

Corresponding-States Analysis of the Surface Tension of Simple, Polar, and Ionic Fluids

V.C. Weiss^{C,S}

School of Engineering and Science, International University Bremen, Bremen, Germany
v.weiss@theo.chemie.tu-darmstadt.de

W. Schröer

Institut fuer Anorganische und Physikalische Chemie, Universitaet Bremen, Bremen, Germany

The liquid-vapor interfacial tension of various simple, polar, and ionic fluids is studied in a corresponding-states analysis originally suggested by Guggenheim [1]. The results for real fluids are compared to the corresponding ones for model fluids of each of the three types. For simple and weakly polar fluids, the data is mapped onto a master curve, as already demonstrated by Guggenheim. For strongly dipolar, associating fluids, which also exhibit hydrogen-bonding (e.g. water), one finds deviations from this master curve at low temperatures. These associating fluids display a characteristic sigmoid behavior of the reduced surface tension as a function of temperature. A similar behavior is found from simulations [2] of an ionic model fluid, the restricted primitive model (RPM), but not (yet) from available electrolyte theories [3]. Truly exceptionally low values of the reduced surface tension are obtained for hydrogen fluoride (HF) and for the Onsager model of dipolar fluids, the surface tension of which we evaluate using an approximate hypernetted chain relation to calculate the square-gradient term in a modified van der Waals theory [4]. Remarkably, in the corresponding-states plot, the surface tensions of HF and of the Onsager model agree very closely, while being well separated from the values for the other fluids. We also study the gradual transition of a model fluid from a simple fluid to a strongly polar one by varying the relative strength of dipolar and dispersion forces, as suggested by van Leeuwen and Smit [5], and discuss the consequences for the reduced surface tension [4].

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