The Slope of the Critical Line and Excess Properties in Liquid-Liquid Phase Transitions

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Under certain conditions, the slope of the liquid-liquid critical line $(dT/dp)_c$ is related to the excess volume v^E and the excess enthalpy h^E at the critical point through an equation first proposed by Prigogine and Defay [1]. The usefulness of this equation lies on the fact that it enables to obtain one of these three quantities (v^E, h^E, $(dT/dp)_c$) from the remaining ones. In this work, this equation was applied to binary mixtures composed by nitrobenzene or nitropropane with alkanes. To this end, h^E at the critical point were experimentally determined. From these data and literature $(dT/dp)_c$ values [2], v^E were derived. The goodness of the results thus obtained is checked against directly determined values. The results for the three properties are discussed in relation to the nature of molecular interactions in each case. Interesting behavior in mixtures containing nitrobenzene could be ascribed to antiparallel dipole-dipole orientation between nearest neighbors.

[1] I. Prigogine, R. Defay, *Chemical Thermodynamics,* Longman, London, (1954).
[2] P. Urbanowicz, S.J. Rzoska, M. Paluch, B. Sawicki, A. Szulc, Ziolo, *J. Chem. Phys.* **201**, 575 (1995).