Modified Dadgostar-Shaw Predictive Correlation for Isobaric Heat Capacity of Organic Liquids

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Estimation techniques for liquid phase isobaric heat capacity of pure compounds include corresponding state and group contribution methods, and empirical correlations. These techniques require critical properties (T_c, P_c), molecular structure, or physical properties (T_b, ρ, sp gr). There are numerous industrially relevant fluids for which proposed molecular structure and critical properties remain speculative. A predictive correlation relating liquid specific heat capacity to absolute temperature and elemental composition was reported recently [1]. It retained the quadratic form of the Lee-Kesler correlation [2], but the parameters were redefined as second order power series in a similarity variable based solely on elemental composition. The resulting predictive correlation valid where the temperature dependent term (C_V) dominates, i.e. where $C_V >> T(\partial V/\partial T)_P(\partial P/\partial T)_V$ provided accurate heat capacity predictions for ill-defined fluids such as bitumen and heavy oil, in addition to reliable estimates for large pure hydrocarbon compounds, and molten polymers. In the present work, the correlation is modified to accommodate the critical region and the consequent variation of liquid phase isobaric heat capacity among isomers at the same absolute temperature. The six universal coefficients appearing in the correlation are redefined based on the heat capacities of materials with high molar mass, such as molten polymers. Deviations of low and intermediate molar mass compounds from this newly defined baseline are tracked, and a reduced temperature dependent term is introduced to accommodate the approach to critical points. The equation development is described. Results obtained for a training data set and a test data set are presented, and compared with results obtained with the unmodified correlation and Lee-Kesler correlation.

[1] N. Dadgostar, and J. M. Shaw, *Fluid Phase Equilibria,* 313 (2011) 211-226.
[2] Private Communication, B.I. Lee and M.G. Kesler, Mobil Oil Corp., Princeton, NJ (January, 1975).