

Liquid–Liquid Equilibrium of the Aqueous Two-Phase System Water + PEG 4000 + Potassium Phosphate at Four Temperatures: Experimental Determination and Thermodynamic Modeling

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The effect of temperature on the liquid–liquid equilibrium for the aqueous two-phase system water + poly(ethylene glycol) 4000 + potassium phosphate was studied by determining 29 tie lines at 10 °C, 14 tie lines at 15 °C, 23 tie lines at 20 °C, and 15 tie lines at 30 °C, to give a total of 81 tie lines at four different temperatures. The results show a transition of miscibility: at 10 °C, the pair water + salt is completely miscible and the pair PEG + water is partially miscible, while, at higher temperatures, the pair water + salt becomes partially miscible and the pair PEG + water becomes completely miscible. Experimental results were correlated with a mass fraction-based NRTL activity coefficient model. New interaction parameters were estimated with the Simplex method and the maximum likelihood principle. The mean deviations between the experimental and calculated compositions in both equilibrium phases are below 1.7%.

Introduction

When two different polymers [e.g. dextran and poly(ethylene glycol), PEG] or one polymer and one salt (e.g. PEG and sodium sulfate) are mixed at certain concentrations in an aqueous solution, the solution separates into two immiscible phases, one rich in one polymer and the other rich in the other polymer (or salt), with water as solvent in both phases. This statement, made by Albertsson¹ in the mid-1950s, is the basis for separation processes using aqueous two-phase systems. Liquid–liquid extraction using aqueous two-phase systems is widely recognized today as a highly efficient separation technique,² particularly in partitioning and purification of biomolecules, since these systems form a gentle environment for enzymes and other biologically active proteins. This extraction technology offers the advantages of high capacity, high activity yields, and ease of scale-up.

Reliable data on the composition and properties of aqueous two-phase systems are necessary for the design of extraction processes and for the development of both thermodynamics and mass transfer models. Phase diagrams have been reported for a large number of polymer–polymer systems;^{1,2} however, experimental data for aqueous polymer–salt mixtures are still relatively scarce. Lei et al.³ reported liquid–liquid equilibrium data for the systems PEG 400, PEG 600, PEG 1000, PEG 1500, PEG 3400, PEG 8000, and PEG 20000, with potassium phosphate at 4 °C; Gao et al.⁴ determined experimental data for systems containing ammonium sulfate and PEG 1000, PEG 1540, PEG 2000, and PEG 4000; Snyder et al.⁵ studied systems containing PEG 1000, PEG 3350, and PEG 8000 and magnesium sulfate, sodium sulfate, sodium carbonate, and potassium phosphate as salts at 25 °C; Voros et al.⁶ used PEG 1000 and PEG 2000 with ammonium sulfate and sodium carbonate at 15, 25, 35, and 45 °C; Hammer et al.⁷

analyzed systems with PEG 1550, PEG 3000, and PEG 6000, using sodium sulfate at 20, 30, and 40 °C; Peng et al.⁸ reported data for systems composed by PEG 1000, PEG 2000, PEG 4000, and PEG 6000 with a mixture of potassium hydrogen phosphate and potassium dihydrogen phosphate at 25 °C; Mishima et al.⁹ measured liquid–liquid equilibrium for systems containing PEG 7500 and potassium phosphate at 15, 30, and 40 °C; Silva et al.¹⁰ studied the phase behavior of systems containing PEG 1000 and PEG 8000 at 4, 25, and 40 °C and pH 6, 7, and 9; Mishima et al.¹¹ published data for systems containing PEG 4000 and PEG 20000 with potassium phosphate at 25 °C. In this work, the effect of temperature on the liquid–liquid equilibrium for the aqueous two-phase system water + PEG 4000 + potassium phosphate was studied by determining 81 experimental tie lines at 10, 15, 20, and 30 °C.

Experimental Section

PEG, with a mass average 4000, and potassium hydrogen phosphate were of analytical grade (Merck) and were used without further purification. Experiments were carried out in equilibrium cells, similar to those suggested by Stragevitch¹² and described elsewhere.^{13,14} The cell temperature was regulated by a controlled thermostatic bath (Tecnal TE-184, accurate to ± 0.01 °C). The overall mixture was prepared directly inside the cell, and the components were weighed on an analytical balance (Ohaus AS200, accurate to ± 0.0001 g). The mixture was vigorously agitated with a magnetic stirrer (Tecnal TE-085) for 3 h, to allow an intimate contact between the phases, and the equilibrium was achieved by letting the mixture rest for 12 h. Preliminary tests¹⁵ showed that these times are enough to achieve the equilibrium. The system separated into two liquid phases, that become clear and transparent, with a well-defined interface. Separate samples of both phases were collected and analyzed. Water was determined by gravimetric analysis, using the same analytical balance (Ohaus AS200, accurate to ± 0.0001 g), while potassium

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