Vapor Sorption by Glassy and Rubbery Polymers Using a Quartz Crystal Balance

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Reliability of the quartz crystal balance as a technique for vapor-liquid equilibrium (VLE) measurements for concentrated polymer solutions is explored. In cases where a coated film couples inertially to the electrode of an AT cut quartz crystal driven in the thickness shear mode by an oscillator circuit, models for the crystal as a balance predict a linear relationship between the series resonant frequency shift and mass loading, for small mass loadings. For rubbery polymers and for polymers softened by the solvent at higher weight fractions, it is possible that the coupling is no longer inertial and frequency shifts could contain contributions from bulk modulus effects in addition to the mass loading effects, making the technique less suitable for polymer/solvent VLE determinations. We explore this suitability with several isothermal sorption data sets obtained using two isopiestic arrangements of the quartz balance for several glassy and rubbery polymers. Thus, results for poly(methyl-, ethyl- and butyl- methacrylates), poly(styrene) and several copolymers of these polymers were obtained at 323.15 K as examples of glassy polymers using several common organic vapors. The rubbery polymers poly(isobutylene), poly(dimethyl siloxane), poly(butadiene) and poly(epichlorohydrin) were studied at 298.15 K (which is above the glass transition temperature of all four polymers) using eight solvents for which most literature data exist, obtained using the conventional vapor pressure lowering, quartz spring balance and inverse gas chromatography techniques. Several exposures for the rubbery polymers were also studied using an impedance analyzer instead of driving the crystal with an oscillator circuit. In these cases, an electrical equivalent circuit analysis of the coated and exposed crystal was performed. Results were utilized in estimating modulus contributions to the frequency shift within reasonable theoretical models.

In cases where the frequency response is purely due to mass loading, these sorption results can be interpreted as bulk VLE data, provided they are film thickness independent to neglect interfacial effects. Results for the glassy polymers and for poly(isobutylene) appear to compare well with literature VLE data. Analysis of the experimental results for the other rubbery polymers is underway and conclusions will be presented.