FIG. 4. Dependence of the inverse strain-rate sensitivity m on strain at several pressures. Elongation $= \Delta L/L_0$.

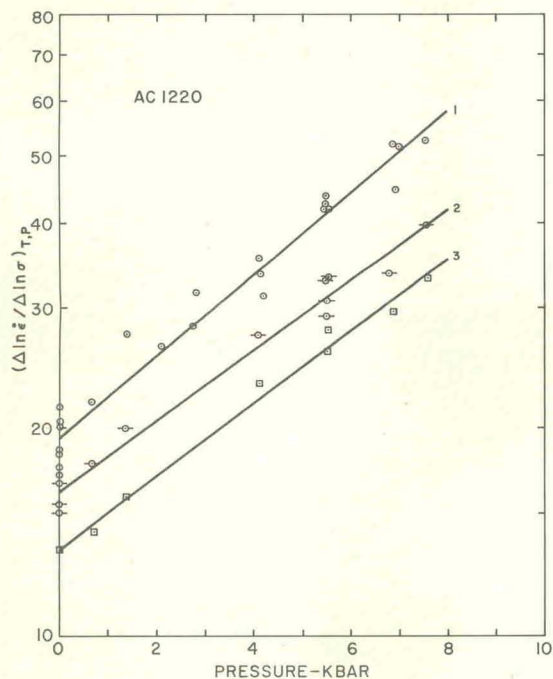

FIG. 6. Influence of pressure on the partial derivative $(\partial \ln \sigma/\partial P)_T$. The dashed curve shown for comparison is derived from the solid curve in Fig. 3.

FIG. 5. Dependence of m on pressure at several strains, corresponding approximately to $\epsilon = \Delta L/L_0 = 0.3$, 0.65, and 1.25 for curves 1, 2 and 3, respectively.
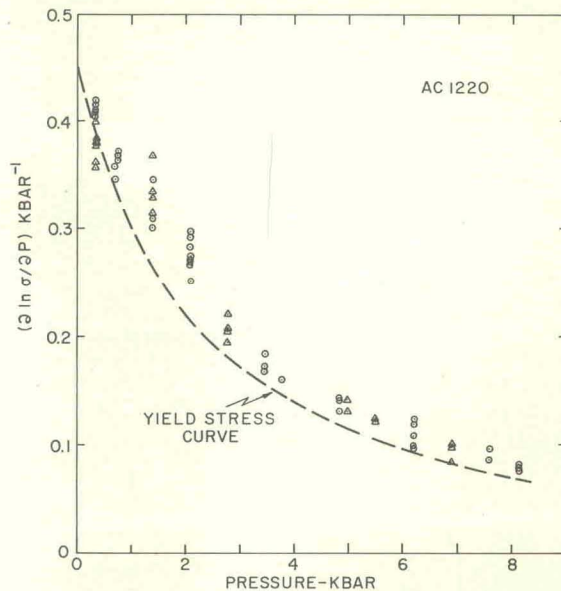
is bracketed by most of the data. (As above, we recognize that fixed ϵ is not necessarily fixed structure.) The result is shown in Fig. 8, where the error bars ($\sim \pm 6\%$) represent our estimate of the total uncertainty arising in the experiments. Within the accuracy of the data one may approximate the decrease of V^* at low pressure as being linear; at high pressure, V^* appears to change very little with pressure. For specimens deformed in water V^* decreases from about 266 Å^3 at 1 atm to about 135 Å^3 at 8 kbar; the initial rate of decrease is ~ -27 Å^3/kbar. For samples tested in pentane the initial rate of decrease is smaller (~ -19 Å^3/kbar) and the value of V^* is reduced at lower pressures (~ 230 Å^3 at 1 atm as opposed to 266 Å^3). At 0.35 kbar this difference arises because both m and $\partial \ln \sigma/\partial P$ are smaller (see Figs. 4 and 6); at 1.4 and 2.78 kbar it appears that the difference lies mainly in m. At any rate it is evident that pentane absoprtion causes a significant change of V^* at low pressure. If Fig. 8 were plotted for a different value of strain, the slope would decrease slightly with increasing strain, e.g., at $\epsilon = 2$, V^* would be ~ 250 Å^3 at 1 atm in water. As V^* in pentane seems to be somewhat less strain dependent, the results for pentane and water would be less divergent at high strains.

DISCUSSION

As is noted above, because deformation is a kinetic process, the appropriate measure of the pressure dependence of plastic flow is the activation
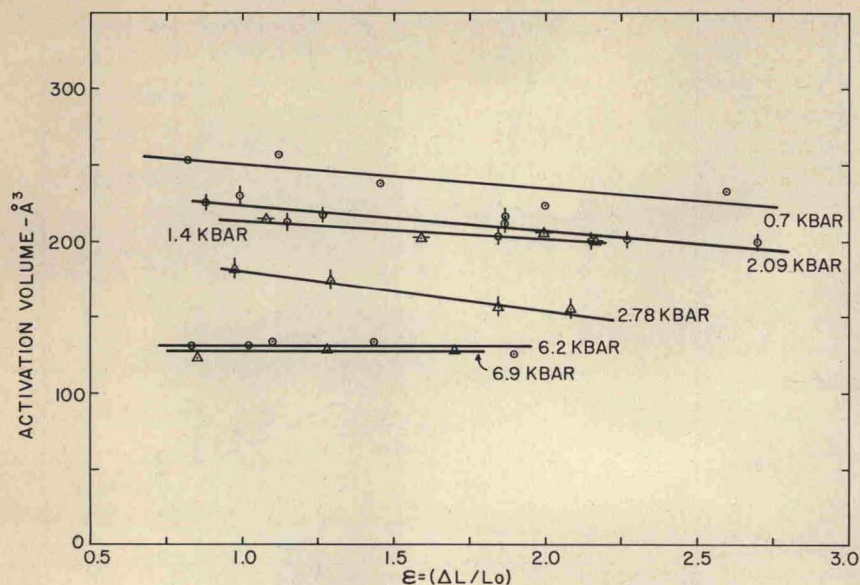
FIG. 7. Change of activation volume with strain for samples tested in water at 0.7, 2.09, and 6.2 kbar (circles) and for samples tested in pentane at 1.4, 2.78, and 6.9 kbar (triangles).

volume V^*. Here we find for high-molecular-weight PE (AC 1220) that V^* is ~ 266 Å^3 at 1 atm. As expected, this value is considerably greater than is found, for example, for creep in metals where V^* is of the order of 10–50 Å^3, i.e., of the order of the atomic volume.[12] We also find (Fig. 8) that V^* decreases with pressure. Examining the parameters which determine V^* [Eq. (4)] we note that $(\partial \ln\sigma/\partial P)_{T,P}$ decreases by a factor of ~ 5 over the pressure range 1 atm to 8 kbar (Fig. 6); over the same range m increases to ~ 2.5 times its 1-atm value (Fig. 5). Hence V^* de-

creases by a factor of ~ 2. For the case of a creep test [Eq. (2)] where the stress is held constant, one could assign this decrease in volume entirely to the increased pressure. In the present case, however, σ increases with P and hence one must examine the relationship between the change of V^* with P at constant stress and at constant strain rate. This is given by

$$\left(\frac{\partial V}{\partial P}\right)_\sigma = \left(\frac{\partial V}{\partial P}\right)_\epsilon - \left(\frac{\partial V}{\partial \sigma}\right)_P \left(\frac{\partial \sigma}{\partial P}\right)_\epsilon . \qquad (5)$$
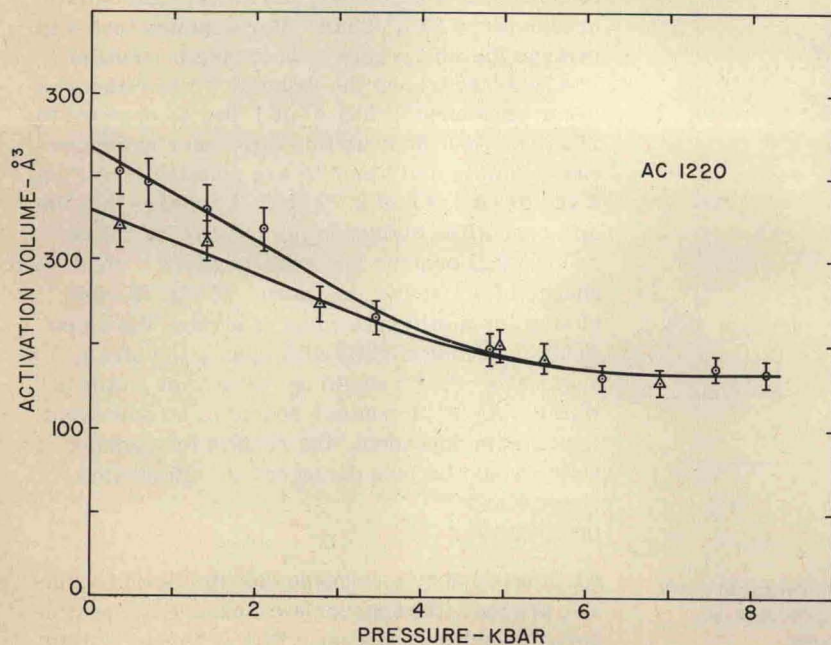
For convenience the last term in Eq. (5) may be

FIG. 8. The activation volume as a function of pressure for samples tested in water (circles) and pentane (triangles) at $\epsilon \simeq 1.25$.