Measurements of the Internal Pressure of Multicomponent Systems

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In this work we directly measured internal pressure

$$(dU/dV)_T = (dP/dT)_v - P \qquad (1)$$

and isochoric heat capacity

$$C_{V} = (dU/dT)_v \qquad (2)$$

of the binary (CO_2+n-decane and H_2O+ammonia) and the quaternary mixture (water+n-octane+SDS+1-pentanol) using a high temperature and high pressure, nearly-constant-volume adiabatic calorimeter. The internal pressure and isochoric heat capacity describe the sensitivity of internal energy U to a change in specific volume V and temperature T, respectively. A high internal pressure implies strong inter-molecular cohesion. The measurements were made at isochoric heating of the system at quasi-equilibrium conditions. The rate of the temperature change was less than 5×10^{-4} K/s. The sample under study was vigorously mixed using a stirrer. The mixing was performed by rotating the calorimeter about the horizontal axis with a frequency of 1 Hz. Therefore, at these conditions, the measured quantities $(DQ/DT)_v$ and $(DP/DT)_v$ can be replaced by the partial derivatives $(dU/dT)_v$ and $(dP/dT)_v$, respectively. Thus measured values of derivatives $(dU/dT)_v$ and $(dP/dT)_v$ together with *PVT* measurement in the same experiment were used to determine the values of internal pressure and isochoric heat capacity by use of relations (1) and (2). The measurements for CO_2+n-decane and H_2O+ammonia were performed in the retrograde range. The results show that the internal pressure for these binary systems is monotonically decreasing with specific volume increase at all temperatures (isotherms) above the cricondetherm temperature. At temperatures below the cricondetherm, the internal pressure also decreases with specific volume increasing, except the points where isotherms cross the liquid-gas coexistence curve. At these points the internal pressure changes discontinuously as well as isochoric heat capacity. For the quaternary mixture (water+n-octane+SDS+1-pentanol) the measured values of the internal pressure essentially depend on the concentration of water. In the homogeneous phase for the low water concentration mixtures the internal pressure increase with temperature increasing along the isochors, while for the high water concentration mixtures the internal pressure decrease with increasing temperature. This means that in the quaternary mixture containing surfactant (dodecylsulfate, SDS) the structure of the microemulsion tends to develop associations when the water content in the mixture is increasing [1].

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[1] Kartsev V.N., Shtykov S.N., Shtykova L.S. Colloid J., 67 (2005) 479-484.