Prediction of the Critical Properties of Homologous Series

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Experimental critical properties are available, as a rule, only for the initial members of homologous series. Measuring the critical constants of heavier homologues is complicated by the progressive thermal instability of these compounds at their critical temperatures. The critical properties of heavy homologues can be estimated, in particular, with the help of extrapolation procedures. We have developed three methods of extrapolation. The first one is based on using an equation of state for a chain-molecule fluid in a self-consistent field approximation (Nikitin, E.D.; Pavlov, P.A. *High Temp*. **2000**, *38*, 690). The extrapolating equations have the form of power series in n, where n is the number of mers in a molecule. The coefficients of the equations are calculated from the experimental data. The number of terms is determined by the method of stepwise regression. We successfully used this method to describe the critical properties of many homologous series. However, it fails at the beginning of series ($n < 3 - 5$).

In the second method (Nikitin, E.D. et al. *Fluid Phase Equilib*. **2005,** *235*, 1), the extrapolating functions satisfy the following conditions: (i) are self-similar, (ii) have a simple exponential form (scaling) for long molecules ($n >> 1$). In addition, for homologous series with the same structure of mers but different end groups, these equations give equal values of the critical constants in the limit of an infinitely long chain. Equations have been obtained that allow calculating the critical temperature and pressure of any member of any homologous series with the molecule structure $R_1(CH_2)_nR_2$ if these quantities are known for one compound that belongs to this series. In the third method, artificial neural networks are used for extrapolating the critical constants of homologous series. The predictive capabilities of these three approaches are compared.