A quaternary system for investigating the effect of acid-base equilibria on volatilities

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The importance of the study of electrolyte containing systems from a thermodynamic point of view has been stressed several times recently [1–3]. The aim of the EleTher (Electrolyte Thermodynamics) Joint Industry Project is to benchmark fluid phase equilibrium modelling approaches on some well-designed electrolyte systems.

Electrolyte thermodynamic problems contain several levels of complexity: beyond the fact that ionic mixtures are far from ideal, thus requiring an activity coefficient model that may contain many adjustable parameters, the reactivity results in the fact that additional species may appear other than the apparent ones, which significantly impacts the thermodynamics of the system. In order to investigate the true complexity of such a system, while keeping it sufficiently simple to allow for a systematic investigation, it was decided within the JIP to work with quaternary fluid phase systems, containing, in addition to water, an acid, a base and a cosolvent. This way, both the effect of pH and the effect of dielectric constant could be investigated. The quaternary becomes in practice a 9 component system when the reactivity is taken into account.

In this work, the vapour-liquid equilibrium of the system of water with acetic acid, potassium hydroxide and methanol is worked on. The existing data are analyzed and modelled using the eNRTL model. It appears that several equivalent parameter sets

can fit the ternary systems, and that it is therefore necessary to include additional information, as for example speciation or quaternary data.

Clearly, more predictive approaches are needed in order to satisfy the industrial need to understand and describe the VLE of such systems.

References

[1] G.M. Kontogeorgis, A. ten Kate, M. Hajiw-Riberaud, J.-C. de Hemptinne, Fluid Phase Equilib. 556 (2022) 113399.

[2] G.M. Kontogeorgis, R. Dohrn, I.G. Economou, J.-C. de Hemptinne, A. ten Kate, S. Kuitunen, M. Mooijer, L.F. Žilnik, V. Vesovic, Ind. Eng. Chem. Res. 60 (2021) 4987–5013.

[3] J.-C. de Hemptinne, G.M. Kontogeorgis, R. Dohrn, I.G. Economou, A. ten Kate, S. Kuitunen, L. Fele Žilnik, M.G. de Angelis, V. Vesovic, Ind. Eng. Chem. Res. 61 (2022) 14664–14680.