Critical Properties of Compounds with Star-Like Molecules

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The experimental critical properties are known only for several compounds consisting of symmetric star-like molecules. This paper presents the critical temperatures and pressures of tetraalkoxysilanes Si[O(CH2)nH]4 (n = 1 to 10) and tetraalkoxytitaniums Ti[O(CH2)n]4 (n = 2 to 10). All the substances investigated are thermally unstable at their critical points. The measurements were performed by the pulse-heating method with ultralow residence times from (0.03 to 1) ms (Nikitin, E.D. et al. J. Chem. Thermodyn. 1993, 25, 869). According to the data from proton magnetic spectroscopy (Bruker DRX 400), the mass fraction of impurities in the samples studied did not exceed the values 0.01 for the samples both before and after measuring the critical properties. The uncertainties were not greater than 0.04\(p_c\) for the critical pressure and 0.01\(T_c\) for the critical temperature, where \(T_c\) is the absolute temperature.

The critical temperatures and pressures of tetraalkoxysilanes were also calculated using group-contribution methods (Myers, K.H.; Danner, R.P. J. Chem. Eng. Data 1993, 38, 175; Nannoolal, Y. et al. Fluid Phase Equilib. 2007, 252, 1). The experimental and the calculated critical constants were compared. We failed to find in the literature any method for estimating the critical properties of titanium-containing compounds. From our experimental data, the contribution of titanium was calculated for the method by Constantinou and Gani (Constantinou, L.; Gani, R. AIChEJ. 1994, 40, 1697).