Summary of the dissertation

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Properties of selected ionic liquids determined based on the ultrasound absorption and speed measurements – the influence of structure, temperature and frequency

The dissertation presents the results of polythermal investigations of the properties of selected ionic liquids based on measurements of absorption and ultrasonic speed along with additional measurements of density, isobaric heat capacity, and viscosity. The research was carried out for 33 ionic liquids (32 aprotic ionic liquids and one with amphiprotic anion), in such a way that they are composed of cations and anions and to make it possible to analyze them comparatively in terms of structure. The dissertation includes an introduction, a theoretical part, a research part, discussions of results and conclusions, a bibliography, and an appendix with numerical data. The theoretical part addresses a problem of determining thermodynamic quantities using the acoustic method, such as the isentropic compressibility coefficient, isothermal compressibility coefficient, isochoric heat capacity or internal pressure, as well as the issues of measuring ultrasonic absorption in viscous media. The latter is most often associated with ultrasonic relaxation processes, a special attention has been paid to this phenomenon. In addition, the current state of research in the field of velocity and absorption of ultrasound in ionic liquids is presented. The research part describes the research techniques used (sample preparation, ultrasonic speed, and absorption, as well as density, viscosity, and isobaric heat capacity) and the conditions in which the measurements were performed. Firstly, the results of additional tests, i.e. density, dynamic viscosity, and isobaric heat capacity, were presented graphically and compared with available literature data. Afterwards, the results of acoustic tests are presented in a similar form, i.e. the speed and absorption of ultrasound, as well as the specific acoustic impedances and bulk viscosities determined on the basis of measurements. It is worth mentioning that the latter are only available through acoustic tests. Moreover, the acoustic method (based on the Newton – Laplace relationship) was used to determine and analyze thermodynamic quantities such as isentropic and isothermal compressibility coefficients, isochoric heat capacity and internal pressure. The next chapter devoted to the discussion of the results includes analyses of density, isobaric and isochoric heat capacity, isentropic and isothermal compressibility coefficients, and internal pressure in relation to the temperature and structure of the studied ionic liquids. A clear influence of the length of the alkyl substituent on the density, both in the anion

and the cation, was noticed. There is also a clear relationship between the density and the position of the alkyl substituent in the aromatic ring of the tested liquids. In general, higher density values are found in ionic liquids composed of anions and cations with a relatively high molar mass. For the ultrasonic speed, it is noticeable that lower values are also shown by ionic liquids that have relatively large molar masses. In turn, for the isobaric heat capacity, a systematic increase in this value was observed with the increase in the length of the alkyl chain in the homologous series. A similar relationship was probably demonstrated for the first time in the case of isochoric heat capacity. In the case of dynamic viscosity – ionic liquid structure relationship, it was observed that the dynamic viscosity increases with the increase in the length of the alkyl chain, either in the cation or in the anion. However, an exception from this general relationship was observed in the form of anomalous behavior for the pair of sulfonium bistriflimides. In the next stage, an attempt was made to analyze the correlation, which allows a semi-quantitative prediction of the isothermal compressibility coefficient based on the isobaric expansion coefficient. In turn, the analysis of the determined internal pressure values confirmed the reports regarding the influence of specific interactions occurring in some ionic liquids on the internal pressure. Next, through systematic comparative analysis, it was proven that in the ionic liquids tested, ultrasound absorption is correlated with dynamic viscosity, and therefore the same structural parts most likely influence both quantities. It has been shown that the absorption of ultrasound in the tested ionic liquids varies greatly – in extreme cases, the values changes up to 70-times between respective ionic liquids. Ultrasonic relaxation phenomena were observed in the frequency range 10 MHz – 270 MHz for 5 ionic liquids. Absorption spectra in this range also revealed the occurrence of dynamic viscosity (shear) relaxation, which indicates viscoelastic properties. Moreover, for one of these liquids, i.e. the ionic liquid with amphiprotic anion (1-ethyl-3-methylimidazolium hydrogen sulfate), an inversion was observed in range 125 MHz – 175 MHz for the absorption in function of frequency relationship recorded at individual temperatures. On the basis of the determined parameters of the Debye spectral function with one or two relaxation times, ultrasound velocity dispersion was determined, which allowed to assess the impact of the ultrasound velocity dispersion on the values determined by the acoustic method, and the suitability of devices for measuring speed of sound using the group method in dispersion conditions.