# Volume Change during the Solvent Separation of a Tight Ion Pair in a Solvent of Low Dielectric Constant[1]

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It is well known[2] that ionization in solution (unlike homolytic fission) is characterized by a volume decrease ($-\Delta V$). This decrease is largely the result of the polarization and attraction of surrounding solvent molecules by the ions (electrostriction). In ionic equilibria, $\Delta V$ can be determined from density measurements extrapolated to infinite dilution if stable solutions of the ions and of the neutral species are available; alternatively, it can be calculated from the effect of pressure on the equilibrium constant *via* the relation $\Delta V = -RT\,\partial \ln K/\partial p$. Both methods have been used for a number of weak acids in water; $\Delta V$ is generally found to be $-10$ to $-15$ cm³/mol, which corresponds to an increase in $K$ by roughly 50% for every thousand atmospheres. The dissociation of some ion pairs in water has also been studied at high pressure; the $\Delta V$ values for the $MnSO_4$ and $MgSO_4$ pairs are both about $-7$ cm³/mol.[3] Similar considerations govern the volume changes that accompany the partial ionization accomplished as the transition state is reached in solvolytic processes; one is then dependent on the effect of pressure on the rate constant and the relation $\Delta V^* = -RT\,\partial \ln k/\partial p$. For Sn1 hydrolysis, $-\Delta V^*$ is usually somewhat smaller than the $(-\Delta V)$ values characterizing weak acids since the ionization is incomplete.

The electrostriction phenomenon is described in a first approximation by the Drude–Nernst equation $\Delta V = -(q^2/2rD^2)\partial D/\partial p$. Both the $q$ (charge) and $r$ (radius) dependences of $\Delta V$ have been confirmed at least qualitatively; little is known, however, about solvent effects ($D$ is the dielectric constant). Solvolysis reactions generally seem to be accelerated more by pressure if they are carried out in solvents such as alcohol or aqueous acetone than in pure water, but there is no confirmation of the very large pressure effects to be expected for ionization in nonpolar solvents. We report here the effect of pressure on the solvent separation of the tight fluorene–lithium ion pairs in tetrahydrofuran. This process has been found by Hogen-Esch and Smid[4] to be accompanied by characteristic spectral changes. We use the apparatus shown in Figure 1, so designed because of the great sensitivity of these solutions to the atmosphere. Lithium (0.1 g) and mercury (4 g) are introduced into A and fluorene (15 mg) into B; the openings are sealed and the apparatus is evacuated. The mercury is warmed slightly until amalgation occurs. THF (10 ml) is distilled from potassium into B and the solution is allowed to flow into A by tilting; remaining traces of fluorene can be transferred by distilling a little THF back to B. After 24 hr a few drops of the solution in A are allowed to flow into B; this solution is then diluted by distilling all the solvent into B. The pale yellow color indicates whether the concentration is in the proper range. The apparatus is then tilted in the opposite direction to allow the solution to flow into C. Some nitrogen is then admitted to force the solution into the Pyrex cell D (0.5-cm path). The apparatus is then tilted such that the mercury in the cell covers the sealed-in platinum tube (0.5-mm diameter; length is 2 mm inside the cell,

**Table I:** Effect of Pressure on the Ion Pair Equilibrium of Fluorene–Lithium in THF at 25.0 ± 0.1°

| $P$, bars | OD at 373 nm | OD at 349 nm | $K$[a] |
|---|---|---|---|
| 1 | 1.07 | 0.705 | 2.51 |
| 36 | 1.08 | 0.703 | 2.70 |
| 70 | 1.09 | 0.702 | 2.92 |
| 104 | 1.10 | 0.700 | 3.00 |
| 139 | 1.14 | 0.700 | 3.55 |
| 277 | 1.135 | 0.683 | 3.90 |
| 415 | 1.185 | 0.682 | 5.06 |
| 553 | 1.235 | 0.683 | 7.00 |
| 691 | 1.28 | 0.680 | 9.41 |
| 966 | 1.39 | 0.700 | >10 |

[a] Calculated on the basis of ratios of $\epsilon_{373}/\epsilon_{349}$ of 2.05 and 0.178 for the solvent-separated and tight ion pairs, respectively (Figure 5, ref 4); it can readily be shown that the observed ratio is a linear function of the mole fraction of one of the ion pairs if Beer's law is obeyed by both and if both species have the same $\epsilon$ at one of the two wavelengths used (note that the OD at 349 nm is constant within 2–3% of all pressures).

(1) Paper XX in the series, "Chemical Reactions Under High Pressure."

(2) W. J. le Noble, *Progr. Phys. Org. Chem.*, **5**, 207 (1967), and reviews quoted there.

(3) F. M. Fisher and D. F. Davis, *J. Phys. Chem.*, **69**, 2595 (1965).

(4) T. E. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, **88**, 307 (1966).

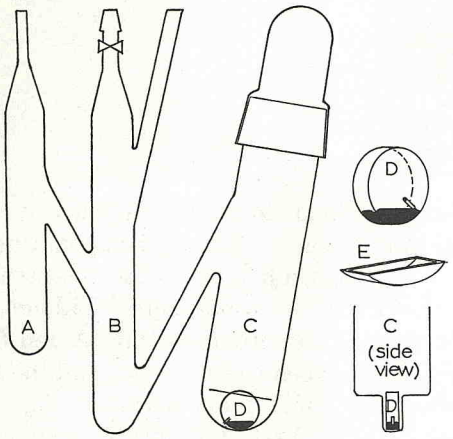


Figure 1. Apparatus for preparing and transferring THF solutions of fluorene–lithium ion pair to the high-pressure absorption cell.

0.5 mm outside); the cell can then be removed and placed in the stainless steel recepticle E, which contains a few drops of mercury and has a small indentation in the bottom to fit the platinum protrusion. The cell is washed with THF, warmed briefly with a hairdryer to expel any trace of gas remaining in the platinum tube, and entered into the cylindrical cavity of the Aminco high-pressure absorption cell. The platinum tube is wetted by the mercury; without it, oxygen apparently diffuses into the cell through the THF film between the Pyrex and the mercury.

We find that even a pressure of 1 kbar reversibly converts virtually the entire solute into solvent-separated ion pairs, and calculate $\Delta V$ to be $-35 \pm 5$ cm$^3$/mol (Table I). This value—for the mere insertion of a solvent molecule—is huge even when compared to the complete ionization of most neutral species in water. If we assume $\Delta V$ for the complete dissociation in water of a monovalent ion pair to be about $-2$ cm$^3$/mol (one quarter that of the bivalent pairs of $MnSO_4$ and $MgSO_4$), we find that the volume change in THF is about twenty times as large; this difference is undoubtedly due to the greater compressibility and less rapid attenuation of electrostatic forces in low $D$ solvents. Knowledge of these results should enable one to test mechanisms of reactions involving ions postulated for such media.

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