

Experimental Errors in Measurements of Binary Molecular Diffusion Coefficients by the Taylor Dispersion Method

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The Taylor dispersion method has been applied to measurements of binary molecular diffusivity in liquids and supercritical fluids for more than five decades. However, the experimental uncertainties and errors that affect data accuracy need to be further addressed. In this study, the benzene-supercritical CO₂ system was investigated, and major sources of experimental errors were identified including injection volume, detector linearity, mobile phase velocity, and column orientation. Experiments were carefully designed and conducted to address these issues. A new dimensionless parameter, ϕ , defined by the ratio of the equivalent length of injection volume ($L_{e,inj}$) over column diameter (D), was proposed to characterize the combined effect of injection volume and column diameter. Various combinations of injection volumes and column diameters were examined. It was found that the measured diffusivity increased with decreasing ϕ and that near constant values were achieved at ϕ below 5. The linearity of the UV detector is crucial to the accuracy of diffusion coefficient measurements. Results showed that the best linearity resulted in maximum diffusion coefficients and that the wavelength corresponding to maximum diffusion coefficients should be selected for dispersion peak detection. The mobile phase velocity demonstrated complex effects on diffusivity measurements; accurate diffusion coefficients could be obtained only within a limited velocity range. Finally, it was found that column orientation affected diffusion coefficient measurements mainly by enhancing or weakening the buoyancy effects. When density difference was substantial and the column was installed vertically, alternate upward and downward flow along the column would significantly enhance the buoyancy effects, leading to lower measured diffusion coefficients. This study improves the Taylor dispersion technique for diffusivity measurements.