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THE SURFACE THERMODYNAMICS OF ALKANE +
PERFLUOROALKANE AND DIMETHYLSILOXANE +
PERFLUOROALKANE LIQUID MIXTURES

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The surface thermodynamics of alkane + perfluoroalkane liquid mixtures reflects the bulk thermodynamics of the same class of mixture. In particular, the dominating feature in both is the influence of the as-yet-unexplained anomalous weakness of the unlike interaction energy compared to that predicted by the Berthelot combining rule. The chief outcome in the bulk thermodynamics is the prevalence of large positive deviations from Raoult's law, most characteristically manifest by liquid-liquid immiscibility in almost every mixture and an abundance of positive azeotropy. In the surface thermodynamics the corresponding characteristic feature is the occurrence of large negative deviations from a simple mole-fraction weighted average surface tension which serves in the absence of a superior definition as an operational statement of surface ideality. In a number of mixtures the deviation is sufficiently extreme as to give rise to negative azeotropy or a minimum in the surface tension.

The thermodynamics of dimethylsiloxane + perfluoroalkane mixtures bears many similarities to that of alkane + perfluoroalkane mixtures. With a less full set of results we highlight the similarities and differences of the behaviour of the two series of mixtures.

We report here the surface tensions as a function of composition of a number of alkane + perfluoroalkane mixtures ranging from methane + tetrafluoromethane at 100 K to octane + octadecafluorooctane at 303 K. In the interpretation of the results we employ with varying degrees of success a variety of theories, chiefly based on the principle of corresponding states.

For those mixtures for which appropriate vapour-liquid equilibrium results have been reported we discuss the relative adsorption both in terms of intermolecular forces and the proximity of the consolute point.