The influence of the structure of selected fatty acid esters on the pressure and temperature dependence of thermodynamic properties

mgr Monika Żarska

Summary of doctoral thesis

This work addresses several issues in the field of physical chemistry of single-component systems subjected to high pressure and temperature. Knowledge of the behavior of matter under the action of high pressure and temperature is important, both in basic research of matter, e.g. to determine the effect of the structure of the studied group of chemical compounds on thermodynamic properties, as well as in application, because pressure and temperature have a very large impact on the course of technological processes. The attached publications are devoted to studies of the pressure and temperature dependence of thermodynamic properties such as: density, isobaric heat capacity, isobaric thermal expansion, isentropic compressibility, isothermal compressibility, and internal pressure of selected fatty acid esters. A number of fatty acid esters, differing in the length of the carbon chain of the alkyl group derived from the fatty acid and the length of the carbon chain of the alkyl group derived from the alcohol, were selected for the study. The following esters were studied: methyl caprylate, ethyl caprylate, methyl caprate, ethyl caprate, butyl caprate, methyl laurate, ethyl laurate, butyl laurate, methyl myristate, ethyl myristate, isopropyl myristate, isopropyl palmitate.

Measurements of density, speed of sound, isobaric heat capacity, viscosity and surface tension as a function of temperature at atmospheric pressure were performed. Speed of sound was also measured in the temperature range from 293 to 323K and pressure up to 101 MPa. The temperature and pressure measurement range for individual esters differed due to different solidification temperatures. Using the acoustic method, the temperature and pressure dependence of density, isobaric heat capacity, isobaric thermal expansion, isothermal compressibility, isentropic compressibility, and additionally internal pressure were

determined. For methyl caprylate, methyl laurate, ethyl caprylate, ethyl laurate, butyl caprate, butyl laurate, isopropyl myristate and isopropyl palmitate, the above properties have not been studied so far. However, for methyl caprate, ethyl caprate, methyl myristate and ethyl myristate, the studies were conducted and published almost simultaneously with Daridon's group.

The obtained results allowed for the analysis of the influence of the structure of the tested esters on the temperature and pressure dependence of their thermodynamic properties.

The temperature at which the density isobars intersect at atmospheric pressure was determined for: methyl caprylate, methyl caprate and methyl myristate, which is 371.65 K; ethyl caprylate, ethyl caprate and ethyl laurate, which is 345.96; butyl caprate and butyl laurate, which is 325.15 K; isopropyl myristate and isopropyl palmitate, which is 303.15 K.

It was found that the density of esters derived from the same alcohol is almost identical at the point of intersection of its isobars and is independent of molar mass. It was observed that with increasing pressure, the point of intersection of the density isobars of a given series of esters shifts towards higher temperatures. It has been shown that the differences in the isentropic compressibility of esters derived from the same alcohol, but differing by two carbon atoms in the carbon chain of the alkyl group derived from the fatty acid, can be compensated by increasing the temperature by about 5 K in the tested pressure range.

It was observed that the isentropic compressibility of methyl caprate is almost the same as that of butyl caprate, and the isentropic compressibility of methyl laurate is almost the same as that of butyl laurate in the entire tested temperature and pressure range.

The internal pressure isotherms of the esters show a maximum in the tested temperature and pressure range. With increasing temperature, the maxima shift towards higher pressures. The pressure and temperature dependence of the internal pressure of the tested esters is most similar to that of alkanes.

Comparing the density and viscosity characteristics of methyl caprate, ethyl caprate, butyl caprate, methyl laurate, ethyl laurate, and butyl laurate in combination with low-sulfur diesel fuel called ecodiesel ultra and biodiesel consisting of rapeseed oil methyl esters, with the EN 590 standard applicable to diesel fuel and the EN 14214 standard applicable to biodiesel, it was found that they constitute a compromise between diesel fuel and biodiesel, which may

affect better lubricating properties. The obtained results indicate that, apart from composition, temperature and pressure play an important role in improving the biofuels' properties.