The Permeability of Polyethylene to Ammonia

In the course of developing a high-density polyethylene (HDPE) heat exchanger to condense ammonia vapor for an ocean thermal energy conversion system,¹ the problem of ammonia transmission through the HDPE wall to the seawater side arose. Because published data² on ammonia permeation through plastics are scarce, a new technique was developed to experimentally determine permeability coefficients.

Conventionally, gas transmission measurements are made by manometric or volumetric methods such as those described by ASTM Standard Method D 1434-66.³ In our case it was desired to make reasonably fast determinations using thick specimens (up to 0.295 cm). In view of the application, it was appropriate to have water in contact with the low-pressure side of the specimen. To accomplish these tests, the apparatus shown in Figure 1 was built. Ammonia transmission through the specimen was monitored by measuring the ammonia concentration in a known volume of water.

The apparatus consisted of a temperature-controlled cabinet enclosing a 142-mm stainless steel filter holder in which the test specimen was mounted. Anhydrous ammonia vapor (99.99% purity) was supplied to the high-pressure side of the specimen from a small cylinder placed in an external water bath which was maintained at a temperature of 298 K. The equilibrium vapor pressure⁴ in the ammonia cylinder at 298 K was 1.003×10^6 Pa. The distilled water was circulated through the low-pressure side of the membrane cell and a 500-ml flask by a seal-less, magnetically driven pump. Ammonia diffusing through the plastic specimen dissolved into the distilled water. Uniform concentration was insured by circulation of the water. Concentration measurements were made using a gas-sensing electrode and meter.

Each test was preceded by a 12-hr preconditioning period during which the apparatus, with specimen mounted, was operated without any concentration data being recorded. The purpose of this period was to allow temperatures to stabilize and establish a steady-state ammonia diffusion process. The system was then refilled with fresh distilled water from a standby flask at the same temperature, and the concentration measurements were commenced. Samples of 6 ml each were withdrawn at 30-min intervals and ammonia concentrations were measured. Typical concentrations ranged from 0.020 to 0.200 mg/l. during a test. From these concentration measurements, the total amount of ammonia transmitted through the specimen was calculated.

A series of tests was made on Soltex F364 HDPE at temperatures ranging 298-322 K in order to assess the temperature dependence of the permeability coefficient. Data for total ammonia transmission versus time are presented in Figure 2. The permeability coefficients in Table I were obtained from the slopes of Figure 2 curves, specimen area, thickness, and ammonia vapor pressure difference across the specimen. A semilog plot of permeability coefficients versus inverse absolute temperature is shown in Figure 3. From the slope of this curve, the activation energy E for the following Arrhenius equation was determined to be 35.2 kJ/mole:

$P = P_0 \exp(-E/RT)$

where P = permeability coefficient, P_0 = constant, T = absolute temperature, and R = universal gas constant.

Permeability of HDPE to Ammonia	
Temperature, K	Permeability, <u>cm³ (S.T.P.) cm</u> <u>cm² sec (cm Hg)</u>
298	$7.56 imes 10^{-10}$
305	8.86×10^{-10}
311	1.34×10^{-9}
316	1.80×10^{-9}
322	1.95×10^{-9}

TABLE I

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Fig. 1. Permeation test apparatus.



Fig. 2. Ammonia transmission through HDPE.



Fig. 3. Temperature dependence of HDPE permeability to ammonia vapor.

This technique is obviously also applicable to other highly water-soluble gases such as chlorine, fluorine, and sulfur dioxide for which electrodes or other convenient analytical methods are available.

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