In this study, we applied the photopyroelectric thermal-wave cavity technique with the common-mode-rejection demodulation scheme to the high-resolution measurements of thermal diffusivity and infrared emissivity of water-alcohol mixtures. The high sensitivity of the photothermal signal to the thermal diffusivity of the sample relies on the exponential decay character of the thermal-wave field at a given modulation frequency. The common-mode-rejection demodulation scheme involves the launching of two unequal duration pulses (sub-harmonics) over one modulation period. In this case, the lock-in amplifier output represents the difference between the response waves produced by each one of two pulses. This differential technique considerably increases overall measurement resolution through signal baseline suppression and detects relatively small signal variations induced by minute difference in the thermal properties of the sample. The measurements show resolution up to 0.2% v/v of alcohol in water, the highest ever reported using thermophysical techniques. A theoretical model describing conduction and radiation heat transfer in the cavity was developed and was found to be in excellent agreement with experimental data. A semi-empirical expression for thermal diffusivity as a function of mixture concentration was introduced. The expression was found to describe the data satisfactorily over the entire concentration range.