

P R E F A C E

During the last decade, solvents of high dielectric constant particularly those having dielectric constant greater than that of water have received considerable attention. Dielectric constant measurements have shown that mono-alkyl derivatives of many simple amides have dielectric constant much higher than that of water. Although simple amides in the liquid state do not in general possess such high dielectric constant, formamide stands out as an exception. It has a dielectric constant ( $\epsilon = 109.5$  at  $25^{\circ}\text{C}$ ) much higher than that of water. It is a colourless liquid with a convenient working range (m.p.  $+ 2.55^{\circ}$  and b.p.  $= 210.7^{\circ}$ ) and resembles water in many respects.

Since these solvents are likely to be highly polar and possess high ionizing power, a major point of interest has been to study the behaviour of ionophores and ionogens in these solvents. Several physico-chemical studies based on conductance, freezing point, calorimetric and transference number measurements have been made with this end in view, but there have been relatively few attempts to study the thermodynamical behaviour of electrolytes employing reversible galvanic cells. Some years back Dawson and co-workers initiated such studies in N-methyl acetamide and reported interesting results on hydrochloric acid from the study of the cell :  $\text{Pt}, \text{H}_2; \text{HCl}(\text{m}); \text{AgCl}, \text{Ag}$ . Following this Agarwal and Nayak from this laboratory carried out detailed study of this cell in formamide over a range of temperature.

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In addition, they also investigated the behaviour of  $\text{Ag, AgBr; Br}^-$  and  $\text{Ag, Ag}_2\text{C}_2\text{O}_4; \text{C}_2\text{O}_4^{2-}$  electrode system in this solvent.

Subsequent work by Broadbank and co-workers on the cell :  $\text{Pt; H}_2; \text{HCl(m); AgCl, Ag}$  in formamide over a lower range of temperature than used by Agarwal and Nayak have not only produced new data, but also have confirmed the general trend of Agarwal and Nayak's results. The success achieved in these studies has led the present author to investigate the behaviour of other electrode systems in formamide. Such well known electrode systems as calomel and quinhydrone which have found wide applicability in aqueous media, have been chosen. The present thesis reports the result of such investigation.

The thesis has been divided into five Chapters.

The first Chapter which consists of five sections is mainly introductory in nature. It gives a general description of the solvents of high dielectric constant with particular reference to formamide. It then introduces the basic theoretical concepts and the principles of the experimental methods which have been used in carrying out the present investigation. Finally, it gives a brief review of the previous work done in this field and outlines the aim and the scope of the work presented in the thesis.

Chapter II consists of six sections and deals mainly with the investigation of the behaviour of calomel electrode systems as found from the study of several cells.

Chapter III has seven sections and these deal with investigation of the behaviour of quinhydrone electrode systems based on the study of a number of several types of cells.

Chapter IV concerns with the evaluation of activity coefficients of hydrochloric acid in formamide both from the e.m.f. of cells and from freezing point measurements and also with the determination of the relative partial molar enthalpy and relative partial molar heat capacity of hydrochloric acid in formamide. The results have been presented and discussed in four sections.

Chapter V which happens to be the last chapter of the thesis has only two sections. The first section deals with the study of the effect of electrolyte concentration and solvent on the e.m.f. of the cell :  $\text{Ag}, \text{AgCl}; \text{KCl}(m); \text{Hg}_2\text{Cl}_2, \text{Hg}$ . In the second section, certain miscellaneous materials pertaining to the whole of the thesis, <sup>such</sup> as Summary of the work presented in thesis, Glossary of the symbols and Bibliography have been presented.