PHASE EQUILIBRIA PREDICTION FOR ALTERNATIVE REFRIGERANTS BY MOLECULAR SIMULATIONS BASED ON AB INITIO FORCE FIELDS

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The year 2000 has ratified the banning of ozone-damaging substances, such as fully chlorinated hydrocarbons, used as working fluids in existing refrigeration units. As a consequence, this action has uncovered new horizons for research activity in the field, looking for new alternatives. It is well known that only a few existing pure fluids can ensure performances equal or at least comparable to those of the banned substances; therefore, the main search for substitute refrigerants will be devoted to mixtures. Azeotropic mixtures, used so far as alternatives to pure components, do not possess the required flexibility to exhibit thermophysical properties at least close to those of banned substance. For this reason, zeotropic mixtures are now considered as alternative refrigerant fluids but, for these mixtures, the availability of a predictive tool for the calculation of phase equilibria is of paramount importance in the selection of the correct process fluids. However, the number of potentially useful mixtures is huge, and it would be extremely uneconomical, if not even inconceivable, to evaluate experimentally the thermodynamic properties of all possible alternatives.

In this work, we present the results of the prediction of phase equilibria of new, alternative refrigerants and their mixtures obtained from molecular simulations based on accurate *ab initio* force fields, in which the possible conformational equilibria of different conformers were taken into account. The force fields were obtained by *ab initio* calculations performed with the density functional method BLYP and the DNP basis set within the DMol^3 package. We also report, for comparison, the results obtained with a different approach, based on the application of a dielectric continuum solvation model.