NOTE

Permeation into Containers Filled with Nonideal Oil

INTRODUCTION

Questions on calculating the rate of water permeation into an exposed container are fraught with severe assumptions about the ideal natures of the participants. Early calculations by Lebovits[1,2] invoked all of the following assumptions: Fick's second law of diffusion is valid; the permeability constant is not a function of concentration; the interior is gas filled; and the driving force for the permeation is constant with time.

In 1975, Cassidy and Perry[3] dealt with the problems of undesiccated gas- and oil-filled cavities. Their approach involved approximations of the integrals involved. Thornton[4] and Smith[5] performed exact integrations of the permeation equations. However, all of these calculations for the oil-filled cavities imply an ideality with Henry's law that has not been demonstrated experimentally.

Data will be presented here on the lack of ideality of two useful fill liquids. The equations will show the effect on water permeation due solely to the nonideality.

EXPERIMENTAL

The water concentrations in the oil solutions were determined using a Fisher Scientific Co., model 392, Karl Fischer titrator. Water vapor pressure over the various solutions were measured with a Panametrics model 2000 hygrometer. Resistivity was measured with a General Radio model 1644A megohm bridge using a parallel plate electrode.

RESULTS AND DISCUSSION

The differential equation describing the permeation rate of water through an elastomer membrane is:

$$\frac{dm_A}{dt} = \frac{Q p_A^0 S}{l} (a_{A_o} - a_{A_i}) \tag{1}$$

where m_A is mass of water permeating in time t; Q is the permeability constant for the membrane; S is the area of membrane exposed; l is the thickness of the membrane; p_A^0 is the vapor pressure of pure water; and a_{A_o} and a_{A_i} are the thermodynamic activities of water outside and inside the container, respectively. Since the activity of water inside the container changes with time, integration must involve the form of this change. When water enters an oil-filled container and the oil–water phase that results obeys Henry's law for partially miscible liquids, then the activity may be expressed simply as:

$$a_{A_i} = k N_{A_i} \tag{2}$$

where k is the Henry's law constant and N_{A_i} is the mole fraction of water in the solution.

Following Smith,[5] eq. (1) proceeds most easily by differentiating eq. (2) and using the mole fraction definition to obtain the change of variable:

$$dm_A = \left[\frac{m_c M_A}{k M_c (1 - N_{A_i})^2} \right] da_{A_i} \tag{3}$$

where m_c is the mass of oil in the container, M_c is the molecular weight of the oil, and M_A is the molecular weight of the permeating component, in this case, water.

After the change of variable, the equation is integrated between the limits $a_{A_i\text{I}}$ and $a_{A_i\text{II}}$ by the method of partial fractions to give

$$t = \frac{k l M_A m_c}{Q p_A^0 S M_c (k - a_{A_o})^2} \left[-\ln\left(\frac{a_{A_o} - a_{A_i\text{II}}}{a_{A_o} - a_{A_i\text{I}}}\right) \right.$$
$$\left. - (k - a_{A_o})\left(\frac{1}{(k - a_{A_i\text{II}})} - \frac{1}{(k - a_{A_i\text{I}})}\right) + \ln\left(\frac{k - a_{A_i\text{II}}}{k - a_{A_i\text{I}}}\right) \right] \tag{4}$$
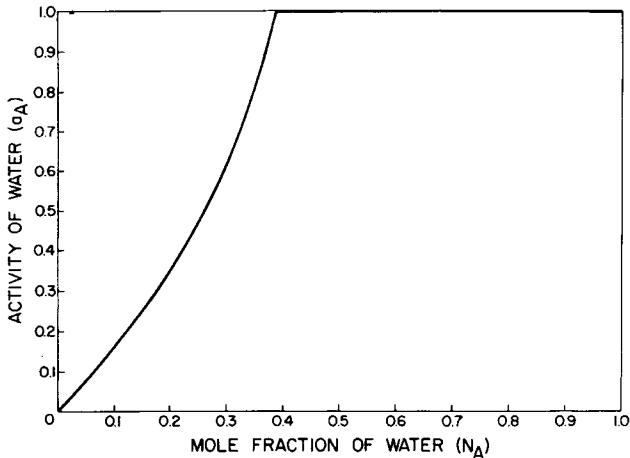
Fig. 1. Activity of PAG–water solutions.

where t is the time required for enough water to permeate through the membrane and enter into solution with the oil to change the thermodynamic activity of the oil from $a_{A_i\text{I}}$ to $a_{A_i\text{II}}$.

However, as might be expected from molecular considerations, the activity of water (as component A) in oil–water mixtures is not necessarily linear with concentration. Recent work at this laboratory[6] has shown that over the narrow region of mutual solubility, water and poly(propylene oxide) butylether (Union Carbide's UCON LB135Y23—hereinafter called PAG) exhibit a negative deviation from Henry's law. These data are presented as Figure 1. Other data show that castor oil–water solutions exhibit a complex, positive deviation from Henry's law. These data are shown in Figure 2. The form of the positive or negative deviation is complex and not mathematically tractable. However, the deviation may be approximately represented by a parabolic equation of this form:

$$a_A = kN_A - k'N_A^2 \tag{5}$$

where k and k' are now the first and second virial, Henry's law constants. These constants may be selected to closely approximate the form of the experimental curves. The presence of the second-order term complicates the mathematics in this case. However, after substituting eq. (5) into eq. (1), the following change of variables permits integration:

$$dm_A = \frac{M_A m_c}{M_c} \left(\frac{2k'}{2k' - k + \sqrt{k^2 - 4k' a_{A_i}}} \right)^2 \left(\frac{da_{A_i}}{\sqrt{k^2 - 4k' a_{A_i}}} \right) \tag{6}$$
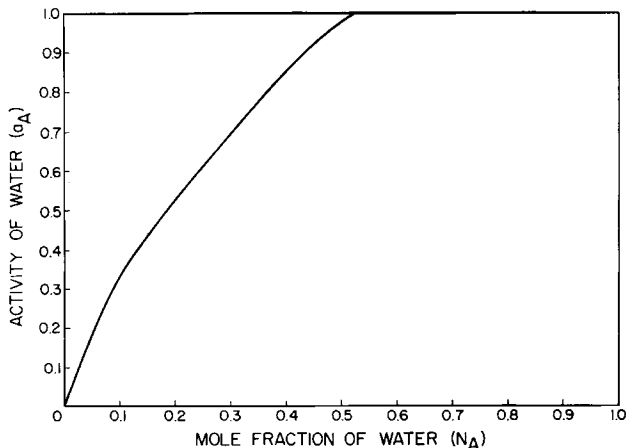

Fig. 2. Activity of castor oil–water solutions.

Integration proceeds by substitution and partial fractions to ultimately yield, between the limits a_{A_iI} and a_{A_iII}:

$$t = \frac{-8k'^2R}{(\beta^2 + \alpha_o^2) - 4\alpha_o^2\beta^2} \left[2\beta\ln\left(\frac{\beta + \alpha_{iII}}{\beta + \alpha_{iI}}\right) + (\alpha_o^2 - \beta)\left(\frac{1}{\beta + \alpha_{iII}} - \frac{1}{\beta + \alpha_{iI}}\right) \right.$$

$$\left. \beta\ln\left(\frac{a_{A_o} - a_{A_iII}}{a_{A_o} - a_{A_iI}}\right) + \left(\frac{\beta^2 + \alpha_o^2}{2\alpha_o}\right)\ln\frac{(\alpha_o - \alpha_{iII})\,(\alpha_o - \alpha_{iI})}{(\alpha_o + \alpha_{iII})\,(\alpha_o - \alpha_{iI})} \right] \quad (7)$$

Where, for simplicity

$$R = \frac{lM_A m_c}{Qp_A^0 S} \quad (8)$$

$$\alpha_o = (k^2 - 4k'a_{A_o})^{1/2} \quad (9)$$

$$\alpha_{iI} = (k^2 - 4'a_{A_iI})^{1/2} \quad (10)$$

$$\alpha_{iII} = (k^2 - 4k'a_{A_iII})^{1/2} \quad (11)$$

and

$$\beta = 2k' - k \quad (12)$$

Interpretation of these results is facilitated by observing them graphically. Figure 3, curve B, shows a plot of eq. (4) using the conditions shown in Table I. These conditions were chosen as representative of an underwater application. Curve A in Figure 3 shows the variation of mole fraction of water with time for a fill liquid that exhibits negative deviation from Henry's law (i.e., has a negative value for k', the second virial coefficient). Curve C in Figure 3 shows the variation of mole fraction of water with time for a material that exhibits positive deviation from Henry's law. The values for Henry's law coefficient(s) for each of these curves were chosen to give a saturation limit of $N_A = 0.38$ (approximately true for both PAG and castor oil). This simplifies comparison of the effect of deviation from ideality.

The results given in Figure 3 might be predicted qualitatively from a cursory examination of eq. (1). That is, negative deviation from Henry's law, as shown in curve A, causes a faster increase in water content than ideality (curve B), which in turn is faster than positive deviation (curve C).

The approach to saturation is asymptotic for all three cases. A useful way of quantitatively comparing these curves is by observing the time necessary to reach a water content such that a small temperature variation will cause a second phase to form. In the case of PAG, measurements indicate that water will form a second phase at $N_{H_2O} = 0.34$ at 15°C, a 5°C decrease. The time to $N_{H_2O} = 0.34$ at 20°C is 12,000 hr for a sample ideal with Henry's law and with the same solubility limits as
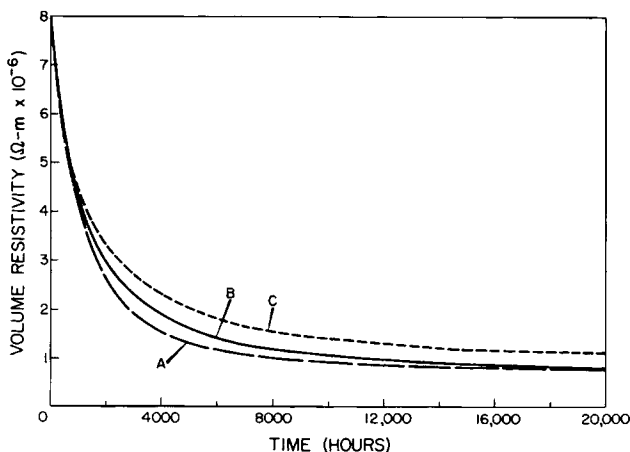

Fig. 3. Mole fraction of water in an oil-filled container as a function of time. Curve A, negative deviation from Henry's law; curve B, obeys Henry's law; curve C, positive deviation from Henry's law.
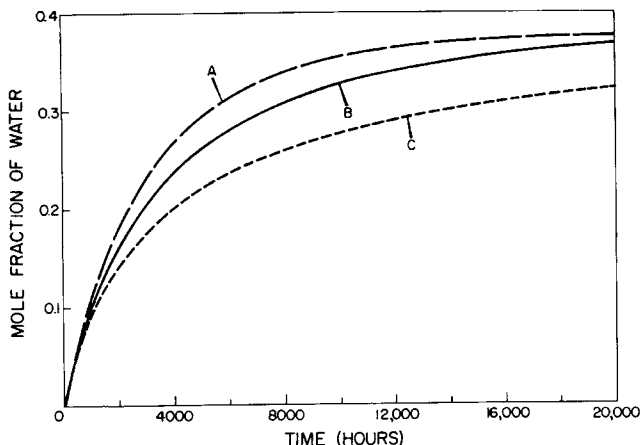
Fig. 4. Volume electrical resistivity of oil as a function of time.   Curve A, effect of negative deviation of the oil from Henry's law; curve B, obeys Henry's law; curve C, positive deviation from Henry's law.

PAG.   Negative deviation from Henry's law causes this time to decrease to 8000 hr. Positive deviation causes the time to increase to 28,000 hr.

Another way of looking at the effect of water permeating through the membrane is to observe the effect of the water on the useful properties of the oil.   Figure 4 is a plot of the volume resistivities of the oils as a function of time for the same conditions as in Figure 3.   Volume resistivities for this figure were calculated from the relationship

$$\rho = 7.8 \times 10^6 \exp(-6.1 N_A) \tag{13}$$

where ρ is the volume electrical resistivity of the oil in ohm·meters and N_A is the mole fraction of water.   This equation was derived from experimental data relating resistivity and water content of PAG.

It can be seen that the time for the oil with positive deviation from Henry's law (curve C) to reach a given resistivity value is longer than the oil that follows Henry's law (curve B), which is in turn longer than the oil exhibiting negative deviation from Henry's law (curve A).   For example, if a volume resistivity value of $1.30 \times 10^6 \Omega$·m should cause a critical property to become unacceptable, the material with positive deviation will reach this point in 12,800 hr; the material linear with Henry's law will reach this point in 7,000 hr, and the material showing negative deviation will reach this point in 5,000 hr.

TABLE I
Conditions Used to Calculate Times for Figures 3 and 4

$a_{A_o} = 1.0$

$a_{A_iI} = 0.0$

$t = 0.238$ cm

$M_A = 18.01$ g/mol

$m_c = 167.8$

$Q = 2.16 \times 10^{-8}$ g cm/cm^2 hr torr[a]

$P_a = 17.5$ torr

$M_c = 600$ g/mol

$S = 290.7$ cm^2

$k = 0.542,\ k' = -5.50$ (curve A)

$k = 2.633,\ k' = 0$ (curve B)

$k = 4.722,\ k' = 5.50$ (curve C)

[a] New value measured at NRL–USRD for a neoprene window material

CONCLUSION

The extent to which a fill liquid obeys Henry's law is an important parameter in considering whether that oil is suitable for filling permeable containers used under water or in humid air. This property should rank along with water solubility, volume resistivity, and material compatibility as criteria for judging the usefulness of a fill liquid.

References

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