



FIG. 3.  $g\mu_0^2/K$  as a function of temperature at various pressures for *sec*-butanol.  $K = 1.68^2$ .  $\circ = 1$  atm;  $\bullet = 0.5$  kbar;  $\ominus = 1$  kbar;  $\oplus = 1.5$  kbar;  $\otimes = 2$  kbar;  $\times = 3$  kbar;  $\bullet = 4$  kbar.

### DISCUSSION

The quantity  $g\mu_0^2/K$  was calculated as a function of temperature and pressure for *n*-propanol, *sec*-butanol, and 6-methyl-3-heptanol from our experimental results. For propanol and *sec*-butanol, the densities were estimated from Bridgman's<sup>11</sup> data by linear extrapolation: Bridgman's 1-kbar data for *n*-propanol at 30° and 75°C extrapolate to Gilchrist's<sup>9</sup> values at low temperatures and we assumed that similar extrapolations would work at higher pressures. Furthermore, we used Bridgman's isobutanol density data since his and our own experience has shown that alcohol isomers have nearly the same compressibility and temperature coefficient of density. The constant  $K$  was chosen to equal  $\mu_0^2$ , using 1.68 D as the best estimate of  $\mu_0$  for aliphatic alcohols. Thus, if  $\mu_0$  were constant, the curves show the variation of  $g$ . The results of these calculations are shown in Figs. 1-3.

Our results for *n*-propanol are that  $\partial(\mu_0^2g)/\partial P < 0$  over the entire range of temperature and pressure, but it appears that the pressure dependence would change sign at higher temperatures. In the vicinity of room temperature, *n*-propanol and methanol (insert to Fig. 2) are similar, as are most of the lower aliphatic primary alcohols. It was this sort of behavior that prompted Jacobs and Lawson to suggest that  $\partial\mu_0/\partial P < 0$ .

For 6-methyl-3-heptanol, the pressure dependence is just the inverse of that of propanol: at all temperatures and pressures  $\partial(\mu_0^2g)/\partial P > 0$  but it appears

that the derivative would change sign if we could extend our measurements to lower temperatures and/or higher pressures. These results are qualitatively similar to those already reported<sup>10</sup> for other octanol isomers.

On the basis of our previous work, it had become apparent that  $\partial(\mu_0^2g)/\partial P$  was greatest for those alcohols whose -OH group was relatively hindered by being situated near the middle of the alkyl group and by being surrounded by (branch) methyl groups, viz., 5-methyl- or 2-methyl-3-heptanol. For these compounds, the Kirkwood correlation factor is close to unity at room temperature and atmospheric pressure. We propose that under such circumstances, the predominant effect of increasing pressure is to favor intermolecular association via hydrogen bonding to form chain *n*-mers. At first the average correlation factor increases rapidly as the degree of association increases, but  $g$  approaches an asymptotic<sup>14</sup> value for infinitely long chains. Thus, once the chains have attained a moderate size, further chainwise association will not be reflected in the correlation factor. It is with the onset of this size that  $\partial(g\mu_0^2)/\partial P$  appears to change sign, the exact temperature and pressure of sign reversal depending in a sensitive manner on the geometry of the alcohol monomer.

In order to test this idea we wanted to investigate a liquid whose correlation factor was close to unity near its normal boiling point and which reached its asymptotic value (at 1 atm) at not too low a temperature for our high-pressure equipment. A perusal of some of our previous results<sup>7</sup> indicated that *sec*-butanol should be suitable, and the results illustrated in Fig. 3 show this indeed to be true. For this compound we are able to measure the reversal of sign of  $\partial(g\mu_0^2)/\partial P$  hinted at in the propanol and octanol results.

It is clear from these results that there are at least two pressure-dependent processes involved in determining  $\partial(g\mu_0^2)/\partial P$  and we suggest that at relatively high temperatures and low pressures, where chain association is small, the principal contribution comes from an increase of the correlation factor with increasing pressure due to enhanced chain association.

What then is the cause for the reversal of sign of  $\partial(g\mu_0^2)/\partial P$  at relatively low temperatures and high pressures? In order to test whether the dipole moment does change with pressure, we determined the dipole moment of several polar solutes in dilute *n*-hexane solution. The dielectric constant data were analyzed according to the simplified Guggenheim method according to Smith.<sup>15</sup> Unlike the procedure used in evaluating  $g$  from Eq. (1), it is now no longer adequate to consider the molar refraction to be independent of pressure. The experimentally determined

<sup>14</sup> G. Oster and J. G. Kirkwood, *J. Chem. Phys.* **11**, 175 (1943); C. Brot, *Ann. Phys. (Paris)* **2**, 714 (1957).

<sup>15</sup> J. W. Smith, *Trans. Faraday Soc.* **46**, 394 (1950).

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