Dispersion Technology Inc. Newsletter #29

Ions, ion pairs and inverse micelles in non-polar media

Bibliography for Related Journal Article:

Dukhin, Andrei, and Sean Parlia. "Ions, ion pairs and inverse micelles in non-polar media." Current Opinion in Colloid & Interface Science 18.2 (2013): 93-115.

Link to Article:

http://www.sciencedirect.com/science/article/pii/S1359029413000204

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Abstract:
This paper begins with a review of the studies dedicated to the electrochemistry of non-polar liquids performed during last century. There is a list of dozens of liquids that have been studied, as well as variety of electrolytes. There is an overview of 13 different experimental methods which have been employed for this task. The theoretical part of the review emphasizes the work done by Onsager, Debye, Fuoss, Kraus, Bjerrum and others in 1920s and 30s. They initiated and justified the fundamental ideas that serve as the scientific basis for modern handbooks on non-aqueous electrochemistry. Many of these papers from 1930s and later are reviewed here.
The second part of this paper is dedicated to the electrochemistry of non-polar liquids containing surfactants. These substances can serve as electrolytes if ionic. However, their main function is to enhance the solvation of ions, providing steric stabilization that minimizes ion re-association and ion-pair formation. Consequently, the classical "dissociation model" requires some modification when applied to surfactant solutions. There are also two additional theoretical models suggested specifically for surfactant solutions in non-polar liquids: the "disproportionation model" for dry inverse micelles, and the "fluctuation model" by Eicke, Borkovec, and Das-Gupta for microemulsions. Charged microemulsion droplets can serve as ions, which justifies the inclusion of this theory in this review. In addition, we can study (with a well defined theory) the transition from microemulsion droplet to dry inverse micelle ion by reducing water content. Studying this transition reveals some important features of both systems. We present here these three theories and apply them for interpreting experimental data (mostly conductivity) in four different systems, all of which are non-polar systems containing surfactants: solutions of ionic surfactants, solutions of non-ionic surfactants, microemulsions with ionic surfactants, and microemulsions with non-ionic surfactants.