

## Salting-out Coefficients and Activity Coefficients of Alkali and Alkaline Earth Metals in Aqueous and Aqueous Organic Mixed Solvents

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**Summary:** The effect of added electrolytes on the salting-out coefficients has been studied at 278±1K in aqueous and aqueous organic mixed solvents. The salting-out coefficients and corresponding activity coefficients for the various systems have also been studied. Thermodynamic parameters i.e free energy(ΔF) is also calculated.

### Introduction

Solution chemistry has essentially become very important with reference to the behavioral studies of various solutes in the presence or absence of electrolytes. The equilibrium existing between two immiscible liquid layers or solutions of liquid components have also helped a lot in the understanding of the solution chemistry. Salting-out behavior is of great significance in analytical chemistry and it finds wide applications.

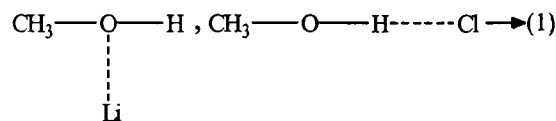
A number of ion-pairs can be extracted into immiscible solvents like nitro-benzene [1] or propylene carbonate [2] by equilibrating the said solvents with aqueous solutions of complex compounds. The salting-out phenomenon is valuable in increasing the extractability of metal complexes in liquid-liquid distributions [3,4,5]. When a polar solvents miscible with water is salted-out from an aqueous solution, the phase separation occurs due to decreased solubility of the solvent. Fujinaga and Nagaosa [6] have shown that acetonitrile has been found to be a very suitable solvent for practical purposes because of subsequent analysis by polarographic methods, which can be applied to determine the amount of extracted species even if they are present in very small quantities. The salting-out effect has advantageously been used in the form of metal salts.

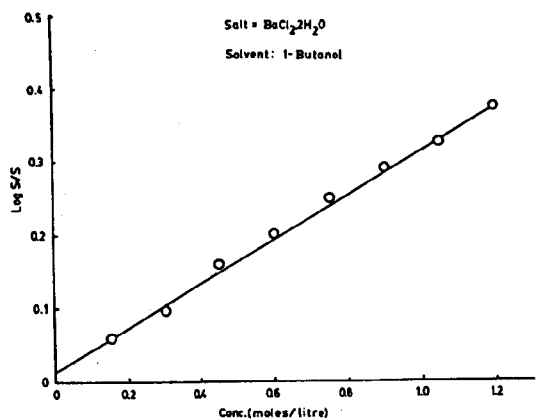
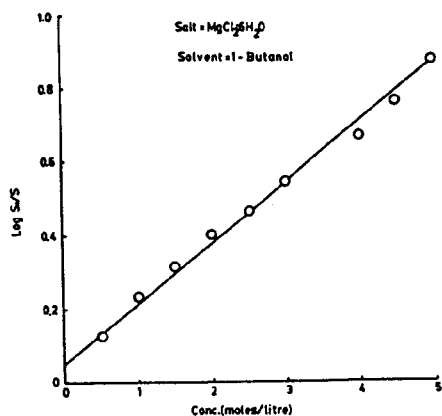
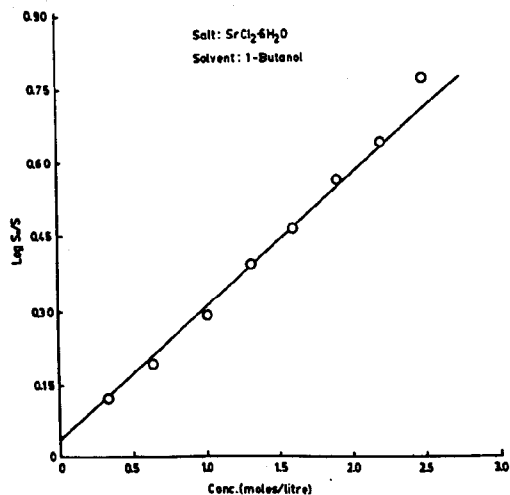
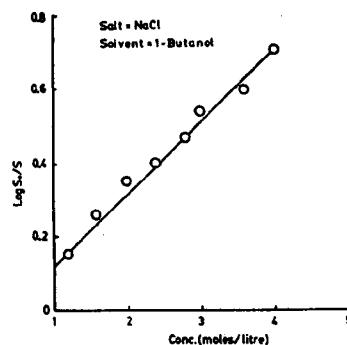
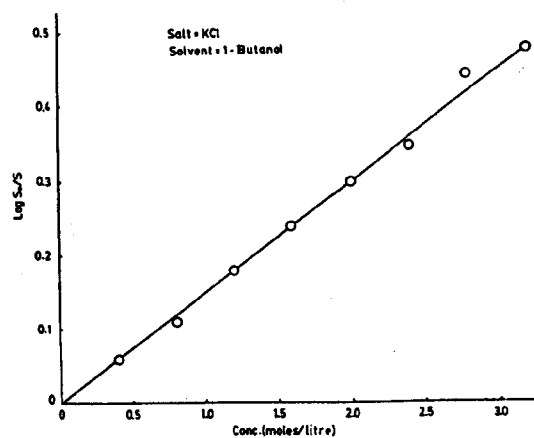
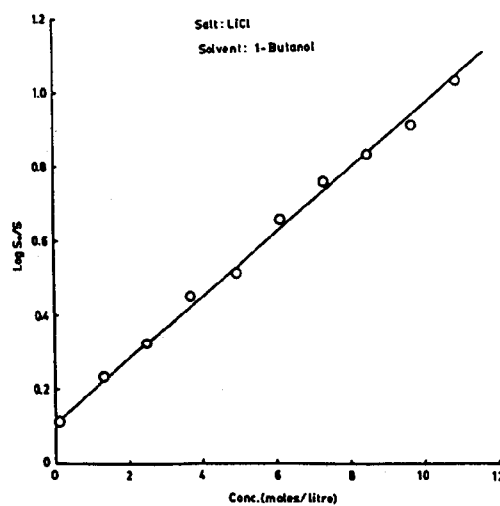
An electrolytes when added to an equilibrating system, either enhances the solubility of an already present solute in the solution or decreases it to a certain extent. The effect called as "salting-in or salting-out", as the case may be, depends upon the nature of the added electrolytes. The effect itself has been associated with the changes in the activity coefficient of the ions of the solute due to the changed ionic strength of the medium. A substances which dissolves in both phases of a two liquid

system, an increase in the mutual solubility of the liquids often occurs to such an extent that the liquids may become completely miscible with one another. If the third substance has high solubility in one liquid and very low solubility in other, its addition to the mixture lowers the mutual solubility. This principle forms the basis of salting-out phenomenon, e.g., a salt is added to a mixture of ether and water to improve the recovery of ether from the mixture. Mutual solubility of solvent systems and the salting-out behavior of one from the other, although investigated extensively, is still of great interest.

### Results and Discussion

Different salts have been used with common anion for the study of salting-out behavior in this case. The charge of the cation was also taken into account during these studies. The results are shown graphically by making a plot of  $\log S_0/S$  versus concentration in figures 1-7. It is observed that amongst 1-1 electrolytes used in this present experimentation lithium salts behaved rather differently as compared with the chloride of sodium and potassium, which yield almost identical slopes. It is postulated that the properties of lithium being different from the rest of the metals within the group, this anomalous behavior for lithium is expected. This unusual behavior of lithium has also been reported in the literature [7,8]. A probable explanation has been given in term of  $e/r$  ratio and the hydration energy. Positive evidence has been obtain from infrared spectroscopic data [9,10] which show that a powerful doner-acceptor bond of the type.



Fig.1: Plot of log  $S_0/S$  vs concentration (moles/litre), temperature: 288°K.Fig.2: Plot of log  $S_0/S$  vs concentration (moles/litre), temperature: 287°K.Fig.3: Plot of log  $S_0/S$  vs concentration (moles/litre), temperature: 289°K.Fig.4: Plot of log  $S_0/S$  vs concentration (moles/litre), temperature: 287°K.Fig.5: Plot of log  $S_0/S$  vs concentration (moles/litre), temperature: 286°K.Fig.6: Plot of log  $S_0/S$  vs concentration (moles/litre), temperature: 287°K.

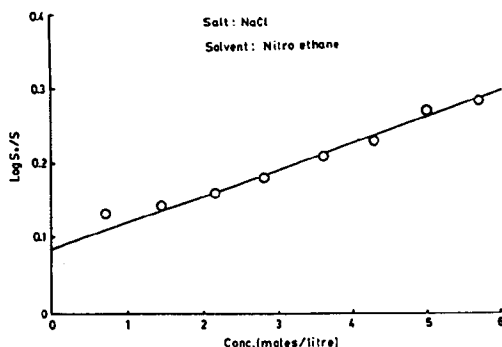


Fig.7: Plot of  $\log S_0/S$  vs concentration (moles/litre), temperature: 303°K

is formed which is stronger than the ion-dipole interaction and is characteristic of solvents such as alcohols. Furthermore, it is also a well known fact [11] that  $\text{Li}^+$  cation have higher solvation numbers than  $\text{Na}^+$  and  $\text{K}^+$  due to which the solvation energies of  $\text{Li}^+$  are much higher. The divalent cations,  $\text{Mg}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  show a regular pattern with reference to the slopes of the graphs shown in Figures 3,4,6. This observation is in direct correspondence with the cationic size of the metals under report.

Compared with 1-1 electrolytes, the 2-1 electrolytes have been found more effective in causing salting-out of 1-butanol from its salt solution at room temperature. This is in agreement with lyotropic series as reported by Glasstone [12]. Although no systematic study was made to differentiate the effectiveness of cations and anions with reference to the salting-out behavior. However, it has been reported [7] that the anions are more efficient as salting-out agents because they are more extensively hydrated than the cations. Further study is required to justify this statement. However, the present study does support that the hydration of ions play a significant role in salting-out of organic solvents. In general, it is concluded that greater the hydration, more efficient is the salting-out.

The Setschenow equation, demands that the plot of  $\log S_0/S$  as a function of concentration, should yield a straight line passing through the origin, whereas in our studies, the equation is not strictly followed because in some cases an intercept appears in the various plots. It indicates that the equation is not strictly valid for the reported systems and it has to be modified in the light of our findings. In addition to the actual equation, a constant has to be

added to account for the intercept observed in the plots. As such, the equation would look like:

$$\log S_0/S = Kc + \text{constant} \quad (2)$$

The value of this constant appears to be dependent on the individual system under investigation. The cavity theories of solutions and the ejections of solute molecules from this cavity to accommodate the electrolyte ions is a very complex process. It appears that the value of the proposed constant depends upon several factors, namely the creation and elimination of the cavity and the solvent-solvent and solvent-solute molecular interactions. However, further investigations are needed to account for the introduction of the new constant in to the Setschenow equation and to evaluate the proposed constant.

Free energies of salting-out of various organic solvents have also been calculated and individual values have been reported in the tables (1-3). The calculations are based on the following equation:-

$$kT \ln f = \Delta F \rightarrow \quad (3)$$

Table-1: Free energy change of different alkali and alkaline earth metals in 1-butanol.

NaCl	KCl	LiCl	BaCl <sub>2</sub>	MgCl <sub>2</sub>	SrCl <sub>2</sub>
0.8	4.2	6.5	2.5	4.8	5.0
1.4	3.6	5.7	2.4	4.1	4.8
1.9	2.6	4.7	2.0	3.6	4.3
2.2	2.2	4.6	1.8	3.0	3.4
2.5	1.9	4.1	1.5	2.5	3.0
2.9	1.6	3.6	1.3	2.1	2.6
3.2	1.3	2.7	1.1	1.7	2.1
3.8	1.0	2.5	0.8	1.3	1.6
	0.6	1.8	0.5	0.3	1.0
	0.3	1.3	0.3	-	0.7

Table-2 Free energy change of different alkali and alkaline earth metals in benzyle alcohol

NaCl	KCl	LiCl	BaCl <sub>2</sub>	MgCl <sub>2</sub>
2.7	3.7	2.4	2.6	4.4
2.6	3.2	1.9	2.4	3.5
2.4	2.8	1.7	2.1	3.2
2.1	2.4	1.3	2.1	3.0
1.6	2.0	1.1	2.6	2.4
1.2	1.8	0.5	2.0	1.8
1.0	1.5	0.4	1.7	1.6
0.7	1.2	0.3	1.2	1.5
0.4	1.0	0.1	1.0	1.2
	-	0.5	0.7	0.7

It is observed that the free energy values are extremely small. It is due to the fact the non-ideal

Table-3:Free energy change of different alkali and alkaline earth metals in nitro ethane

NaCl	LiCl	BaCl <sub>2</sub>	MgCl <sub>2</sub>
2.0	3.4	1.8	3.6
1.9	3.2	1.5	3.2
1.6	3.0	1.4	2.8
1.5	2.7	1.1	2.5
1.3	2.4	1.0	2.0
1.1	1.9	0.8	1.5
1.0	1.5	0.6	1.3
0.9	1.0	0.4	1.0
0.8	0.8	0.2	0.8
0.7	0.4	-	0.4

free energy for the transfer of a molecule of organic solvent from pure water to salt solution is essentially independent of the organic solvent and its concentration. Therefore, it is concluded that free energy changes do not play any significant role in the salting-out efficiency.

### Experimental

For this purpose 500ml of conductivity water was taken in a 1000ml flask and some amount of salts was added to it.

The flask was closed with the help of a rubber cork, was shaken well, and was then kept in a thermostat for two hours at room temperature. The solution was kept shaken at 10 minutes interval in order to let the salts completely dissolve itself in the conductivity water. The addition of salts was continued until no more salts dissolved in the solvent. Thus a saturated solution of salts was prepared at room temperature. The saturated salt solutions served as stock solutions. 10ml to 90ml at an interval of 10ml each, stock solutions were taken and each diluted to 100ml, in a volumetric flask with conductivity water. A 10ml aliquote of the diluted solution was mixed with an equal volume of conductivity water in a conical flask. It was then titrated against various organic solvents. The end point was detected by the appearance of turbidity.

For the volume of organic solvent used, the solubility of organic solvents was determined at room temperature.

### Solution

#### i) Potassium Chromate Solution ( $K_2CrO_4$ )

Potassium Chromate solution was used as indicator for the determination of chloride. It was prepared by dissolving 5gm. of the salts in

conductivity water and the volume was made up to 100ml to 5% solution of potassium chromate [13].

#### ii) Silver nitrate solution

Silver nitrate used had a purity of 99.9%. Therefore, a standard solution could be directly weighing 8.49gm of silver nitrate was weighed and dissolved in water and the volume was made up to 500cm<sup>3</sup> in a graduated flask in order to have 0.1M solution of silver nitrate. This solution had to be protected from light and was thus stored in amber-coloured glass bottles.

### Calculations

#### i) Solubility of solute

A simple calculation for computing the solubility data is given below:-

$$\text{Solubility} = \text{weight of solute} / \text{weight of solvent} \times 100 \quad (4)$$

Which gave us the solubility of various polar organic solvents in gm per 100ml of saturated solution. The experiments were performed at room temperature for the above calculation method.

#### ii) Salting-out constant (K)

The salting-out constant was calculated with the help of the equation given by Setschenow, in the following form:-

$$\log S_0/S = KC \quad (5)$$

where

$S_0$  = The solubility in pure water.

$S$  = The solubility in the salt solution.

$C$  = Being the concentration of electrolyte in moles<sup>3</sup> and

$K$  = Salting-out constant.

#### iii) Non-ideal free energy (F)

The non-ideal free energy ( $\Delta F$ ) was calculated using the relationship:

$$\Delta F = RT \ln f$$

Where

$K$  = Salting-out constant and

$f$  = Activity co-efficient.

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### Conclusions

The salting-out behavior depends upon the nature of the cations used. This has been interpreted in terms of the size and hydration of individuals cations. The increasing polarity of solvents is directly related with the salting-out effectiveness.The calculated thermodynamic parameters indicate that free energy changes for the solute transfer do not play any significant role in the phase separation.

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