217a A Hydrodynamic/Brownian Motion Model of Thermal Diffusion in Liquids

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A recently modified formulation of fluid-mechanical transport processes, which has been shown to correctly predict the thermophoretic force on a rigid isolated particle in a single-component fluid continuum (gas or liquid), is combined with steady-state Stokes-Einstein-type sedimentation-equilibrium/Boltzmann distribution-like arguments appropriate to a dilute suspension of such particles, each regarded as Brownian, so as to furnish an elementary hydrodynamic theory for thermal diffusion separation phenomena in dilute binary liquid-phase mixtures (the Ludwig/Soret effect) for the case of a disparate solute/solvent molecular size ratio. The results of the theory are shown to accord well with experiments on polymer solutions in regard to both the magnitude and algebraic sign of the Soret coefficient, as well as with respect to the effects of temperature and mixture composition on this coefficient. An extension (albeit less rigorous) of the preceding theory to the case of nondilute, thermodynamically ideal, binary solutions of miscible liquids of comparable molecular size also yields results in reasonable accord with experiments.