Study of the Comparative Solvation Behaviour of Na^+ and Cu^+ Cations in Acetonitrile + N,N-Dimethylformamide Mixtures at 298.15 K

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Z. Naturforsch. **59a,** 615 – 620 (2004); received April 26, 2004

Viscosity and molar conductance of Bu_4NBPh_4, Bu_4NClO_4, $[Cu(CH_3CN)_4]ClO_4$, $NaClO_4$ and $NaBPh_4$ have been measured in the concentration ranges 0.02 – 0.5 mol dm^{-3} and 0.0005 – 0.0065 mol dm^{-3} at 298.15 K in AN + DMF mixtures containing 0, 10, 20, 40, 60, 75, 80, 90, and 100 mol % DMF. The viscosity data have been analyzed by the extended form of the Jones-Dole equation in the form: $(\eta/\eta_0) = 1 + AC^{1/2} + BC + DC^2$ to evaluate B and D parameters and the conductance data by the Shedlovsky equation to evaluate Λ_o and K_A values of the salts. Ionic viscosity B–coefficients ($B_\pm$) and ionic molar conductances (λ°_i) have been calculated by using Bu_4NBPh_4 as a reference electrolyte. Solvated radii (r_i) for Na^+, Cu^+ and ClO_4^- have been estimated by using Gill's modification of Stokes' law. The variation of $B_\pm$ and r_i as a function of mol % DMF shows that both Na^+ and Cu^+ are highly solvated in AN + DMF mixtures over the entire composition region. The solvation passes through a maximum between 40 to 80 mol % DMF. Both Na^+ and Cu^+ are more strongly solvated between 40 to 80 mol % DMF. Cu^+ is relatively more strongly solvated than Na^+ in AN + DMF mixtures. ClO_4^- shows poor solvation in AN + DMF mixtures.

Key words: Viscosity B-coefficients; Solvation; Solvated radii; Na^+; Cu^+; Acetonitrile and N,N-Dimethylformamide.