

## The Effect of Degree of Protonation on the Phase Diagrams of Alkyldimethylamine Oxides

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**Abstract**—For aqueous NaCl solutions of alkyldimethylamine oxides ( $C_n$ DAO,  $n = 12, 14, 16$ ), the potentiometric titration curves and the phase diagrams have been drawn as a function of the degree of protonation,  $\alpha$ , surfactant and NaCl concentrations,  $c$ ,  $C_s$ , and the temperature,  $T$ . The logarithm of apparent dissociation constant changes complicatedly with an increase in the degree of protonation, being related to the variations in the content of monomeric molecules and micelles and in micelle aggregation number. The  $T$ - $\alpha$ - $C_s$  diagrams for aqueous NaCl solutions of  $C_n$ DAO with a surfactant concentration of  $0.3 \times 10^{-2} \text{ g cm}^{-3}$  exhibit the liquid-liquid phase separation region above the Krafft temperature and at high NaCl concentrations. The consolute phase boundary spreads parabolically on both sides of  $\alpha \sim 0.5$ , slightly dependent on the temperature. The critical value of lower consolute NaCl concentration is 1.4 M for  $C_{12}$ DAO, 0.32 M for  $C_{14}$ DAO and 0.08 M for  $C_{16}$ DAO. In the  $T$ - $\alpha$ - $c$  diagram for 0.37 M NaCl solutions of  $C_n$ DAO, two liquid phase region is spheroidal in shape with ranges of  $T = 25$ -75 °C,  $\alpha = 0.38$ -0.60 and  $c = 0.05$ -1.67  $\times 10^{-2} \text{ g cm}^{-3}$ . The effect of the degree of protonation on the liquid-liquid phase separation is discussed in connection with the solute-solvent and solute-solute interactions and the micellar growth.

**Keywords:** *Alkyldimethylamine oxide, phase diagram, protonation*

### INTRODUCTION

The liquid-liquid phase separation of aqueous surfactant solutions is an interesting phenomenon, having relation to the solute-solvent or solute-solute interaction and the micellar growth. Such a phenomenon has been observed for aqueous solutions of oligo- and polyoxyethylene alkyl ethers [1-15], alkyldimethyl phosphine oxides [9,16,17],  $C_n$ DAO [18-20], zwitterionic surfactants [21], alkyldimethylammonium halides and dodecylammonium chloride [22].

The profile of the consolute phase boundary can be classified into three types: one has the lower critical solution temperature (LCST) and the second has the upper critical solution temperature (UCST). The third exhibits both of the LCST and the UCST, and, therefore, forms a closed loop.

When HCl is added into aqueous solutions of  $C_n$ DAO, molecules of  $C_n$ DAO are protonated and converted into *N*-hydroxyammonium ions. The effect of pH on the consolute phase boundary has been reported for 0.2 M NaBr solutions of  $C_{12}$ DAO [18].

We have observed the liquid-liquid phase separation for aqueous NaCl solutions of oleyldimethylamine oxide (ODAO) and discussed the effect of the addition of NaCl and HCl [19,20]. The 0.05 and 0.1 M NaCl solutions of ODAO at 25 °C separated into two liquid

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