Aggregation of Tri-n-Octylammonium Chloride (TOAHCl), Tri-n-Octulammonium Bromide (TOAHBr) and Tri-n-Octylammonium Iodide (TOAHI) in Benzene Solutions

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In non-polar solvents tertiary n-alkylammonium salts exist as hydrogen bonded ion-pairs, which with increasing concentration aggregate to quadrupoles and higher oligomers, while at highest dilution ($<10^{-5}$ mol kg^{-1}) species in the form of positive and negative triple ions can be produced. These species may be further solvated. The extent and degree of association depend on the magnitude of the dipole moment, as well as the size and shape of the solute molecules and, additionally, on the nature of the solvent [1, 2].

The aggregation of the investigated solutes in benzene solutions is studied by crysocopic method over the concentration range 0.05–0.25 mol kg^{-1}. We show, that the non-ideal behaviour of these systems as a consequence of a series of association equilibria, due to the dipole–dipole interactions of simple ion-pairs, $l\mathrm{BHX} \rightleftharpoons (\mathrm{BHX})_l$, with the self-association constant β_l, can be described with two independent parameters: the dimerization constant β_2 and constant K, which are related to the self-association constant via the relation

$$\beta_l = \beta_2 \frac{K^{l-2}}{l-1}, \qquad (l \geqslant 2)$$

and to the stepwise association constant through

$$K_l = \frac{l-2}{l-1} K, \qquad (l \geqslant 3).$$

From the hypothesis used [3], it follows, that the first stepwise associations occur less readily than the rest. The values of $\beta_2 \times 10^{-3} = 5.5$ (TOAHCl); 3.0 (TOAHBr); 2.5 (TOAHI), $K \times 10^{-2} = 1.75$ (TOAHCl); 2.25 (TOAHBr); 3.00 (TOAHI) and free monomer concentration $n_{1,0}^{*} \times 10^{3} = 1.0$ (TOAHCl); 1.1 (TOAHBr); 1.1 (TOAHI) are determined by curve-fitting method [3, 4]. The results indicate, that with increasing size of anion of tri-n-octylammonium halides in benzene solutions the dimerization decreases, while the presence of higher oligomers increases.

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Interactions in the Systems $Et_3N/AgNO_3/C_6H_6$ and $Et_3N/AgNO_3/CH_3COCH_3$. Their Effect on the Catalysed Quaternization of Et_3N with EtI

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A strong catalytic effect having been observed due to the presence of $AgNO_3$ in a Menschutkin reaction mixture in benzene [1] and acetone [2], it has been considered of interest to study more deeply this effect. Studies of interactions in the systems $Et_3N/AgNO_3$/solvent are required to understand the mechanism and rate law of the proposed catalysed reaction.

The studies started with benzene and acetone as solvents. Density measurements in the binary mixtures Et_3N/C_6H_6 and Et_3N/CH_3COCH_3 as well as in the ternary mixtures $Et_3N/AgNO_3/C_6H_6$ and $Et_3N/AgNO_3/CH_3COCH_3$ have been undertaken in this laboratory using a Digital Anton Paar DMA O2D Density Meter. Computation of partial molal volumes were made.

Discussion of the foregoing results together with infrared spectroscopic information and the analysis of data found in the literature [3–7] led us to propose structural models for the investigated mixtures and to make correlations with the experimental rates measured for the catalysed reactions.

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