



A new semi-empirical kinetic method for the determination of ion exchange constants for the counterions of cationic micelles

M. Niyaz Khan*

Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia

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ABSTRACT

A new method, based upon semi-empirical kinetic approach, for the determination of ion exchange constant for ion exchange processes occurring between counterions at the cationic micellar surface is described in this review article. Basically, the method involves a reaction kinetic probe which gives observed pseudo-first-order rate constants (k_{obs}) for a nucleophilic substitution reaction between the nonionic and anionic reactants (R and S) in the presence of a constant concentration of both reactants as well as cationic micelles and varying concentrations of an inert inorganic or organic salt (MX). The observed data (k_{obs} , versus [MX]) fit satisfactorily (in terms of residual errors) to an empirical equation which could be derived from an equation explaining the mechanism of the reaction of the kinetic probe in terms of pseudophase micellar (PM) model coupled with another empirical equation. This (another) empirical equation explains the effect of [MX] on cationic micellar binding constant (K_S) of the anionic reactant (say S) and gives an empirical constant, $K_{X/S}$. The magnitude of $K_{X/S}$ is the measure of the ability of X^- to expel S^- from a cationic micellar pseudophase to the bulk aqueous phase through ion exchange X^-/S^- . The values of $K_{X/S}$ and $K_{Y/S}$ (where Y^- is another inert counterion) give the ion exchange constant, $K_X^Y (= K_X/K_Y$ where K_X and K_Y represent cationic micellar binding constants of X^- and Y^- , respectively). The suitability of this method is demonstrated by the use of three different reaction kinetic probes and various MX.

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* Tel./fax: +60 3 7967 4193.

E-mail address: niyaz@um.edu.my.

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1. Introduction

1.1. Micellar structure

The structure of normal micelles or micelles, is determined by the balance between hydrophilic interaction (which consists of all or some of the following non-covalent interactions: ion–ion, ion–dipole, ion–pi-electrons, dipole–dipole, induced dipole–dipole and hydrogen bonding interactions), hydrophobic interaction and van der Waals’/steric interaction between surfactant molecules and solvent molecules for

both nonionic and ionic micelles as well as electrostatic interactions between two adjacent headgroups and headgroups–counterions for ionic micelles only. Micelles are dynamic aggregates that exist in rapid equilibrium with monomers (cmc) as expressed by Eq. (1) [1,2]. In Eq. (1), N and n represent respective total number of surfactant molecules (D) and aggregate number of micelles (D_n), k_{in} represents

$$(N-n)D \rightleftharpoons D_n \xrightleftharpoons[k_{in}]{k_{ex}} D_{n-1} + D \tag{1}$$

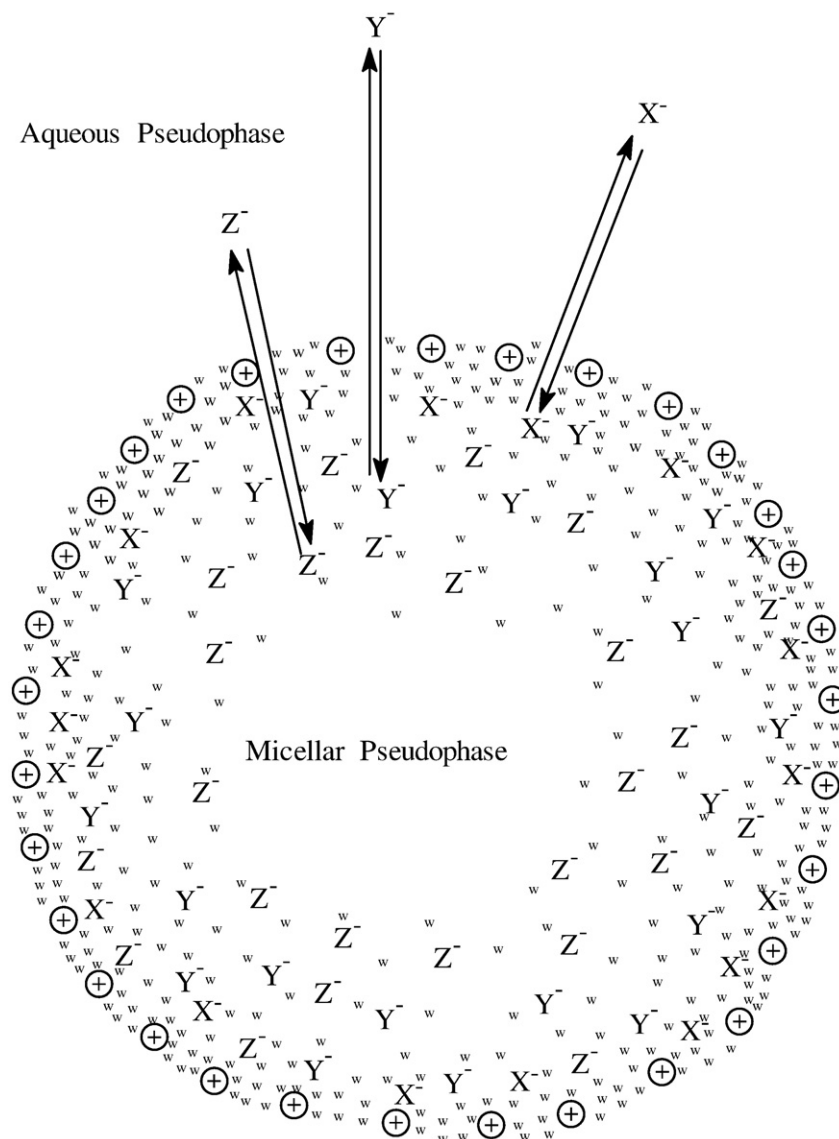


Fig. 1. Schematic representation of the probable locations of X^- , Y^- and Z^- ions in the micellar pseudophase. The X^- , Y^- and Z^- ions are assumed to have similar steric requirements and they differ in terms of hydrophobicity in the order $X^- < Y^- < Z^-$.

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