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Studies on Molar Volume of Alkali Metal Complexes in Non-Aqueous Solvents

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The apparent molar volume (ϕv) of M-BAN-Ox for various concentrations of salt M-BAN have been determined in methanol and 95% ethanol at 300 K, where M-BAN = Na and K salt of 1-benzene-azo-2-naphthol and Ox = oxalate ion. We have observed that in methanol as concentraton of salt increases (5 to 15%) the ϕv decreases; after that no change in ϕv takes place when we increase the concentration of salt in the solution of oxalate ion. In ethanolic medium, ϕv shows decreasing trend as concentration of salts increases from 5 to 25%. It shows that in methanol the complex forming tendency terminates at 15% and above concentrations while in ethanolic medium the soluble complex formation tendency is retained even upto 25% concentration. This change of ϕv is much more pronounced in the case of corresponding potassium complexes throwing light on the fact that potassium complexes are more stable compared to their corresponding sodium complexes.

INTRODUCTION

The recent communcation[1] from this laboratory dealt with molar volume of s-block metal ion complexes in non-aqueous solvents. The apparent molar volume (ϕv) of Ca-OAc-BAN and Mg-Ox-BAN were determined in methanol and 95% ethanol at 283, 293 and 303 K temperatures and observed that in Ca-OAc-BAN complexes, there is complex breaking property above 293 K while in Mg-Ox-BAN complex forming tendency persisted even above 303 K; in 95% ethanol the complexes showed decreasing complex breaking property and increasing trend of complex forming tendencies.

In continuation of this type of study we have selected the present work in which we have sudied the solvent-solute interaction by determining ϕv during the process of complexation by the interaction of sodium and potassium salts of 1-benzene-azo-2-naphthol and oxalate ions in methanolic and 95% ethanolic media at room temperature. This work may provide a method for characterisation and justification of soluble complexes by determining the molar volumes.

RESULTS AND DISCUSSION

The apparent molar volumes of soluble M-BAN-Ox-complexes have been calculated out from density data by using the equation[2]

$$\phi v = \frac{m}{d^\circ} - \frac{1000(d - d^\circ)}{md^\circ}$$

where d° is the density of methanol and ethanol, d is the density of soluble complexes, m is the molality of solution and m is the molecular weight of M-BAN, where M = Na and K.

The value of ϕv for soluble complexes of Na-BAN-Ox and K-BAN-Ox in methanol and 95% ethanol at 300 K for 5%, 10%, 15%, 20%, 25% concentrations have been given in Table-1 and Table-2.

TABLE-1

Compound formed in methanolic medium	Concentration of salt being added	Apparent molar volumes ϕv
Na-BAN-OX	5%	426.90
Na-BAN-OX	10%	416.09
Na-BAN-OX	15%	400.49
Na-BAN-OX	20%	398.09
Na-BAN-OX	25%	398.09
Compound formed in Ethanolic medium	Concentration of salt being added	Apparent molar volumes ϕv
Na-BAN-OX	5%	443.02
Na-BAN-OX	10%	421.41
Na-BAN-OX	15%	414.21
Na-BAN-OX	20%	408.81
Na-BAN-OX	25%	401.25

TABLE-2

Compund formed in Methanlic medium	Concentration of salt being added	Apparent molar volumes ϕv
K-BAN-OX	5%	420.84
K-BAN-OX	10%	432.13
K-BAN-OX	15%	420.84
K-BAN-OX	20%	417.08
K-BAN-OX	25%	413.32
Compund formed in Ethanolic medium	Concentration of salt being added	Apparent molar volumes ϕv
K-BAN-OX	5%	430.18
K-BAN-OX	10%	452.74
K-BAN-OX	15%	435.70
K-BAN-OX	20%	433.94
K-BAN-OX	25%	431.68

It has already been established[3] that higher the value of ϕv, the solute-solvent interaction becomes lower. Thus solute-solvent interaction decreases with increase in the concentration of salt added in the solution.

In the case of Na-BAN-Ox complexes in methanolic medium as concentration of salt increases from 5 to 15% the ϕv decreases. As concentration increases further no change in ϕv has been found. This shows that as we go on adding salt (Na-BAN) from 5 to 15% concentration, the solute-solvent interaction decreases and then becomes obscured perhaps due to breaking of intramolecular H-bonding of the soluble complexes. In ethanolic medium, the continuous decreasing trend of ϕv for increasing concentrations of Na-BAN shows that solute-solvent interactions are decreasing slowly and slowly, *i.e.*, the intramolecular H-bonding persists in soluble complexes.

During formation of soluble complexes with potassium salts (K-BAN), initially the ϕv rises sharply due to rise in solute-solvent interaction. But when complexation proceeds the ϕv decreases more sharply for 15% concentration and then slowly for 20% and 25% concentration. Thus we can say that potassium complexes are more stable than their corresponding sodium complexes.

EXPERIMENTAL

The benzene azo-2-naphthol is prepared by standard method[4]. We dissolved it in 95% ethanol and to the hot solution of it added the pellets of sodium hydroxide and potassium hydroxide yielding sodium and potassium salts of BAN. We use the anhydrous oxalic acid as ligand.

To the hot 100 mL methanolic solution of oxalic acid, we go on adding 5%, 10%, 15%, 20% and 25% Na-BAN salt and go on continuously stirring for each addition and cooled at 301 K. Red coloured soluble complexes Na-BAN-Ox is formed. Its molality for each concentration is determined by usual method[5] and also density of soluble complexes formed by each addition of salt is determined by help of Wand and Millero[6].

The apparent molar volume is determined by using the formula[2].

REFERENCES

1. T.K. Singh, *J. Teach & Res. Chem.*, (In press).
2. O. Redlich and D.M. Meyer, *Chem. Rev.*, **64**, 221 (1964).
3. Shashikant and Rekha Kumari, *J. Indian Chem. Soc.*, **72**, 29, 31 (1995).
4. Beilstein, Prager and Jacobsen, *Org. Chemic. Band XVI System*, 2085–2358 (1964).
5. D.P. Shoe Maker and C.W. Garland, Experiments in Physical Chemistry, McGraw-Hill, New York (1967).
6. G.K. Ward and F.J. Millero, *J. Solution Chem.*, **3**, 417 (1974).

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