Chemical Dynamics and Critical Phenomena: Conductivity and Reactivity of Benzylbromide Near the Consolute Point of Triethylamine + Water

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The mixture triethylamine (TEA) + water has a lower consolute point at a composition of 32.27 % by mass TEA and a temperature of 291.24 K. In the mixture at its critical composition, TEA is a weak electrolyte, whose conductivity increases at a fractional rate of 6.7 %/K, reaches a maximum at the critical temperature, and then plunges for temperatures above critical at a fractional rate of -259 %/K. The drop in conductivity in the critical region is presumably an example of the phenomenon of critical slowing down. When a small amount of benzyl bromide (BB) is added to the mixture at its critical composition, the BB reacts with TEA to form benzyl triethylammonium bromide (BTAB), which is a strong electrolyte. The kinetics of this Menschutkin reaction are pseudo first order. At temperatures below critical, the temperature dependence of the rate coefficient, which governs the rate of approach to chemical equilibrium, fits an Arrhenius equation with a pre-exponential factor of 11.4 per minute and an activation energy of 34.1 kJ per mole. In the critical region, the measured rate coefficient slows down to 78 % of the Arrhenius prediction. At equilibrium, the conductivity of the reaction mixture consisting of TEA + water + BTAB + unreacted BB is a monotonically increasing function of temperature. The rate of increase of the conductivity below the critical temperature is 3.4 %/K, whereas it is 91 %/K above the critical temperature. This jump in the fractional rate of increase of the conductivity in the critical region is presumably an example of critical speeding up.