

**CALCULATION AND EXPERIMENTAL STUDY OF
PHASE EQUILIBRIA IN BINARY AQUEOUS SYSTEMS CONTAINING
MONOVALENT CATIONS AND METHANESULFONATE**

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Methanesulfonic acid and its salts are of interest for green hydrometallurgical processing routes. Phase diagrams are the key instrument for element separation in such processes. Thermodynamic modeling allows to calculate phase composition in complex multi-component systems. At the same time, the literature data for thermodynamic properties of phases in even binary systems containing alkali metal and ammonium methanesulfonates remain fragmentary, which hampers the development of a consistent thermodynamic model.

In the present work, the binary systems $\text{H}_2\text{O}-\text{CH}_3\text{SO}_3\text{Me}$ ($\text{Me} = \text{Li}, \text{K}, \text{NH}_4$) are considered. Only for the $\text{H}_2\text{O}-\text{CH}_3\text{SO}_3\text{NH}_4$ system, solubility data are available in the literature [1]. For the $\text{H}_2\text{O}-\text{CH}_3\text{SO}_3\text{Me}$ ($\text{Me} = \text{Li}, \text{K}$) systems, solvent activity data at 298.2 K have been reported [2]. These data require extension to the high-concentration region and to other temperatures. The aim of this work is to obtain a new set of experimental data on vapor-liquid and solid-liquid equilibria in these binary systems and to provide their thermodynamic description.

Solubility in the $\text{H}_2\text{O}-\text{CH}_3\text{SO}_3\text{Me}$ ($\text{Me} = \text{Li}, \text{K}$) systems was determined by the isothermal solubility method in the temperature range 253.2–323.2 K ($u(T)=0.2$ K). Methanesulfonate concentrations in saturated solutions were determined by evaporation of a sample of the saturated solution followed by weighing of the dry residue ($u_r(w)=0.5\%$). For these systems, data on the freezing-point depression of ice were obtained by DSC ($u_r(w)=0.5\%$, $u(T)=0.8$ K), using NETZSCH DSC 204 F1. Water activity of non-saturated liquid solutions was obtained at 298.2 K, 310.7 K and 323.2 K ($u(T)=0.2$ K, $u(aw)=0.003$) using the hygrometer Novacina LabMaster-aw neo.

Parameters of the Pitzer–Simonson–Clegg (PSC) model were determined for the liquid phase. Solubility products and their temperature dependence were evaluated for all salts. Phase diagram sections were calculated for the $\text{H}_2\text{O}-\text{CH}_3\text{SO}_3\text{Me}$ ($\text{Me} = \text{Li}, \text{K}, \text{NH}_4$) systems.

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2. Bonner O.D. Study of Methanesulfonates and Trifluoromethanesulfonates. Evidence for Hydrogen Bonding to the Trifluoro Group // J. Am. Chem. Soc. 1981. Vol. 103. No 12. P. 3262–3265.

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