Freezing Pressures, $p$, $V$, $T$, and Self-Diffusion Data at 298 and 313 K and Pressures up to 300 MPa for 1,3,5-Trimethylbenzene

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Measurements are reported for the melting point of 1,3,5-trimethylbenzene at pressures up to 345 MPa. Self-diffusion coefficients and $p$, $V$, $T$ data have been obtained at 298 and 313 K for pressures up to 280 MPa. Isothermal compressibilities have been calculated from the $p$, $V$, $T$ results. The freezing pressures at 0.1 MPa correspond to previously reported values for modification III of trimethylbenzene. Equivalent hard-sphere diameters estimated from the melting point and $p$, $V$, $T$ data are used to apply the rough hard-spheres theory to the self-diffusion data; the calculations indicate that there is random packing of the particles.

KEY WORDS: freezing pressure; high pressure; isothermal compressibility; $p$, $V$, $T$ data; self-diffusion; 1,3,5-trimethylbenzene.

1. INTRODUCTION

The measurement and interpretation of tracer and self-diffusion coefficients for liquids have been the subject of a number of communications from this laboratory. The application of hard-spheres theory for liquid-state transport properties to experimentally determined transport (particularly diffusion) data has been of considerable interest both in this laboratory and elsewhere.

As has been noted in recent papers [1, 2], the rough hard-spheres (RHS) theory due to Chandler [3], in conjunction with molecular dynamics (MD) simulation results, provides a very useful theoretical basis...
for interpretation of the density dependence of diffusion coefficients. Our recent applications of the RHS theory have differed in one important respect from Chandler's original treatment, in that we have chosen to remove some arbitrariness from the selection of numerical values for equivalent hard-sphere diameters, \( \sigma \), by estimating \( \sigma \) for pure liquid from experimental data which have been determined independently of diffusion data. This has been done by calculating \( \sigma \) from liquid densities at the freezing pressure, at the temperatures of interest. This approach has been used for methane, carbon tetrachloride, benzene, octamethylocyclotetrasiloxane, and water in particular: for several other liquids the required freezing pressure and/or \( p, V, T \) data are not available at the temperatures at which diffusion coefficients have been measured.

The present study is an extension of our previous work to a liquid (1,3,5-trimethylbenzene) with roughly spherical molecules and easily attainable freezing pressures in the temperature range for which we are able to determine conveniently \( p, V, T \) data and self-diffusion coefficients as a function of pressure.

2. EXPERIMENTAL

The 1,3,5-trimethylbenzene (mesitylene) was Fluka "puriss"-grade material which was dried with molecular sieve prior to fractional distillation under reduced pressure.

The melting point was measured for 16 pressures at approximately 20-MPa steps in the range 0.1 to about 345 MPa, using the differential thermal analysis (DTA) technique which has been described previously [4]. Melting points were determined with an accuracy of \( \pm 0.2 \) K using a calibrated copper-constantan thermocouple, and pressures were determined to \( \pm 0.1 \) MPa using a 400-MPa Heise bourdon tube gauge which had been calibrated against a deadweight tester.

Volume ratios, \( k \), defined by

\[
k = \frac{V_p}{V_o}
\]

where \( V_p \) and \( V_o \) are volumes at 0.1 MPa and pressure \( p \), respectively, were determined at pressures from about 2.5 to about 280 MPa using the bellows volumometer whose construction, calibration, and operation have been previously described [5, 6]. Temperatures were controlled to within \( \pm 0.005 \) K and measured to \( \pm 0.01 \) K using a calibrated platinum resistance thermometer. Above 25 MPa pressures were measured with an uncertainty of \( \pm 0.1 \) MPa with a calibrated 400-MPa Heise gauge. In the 0- to 25-MPa region a calibrated 25-MPa gauge was used, with an accuracy of