

by about 8 ml, i.e., by  $\sim 10\%$  of its molar volume. Our data, given in table 3, show that the volume of THF decreases by about  $10\%$  at 2000 atm.

Inspection of fig. 4 reveals that the plot of  $\log K$  against  $P$  for sodium fluorenyl in THF is curved;  $\Delta V$  is, therefore, a function of pressure, slightly decreasing with its increase. The observed curvature seems to be real, although the deviations from linearity are within the experimental uncertainties. The decrease of  $\Delta V$  with pressure

TABLE 3.—COMPRESSION OF THF AT  $\sim 22^\circ\text{C}$

$P$ , atm	% volume compression	relative O.D. ( $\lambda_{\max}$ tight)+ O.D. ( $\lambda_{\max}$ loose) corrected for the compression
1	0.0	1.00
940	6.2	1.11
1920	10.1	1.20
2920	12.8	1.34
3900	15.1	1.47
4900	extr. $\sim 17.4$	$\sim 1.58$

might be expected—the compression of solvent molecules around the ions being less significant, as the bulk of the liquid is compressed. The curvature could not be observed for the lithium salt because the relevant  $K$  could not be accurately determined at higher pressures.

Finally, we note the substantial increase of the linear extinction coefficients of the ion-pairs at higher pressures. The data collected in table 3 show that the sum of the optical densities at both  $\lambda_{\max}$  increases by about  $60\%$  (after being corrected for the volume contraction) as the pressure rises from 1 to about 5000 atm. The partial destruction of fluorenyl carbanions by glycerol, which leaked at higher pressures into the cell, makes the determination of the pressure dependence of the O.D. difficult. We believe that the leakage was negligible in expt. 2 given in table 1, and, at lower pressures, in expt. 2 and 3 given in table 2. Apparently, the absorption curves become sharper at higher pressure, presumably because the rotation and the soft vibrations of the pairs are impeded by the compression of the solvent.

#### APPENDIX

The equilibrium constants  $K$  are calculated from the experimentally determined  $R$  in conjunction with the auxiliary constants  $r_1$  and  $r_2$ . Fortunately, the numerical values of  $K$  are not greatly affected by the values of  $r_1$  and  $r_2$  if  $R$  is substantially greater than  $r_1$  and smaller than  $1/r_2$ . The most reliable values of  $K$  are obtained in this range of  $R$ , e.g., in the experiments involving sodium fluorenyl (see table 1).

Under conditions when both types of pairs co-exist, the  $r_1$  and  $r_2$  values cannot be obtained directly. Our choice may be criticised, e.g., one may argue that  $r_1$  and  $r_2$  decrease with pressure because the absorption curves become sharper. However, at increasing pressure the absorption peaks come closer together and this should increase the  $r_1$  and  $r_2$  values. It seems, therefore, that the assumption of constant, pressure-independent  $r_1$  and  $r_2$  may be valid.

Unfortunately, previous workers did not give their procedure to determine  $r_1$  and  $r_2$  and their temperature dependence. In a private communication<sup>6</sup> they confirmed our claims, i.e., at  $25^\circ\text{C}$  and 1 atm pressure both ion-pairs have the same extinction coefficients,  $r_1 = 0.24$  for the sodium salt and 0.11 (compared with our 0.10) for the lithium salt. They found, however, that on lowering the temperature  $\epsilon_{\text{loose}}/\epsilon_{\text{tight}}$  increases and  $r_1$  and  $r_2$  decrease, the latter diminishing more than the former. These conclusions were obtained from studies of the caesium salt in THF (only tight pairs are present in such a solution) and the lithium salt in DME (only loose pairs appear in the latter system). It is assumed then that the numerical results apply to the investigated systems—a plausible but not necessarily a correct procedure.

In spite of these difficulties, extrapolation to 1 atm gives a value of  $K$  for sodium fluorenyl at  $\sim 25^\circ\text{C}$  which is identical with that obtained by extrapolation to  $25^\circ\text{C}$ , of the previously reported data<sup>1</sup> pertaining to lower temperatures (i.e.,  $K_{25^\circ, 1\text{atm}} \sim 0.058$ ). Some discrepancy is found, however, for the lithium salt (our  $K = 2.7$ , reported 4.6).

The equation for  $K$  is modified if  $\epsilon_{\text{loose}}/\epsilon_{\text{tight}} \neq 1$ . Denoting this ratio by  $\gamma$  we find

$$K = (R - r_1)/(\gamma - Rr_2).$$

It is possible that our  $r_2$  is too small, because it was determined from the spectrum of lithium fluorenyl recorded at the highest pressure. This may account for our low value of  $K$  for the lithium salt at 1 atm. At higher pressures the error is probably partly compensated by  $\gamma$  being larger than 1.

Finally, we have checked that any reasonable changes of  $r_1$  and  $r_2$  have negligible effect upon the final values of  $\Delta V$  for the sodium salt, although the results obtained for the lithium salt are less certain.

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