The availability of accurate thermophysical data represents a limitation to the adequate design and development of separation units in chemical engineering applications. Our research activity has been focused over the last few years in the analysis of alternative separating agents in modified distillation processes. The first step towards this objective is to obtain an adequate description of the thermodynamic behavior of the mixtures involved, in order to try to obtain an insight of the effect that the added agent induces at molecular level on the studied mixture, on the basis of a group contribution approach. In this particular case, previous studies on the separation of the azeotropic binary mixture benzene + cyclohexane are now extended by considering a binary mixture as well as solvent and separation agent. With this aim the density, refractive index and sound velocity has been determined for the cited quaternary mixture over the whole composition range at 298.15 K and atmospheric pressure. Density and sound velocity were measured using an Anton Paar DSA 48 vibrating tube densimeter and sound velocity analyzer, and refractive index has been determined with an ABBEMAT-HP Dr. Kernchen automatic refractometer. Mixing properties (excess molar volume, changes on refractive index or sound velocity on mixing) have been computed from the original experimental data, and have been correlated using polynomial expressions of increasing order (binary, ternary and quaternary).