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Thermodynamics and phase equilibrium of the high concentration solid solution-aqueous solution system KCl–RbCl–H₂O from T=298.15 K to T=323.15 K

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Abstract: Water activities of the high concentration solid solution-aqueous solution system (SS-AS) KCl-RbCl-H₂O and its sub-binary systems at T=298.15 K and T=323.15 K have been elaborately measured by an isopiestic method. The solubility of this ternary system at T= (298.15, 308.15 and 323.15) K was also measured by a Flow-Cloud-Point method. A Pitzer model was used to estimate the reliability of the solubility reported in the literature, and to judge the type of solid phase, by correlating the measured water activity and the reported solubility values. The binary model parameters as a function of temperature between T=298.15 K and T=323.15 K were obtained by fitting the water activities in the binary systems. The predicted water activities at T=298.15 K and T=323.15 K with the obtained binary parameters only, are in good agreement with the experimental values, which indicate that the Pitzer model can reliably represent the properties of the ternary system, with binary parameters only within the temperature range from T=298.15 K to T=323.15 K. Under the different assumptions that the equilibrium solid phase involved the pure salts (KCl_(s) and RbCl_(s)) for the ideal solid solution or regular solid solution (K,Rb)Cl_(ss), the solubility isotherms at T = (298.15, 308.15 and 323.15) K were calculated and compared to experimental results, respectively. It was found that only the calculated solubility isotherms for (K,Rb)Cl_(ss) regular solid solution are consistent with the corresponding experimental values. The solid phase equilibrated with the aqueous solution in the KCl-RbCl-H₂O ternary system should be a regular solid solution (K,Rb)Cl_(ss). This conclusion also can be verified from the Lippman $\log \sum K - X^{s} - X^{act}$ and $\Phi \sum m - X^{s} - X^{aq}$ equilibrium diagrams.

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