PHYSICOCHEMICAL STUDIES OF ROOM TEMPERATURE MOLTEN SALT SYSTEMS CONTAINING HYDRATED INORGANIC SALTS AND ORGANIC COMPOUNDS

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CERTIFICATE

I certify that the thesis entitled " **Physicochemical Studies of Room Temperature Molten Salt Systems Containing Hydrated Inorganic Salts and Organic Compounds"** submitted by Mr. Sontosh Dev for the Degree of Doctor of Philosophy of the North-Eastern Hill University, embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the Ph. D Degree. This work has not been submitted for any degree of any other University.

(Dr. K. ISMAIL)
Supervisor

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CONTENTS

ABSTRACT

The thesis entitled, ' Physicochemical Studies of Room Temperature Molten Salt Systems Containing Hydrated Inorganic Salts and Organic Compounds', consists of seven chapters.

In Chapter 1 a general introduction to the subject of study has been given along with the scope and scheme of the work. In Chapter 2 a general description of the experimental techniques used has been given.

In Chapter 3 visible absorption spectra of molten systems containing calcium nitrate tetrahydrate melt (CNTH) and various organic indicators were recorded at 25°C. The indicators used are methyl red, p-nitrophenol, bromophenol blue, methyl orange, and p-nitroaniline. It has been demonstrated that spectroscopic technique using organic indicators can be employed for the determination of acidity function of hydrate melts even if the indicators undergo reaction in the acidic melt and the melt has no UV transparency. For obtaining meaningful value of acidity function, it has been shown that the indicator to be used must have low pK_a value preferably $\leq \sim 1$. Indicators having high pK_a value in the range ~ 4 are also found to be useful for the determination of acidity function if such indicators have well-separated absorption

bands for their basic and acidic forms in neat hydrate melt. The average value of the acidity function of CNTH is estimated to be ca. 2.2 ± 0.4.

In Chapter 4 the kinetics of the reaction of methyl red in acidic CNTH melt has been studied by recording the time-dependent absorption spectra. The reaction follows a pseudo-first-order kinetics up to a particular time duration. The time limit of applicability of pseudo-first-order rate expression is found to be dependent on the amount of acid (acetic acid) present in CNTH. The value of the rate constant is also found to be dependent on the acid concentration. The reaction which methyl red undergoes in acidic CNTH is shown to be nitration and it has been proposed that nitration takes place at the azo nitrogen of methyl red.

In Chapter 5 density and electrical conductance measurements of a room temperature molten salt system containing CNTH and acetamide were carried out with a view to understanding the volumetric and transport behaviour of this melt. The molar volume of this molten mixture exhibits additivity and thus provides a method to estimate the molar volume or density of acetamide at ambient temperature. This type of molten mixture behaves as an ideal mixture of hydrate melt (CNTH) and hypothetical supercooled liquid solute (acetamide). The temperature dependence of specific conductance of the molten mixture is found to be non-Arrhenius and is explained in the light of the Vogel-Tammann-Fulcher (VTF) equation. Using the VTF equation ideal glass transition temperatures of the molten mixture were estimated. The decrease in specific conductance caused by the addition of acetamide to CNTH seems to be due to the ion-acetamide interactions.

In Chapter 6 micellization behaviour of sodium dodecyl sulfate (SDS) in CNTH + acetamide molten mixture has been investigated using conductance method. In order to ascertain occurrence of micellization of SDS in CNTH + acetamide molten mixture, electrical conductances of SDS, cetylpyridinium chloride (CPC), and $NaNO_3$ in pure acetamide melt were also measured. In pure acetamide melt both SDS and CPC are found to form micelles. The electrical conductance behaviour of SDS and CPC in pure acetamide melt at higher concentration is shown to be similar to that of a normal electrolyte like $NaNO_3$. SDS and CPC even exhibit conductance maxima in acetamide melt. SDS is also shown to form micelles in CNTH + acetamide melt. The critical micelle concentrations were estimated. The size of the micelles formed in molten media seems to be smaller than those formed in aqueous medium. In CNTH +acetamide melt the nature of the conductance behaviour of SDS is controlled either by acetamide or by CNTH depending upon their relative amounts in the mixture. It has been highlighted that, while employing conductance method to study the micellization behaviour, making distinction between interionic interactions and interactions reponsible for micelle formation is necessary in order to avoid possibility of estimating erroneous values for the critical micelle concentration.

In Chapter 7 electrical conductances of CNTH +Methanol, CNTH + Ethanol, and CNTH + Propanol binary mixtures were measured in the entire concentration range and in the temperature range from 45 to - 75°C. The non-Arrhenius type of temperature dependence of specific conductance of these three binary mixtures is explainable satisfactorily by the VTF, Adam-Gibbs (AG), and power-law (PL) equations. However, conceptually the VTF and AG equations do not seem to be applicable to these binary mixtures since the ideal glass transition temperatures obtained for the three alcohols from these equations are found to be higher than their respective calorimetric glass transition temperatures. The critical tempe-rature obtained from the PL equation does not seem to correspond to the ideal glass transition temperature and may probably refers, on the other hand, to the temperature at which α- and β- relaxations merge. The shape of the specific conductance versus concentration isotherms of the three binary systems differs from each other particularly above 20°C. The concentration at which conductance maximum occurs shifts towards alcohol side as the temperature is decreased. The concentration dependence of specific conductance seems to have a correlation with the dielectric constant and viscosity of the alcohol.