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A General Empirical Relationship between Tracer or Self-Diffusion Coefficients of Liquids and Pressure

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In the course of recent work on tracer diffusion of HTO and carbon-14 labelled CH_3CN, in $H_2O + CH_3CN$ mixtures under pressure, it was found to be useful to represent the variation of diffusion coefficients with pressure (at constant temperature) in such a way as to facilitate comparison of the diffusion behavior of the mixtures. Testing a variety of analytical relationships between D and P has led to the discovery of a simple relationship which linearises D,P data over wide pressure ranges, and which holds at widely differing temperatures. The relationship has been tested for a considerable number of tracer and self-diffusion coefficients as a function of pressure and in all but a few cases (noted below), and except for pressures close to normal atmospheric pressure, it represents experimental data to within the probable limits of uncertainty of the data.

The relationship has the simple form

$$\ln D = a + b\, P^{0.75} \qquad (1)$$

and is potentially useful in engineering situations because it allows prediction, to within the uncertainty of the experimental data, of diffusion coefficients at high pressures from as few as two values at lower pressures. A limitation of this relationship is that in many cases it overestimates values of D at pressures near 0.1 MPa. However, since diffusion coefficients are more readily available at 0.1 MPa then at high pressures, the applicability of the relationship at high pressure is an advantage which outweighs the disadvantage of inapplicability at low pressure. Furthermore, the discrepancy between experimental and predicted diffusion coefficients at or near normal atmospheric pressure decreases with increasing temperature.

The recently determined self-diffusion coefficient data for n-hexane (Harris, 1982) provide a stringent test for Eq. 1 because the data have relatively high precision ($\pm 1.5\%$), and they are available up to high pressures (maximum 393.8 MPa) and cover a wide temperature range (from 223.15 to 333.15 K). The data for three
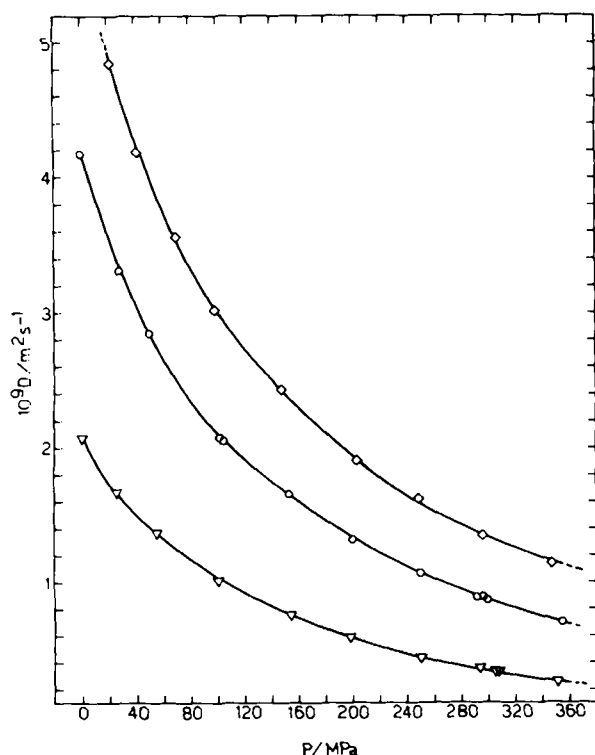

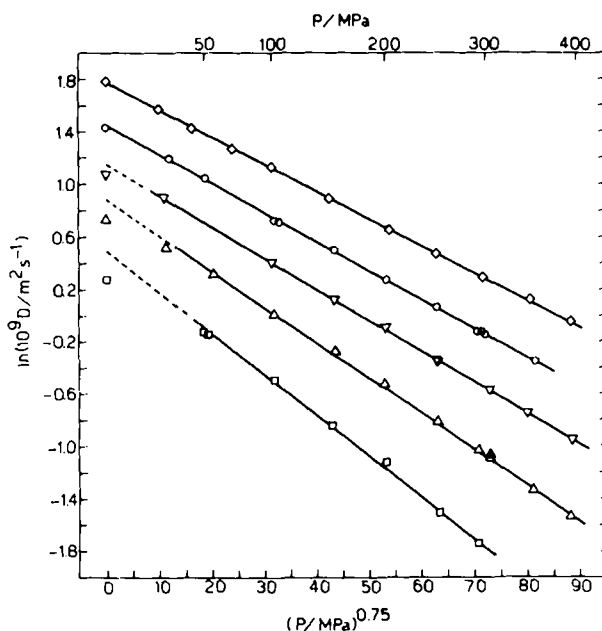**Figure 1. The variation with pressure of the self-diffusion coefficient for n-hexane. $\Diamond$, 333.15 K; $\bigcirc$, 298.15 K; $\triangledown$, 248.15 K.**

Figure 2. Fit of Eq. 1 to self-diffusion data for n-hexane. $\Diamond$, 333.15 K; $\bigcirc$, 298.15 K; $\triangledown$, 273.15 K; $\triangle$, 248.15 K; $\square$, 223.15 K.

TABLE 1. FIT OF SELF-DIFFUSION DATA FOR n-HEXANE TO EQ. 1

T/K	a^1	b^1	σ^2	Range[3]
223.15	0.4622	−0.0308	2.0	48.7–292.3
248.15	0.8968	−0.0273	1.9	55.7–391.2
273.15	1.1763	−0.0241	0.4	25.0–393.8
298.15	1.4513	−0.0221	0.9	0.1–353.5
333.15	1.7746	−0.0206	0.9	0.1–392.4

[1] Values obtained by expressing $\ln (10^9 D/m^2 \cdot s^{-1})$ as a linear function of (P/MPa).
[2] Mean deviation (%) of experimental points from values calculated from equations to the lines of best fit.
[3] Lowest experimental pressure (MPa) for which D is predicted within experimental uncertainty by Eq. 1, and highest experimental pressure.

temperatures are plotted in Figure 1. The variation of D with P for n-hexane is typical normal liquid behavior. The slopes of the curves decrease considerably with increasing pressure, particularly at elevated temperatures. Clearly the pressure dependence of D is so strong that if data were available up to only 200 MPa, for example, it would be difficult to reliably extrapolate the curves to much higher pressures. The data at each temperature could no doubt be fitted to functions such as polynomials in P for extrapolation purposes, but (depending on the order of the polynomial) a considerable number of data points may be required, so that polynomials have limited value as predictive functions. Fits of the n-hexane data to Eq. 1 are shown in Figure 2, which demonstrates that apart from the low pressure (<50 MPa) region at low temperatures, the plots are linear up to the highest pressures attained in the measurements. The best-fit parameters of Eq. 1 are listed in Table 1. The estimated accuracy of the experimental data is ±2.5%, so that for each temperature the mean deviation is smaller than the uncertainty in individual data points. Since Eq. 1 has only two adjustable parameters, as few as two experimental diffusion coefficients at pressures above say 50 MPa are adequate to make good estimates of D at other pressures.

The general applicability of Eq. 1 suggests that it can serve also as a useful criterion of normal liquid behavior. The relationship does not hold for tracer and self-diffusion coefficients of water. However, the variation of D with P for water is abnormal in that with increasing pressure D first increases, then subsequently decreases (Woolf, 1975; Woolf and Harris, 1980). Work in progress on tracer diffusion of methanol has revealed a similar anomaly at low temperature. At higher temperature the diffusion of methanol in water approaches normal liquid behavior.

NOTATION

D = self-diffusion or tracer diffusion coefficient, $m^2 \cdot s^{-1}$
P = pressure, MPa

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Reconstruction of Oil Saturation Distribution Histories During Immiscible Liquid-Liquid Displacement by Computer-Assisted Tomography

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INTRODUCTION

Characterization of the fluid mechanics of immiscible displacement of one liquid phase by another in porous media in connection with oil recovery processes requires knowledge of the time history of the intramedia spatial distribution of each phase.

Such distributions in optically dense media are difficult to obtain because of the inaccessibility to traditional measurement probes.

Several methods have been used, however, to study flow behavior in such systems. Fluid solidification by polymerization with subsequent sectioning has detailed the final fluid distribution. Microwave attenuation (Parsons, 1975) and conductivity measurements (Leverett, 1939) give area-average fluid saturations. Measurements of the distribution of a radionuclide tracer using a