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A Method of Estimating Self-Diffusion Coefficients in Liquids

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An empirical relationship has been developed which is useful for the estimation of the self-diffusion coefficient of liquids. The relationship is given by

$$D_{11} = \frac{4.5 \times 10^{-9}(V^* - v)T}{\eta V^{*4/3}} \quad (1)$$

where D_{11} is the self-diffusion coefficient in the units of square centimeter per second, V^* and v are the molar volumes at the critical temperature and temperature T (in degrees Kelvin), respectively, and η is the viscosity at the temperature T expressed in poise.

A test of this equation is shown in Figure 1, where V^* on the ordinate is plotted against the quantity $D_{11}\eta/T(V^* - v)$ on the abscissa for a remarkably diverse set of liquids. It is noteworthy that V^* varies over five orders of magnitude, while the other variable covers a range of seven orders of magnitude (D_{11} varies by nine orders of magnitude and η varies by about eight orders of magnitude). The slope and intercept of the line depicted in the figure provide the value of the constant 4.5×10^{-9} and of the exponent 4/3 associated with V^* as given by Equation (1).

THE DATA

The filled points represent data which are directly identified in the figure, while the unfilled points represent data for low molecular weight organic liquids; requisite data, that is, D_{11}, η, V^*, and v, at various temperatures were obtained from Dullien (1972) and Reid et al. (1977).

The data on the liquid metals shown as the labeled filled points were obtained as follows. Values of D_{11} were taken from Nachtrieb (1967) and Breitling and Eyring (1972). Values of η and v were obtained from Miller (1952). Data for D_{11}, η, and v for thallium and η for indium were obtained from Cahill and Grosse (1965); V^* values for liquid metals were obtained from a compilation of McGongal (1962) or were estimated from liquid density measurements.

Data for the high molecular weight liquids also shown as the labeled filled points were obtained as follows. D_{11} data for polyethylene from McCall et al. (1959) and all other D_{11} values from Skewis (1966). v values were estimated from the reported polymer densities (Van Krevelen, 1976). The appropriate viscosity data for butyl rubber, SBR, and EPR were estimated using procedures detailed by Van Krevelen (1976) because data at the same temperatures at which D_{11} were measured could not be found in the literature. η for natural rubber was obtained from a plot of bulk viscosity vs. molecular weight given by Holden (1965). η for polyethylene was obtained from a plot of viscosity-molecular weight data given in Doolittle (1952) and in Mendelson et al. (1970).

For these high molecular weight liquids, we used the viscosity values which do not include the chain entanglement contribution (Van Krevelen, 1976). In general, the viscosity of a homologous family of liquids depends on the molecular weight M according to $\log \eta = a + \log M$, where a is a constant for a given series; at a particular value of M, the dependence changes to $\text{long}\ \eta = A + 3.4 \log M$. This stronger dependence of η on M is attributed to mechanical entanglements between adjacent molecules which serve to reduce flow. For bulk flow of high molecular weight liquids, this entanglement phenomenon must be taken into account when viscosity is considered. However, for the very long time scales involved in diffusion phenomenon, entanglements should not play a role. Hence, the viscosity appropriate to diffusion was estimated for each polymer by extrapolating the bulk viscosity-molecular weight data for low molecular weight homologues whose entanglements are absent to higher molecular weight. This procedure provides values of η which are free of mechanical entanglement contributions.

Critical volumes for the polymers were obtained using an estimation method described by Fedors (1978). Estimates of V^* using alternative methods described in Reid et al. (1977) yielded similar numbers.

CONCLUSIONS

The data of Figure 1 demonstrate that Equation (1) is suitable for estimating self-diffusion coefficients for a very wide range of liquids. For organic liquids, the calculated and measured coefficients differ on the average by about 4%, with methanol and ethanol as two exceptions. However, if it is assumed that in these two liquids diffusion involves dimers, then these data also fall into their proper place. For the liquid metals, the average difference in calculated and measured diffusion coefficients is somewhat higher but well within the errors or spread in values associated with obtaining the experimental values. The high molecular weight liquids show the largest deviation from the prediction of Equation (1), and this is attributable to the uncertainties in the experimentally measured coefficients which are only of the order of 10^{-13} to 10^{-14} cm^2/s. Such small coefficients are very difficult to measure precisely. However, even with this difficulty in mind, D_{11} values estimated via Equation (1) are within a factor of two or three of the experimentally measured values. It is also significant that the data for the long chain high molecular weight liquids follow the same relationship which obtains for low molecular weight liquids; the polymeric nature of a liquid does not confer special properties to the self-diffusion coefficient.

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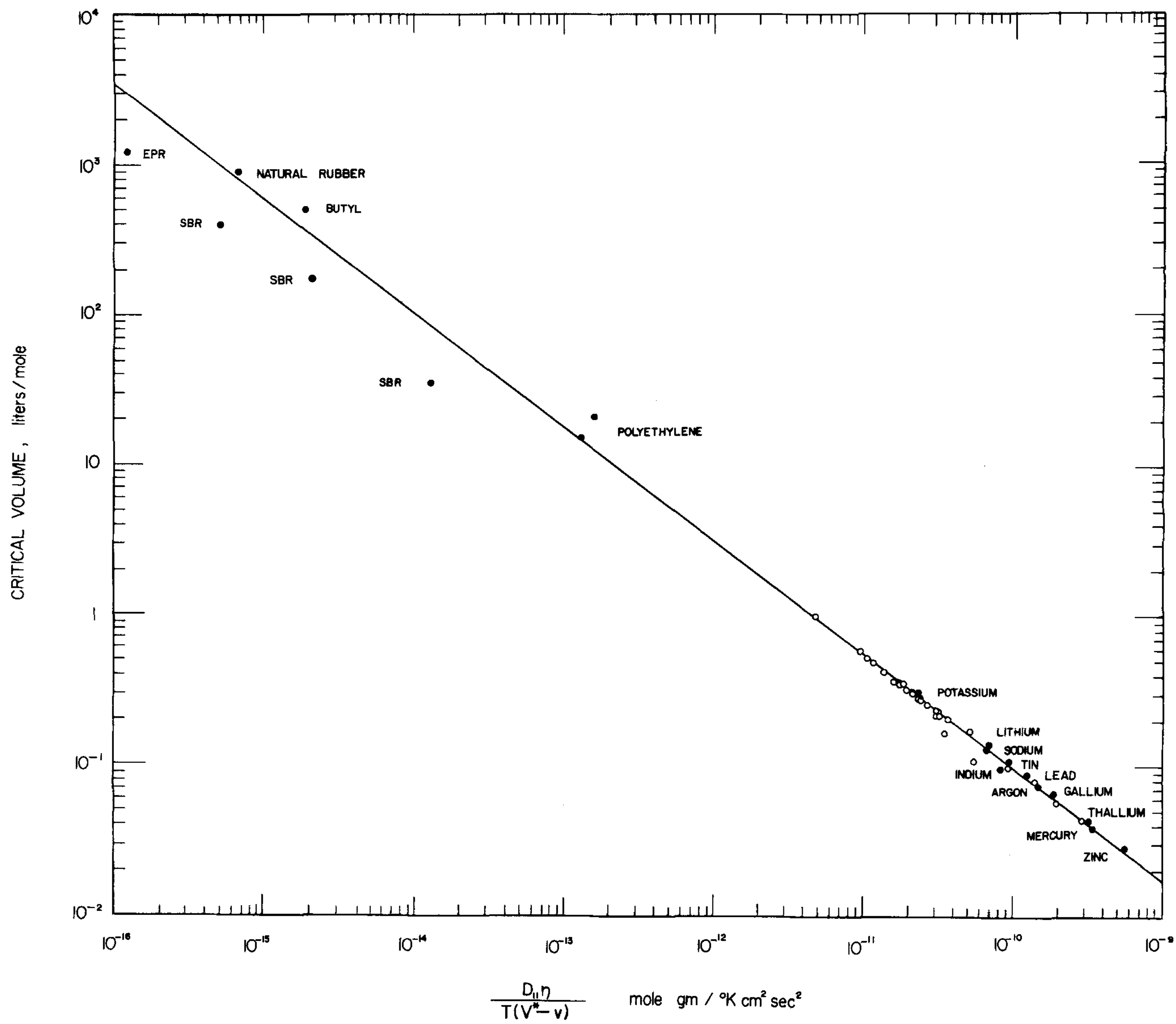

Fig. 1. Dependence of the volume of the critical temperature with the reduced variable $D_{11}\eta/T(V^* - v)$ for liquids.

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