Calorimetry and the 3Ω Method and the Application to the Glass Transition Phenomena in 2-Butoxyethanol

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Since the reports of a new experimental technique, so-called 3-ω method, by N.O. Birge and S.R. Nagel [1], the heat capacity spectroscopy has been attracted increasing attention in the field of thermodynamic studies of glass transition phenomena especially in molecular liquids. The present authors have constructed a heat capacity spectrometer, and studied the glass transition of some molecular liquid glasses [2]. Recently, it has been extended to the thermodynamic investigation of 2-butoxyethanol isomers [3]. More recently, we modified and developed the apparatus of heat capacity spectrometer, in which the dielectric constant can be measured on the same sample, at the same time, and in the same vessel. The balance of bridge circuit is realized with compensating variable capacitor at various frequencies. The complex heat capacity, $Cp(\omega) = C'p(\omega)\ i\ C''p(\omega)$, can be measured quantitatively for an extended frequency region from 1 Hz to 5 kHz, with a platinum thin film probe, which is stable thermally and chemically against various samples. Now the precision and accuracy of the data are substantially improved. This dynamic study has been applied to the glass transition phenomena of isomeric compounds of 2-butoxyethanol (normal-, iso-, tertiary- and secondary-). For the precise analysis, the data are compared with the heat capacity obtained by adiabatic calorimetry. The results are also discussed comparing with those of molecular dynamics simulations, in which we found that properties of static hydrogen bonding and dynamical heterogeneity change around experimental melting point, and hydrogen bond dynamics of ether part is strongly related to crystallizations.

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