



FIG. 2. Absolute viscosity versus  $F(v) = [(v_0/v)^4 - (v_0/v)^2]$  for PSU 18, 19, 25, and 111 at 37.8°C and PSU 19 at 98.9°C. The first cycle is 10–100 cp for the PSU 111 curve and is 1–10 cp for all other curves.

equation is known to describe the viscosity variation with temperature over short temperature ranges.  $A$  and  $B$  in Eq. (7) are parameters characteristic of the liquid and both are functions of the specific volume. Letting the subscript null refer to atmospheric pressure and assuming constant temperature, Eq. (7) leads to the

relationship

$$\log(\eta/\eta_0) = (B - B_0)/(2.303RT), \quad (8)$$

when  $\eta$  and  $B$  refer to values at elevated pressures, the variation of  $A$  with pressure having been neglected. It is necessary to seek a suitable form for expressing  $B$  as a function of the specific volume or the pressure. Among the several approximation functions tried, the best results were obtained by assuming

$$B(v) = b/v^4 - a/v^2 \quad (9)$$

and

$$b = av_0^2. \quad (10)$$

The form of (9) was suggested from the Lennard-Jones intermolecular potential function  $\phi = C_1 r^{-6} + C_2 r^{-12}$ .<sup>25</sup> It can be objected this function is valid only for spherical molecules but it has been successfully extrapolated in other instances.<sup>18,19</sup> With the use of (9) and (10) Eq. (8) becomes

$$\log(\eta/\eta_0) = (K/T) [(v_0^4/v^4) - (v_0^2/v^2)]. \quad (11)$$

To test the agreement of Eq. (11) with the data, curves were plotted on  $\log \eta$  versus  $[(v_0^4/v^4) - (v_0^2/v^2)] \equiv F(v)$ .

Figures 1 and 2 show the agreement between the resulting Eq. (11) and the experimental viscosities. In terms of viscosity the points for each of the three nonaromatic hydrocarbons, PSU 19, PSU 25, and PSU 111, at 37.8° and 98.9°C fall on straight lines with an average deviation of 2% and a maximum deviation of 8%, but PSU 18, the compound containing two phenyl groups, exhibits a definite curvature which is greater at the higher temperature. Evidently the stronger forces existing between aromatic molecules require a more exact expression than the form of the expression (9), or the Lennard-Jones function, to describe their variation with intermolecular distance.

<sup>25</sup> J. E. Lennard-Jones, Proc. Roy. Soc. (London) A106, 46 (1924).

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