis of polarity of the two solvents. This observation is interesting and require explanation. It is propposed that in comparison to aqueous solutions, the hydrophobic interactions of the soap in non-aqueous media are much weaker. In non aqueous medium, the polar group of the diphilic soap molecule becomes liophobic. This causes formation of aggregates in which core consists of polar groups while the hydrocarbon chains of the molecules are oriented towards the solvents. Such aggregates are called reversed micelles. The forces of dipole-dipole interaction between the ion pairs as well as possible hydrogen bonds seem responsible for formation of a polar core. This association of the soap molecules in non aqueous medium has a number of features distinguishing it from association in aqueous medium. Among them may be the presence of aggregates at premicellar concentrations and the continuity of the aggregation process up to critical micelle concentration. It is therefore, proposed that molecular aggregates bigger in size in more polar solvent (cyclohexanol) than those present in less polar solvent (aniline) exist in pre-micellar range. The bigger aggregates would, obviously, have less ionic mobility as well as less number of ionic species present per unit volume of the solution, resulting into a lower specific conductivity in cyclohaxanol than that in aniline at all concentrations below critical micelle concentration. Further, since bigger molecular aggregates exist in cyclohexanol, micellar structures can form easily. Consequently, critical micelle concentration of the soap in cyclohexanol is lower than that in aniline. In post-critical micelle concentration region, the plots between K and C are almost parallel in both the solvents. This may indicate that the behaviour of micellar solutions is identical in both the solvents and that aniline contains bigger micellar clusters.

The molar conductance (λ_c) of copper oleate solutions decreases with increasing soap concentration in cyclohexanol and aniline in premicellar region (Fig. 2).

The decrease in λ_c is attributed to the combined effects of ionic atmosphere, solvation of ions and decrease of ionic mobility with growth in aggregates size until micellar aggregates are finally formed. Since λ_c of the soap solutions is not found to vary linearly with $\sqrt{c}$, the Debye- Huckel-Onsager equation[19] is not applicable. However, Fig. 2 indicates that copper oleate behaves as a weak electrolyte in the solution. Ioniza-

tion of copper oleate may, therefore, be explained by Ostwald's dilution law. The ionization equilibrium may be given as:

$$(C_{17}H_{33}COO)_2Cu \rightleftharpoons 2C_{17}H_{33}COO^- + Cu^{2+} \quad (1)$$
$$C(1-\alpha) \qquad\qquad 2C\alpha \qquad\qquad C\alpha$$
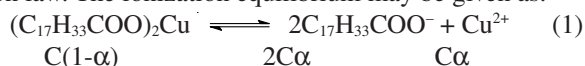
where, α represents degree of dissociation. If K_d is dissociation constant of equilibrium (1),

$$K_d = \frac{[C_{17}H_{33}COO^-]^2[Cu^{2+}]}{[(C_{17}H_{33}COO)_2Cu]} = \frac{[2C\alpha]^2[C\alpha]}{[C(1-\alpha)]} = \frac{4C^2\alpha^3}{(1-\alpha)} \quad (2)$$

Since the concentration of the soap solutions is low, the activities of the ions can be taken almost equal to their concentrations. Then $\alpha = \lambda_c/\lambda_\infty$, where, λ_∞ represents equivalent conductance at infinite dilution. Equation (2) can be resolved in the form:

$$\lambda_c^2 C^2 = \frac{K_d\lambda_\infty^3}{4\lambda_c} - \frac{K_d\lambda_\infty^2}{4} \quad (3)$$

The values of $\lambda_c^2 C^2$ when plotted against the corresponding $1/\lambda_c$ values, yielded straight lines in premicellar region for both the solvents $i.e.$, in cyclohexanol and aniline (Fig. 3).
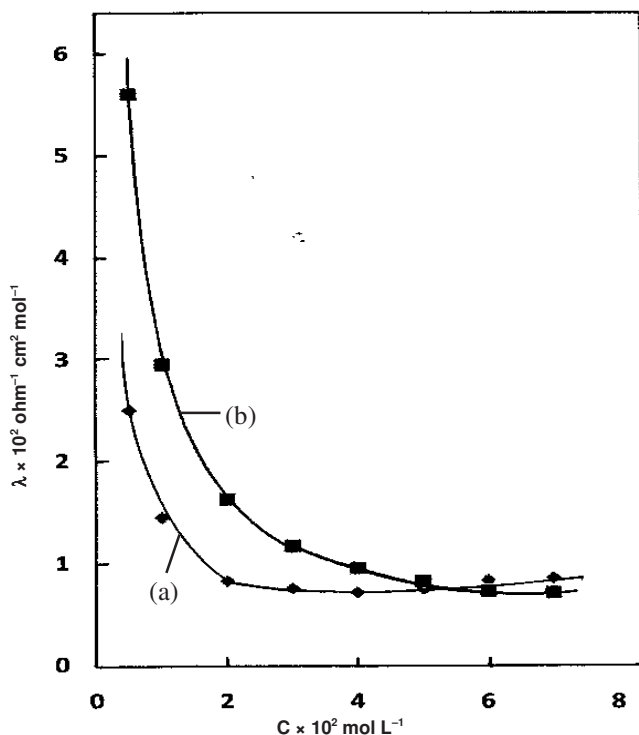
Fig. 2. Variation of molar conductance (λ_c) of copper oleate solutions with increasing soap concentration in different solvents: (a) cyclohexanol; (b) aniline

The slope (= $K_d \lambda_\infty^3/4$) and intercept (= $-K_d \lambda_\infty^2/4$) of these plots were used to find the dissociation constant of the soap in both the solvents (Table-1). The higher value of K_d in aniline than that in cyclohexanol indicates the presence of large number of monomeric soap units in former at all concentrations than that in the latter. This should lead to a higher specific conductivity in aniline than that in cyclohexanol at any soap concentration in premicellar range. This is in line with our observations (Fig. 1). The dissociated molecules also prefer to form aggregates of different size leading to negative value of K_d.
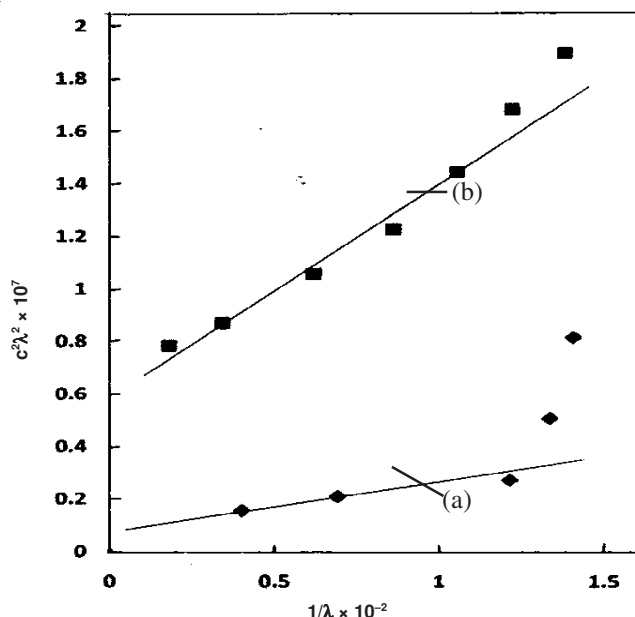
Fig. 3. Plots of $\lambda_c^2 C^3$ $versus$ $1/\lambda_c$ in premicellar range of different solvents: (a) cyclohexanol; (b) aniline; Temp. = 31 ºC

TABLE-1
DATA OBTAINED FROM SPECIFIC CONDUCTIVITY
VERSUS CONCENTRATION PLOTS

Solvent	CMC (mol L^{-1})	Dissociation constant (K_d)
Cyclohexanol	3.7×10^{-2}	-1.3501×10^{-3}
Aniline	6.5×10^{-2}	-0.512×10^{-3}

The importance of an ionic surfactant along with other physical parameters, does depend on its Kraft point (T_k). Majority applications of a surfactant are at concentrations above critical micelle concentration. Thus a surfactant may be more efficient if it has a relatively lower critical micelle concentration. Kraft point indicates minimum temperature at which micelles can be formed. Fig. 4 shows variation of solubility of the soap with temperature in all the three solvents studied.

The trend of change of solubility with temperature is same in all the three solvents. It is seen that the solubility increases gradually up to a certain temperature (Kraft point) after, which almost infinite solubility is observed. The values of T_K, critical micelle concentration and heat of solution (Q) below and above the Kraft temperature for each of the solvents were calculated from the plots shown in Fig. 4 according to equation:

$$\frac{d \ln S}{dT} = \frac{Q}{RT^2} \quad (4)$$

where, R is Rydberg constant and T is working temperature in K. The critical micelle concentration value of the soap in cyclohexanol and in aniline (Table-2) is invariably the same as determined earlier by conductance measurements (Table-1).

TABLE-2
DATA OBTAINED FROM SOLUBILITY *VERSUS*
CONCENTRATION PLOTS

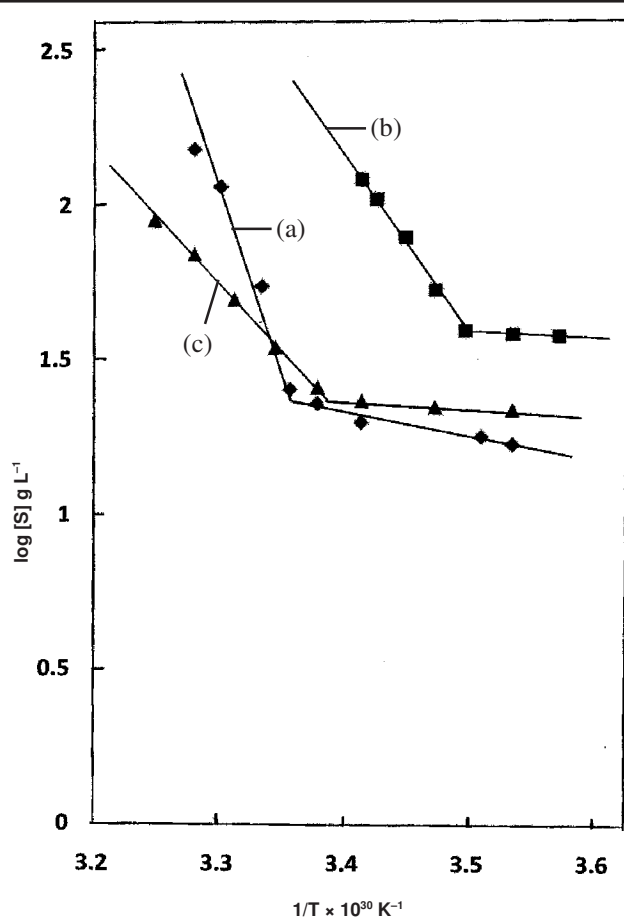| Solvent	CMC (mol L^{-1})	Kraft point, T_k (K)
Cyclohexane	3.7×10^{-2}	295.4
Cyclohexanol	3.7×10^{-2}	297.6
Aniline	6.5×10^{-2}	286.1

Fig. 4.   Variation of solubility of copper oleate solutions with temperature in different solvents: (a) cyclohexanol; (b) aniline; (c) cyclohexane

However, the solubility data has yielded the critical micelle concentration in cyclohexane that the conductivity measurements could not for the soap solution in it was non conducting. This suggests that copper oleate behaves as a non ionic molecule. Thus conductivity and solubility data contradict each other. Nelson and Pink[20] for dilute metal oleate solution clearly indicated that the polarity of the metal carboxyl bond increases in approximate order of Zn, Cu, Pb, Mn and Ca. A dipole moment of 1.2 D has been reported for copper oleates[21]. The magnetic properties of copper soaps provide evidence for relatively covalent character of the copper-carboxylate bond[22]. Thus, it may be conceived that the negative charge in the oleate anion is distributed over the entire ion and that the centre of gravity of the charge lies farther from copper, which might explain the high dipole moment, though the polarity of the bond may not be so high. It may, therefore, be concluded that the properties characteristics of covalent compound are conferred by the long hydrocarbon chain while ionic conductance is a consequence of the polar metal-carboxylate bond. It was verified experimentally that variation of temperature from 30° to 45° had no significant effect on the value of critical micelle concentration in any given solvent. The conductivity measurements were, therefore, carried out at room temperature (31 °C). It would therefore, be in reference if the thermodynamic parameters like standard enthalpy (ΔH^0_m), free energy (ΔG^0_m) and entropy (ΔS^0_m) of micellization are calculated at 31 °C.

A given soap solution above its Kraft temperature is always micellar and so the value of heat of solution (Q) above T_k can be taken as standard heat of micellization (ΔH^0_m). The standard free energy change (ΔG^0_m) for micellization of 1 mol of the soap monomers was calculated from[23],

$$(\Delta G^0_m) = R\, T \ln [CMC] \tag{5}$$

And the molar entropy of micellization (ΔS^0_m) was obtained from:

$$\Delta S^0_m = \frac{\Delta H^0_m - \Delta G^0_m}{T} \tag{6}$$

The soap solution below T_k should be non micellar. However, the probability of existence of lower associates is not denied. But in this concentration range Q cannot be equal to ΔH^0_m.

Nevertheless, entropy of solution ($\Delta S_{p\,m}$) in premicellar range may be given:

$$\Delta S_{pm} = \frac{Q}{T} \tag{7}$$

where, T has been taken as experimental temperature *i.e.* 304 K. If Q is replaced by ΔH^0_m, equation (7) may also give ΔS^0_m. It is indeed found that values of ΔS^0_m calculated from equation (6) and (7) for each of the solvents are almost the same. Table-3 shows that the values of ΔG^0_m in cyclohexane and cyclohaxanol are lower than that in aniline and so the micellization should be favoured in former two solvents. This is in agreement with the values of critical micelle concentration in these solvents.

TABLE-3
THERMODYNAMIC PARAMETERS FOR MICELLIZATION OF COPPER OLEATE IN DIFFERENT SOLVENTS

Solvent	Apparent heat of solution (Q) (K. cal mol^{-1})		ΔG^0_m (K. cal mol^{-1})	ΔS_{pm} (cal K^{-1} mol^{-1})	ΔS^0_m (cal K^{-1} mol^{-1})
	Below T_K	Above T_K			
Cyclohexane	1. 30	19. 29	-1. 985	4. 28	69. 98
Cyclohexanol	3. 91	49. 75	-1. 985	12. 86	170. 18
Aniline	0. 912	27. 36	-1. 646	3. 00	95. 41

Further a comparison of ΔS_{pm} and ΔS^0_m indicates that entropy in all the solvents increases after the micelles are formed. Since micellization is a process of molecular aggregation. This observation needs an explanation. An observation of the values of ΔH^0_m and ΔS^0_m indicates that the process of micellization is predominantly controlled by entropy change. The polar head groups of the soap molecules associate in a non-aqueous medium simultaneously with soap dissolution. This may be termed as lyophobic interaction. During the process of lyophobic interaction, the polar head groups pass over from non aqueous soap solution to micelle core, where van der Waals bonds originate between them. The number of head groups occupying the core depends on the nature and charge on the group. Nevertheless, since the medium is non aqueous and Cu^{2+} carries a double positive charge, the size of reverse micelle formed should be comparatively small. However, during lyophobic interaction, the solvent structure is destroyed and an increase in conformation entropy of polar head groups in a reverse micelle nucleus, in comparison with their entropy in a non-aqueous phase takes place.

It is concluded that copper oleate forms reversed micelles in non aqueous solvents and small molecular aggregates, instead monomers of the soap, exists at all concentrations in premicellar range. The heat of solution is found to increase many fold above the Kraft temperature than that below it for each solvent. The entropy is also found to increase after micellization and destruction of solvent structure is responsible for it.

REFERENCES

1. G.G. Sward, Paint Testing Manual, American Society for Testing and Materials, edn. 13, Ch. 2 (1972).
2. W.F. Whitmore and M. Lauro, *Ind. Eng. Chem.*, **22**, 646 (1930).
3. N. Pilpel, *Chem. Rev.,* **63**, 221 (1963).
4. R.G. Bossert, *J. Chem. Educ.*, **27**, 10 (1950).
5. J.D. Richter and P.J. Van den Berg, *J. Am. Oil Chem. Soc.*, **46**, 155 (1969).
6. J.D. Richter and P.J. Van den Berg, *J. Am. Oil Chem. Soc.*, **46**, 158 (1969).
7. M.N. Khan, *Micellar Catal.,* **133**, 1 (2007).
8. D.D. Eley, in ed.: W.G. Franken Burg, Advances in Catalysis and Related Subjects, Academic Press, New York, p. 20 (1969).
9. Y.J. Lee, T. Zhang and P.F. Barbara, *J. Phys. Chem.*, **108**, 5175 (2004).
10. J.W. Shield, H.D. Ferguson, A.S. Bommarius and T.A. Hatton, *Ind. Eng. Chem. Fund.*, **25**, 603 (1986).
11. J. Michizoe, Y. Uchimura, T. Maruyama, N. Kamia and M. Goto, *J. Biosci. Bioeng.*, **95**, 425 (2003).
12. I.A. Wani, S. Khatoon, A. Ganguly, J. Ahmed, A.K. Ganguli and T. Ahmad, *Mater. Res. Bull.*, **45**, 1033 (2010).
13. M.M.R. Talukder, Y. Hayashi, T. Takeyama, M.M. Zamam, J.C. Wu, T. Kawanishi and N. Shimizer, *J. Mol. Catal. B: Enzym.*, **22**, 203 (2003).
14. L. Dong, W. Li, X. Zhou, Q. Khan and W. Shen, *Braz. J. Chem. Eng.*, **26**, 415 (2009).
15. M.E. Leser and P.L. Luisi, **44**, 270 (1990).
16. M.E. Leser, G. Wei, P.L. Luisi and M. Maestro, *Biochem. Biophys. Res. Commun.*, **135**, 629 (1986).
17. A.H. Ghaleb and G.P. Williams, *Eur. J. Pharm. Biopharm.*, **60**, 1137 (2008).
18. R.C. Mehrotra and A.K. Rai, *J. Inorg. Nucl. Chem.*, **21**, 311 (1961).
19. I.N. Levine, Physical Chemistry, Mc Graw-Hill Inc., edn. 4, p. 485 (1995).
20. S.M. Nelson and R.C. Pink, *J. Chem. Soc.*, 4412 (1954).
21. B.C. Beberzee and S.R. Palit, *Ind. Chem. Soc.*, **27**, 385 (1950).
22. K.N. Mehrotra, V.L. Mehta and T.N. Nayar, *Z. Fur-Naturforschung*, **24(b)**, 1511 (1969).
23. C. Jolicoeur and P.R. Philip, *Can. J. Chem.*, **52**, 1834 (1974).