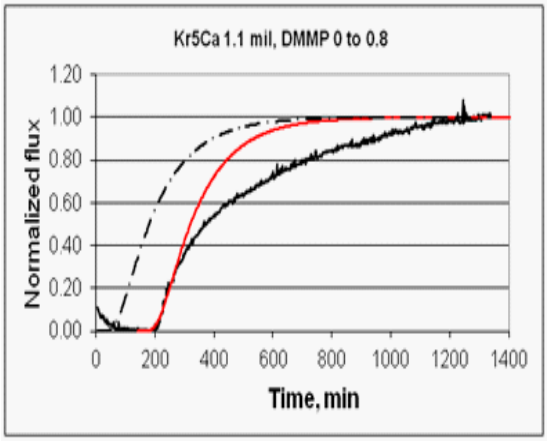
FUNDAMENTAL CHARACTERIZATION OF MEMBRANE TRANSPORT PROPERTIES



The Chemical Technology Team has an active program on characterizing the transport properties of membranes. This effort supports the development and application of membranes as barriers for toxic chemicals but which support moisture vapor transport to relieve heat stress. The goal of transport studies is to determine parameters controlling permeation kinetics, steady state permeability and stability of candidate membrane exposed to fixed concentration of challenge vapor. In some membranes, notably ionomers, there are complex interactions with dimethylmethyl phosphonate, DMMP, a commonly used Sarin stimulant. Vapor permeation testing is conducted to determine kinetics and steady state flux. Vapor sorption testing is conducted to determine solubilities. An analytical approach has been developed to characterize the contributions of diffusion constant, immobilization and relaxation to permeation kinetics and steady state permeability at selected vapor concentrations. Results have appeared in several publications on DMMP interactions with ionomers and on the effect of cation modification of ionomers.

Permeation is conducted with samples sealed in a channel type cell that provides a precisely defined exposed area. Vapor is supplied at controlled activity from a specially designed double chamber bubbler to provide a saturated bubbler which is combined with a diluents nitrogen stream set with electronic mass flow controllers. Both cell and bubbler are housed in a temperature controlled cabinet. Permeant concentration of DMMP or other organic chemicals is determined in continuous flow with a calibrated FID detector (SRI). The detector module also houses a flame photometric detector for additional sensitivity. Water concentrations are determined with an auto sampling instrument with conductivity based detector (Agilent technologies). Boundary layer corrections are applied for water vapor permeabilities.

The following chart is an example of DMMP permeation kinetics at activity 0.8 for a calcium modified pentablock sulfonate ionomer. The dashed line is the predicted Fickian curve for a diffusion constant, D = 1.0E-10 cm2/s. This corresponds to a short breakthrough time dependent only on the value of the diffusion constant. The actual breakthrough is close to 200 minutes. The analytical curve in color has to be shifted by 140 minutes to superimpose on the experimental data. The delay in onset of detectable permeation is due to immobilization of DMMP by interaction with the calcium sulfonate and the time shift is related to the extent of immobilization. The difference between the superimposed analytical curve and experiment is an indication of the effect of relaxation on the rate of approach to steady state.

Membrane solubilities are determined with a Cahn electro-balance housed in a temperature controlled cabinet. An automated sorption system operating under high vacuum, (Hiden Analytic) is also available to conduct solubility measurements with water or organic liquids. Since the system follows conditions set in a table, including the series of pressure steps, this system is especially useful for determining sorption isotherms. Vapor is supplied from a liquid reservoir at a preset series of pressures determined by a computer controlled inlet and exhaust valve. The advantage, compared to working with the Cahn electro-balance, is more precise control of vapor concentration and temperature as well as the absence of corrections for boundary layer resistance or vapor concentration changes that occur in a flow cell.

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