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A new correlation for the relative permittivity of polar compounds and its application to the NRTL-PRA EoS for modeling of mixtures containing water and salts

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The NRTL-PRA EoS [1] was recently extended to the modeling of phase equilibria in mixtures containing alcohols and light gases with water and strong electrolytes [2]. For this purpose, the *residual term* of the original model was modified in order to describe all the interactions between solvents and ions with only two contributions: the *SMR* term, specific of "Short and Middle Range" interactions between solvents and salts, and the *LR* relation proposed by Pitzer-Debye-Hückel [3], for the description of "Long Range" electrostatic interactions.

The first problem encountered in the development of this model concerned the estimation of the *relative permittivity*, $\varepsilon_r(T)$, of the polar salt-free solvent mixture which appears in the *LR* term. In particular, it was observed that classical correlations proposed in literature [4-6] for water and methanol with sodium chloride led to "strange" behaviors of the permittivity, especially for water, at temperatures greater than 350 K.

Taking into consideration “data generated” from various literature correlations ([4] for water, [5] for methanol and CRC tables [6] for other alcohols), a generalized function for ε_r was proposed for *polar compounds* in [2] with two objectives: first, to obtain the best representation of the "experimental domain" defined by the CRC tables; second, to allow a "reasonable extrapolation" of the relative permittivity ε_r at high temperatures, it means up to 600 K (as required for the modeling of VLE of methane or carbon dioxide mixtures with water and salts near the water critical temperature). Rather satisfactory VLE results were obtained in such conditions [2].

However, a further critical comparison between *real experimental data* and the *estimations proposed in [2]* of the relative permittivity of water in a very wide temperature range (from 250 K to 680 K) gave evidence of strong discrepancies above 400 K. A similar comparison, using obviously a more restricted data set, was also performed with methanol and led to the same conclusions.

The purpose of this work was therefore the development of a general correlation of $\varepsilon_r(T)$ based on a substantial amount of experimental data in a wide temperature range up to 823 K. A comparison between results obtained from the various methods is presented for water and methanol.

The last step of the work concerned the application of the proposed correlation to the modeling of phase equilibria by means of the NRTL-PRA model [2]. Due to the presence of water in all mixtures previously considered (alcohols and light gases with water and strong electrolytes), a new estimation of group contribution interaction parameters between solvents and ions was required. A good agreement with experimental data is obtained for VLE representations.

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