Liquid-liquid equilibrium (LLE) has an important role in the design and development of separation processes and it requires a reliable knowledge of the phase behaviour for the system in order to be separated. LLE data are also essential in theoretical studies, such as the applicability of the activity coefficient and group contribution thermodynamic models. However, the experimental values of the solubility reported in the literature frequently show discrepancies and, in addition, liquid mutual solubility data for binary systems sometimes are scarce. In this regard, we have measured the mutual solubility for different binary systems: glycerol + alkanes (pentane, hexane, heptane) and glycerol + ethyl acetate at atmospheric pressure. Also, we have determined the binodal curve for the ternary system glycerol + methanol or ethanol + ethyl acetate between 303-323 K and atmospheric pressure with the possibility of using glycerol as possible solvent in the liquid-liquid extraction of the azeotropic mixtures acetate-alcohol. Another ternary system studied is the ELL (tie-lines and the binodal curve) of the methyl oleate + ethanol + glycerol between 303-333 K and atmospheric pressure involved in the biodiesel separation. No available information was found in the literature about the liquid liquid equilibria studies in these binary and ternary mixtures. The Group Contribution with Association Equation of State (GCA-EOS) was applied to represent the phase equilibria of the binary and ternary system studied in this work. Self-association in glycerol and alcohols and cross-association with esters were taken into account.