Desalination and Water Treatment
www.deswater.com

24 (2010) 55–60
December

1944-3994/1944-3986 © 2010 Desalination Publications. All rights reserved
doi: 10.5004/dwt.2010.1176

The influence of polyphosphonates on the precipitation of strontium sulfate (celestite) from aqueous solutions

S.K. Hamdona[a]*, S.M. Hamza[b], A.H. Mangood[b]

[a]*Department of Chemistry, National Institute of Oceanography & Fisheries, Alexandria, Egypt*
Tel. +2035450652; email: samiahamdona@yahoo.com
[b]*Department of Chemistry, Faculty of Science, Menoufia University, Shebin El- Kom, Egypt*

Received 10 April 2009; accepted 23 May 2010

ABSTRACT

The precipitation of strontium sulfate in 0.7 mol l^{-1} sodium chloride solutions was investigated at various degrees of supersaturation (0.2–0.62), with pH = 7.5, at 25°C. The rate of precipitation showed a quadratic dependence upon the relative degree of supersaturation which suggests a surface-controlled mechanism. The presence of phosphonates even at relatively low concentrations ($2.5–20 \times 10^{-6}$ mol l^{-1}) was retarding the rate of precipitation. This retardation effect was enhanced with the increase in concentration of the additives. Moreover, the retardation further augmented as the relative degree of supersaturation was decreased. The effect of the additives has been attributed to the blocking of active sites by adsorption of the additive molecules on the crystal precipitation surfaces. The action of the additives can be interpreted in terms of a Langmuir-type adsorption isotherm.

Keywords: Precipitation; Strontium sulfate; Polyphosphonate; Aqueous solutions

---

1. Introduction

The precipitation and dissolution of sulfate and carbonate salts of alkaline earths are of considerable importance in a wide variety of fields such as oceanography, sedimentology, and limnology [1]. The precipitation of sparingly soluble alkaline earth metal sulfates from their supersaturated solutions has attracted the attention of several authors. Divalent metal sulfate precipitation [2–5] is of particular interest because of its importance in the petroleum industry as well as from the point of view of analytical chemical applications. A number of previous investigations have been concerned with spontaneous precipitation processes [6–10]. The formation of scale deposits is a serious problem in the operation of oil fields, desalination plants and geothermal wells. Oil field scales are formed mainly from the sparingly soluble sulfates and carbonates of calcium, strontium and barium. Impurities play an important part in the theory of crystallization in supersaturated solutions. The factors that govern the mechanism of precipitation of these salts are therefore of considerable interest, especially the influence of foreign materials which may exert a marked effect on the rate of crystallization either through adsorption at the surface of the crystals or by lattice substitution [11,12].

In the present work, the precipitation and crystal growth of strontium sulfate from seeded supersaturated solutions at different stirring rates has been investigated. The influence of triethylenediaminetetramethylene phosphonic acid (TENTMP), ethylenediaminetetramethylene phosphonic acid (ENTMP), hydroxylethylidene 1,1-diphosphonic acid (HEDP)

---

*Corresponding author

and nitrilotrimethylene phosphonic acid (NTMP) upon the rate of crystal growth of strontium sulfate has also been investigated over a range of relative degrees of supersaturation. The structural formulae of these phosphonates are shown in Scheme 1.

2. Experimental section

Supersaturated solutions of strontium sulfate were prepared using reagent grade (Fisher Scientific Co. and J.T. Baker Co.) chemicals.

Solutions were filtered (with 0.22 μm Millipore filters) before use. Metal ion concentrations were determined by passing aliquots through a cation exchange resin (Dowex 50) in the hydrogen form and titrating the eluted acid with standardized sodium hydroxide.

All experiments were done in a thermostated double-walled Pyrex glass vessel at 25 ± 0.1°C. The total volume of the working solution was 500 cm^3. The supersaturated solution of strontium sulfate was prepared by mixing solutions of known concentrations of strontium chloride and sodium sulfate in double-distilled water. The rate of precipitation, after purging the system with nitrogen, was followed by drawing liquid samples through a filter assembly (0.22 μm) at various time intervals until the solution showed little change in strontium concentration with time. The strontium ion concentration for each sample was determined by atomic absorption spectrophotometer (Perkin Elmer Model 2380) or by exchanging the metal for hydrogen ions on a Dowex-50 ion-exchange resin and titrating the liberated acid with standardized sodium hydroxide solution. The ionic strength was adjusted to the desired value ($0.7\ mol\ l^{-1}$) by the addition of sodium chloride solution.

The pH of the solutions was measured by a glass-saturated calomel electrode (Metrohm), and was standardized before and after each experiment with NBS buffer solutions. The pH of the working solutions was adjusted to 7.50 ± 0.01 by the addition of standard sodium hydroxide and it remained constant.

Seed crystals of strontium sulfate were prepared by precipitation from a mixed solution of sodium sulfate and strontium chloride at 25°C. The seeds were washed with saturated solutions of strontium sulfate and allowed to age for at least one month at 25°C, until the specific surface area (SSA) reached a constant value of $6.12 \pm 0.1\ m^2\ g^{-1}$.

3. Results and discussion

Concentrations of ionic species in the supersaturated solutions were calculated as described previously [13], using expressions for mass balance, electroneutrality and thermodynamic equilibrium constant. The calculations were made by successive approximations for the ionic strength. Activity coefficients were calculated from the extended form of the Debye-Huckel equation proposed by Davies [14].

For many sparingly soluble salts, M_aB_b, the rate of precipitation R, normalized for seed surface area, can be expressed by the following equation:

$$R = d[M_aB_b]/dt = ks\sigma^n, \tag{1}$$

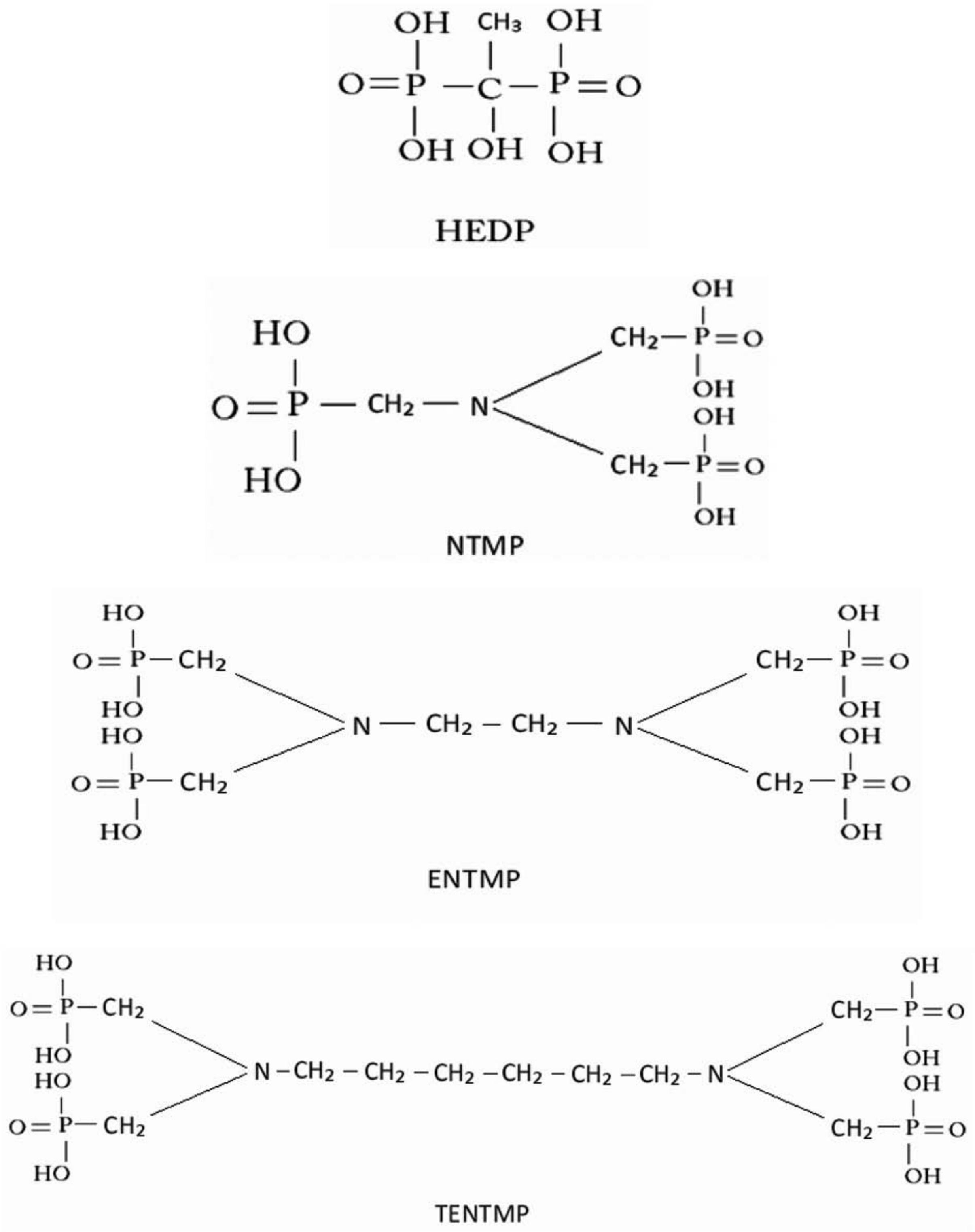
where k is a rate constant, s is proportional to the number of growth sites available, n is the apparent order of the reaction and σ is the relative degree of supersaturation for strontium sulfate solutions, which may be defined by:

$$\sigma = \left([Sr^{2+}]\,[SO_4^{2-}]\right)^{1/2} - \left([Sr^{2+}]_0[SO_4^{2-}]_0\right)^{1/2} \Big/ \left([Sr^{2+}]_0[SO_4^{2-}]_0\right)^{1/2}, \tag{2}$$

where $([Sr^{2+}],[SO_4{}^{2-}])^{1/2}$ and $([Sr^{2+}]_0, [SO_4{}^{2-}]_0)^{1/2}$ are the concentrations of free calcium and sulfate ions at time t and at equilibrium, respectively.

The results of the precipitation of strontium sulfate experiments from supersaturated solutions are summarized in Table 1. The data in Table 1 had an excellent reproducibility; each experiment was made in duplicate or triplicate. It can be seen that the rates of precipitation were proportional to the mass of strontium sulfate seed crystals used to initiate the reactions (Compare experiments 12–20). In Table 1, the rate of precipitation according to Eq. (1) (shown in Fig. 1) confirms that the reaction rates follow a parabolic rate law with ($n \approx 2$). The suggestion of a predominantly surface-controlled process over a range of relative degrees of supersaturation in this study may also be supported by the observed independence of the experimental rate of precipitation on changes in fluid dynamics, as shown in Table 1 (Compare experiments 7–9 and 4,5). It can be seen that precipitation takes place on the seed crystals without additional nucleation or spontaneous precipitation. A similar mechanism for the crystal growth of calcium sulfate dihydrate has been observed [15].

The precipitation rates of divalent metal ion salts in general are greatly inhibited by the addition of certain materials [15–18]. The rate of precipitation of strontium sulfate was studied with HEDP, TENTMP, NTMP and ENTMP present as additives. Table 2 and Fig. 2 summarize the data at the same relative degree of supersaturation for each additive, each experiment being made in duplicate or triplicate. It can be seen that



Scheme 1. Structural formulae of phosphonates.

Table 1
Precipitation of strontium sulfate crystals at 25°C, Ionic Strength = 0.7 mol l^{-1} (NaCl)

Expt. no.	10σ	Seed (mg)	Rate (10^{-6} mol min^{-1} m^{-2})
1	2.0	80	0.671
2	2.5	100	1.098
3	3.0	80	1.599
4	3.5	80	2.120
5	4.0	80	2.997
6	3.0	80	1.603
7	3.5	80	2.117
8	3.5	80	2.125
9	4.0	80	3.011
10	4.3	90	3.401
11	4.6	90	3.665
12–20	5.0	40-120	4.520
21	5.4	80	5.402
22	5.8	80	6.595
23	6.2	80	7.159

Stirring speed 200 rpm, with 300 rpm for experiments 7–9.

Table 2
Influence of polyphosphonates on the precipitation of strontium sulfate at σ = 0.43

Expt. no.	[Phosphonate] (10^{-7} mol l^{-1})	Rate (10^{-6} mol min^{-1} m^{-2})	% Inhibition
9		3.401	–
24	25 HEDP	1.974	41.96
25	50 HEDP	1.348	60.36
26	75 HEDP	1.050	69.13
27	100 HEDP	0.890	73.83
28	150 HEDP	0.610	82.06
29	200 HEDP	0.491	85.56
30	25 TENTMP	2.400	29.43
31	50 TENTMP	1.841	45.87
32	75 TENTMP	1.480	56.48
33	100 TENTMP	1.205	64.57
34	150 TENTMP	0.933	72.57
35	200 TENTMP	0.717	78.92
36	25 NTMP	2.622	22.91
37	50 NTMP	2.178	35.96
38	75 NTMP	1.875	44.87
39	100 NTMP	1.586	53.37
40	150 NTMP	1.244	63.42
41	200 NTMP	1.084	68.13
42	25 ENTMP	2.801	17.64
43	50 ENTMP	2.380	30.02
44	75 ENTMP	2.082	38.78
45	100 ENTMP	1.821	46.46
46	150 ENTMP	1.475	56.63
47	200 ENTMP	1.235	63.69

concentrations as low as 20×10^{-6} mol l^{-1} of each additive (experiments 29, 35, 41 and 47) markedly reduce the precipitation rate, by as much as 85.56%, 78.92%, 68.13% and 63.69% in the presence of HEDP, TENTMP, NTMP and ENTMP, respectively. It can be seen that the order of effectiveness of these additives is as follows: HEDP > TENTMP > NTMP > ENTMP. As the concentration of additive molecules increases, the active growth sites on the crystal surfaces may be blocked through adsorption and the rate of precipitation decreases.

When a solute precipitates from its supersaturated solution, the presence of a third component can often have a dramatic effect on the crystal growth kinetics and habit form of the crystalline phase. Such a third component is effective at relatively low concentrations ($10^{-9} < X/\text{mol dm}^{-3} < 10^{-3}$ mol l^{-1}) and exhibits a marked specificity in its action, factors which have led to the generally held conclusion that they are adsorbed onto growing crystal surfaces.

The factors that might govern the efficiency of a polyphosphonate are: (i) the nitrogen element, (ii) the molecular size, (iii) the number of phosphonic acid groups, (iv) the pK_a value. The first three factors can

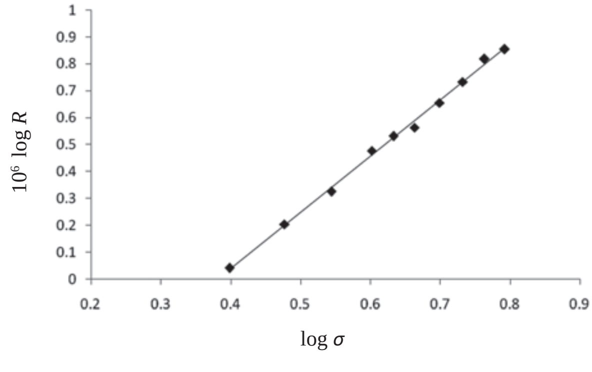


Fig. 1. Plots of log R against log σ for the precipitation of strontium sulfate.

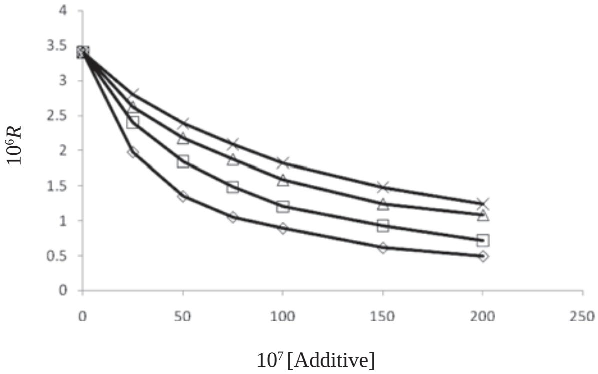


Fig. 2. Precipitation of strontium sulfate in the presence of additives: HEDP (◇); TENTMP (□); NTMP (△) and ENTMP (×).

Table 3
Acid dissociation constants of the different phosphates. (Concentration = 0.1 mol l^{-1} and 25°C)

pK_a	HEDP	TENTMP	NTMP	ENTMP
1	10.98	11.82	12.30	12.99
2	6.87	7.71	6.66	9.78
3	2.59	6.23	5.46	7.94
4		5.68	4.30	6.42
5		5.12		5.17
6		3.25		3.02
7				1.33

be ruled out since: (a) the nitrogen content of phosphonate is not a decisive factor with regard to its reactivity, as the most efficient phosphonate in the present study, HEDP, contains no nitrogen. TENTMP, NTMP and ENTMP contain two, one and two nitrogen atoms, respectively; (b) the molecular size has no bearing on the reactivity. The order of molecular size of the phosphonates can be given as follows: TENTMP > NTMP > HEDP, which is not the order of their reactivity; (c) the reactivity is not dependent upon the number of phosphonic groups. The polyphosphonates, in decreasing order of reactivity, posses the following number of phosphonic groups: 1, 4, 2, 4.

A better assessment could only be gained by a comparison of the pK_{a1} values of these polyphosphonates [3], since the degree of dissociation has to be taken into account as reported in Table 3. The values of pK_{a1} for these phosphonates fall in the following order: HEDP < TENTMP < NTMP < ENTMP, which is the same as their order of reactivity in inhibiting the precipitation rate of strontium sulfate crystals.

The negatively charged phosphonate ions will be strongly attracted by the positively charged strontium ions of the strontium sulfate crystals, which inhibits further precipitation of the crystals in the medium. This suggestion is supported by the fact that HEDP showed the greatest inhibition of precipitation of strontium sulfate and at the same time possesses the highest degree of ionization of the phosphonates used here under these experimental conditions.

In spite of the worldwide application of additives as growth and dissolution inhibitors, their mechanisms of inhibition are still largely unknown. Precipitation inhibitors are able to retard or to block the precipitation process even if added in trace amounts. Their effectiveness can therefore only be explained either by complexation of the inhibitor, usually a chelating or sequestering agent, with the lattice cation, or by adsorption of the molecules at active sites on the crystal surfaces. The latter effect may be interpreted in terms of the Langmuir adsorption isotherm [19]. This requires a linear relationship between the inverse of the relative reduction in rate, $R_o/(R_o–R_i)$ and the reciprocal of the inhibitor concentration $1/C$:

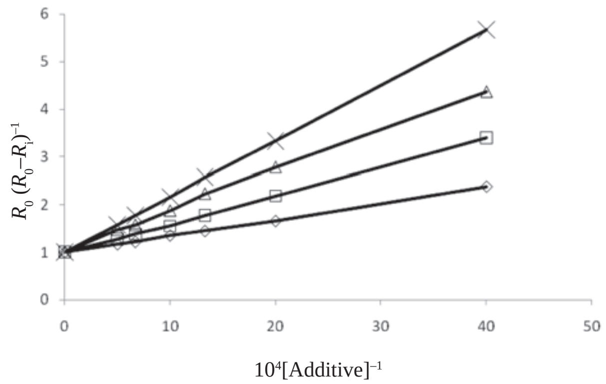


Fig. 3. Precipitation of strontium sulfate in the presence of polyphosphonate: HEDP (◇); TENTMP (□); NTMP (△) and ENTMP (×).

$$R_o/(R_o - R_i) = 1 + 1/K_L C, \tag{3}$$

where C is the equilibrium concentration of additives, K_L is the adsorption affinity constant, and R_o and R_i are the rate of precipitation in the absence and presence of an inhibitor, respectively. The applicability of the Lamgmuir model is demonstrated by the linearity of plots in Fig. 3. The values of the adsorption affinity constants K_L are 29.41×10^4, 18.18×10^4, 11.49×10^4 and 8.88×10^4 l mol^{-1} for HEDP, TENTMP, NTMP and ENTMP, respectively. These values reflect the high adsorption affinity at the same relative degree of supersaturation ($\sigma = 0.43$) in the following order: HEDP > TENTMP > NTMP > ENTMP, which is the same as the order in which they fall in terms of their pK_a values.

At different relative degrees of supersaturation, experiments for the precipitation of strontium sulfate in the presence of ENTMP were made. Concentrations as low as 10×10^{-6} mol l^{-1} ENTMP reduced the precipitation rate by at least 60.37%, 46.46% and 31.71% compared to that in pure solution at the following relative degrees of supersaturation: $\sigma = 0.35$, 0.43 and 0.54, respectively. These values show that the effectiveness of the inhibitors decreased with increases in the relative degree of supersaturation of strontium sulfate solutions. In other words, the higher the relative degree of supersaturation, the higher the dose level of the additive required to inhibit precipitation of strontium sulfate. The marked dependence of the effectiveness of growth inhibitors upon the degree of saturation (σ) has important consequences in assessing the usefulness of these compounds for industrial applications such as the control of scale formation. A similar dependence of the degree of inhibition on change in driving force has been observed for the influence of arginine and cadmium on the precipitation of gypsum and the effect of phosphate on the precipitation of calcite crystals [15,20].

4. Conclusions

Over a range of degrees of saturation, $0.2 < \sigma < 0.62$, the precipitation reaction appears to be controlled by a surface process.

Crystal growth experiments in the presence of phosphonates as inhibitors indicate that the effectiveness of the inhibitors was as follows: HEDP > TENTMP > NTMP > ENTMP. The retardation caused by these additives indicates that this effect was increased as the degree of saturation decreased. Complete inhibition of precipitation was not found with any concentration of these phosphonates or any degree of saturation.

References

[1] W. Stumm and J.J. Morgan, Aquatic Chemistry, Wiley-Interscience, New York, 1970.
[2] G.M. Van Rosmalen, M.C. Van der Leeden and J. Gouman, J. Krist. Tech., 15 (1980) 1269.
[3] E.N. Rizkalla, J. Chem. Soc. Faraday Trans. 1, 79 (1983) 1857.
[4] O.D. Linnikov, Desalination, 128 (2000) 35.
[5] C.R. Paige, O.E. Hileman Jr, W.A. Kornicker and W.J. Snodgrass, J. Radioanal. Nuclear Chem., 137 (1989) 319.
[6] A.E. Nielsen, Acta Chem. Scand., 15 (1961) 441.
[7] A.E. Austin, J.F. Miller, N.A. Richard and J.F. Kircher, Desalination, 16 (1976) 331.
[8] Z. Amjad, Environ. Treat. Contr., MP November (1989) 52.
[9] F.H. Butt, F. Rahman and U. Baduruthamal, Desalination, 109 (1997) 323.
[10] Y. Yeboah, M. Saeed and A. Lee, J. Crystal Growth, 135 (1994) 323.
[11] X.M. Alollari, P.G. Klepetsanis and P.G. Koutsoukos, J. Cryst. Growth, 155 (1995) 240.
[12] S.K. Hamdona and U.A. Al Haddad, J. Cryst. Growth, 299 (2007) 1857.
[13] G.H. Nancollas, Interactions in Electrolyte Solutions, Elsevier, Amsterdam, 1966.
[14] C.W. Davies, Ion Association, Butterworths, London, 1960.
[15] S.K. Hamdona and U. A. Al Haddad, Desalination, 228 (2008) 277.
[16] S.M. Hamza and S.K. Hamdona, J. Chem. Soc. Faraday Trans. 1, 88(18) (1992) 2713.
[17] J. Boisvert, M. Domenech, A. Foissy, J. Persello and J. Mutib, J. Cryst. Growth, 220 (2000) 579.
[18] L. Wang, R. Tang, T. Bonstein, C. Orme, P. Bush and G.H. Nancollas, J. Phys. Chem., 109 (2005) 999.
[19] P.G. Koutsoukos, Z. Amjad and G.H. Nancollas, J. Coll. Interf. Sci., 83 (1981) 599.
[20] S.K. Hamdona, Egypt. J. Aquat. Res., 33 (2) (2007) 1.