A Critical Review on the Solubility of Barium Sulphate

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Summary: Barium sulphate scale is becoming a formidable problem in the oil and gas production from natural reservoirs. Once formed it clogs the oil pipelines, resulting in a large economic loss. To understand the behaviour of this highly insoluble material a complete and comprehensive review is presented with a critical discussion on the solubility of barium sulphate in presence of different electrolyte systems. It has been suggested that the increased solubility is mainly due to the side reactions of both barium and sulphate ions, where as the contribution from ionic strength is relatively small.

Introduction

Investigations of the solubility of barium sulphate started well over a century ago, mainly because of its analytical importance. Some workers checked the reliability of older theories of electrolyte solutions on the basis of barium sulphate solubilities. The most recent studies of barium sulphate solubility, however, are generaly due to its importance in the petroleum industry, where it occurs as a scale and creates problems in the oil production [1,2].

Scale is one of the major enemies in our daily oil and gas operations. The usual type of scale found in oil fields is either calcium sulphate or calcium carbonate, which is easy to deal with. However, barium sulphate scale is becoming a formidable problem on which little research has been reported [3]. A comprehensive review of barium sulphate solubility is thus needed to study the overall behaviour of this highly isnoluble compound, towards aqueous media of different compositions, under different conditions.

Review of the older solubility data is approached from different angles, i.e. on the basis of the methods used for solubility measurements the the effect of different parameters on the solubility values. At the end a theoretical cencept is established towards the true explanation of solubility in different electrolyte solutions.

Methods for solubility measurement

Various techniques have been used for the solubility measurements of barium sulphate. The early studies on the solubility of barium sulphate were mainly done by measuring the electrical conductance of its saturated solutions [4,7]. After substracting the measured conductance of water the

corresponding solubility was calculated. The values of solubility thus reported, have big variations [8]. Polarographic method was reported to be superior than conductometric method for the solubility measurements, due to its stable response towards various types of interferences [9-11]. This statement was latter denied because in the case of extreme conditions the dimensions of the waves are very sensitive to traces of other electrolytes, such as, those coming from the dissolution of glass, thus making the exact evaluation of solubility in pure water difficult and uncertain [12]. Tyndallometric method was successfully employed for the solubility studies in different electrolyte solutions [13]. Another widely used method for the solubility measurements is radiochemical method [14,15]. It was observed that barium sulphate containing [140]Ba was much less soluble in water than the one precipitated with ^{35}S-labelled sulphate [16-17]. Saturated solutions of barium sulphate containing both [140]Ba and [35]S- have a surplus of sulphate ions and a defincency of barium ions, thus the solubility values were higher when sulphate was determined, than those when barium was measured. This was because of the adsorption of excess sulphate on the surface of crystallites during the precipitation of barium sulphate used in the solubility measurements. Contrary to Spitsyn et al. [16-17], Bovington [18] found solubility of radioactivity labelled barium sulphate ^{35}S about 10% higher than the inactive barium sulphate. Microscopic studies of the labelled barium sulphate crystals revealed that their surface were covered with minute crystallites, which probably arose as a result of self irradiation damage in the crystals. Because of their small size these crystallites would have a high surface free energy and hence enhanced solubility [19].

Some other methods which have also been employed for solubility studies include electric arc spectrography [20], solubility measurements based on the evaporation of equivilibrium solutions [21] and use of a synthetic ion-exchange resin membrane for barium measurement [22].

The overall data of barium sulphate solubility in water differs a lot and ranges from 0.95×10^{-5}M to 1.5×10^{-5}M and even to 3.27×10^{-5}M. One of the reasons for this large deviation may be that the equipment used in the early days was not very sensitive and accurate. For example the solubility method [21] involved the stirring of precipitated barium sulphate with water and the resulting saturated solution was filtered off and evaporated. As the amount of barium sulphate recovered had been very small the weighing error would have caused a large relative error in results. For these reasons it is difficult to regard the old solubility data as completely reliable.

Table 1 lists the solubility data reported in the literature. The only closely similar values of the solubility of barium sulphate are those obtained by Rossinsky [24], Nancollas and Purdi [25] and some other workers, [7,8,9,10]. In the former cases solubility was measured by conductometry where as in the latter cases polarographic method was used. The concordance of these results with each other show their reliability. Overall it can be seen that solubility studies have mainly been approached by conducitivity methods.

Effect of particle size on the solubility

Provided that the surface tension is independent of particle size, that the particles are spheres and that no electrical forces are involved, the relationship of solubility 'S' and particle size, as representated by the radius(r) of the particle is expressed by equation:

$$RT \ln \frac{S_2}{S_1} = \frac{2\sigma}{\rho} \left(\frac{1}{r_2} - \frac{1}{r_1} \right) [26,27]$$

Where the subscripts 1 and 2 refer to the particle size, is the solution solid surface tension, M is the molecular weight of the substance and is the density of the solid. On the basis of the above equation it was reported that the solubility of barium sulphate increases by 10% when the particles are ground to 0.4 um [28] and by 90% when ground to 0.2 um diameter [29]. Particles with 1.7 um diameter were found to have solubility three times that of bigger crystals [30]. This enhanced solubility was explained on the fact that the grinding sets up a considerable strain on the surface of the particles which results in increased solubility [31,32], but this claim was denied [9,10] latter on. Increased solubility of small barium sulphate particles compared to the larger particles was predicted on the basis of greater electrical conductivity of solution of small particles. However, this enchanced conductivity has proved to be due to the actual conductance of the suspended small particles themselves [33] and also to occluded barium chloride which was exposed upon grinding the barium sulphate particles [34].

Effect of aging of precipitates

Solubility of freshly precipitated barium sulphate had been found to be 8 times higher than that of the material 30 hours old [12]. The fresh precipitates are generally in a metastable, non-uniform amorphous form and hence more soluble, which turns to stable uniform crystalline shape on aging and thus becomes relatively less soluble [35,36].

Effect of temperature

Increase of temperature increases the solubility of barium sulphate [37]. Effect of temperature ranging from 20°C-600°C had been seen [38] and the general trend remains same on this wide range of temperature variation.

Solubility in electrolyte solutions

The knowledge of the solubility of barium sulphate in strong electrolyte solutions is useful to solve different geological and petroleum production problems. Water produced along with petroleum is often high in minerals, which has created many problems for this industry. Dilution of these waters with relatively "Pure" surface water, often causes precipitation of sulphate which clogs pumps, filters and pores of sedimentary rock [39]. The solubility interrelation of barium sulphate in presence of strong electrolytes is required for solving these problems [40]. The effect of electrolyte concentration on the solubility of barium sulphate had been determined by a number of workers [41,43]. The solubility increases by increase in electrolyte concentration and the effect is more pronounced for electrolytes with higher-valent cations [44]. The nitrate salts show more effect to the solubility of barium sulphate compared to their corresponding chloride salts [13]. Tempelton [20] studied the solubility of barium sulphate in sodium chloride solutions (0.1-5.0M) at temperatures ranging 25°C - 95°C. He reported an increase in the solubility by increase of both temperature and salt concentration. Davies and Collin [45] obser-

ved an interesting effect when the solubility of barium sulphate was studied in calcium chloride concentration. The solubility increased initially, reached a maximum and then started decreasing with increasing concentration of calcium chloride (Fig.1). This decrease in solubility was attributed to the low solubility product of calcium sulphate, which does not provide a satisfactory answer and a detailed discussion will be made in the theoretical part of this paper. Malinin [46] determined the solubility of barite in 0.1-2 N solutions of salts (Na, K Mg and Calcium Chloride) at 100-300°C, by using the theory of strong electrolytes.

Hydrothermal solubility of barite increases only slightly along the boundaries of the three-phase region in the binary system [38]. A number of other workers [46-49] determined the solubility of barium sulphate in different brine solutions using radiochemical methods. The values thus obtained, vary from 30-81 ug/1 of sea water.

Solubility in acid solutions

Effect of different acids on the solubility of barium sulphate had been studied by a number of workers. Banthisch [50] and Gates and Caraway [51] noted that the solubility of barium sulphate increased with increasing hydrochloric acid concentration, reached a maximum and then started decreasing. No reason was provided for the phenomenon. The solubility was found greater in nitric acid than in similar concentrations of hydrochloric acid which could well be due to the nitrate complexes of barium. Haslam [52] reported that the solubility of barium sulphate is much higher in hydrobromic acid than in hydroiodic acid. The solubility of barium sulphate increases in 0.01-0.06 M sulphuric acid, but when 0.15M sulphuric acid is present, coprecipitation of sulphate ions during the precipitation, more than counter-balances the increased solubility [53]. Equilbrium in this study was approached through super-saturation, hence increased concentration of SO_4 ions result in a decreased solubility. Other workers [54-5] also investigated the solubility of barium sulphate in sulphuric acid and reported the similar conclusions.

Theoretical aspect of barium sulphate solubility

In the literature the solubility of barium sulphate in different electrolyte solutions has been reported by many workers. In almost all cases the changes in the solubility with change of electrolyte concentration has been attributed to the change in ionic strength and no mention is made of any other phenomena. If we consider the only affecting factor to be the ionic strength then why should the solubility of calcium sulphate differ [57] in solutions of sodium chloride, perchlorate and nitrate of the same ionic strength. Similarly from the difference in the solubility values of barium sulphate in similar concentrations of hydrochloric and nitric acid [50,58], it appears that besides the ionic strength other factors such as side reactions (e.g. complex and ion-pair formation) can also make an appreciable difference, and should be taken in to account when studying the solubility at high concentrations of other salts. Theoretical solubility values for barium sulphate in sodium chloride, perchlorate and nitrate solutions, were calculated on the basis of ionic strength only [59], and found to be much lower than those of experimentally determined. However, solubility values at salt concentrations lower than 0.1M agreed with those of Neuman [13].

Table-1: Solubility of barium sulphate in water

S.No.	Temperature °C	Solubility mg/1	μmole/1	Solubility Product	Method	Ref.
1	18	2.29	9.81	10.02	cond	5
2	26	2.60	11.14	9.90	"	
3.	25	2.29	9.81	10.01	Cond	28
4.	18	2.22	9.51	10.06		
5	25	2.42	10.36	9.98		
6	50	3.36	14.39	9.92	0-corr.	7
7.	90	3.90	16.71	9.58		
8.	18	2.36	10.11	10.01	cond	27
9.	18	2.41	10.35	10.93	cond	6
10	100	11.8	50.55	9.30	cond.	30
11	18	2.22	9.51	10.06	Soly	69'
12.	18	2.22	9.51	10.06	ΔG	70
13.	25	2.23	9.51	10.06	Tyndall	13
14.	25	2.41	10.04	9.97	Pol.	9
15.	25	2.44	`10.28	9.96	Pol.	10
16.	24	2.71	11.61	9.87	soly	11
17.	25	2.33	10.00	10.00	cond	71
18.	25	2.42	10.39	9.99	cond	24
19.	25	2.42	10.39	9.99	cond	25
20.	50	3.36	14.4	9.71	Soly.	20
21.	65	3.59	15.4	9.66	0-corr.	72
22.	30	3.30	14.12	9.7	0-corr (eml)	22
23.	25	2.68	11.5	9.88	radioch.	73

Table-1 (contd.)

S.No.	Temperature °C	Solubility mg/l	Solubility μmole/l	Solubility Product	Method	Ref.
24	20	2.70	11.6	9.87	"	14
25.	25	2.71	11.8	9.87	"	18
26	20	2.5	10.71	9.94	"	45

Soly=Solubility; Cond= Conductivity; O-Cor = corrected to Zero ionic strenght, Pol.=Polaro-graphy; G=Free energy calculation; Tyndall = Tyndallometry; em = Potentiometric; radioch = radiochemical.

Effect of side reactions on the solubility

The concentration solubility product cannot be correct if there is any sort of complex formation occuring in the solubility system. The effect of this type of side reaction is readily taken in to account by using the conditional (apparent, effective) stability constant concept introduced by Schwarzenbach [60] and developed by Ringhom [61]. Unlike the negligible effect of ionic strength, the influence of side reaction on the solubility equibiria can be very large, as in the case of the solubility of barium sulphate in alkaline-EDTA media [62]. The conditional solubility product constant is defined as:

$$K'_{sp} = [A'] [B']$$

Where [A] represents the total concentration of all species containing A not bound to B, and [B] represent the total concentration of all species containing B not bound to A. Hence,

$$[A'] = [A] + [AL] + \cdots\cdots + [ALx]$$

$$= [A] (1 + \Sigma [L]^i Bi)$$

$$= A \, \alpha_A (L)$$

Where $\alpha_{A(L)}$ is the "side reaction coefficient" or –coefficient for the side reaction of L with A, and Bi is the overall formation constant of the complex "ALi" i.e.

$$Bi = \frac{[ALi]}{[A] [L]^i}$$

Similarly

$$\alpha_{B(M)} = (1 + \Sigma [M]^i Bi)$$

Where
$$Bi = \frac{[BMi]}{[B] [M]^i}$$

If these formation constants and the concentration of L and M are known, $\alpha_{A(L)}$ and $\alpha_{B(M)}$ can be evaluated. By use of the –coefficients the conditional solubility constant can thus be defined as
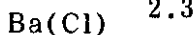
$$K_{as} = [A] [B] \, \alpha_{A(L)} \cdot \alpha_{B(M)}$$

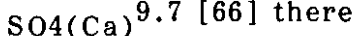$$K'_{sp} = K_{sp} \, \alpha_{A(L)} \cdot \alpha_{B(M)}$$

Because the stability constants for chloro and nitrato-complexes of barium are different [63,64], hence the difference in the solubility of barium sulphate in solutions of sodium nitrate and chloride can be explained.

Some new suggestions

Solubility of barium sulphate in the presence of other electrolyte solutions is an important subject owing its signifcance in oil filed operations. The majority of workers who have dealth with this problem explained their findings on the basis of thermodynamic factors, but few, if any, have discussed what happens during the process of dissolution, how different electrolytes increase or decrease the solubility and what sort of equilibrium is established between the ions in solution and those on the solid surface. For example, considering the solubility of barium sulphate in calcium chloride solutions, Davies and Collins [45] found that the solubility passed through a maximum with increasing calcium chloride concentration, and that at a 2-molal calcium chloride concentration the solubility was about the same as that for a saturated solution of barium sulphate in water, but the total barium plus sulphate concentration was lower than the sulphate concentration predicted from the solubility product for calcium sulphate. In view of the fact that at 4-molal chloride concentration $Ba(Cl)$ 2.3 [65] and that for 2-molal calcium concentration $SO4(Ca)$ 9.7 [66] there is obviously some effect at work that prevents thermodynamic equilibrium from being reached. The effect can only be kinetic and mechanistic in nature. A further complication arises if complex formation between sodium ions and chloride or nitrate ions is taken in to account.

For a true explanation of the barium sulphate solubility various other factors are still to be taken in to account. For example, Meites et al [67] found that in the case of calcium sulphate the ion-pairs derived from the ions of the precipitate may be able to exist in the solution and thus increase the solubility. Again, coprecipitation effects are seldom considered, although it is well known [68] that errors occur in analysis based on barium sulphate, when various cations (Na^+, K^+, Fe^{3+} etc) and anions (Cl^-, NO^-_3, PO_4^{-3} etc) are present. Furthermore, no past studies have considered the possibility of identifying the various species that make up the total solubility of the precipitate (complexes, ion-pairs etc). All that has been determined is the total concentration. In the case of conductivity work, erros could obviously arise from the presence of ion-pairs and complexes. The use of ion-selective electrodes to measure the free ions concentration could be coupled with 'Total' measurement to estimate the contribution of the complex species.

Virtually all workers have considered solubility purely from a thermodynamic point of view, and only those interested in crystal growth have considered kinetics and mechanism.

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