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QUARTERLY TECHNICAL PROGRESS REPORT

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Summary of Technical Progress

Earlier reported results on the adsorption/desorption behaviors of single surfactant as well as mixtures of surfactant of tetradecyl trimethyl ammonium chloride (TTAC) and pentadecyl ethoxylated nonyl phenol (NP-15) indicated that the phenomena in mixed surfactant systems are more complex than those in single surfactant systems. To better understand the mechanisms involved in adsorption and desorption processes of mixed surfactant system, changes in the ratios of TTAC:NP-15 mixtures after adsorption both at the alumina-water interface and in the bulk are discussed in this report. It was found that the initial mixing ratios of TTAC:NP-15 changed significantly after adsorption over the concentration ranges studied. The adsorption behavior is directly related to these changes of mixing ratios. The possible structure of the adsorbed layer is also discussed for different mixing ratios. In the low concentration range, electrostatic attraction between the cationic surfactant, TTAC, and the negatively charged alumina surface is dominant and the adsorption of TTAC is higher than that of NP-15. With an increase in total surfactant concentration pre-adsorbed TTAC molecules function as anchors and induce the adsorption of NP-15. Strong synergism between the two surfactants is observed over this concentration range. Adsorbed pentadecylethoxylated nonyl phenol (NP-15) provides a steric barrier to further adsorption of tetradecyl trimethyl ammonium chloride (TTAC), and the adsorption of TTAC is suppressed. To develop a model that can predict adsorption of both components as a function of their activity in the mixed surfactant system, the monomer concentrations of TTAC and NP-15 in mixtures of different ratios were measured using ultrafiltration. Interestingly, the monomer concentrations measured by ultrafiltration method were different from the predictions of the regular solution theory. This result exposes the limitations of the regular solution theory for the current mixed surfactant system and a more suitable model needs to be developed.

Changes in Surfactant Ratios of Tetradecyl Trimethyl Ammonium Chloride (TTAC) to Pentadecylethoxylated Nonyl Phenol(NP-15) after Adsorption

Changes in surfactant ratio for an initial tetradecyl trimethyl ammonium chloride (TTAC) to pentadecylethoxylated nonyl phenol (NP-15) mixture of 4:1 are plotted in figure 1. It is seen that the ratios of TTAC:NP-15 both at the alumina-water interface and in the supernatant after adsorption are constantly changing over the concentration range studied.

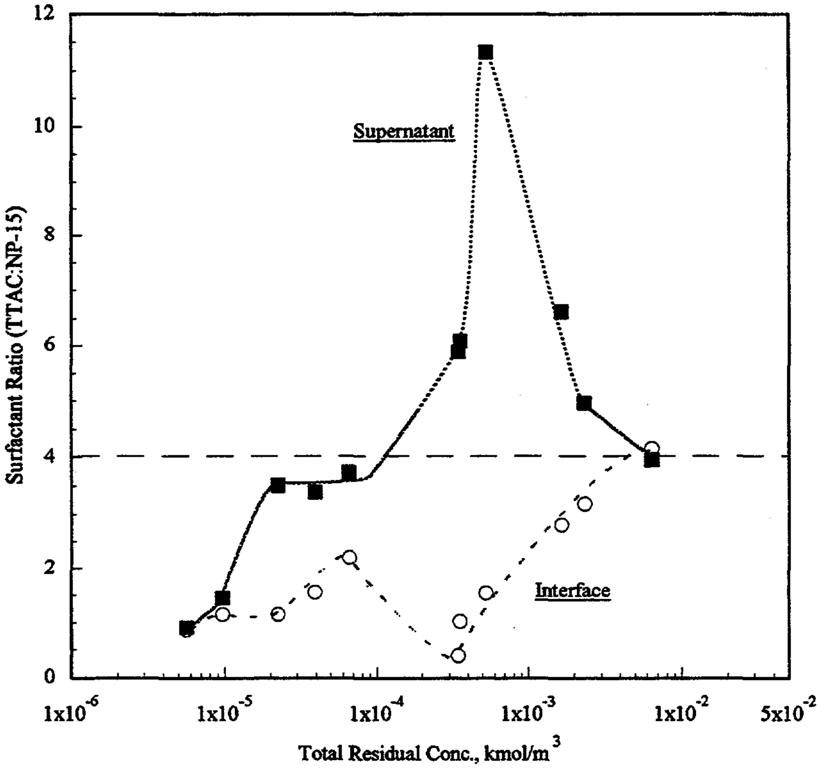

Figure 1 **Changes in surfactant ratios (TTAC to NP-15) after adsorption for an initial 4:1 mixing ratio.**

TTAC adsorbs first on alumina through electrostatic interaction. As a result of this preferential adsorption the ratio of TTAC to NP-15 is lower than 4.0 in the initial stages. Once sufficient TTAC adsorbs at the interface, NP-15 is coadsorbed through interactions between the hydrocarbon chains. Preadsorbed TTAC will function as anchors and induce the adsorption of NP-15 leading to formation of mixed surfactant aggregates at the interface. The activity of NP-15 is higher than that of the TTAC which results in excess TTAC in the supernatant leading to a high ratio of TTAC to NP-15 in the supernatant. This is also seen as a decrease of the surfactant ratio at the interface. The NP-15 molecule is larger than the TTAC molecule hence the steric hinderance to the further adsorption of TTAC leads to depression of TTAC adsorption. Once adsorption of NP-15 is complete, TTAC adsorption continues and eventually equilibrium is attained. At high concentrations of surfactant the initial mixing ratio is reflected both at the interface and in bulk solution after adsorption. Thus it is seen that partitioning of surfactant to the interface does not depend upon the initial mixing ratio particularly at low concentrations. A combination of electrostatic and hydrophobic interactions is responsible for the observed phenomena.

Similar changes for a 1:1 TTAC:NP-15 mixture are shown in Figure 2. The adsorption

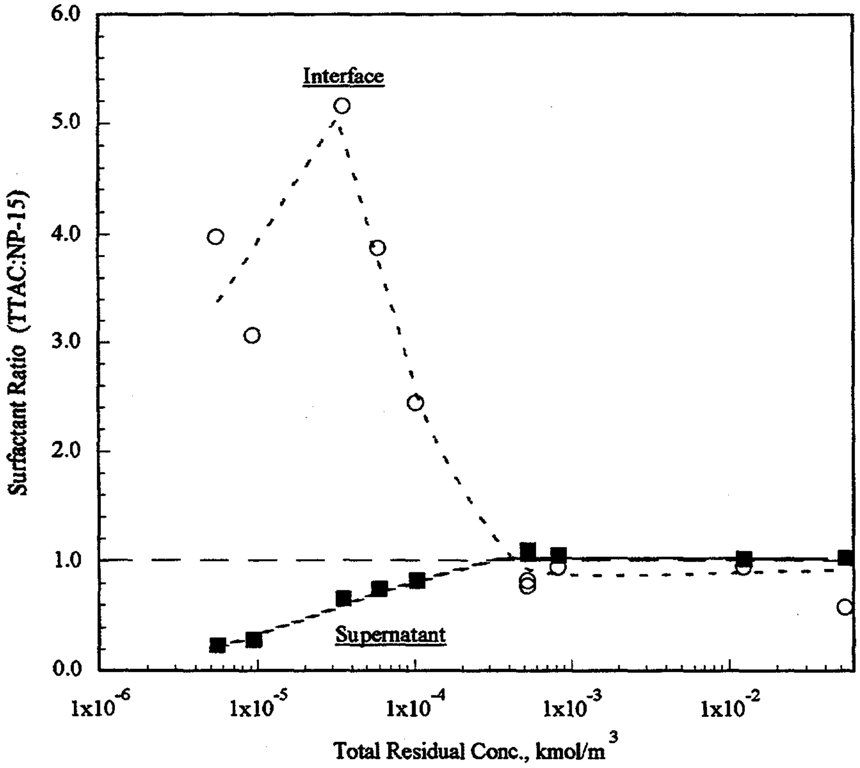

Figure 2 Changes in surfactant ratios (TTAC to NP-15) after adsorption at the alumina water interface for an initial mixing ratio of 1:1.

behavior in this system is similar to that in 4:1 TTAC:NP-15 mixture system. At low concentrations more TTAC molecules will be adsorbed at the alumina-water interface by electrostatic attraction, and the mixing ratio in supernatant is lower than 1.0 but the ratio at the interface is far greater than 1.0. It is interesting to note that the maximum surfactant ratio at the interface is higher than that in the 4:1 TTAC:NP-15 system (figure 1). This indicates that the synergism between these two surfactants is stronger in the 1:1 TTAC:NP-15 system than in the 4:1 TTAC:NP-15 system. The behavior in the supernatant is however not very complicated and at high concentrations the initial mixing ratio is reflected both in the bulk and at the interface.

For a 1:4 TTAC:NP-15 mixture the changes in mixing ratio indicate similar interactions particularly at low concentrations (figure 3).

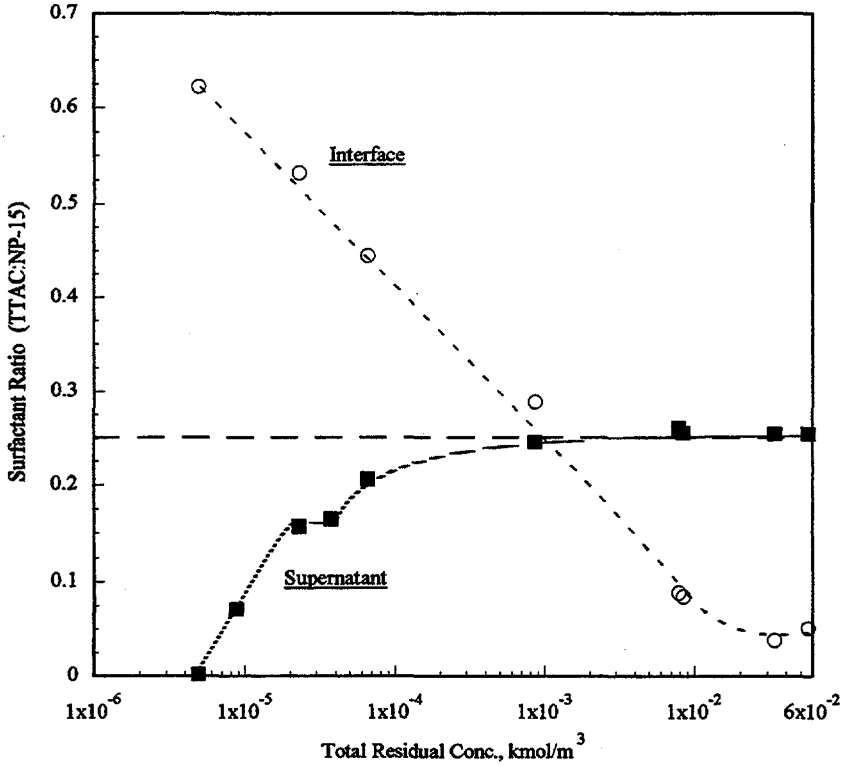

Figure 3 Changes in surfactant ratios (TTAC to NP-15) after adsorption at the alumina-water inteface for an initial mixing ratio of 1:4.

Since the TTAC content is very low, adsorption of TTAC also will be low leading to lower NP-15 adsorption as well. There was no maximum or minimum observed for the ratios either in the supernatant or at the interface. The concentration of preadsorbed TTAC molecules is not enough to induce significant coadsorption of NP-15.

Comparing the changes in mixing ratios after adsorption for the different mixtures it is seen that the adsorption behavior in this system depends on both the relative mixing ratio and the absolute concentration ranges. Considering the synergism and steric hindrance in these systems, it can be concluded that adsorption of TTAC will be decided by the relative and absolute quantity of NP-15 in the mixture. If the relative and absolute quantity of NP-15 is low, synergism between these two surfactants can be seen. At high concentrations, the absolute quantity of NP-15 is significant and steric hindrances will be dominant thus suppressing the adsorption of TTAC. On the other hand, the adsorption of NP-15 will simply depend on the mixing ratio of TTAC:NP-15 in the mixtures. With the increase of TTAC ratio the adsorption of NP-15 will be enhanced.

Monomer concentrations of tetradecyl trimethyl ammonium chloride (TTAC) and Pentadecylethoxylated nonyl phenol (NP-15) in their mixed solutions

The monomer concentrations of both tetradecyl trimethyl ammonium chloride (TTAC) and pentadecylethoxylated nonyl phenol (NP-15) in their mixtures were measured using ultrafiltration. AnYM-3 membrane from Amicon Company with a molecular weight cut-off of 3000 was used for ultrafiltration. All experiments were performed at an ionic strength of 0.2 M NaCl . The monomer concentrations of TTAC in its mixtures with NP-15 are shown in figure 4.

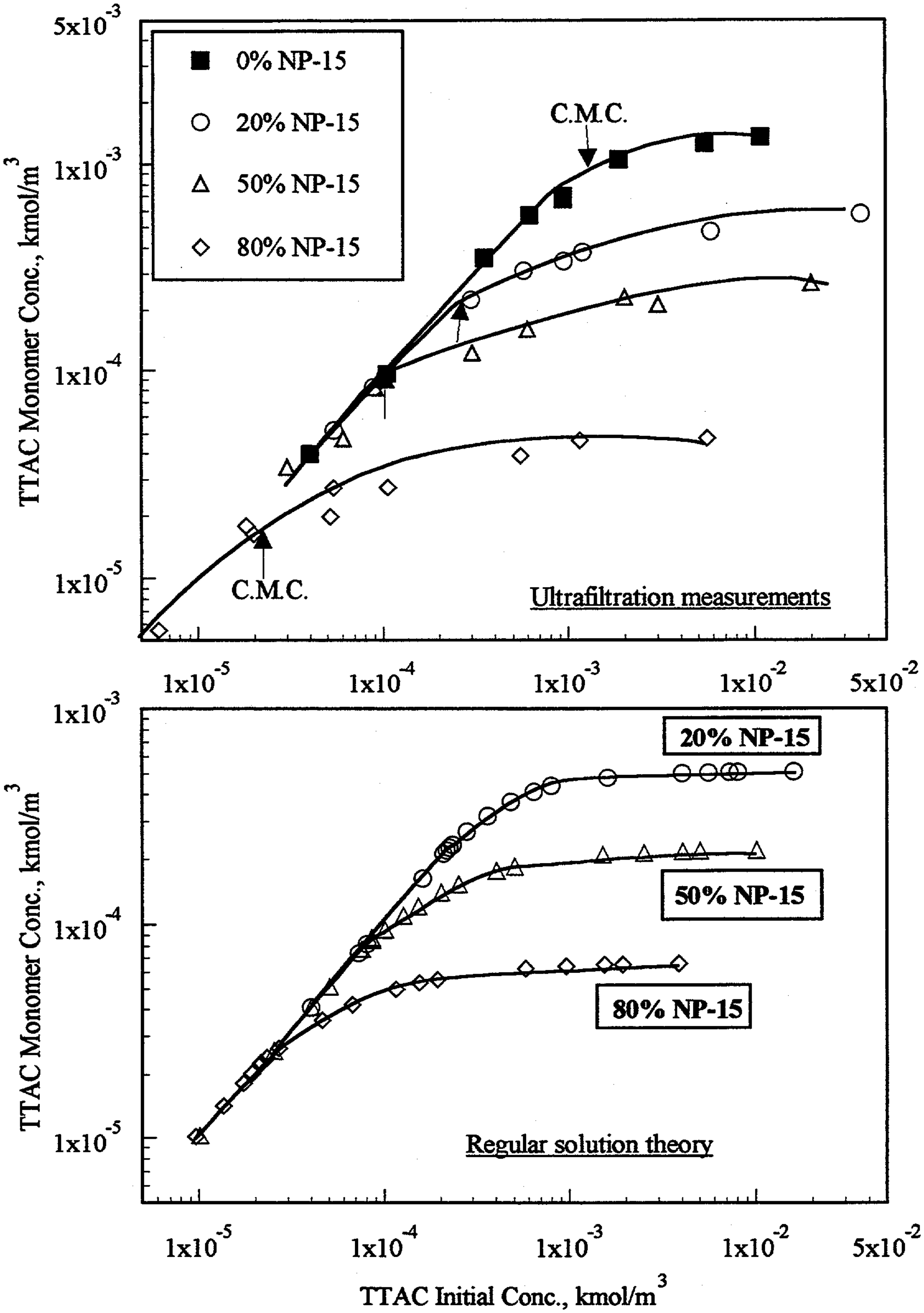

Figure 4 **Monomer concentrations of TTAC in mixtures with NP-15 as measured by ultrafiltration and also calculated using regular solution theory.**

It is seen that TTAC monomer concentrations are lower in mixtures with NP-15 than for TTAC alone. With an increase of NP-15 content in the mixtures, the monomer concentrations of TTAC is further decreased. It is interesting to note that monomer concentrations of TTAC in the mixtures keep increasing even above the critical micelle concentration (CMC) of the mixtures. This is in contrast to the single surfactant system where the monomer concentration is relatively constant above the CMC. The TTAC monomer concentrations were also calculated using the regular solution theory (see our earlier reports). Comparing the two it is seen that the TTAC monomer concentrations in this mixed surfactant system measured by ultrafiltration and calculated using regular solution theory are similar. This is not the case for NP-15 since the monomer concentrations measured by ultrafiltration are different from those calculated using regular solution theory (see figure 5). The ultrafiltration results show the monomer concentrations to be constant over the concentrations immediately above the mixed CMC (depending on mixed ratio), and then to increase at higher concentrations. Regular solution theory, however, predicts a decrease in monomer concentration above the mixed CMC. The above results clearly suggest that regular solution theory is not suitable for the TTAC and NP-15 mixture system. In our subsequent work monomer concentration in the mixtures will measured after adsorption in order to correlate these monomer concentrations to the adsorption mechanisms and enable the development of a more suitable model to describe interactions among surfactant mixtures.

Future work: Monomer concentration measurement for mixed surfactant system after adsorption

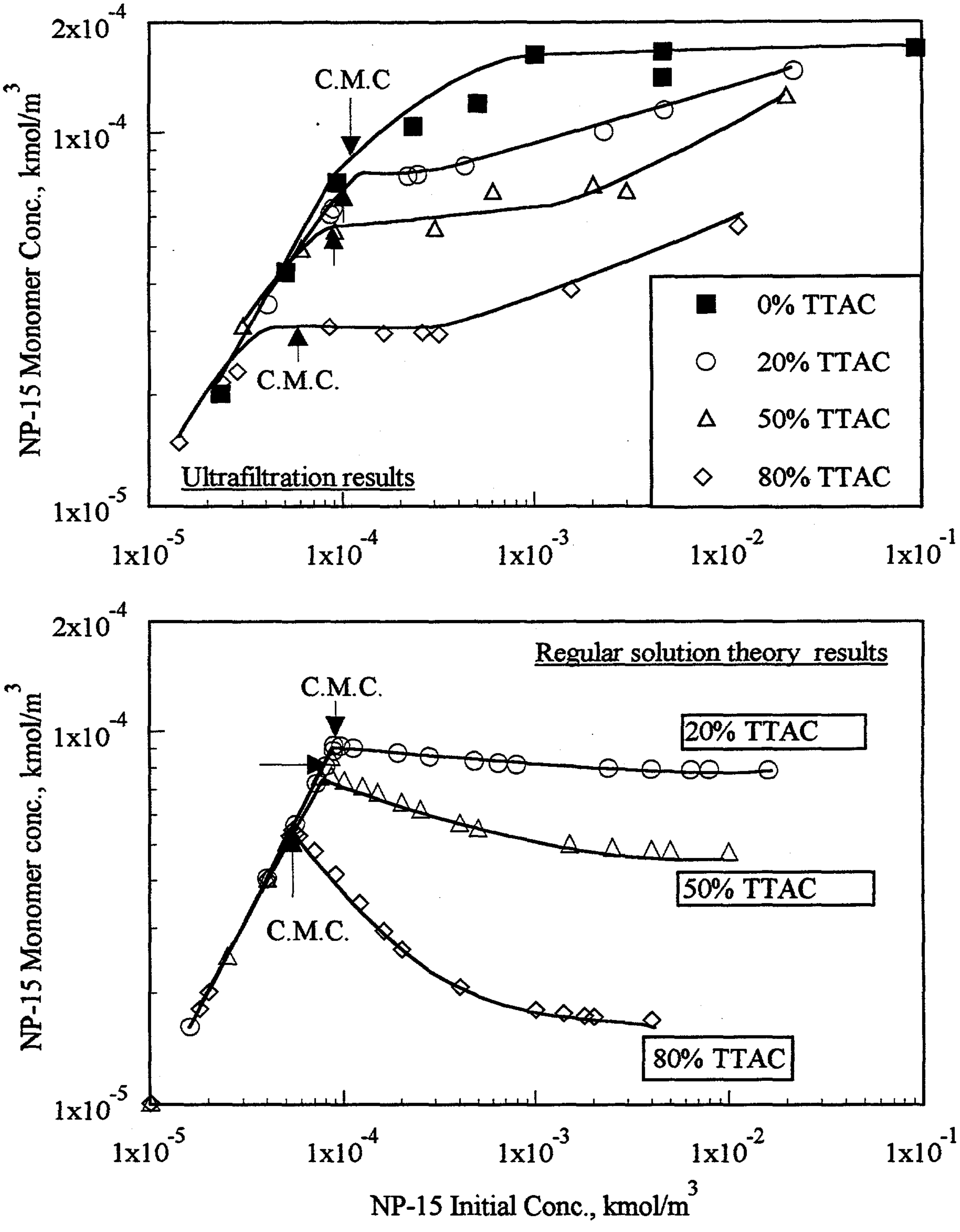

Figure 5 **Monomer concentrations of NP-15 as measured by ultrafiltration compared with those calculated using regular solution theory.**