coordinate with the counterion (*i.e.*, $-\Delta H_i°$ large), the Arrhenius plot will behave as depicted in curve A, Figure 11. In less polar solvents, or when large counterions are involved (*e.g.*, Cs^+), the exothermicity of solvent-separated ion-pair formation is too low to cause the ΔE_{app} to assume a negative value (curve B).

The presence of two propagating ion pairs will tend to broaden the molecular weight distribution of the resulting polymer. This phenomenon has previously been observed when free ions are present.[42] When caused by two different ion pairs, however, the broadening cannot be eliminated by salt addition. The broadening itself will depend on the rate of solvent exchange, and would become important in cases where the carbanion tends to coordinate rather strongly with an added component of the solvent medium.

Finally, we would like to point out that formation of solvent-separated ion pairs (and free ions) will make anionic copolymerization studies rather complicated. The two propagating carbanions will contain different fractions of solvent-separated ion pairs, and the copolymer composition will therefore be a sensitive function of solvent composition, counterion, and temperature. It seems to us not realistic at this stage to attempt to develop a coherent mechanism for anionic copolymerization as has recently been proposed.[43] The number of propagating species can be numerous (solvated and nonsolvated contact ion pairs, associated ion pairs, solvent-separated ion pairs, triple ions,[44] free ions, etc.), while association between the ion pairs of the two propagating carbanions[45] may be a serious problem. The situation would be even more complex in mixtures of solvents. The conditions under which these species are stable, and their individual reactivities still need continued investigation, and any copolymer mechanism which could explain the behavior of a particular system may completely fail when conditions are changed.

Acknowledgment. We wish to thank Dr. Michael Szwarc for his encouragement and helpful discussions. We gratefully acknowledge the support of this investigation by the National Science Foundation and the Research Corporation.

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(42) G. Löhr and G. V. Schulz, *Makromol. Chem.*, 77, 240 (1964).

(43) K. O'Driscoll and R. Patsiga, *J. Polymer Sci.* A3, 1037 (1965).

(44) D. N. Bhattacharyya, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, 86, 5024 (1964).

(45) R. Lipman, J. Jagur-Grodzinski, and M. Swarc, *ibid.*, 87, 3005 (1965).

Studies of Contact and Solvent-Separated Ion Pairs of Carbanions. II. Conductivities and Thermodynamics of Dissociation of Fluorenyllithium, -sodium, and -cesium

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Abstract: The conductance behavior of the lithium, sodium, and cesium salts of the fluorenyl carbanion has been studied in tetrahydrofuran over a temperature range of +25 to −70°. The dissociation constants have been calculated from the slopes of the plots of the Fuoss conductance equation for associated electrolytes. The dissociation of the cesium salt can be described by the "sphere in continuum" model, the center-to-center distance between the ions being 3.76 Å., leading to an electrostatic radius of 2.1 Å. for the fluorenyl carbanion. The data for the lithium and sodium salts clearly reveal the presence of two ion pairs, *viz.*, contact and solvent-separated ion pairs for which spectrophotometric evidence was given in the preceding paper. The dissociation of the solvent-separated ion pairs is fairly well represented by the sphere in continuum model. At −70°, an interionic distance of 6.3 Å. is found for the lithium salt and 7 Å. for the sodium salt. The conventional model, however, is completely inadequate to describe the dissociation of the respective contact ion pairs, due to strong specific solvation of the cation. The enthalpy of dissociation for the contact ion pair of the sodium salt at 25° is found to be −9.5 kcal./mole, or about 7.5 kcal. lower than for the solvent-separated ion pair. The entropy of dissociation at this temperature is −60 e.u., or about 30 e.u. lower than for the solvent-separated ion pair.

In the preceding paper[2a] evidence was presented supporting the existence of two chemically distinct ion pairs in solutions of carbanions and radical ions. The contact and solvent-separated ion pairs were shown to exhibit different absorption maxima. The relative amounts of the two species were found to depend on the type of carbanion, the counterion, the nature of the solvent, and the temperature. In ethereal solvents, the ion pairs are dissociated into free ions to such an extent that reasonably accurate conductivity data can be obtained, allowing us to calculate the dissociation constants of free ion formation. The two kinds of ion pairs obviously have different interionic distances and solvation states. Hence, one may expect substantial differences both in the absolute values of the dissociation constants and their temperature dependence. In this paper we report the results of conductivity studies of lithium, sodium, and cesium fluorenyls carried out in tetrahydrofuran in the temperature range 25

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(1) To whom correspondence should be addressed.

(2) (a) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, 88, 307 (1966); (b) T. E. Hogen-Esch and J. Smid, *ibid.*, 87, 669 (1965).

to $-70°$. The data can be interpreted in terms of the two kinds of ion pairs and permit us to discuss the thermodynamics of ion-pair formation.

Experimental Section

The preparation of the fluorenyl salts has been described in the preceding paper.[2a] Conductivities of these salts were measured in THF at temperatures ranging from 25 to $-70°$. A Leeds and Northrup a.c. conductance bridge operating at 1000 c.p.s. was used for these studies. A General Radio Corp. tuned amplifier and null detector was used as a balance instrument. The basic features of this bridge have been described by Edelson and Fuoss.[3]

High-vacuum conductivity cells (volume about 40 to 60 cc.) with flat platinum electrodes were used. The cell constants were found to be 0.00925 and 0.0229 cm.$^{-1}$. It was established that the change in cell constant over the 100° temperature range was less than 2%. At very low salt concentrations it was necessary to use a calibrated 10^5-ohm resistance parallel with the cell. To increase the accuracy of the temperature measurements, a copper-constantan thermocouple was sealed in the cell with the metal junction located in a thin glass bead about 2 mm. from the platinum electrodes. The cell was immersed in a thermostated dewar bath containing isooctane cooled by Dry Ice. A small heater of about 10 w. completed the bath.

A full description of the conductivity apparatus has recently been published.[4] In addition to the conductivity cell, three quartz optical cells of varying path length were connected to the all-glass apparatus to measure spectrophotometrically the fluorenyl salt concentration. The apparatus first was thoroughly purged with a fluorenyl solution, and the solvent of this solution then was used to dilute a more concentrated fluorenyl solution on which the actual measurements were carried out. Conductivities were measured between 10^{-4} and 5×10^{-6} M salt concentration. The apparatus was constructed in such a way that the concentration could be changed by transferring part of the solution to a side tube and distilling the solvent back to the remaining solution (see ref. 4 for further details).

The following procedure was used for measuring the conductivities at various temperatures. Starting with a concentration of approximately 10^{-4} M (measured spectrophotometrically), the solution was cooled to $-70°$ by placing the conductivity cell in the isooctane–Dry Ice bath. After reaching thermal equilibrium, the temperature inside the cell was recorded by means of the thermocouple, and the cell resistance was measured. The temperature then was raised about 10° by turning on the heater for a few minutes. After thermal equilibrium was re-established, the temperature and resistance again were recorded. This process was repeated about every 10° until room temperature was reached, after which the concentration of the salt was measured once again. The two concentration determinations agreed within 1%, indicating very little deterioration of the salt solution during this procedure. By means of the dilution method described above, a solution of lower salt concentration then was prepared and the same series of measurements was made, starting at -70 up to 25°. This was repeated for about four to six different concentrations. For every concentration, a plot of resistance *vs.* temperature was made. To obtain the conductance data of the salt as a function of its concentration at one particular temperature, the interpolated resistance values at -70, -60, -50, etc., up to $+25°$ were determined from these plots. The set of data thus obtained were then fed into an IBM 1622 computer to calculate the variables of the Fuoss conductance equation. In addition to temperature, resistance, and concentration, one must know the density, viscosity, and dielectric constant of THF at the various temperatures. Viscosities were measured in an Ubbelohde viscometer calibrated at 25° with solvents of known viscosity. The density of THF was measured accurately at 25°, and the contraction of a known volume then was measured at various temperatures in a pycnometer. Dielectric constants were obtained by measuring the capacity between the platinum electrodes of a conductivity cell of low cell constant filled with pure THF, using isooctane–Dry Ice as a cooling mixture. A Q meter was used in the measurements and corrections were made for the capacities of the lead wires. The cell was calibrated at 25° using solvents of known dielectric constant. The accuracy of the dielectric constant measurements was about 1%, which is sufficient for our purpose.

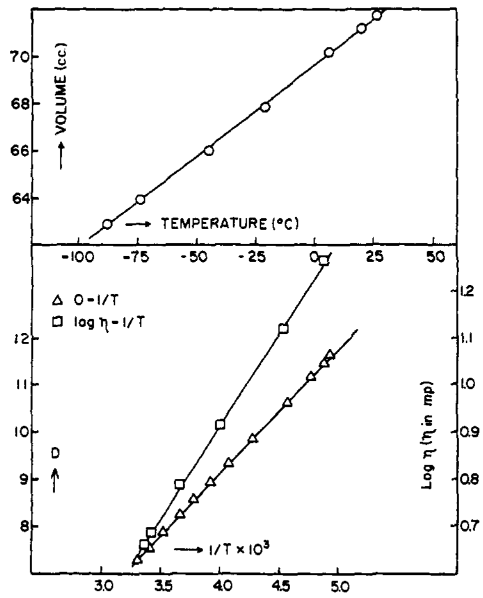

Figure 1. Temperature dependence of density, viscosity, and dielectric constant of tetrahydrofuran.

Results

The data obtained for the densities, viscosities, and dielectric constants of THF over the temperature range of 25 down to $-70°$ are shown graphically in Figure 1. In all three cases, linear relationships were obtained, and the following equations were found to describe the temperature dependence of these physical properties

$$d_t = 0.880[1 + 0.001085(25 - t)]$$

$$\log \eta_T = -0.655 + 393/T$$

$$D_T = -1.49 + 2660/T$$

where d_t denotes the density in g./cc. at $t°$, η_T the viscosity in millipoises at T°K., and D_T the dielectric constant at T°K. These equations were employed in the calculation of the dissociation constants.

A typical plot of resistance *vs.* temperature for two concentrations of F^-,Na^+ is shown in Figure 2. On lowering the temperature, the ionic mobility is decreased due to the enhanced viscosity, but this is more than compensated by the exothermicity of the dissociation process. At very low temperatures the exothermicity decreases considerably, leading to the observed minima in the R *vs.* T plots. For the lithium and cesium salts no such minima were observed due to the lower exothermicity of the dissociation process over the whole temperature range, as will be apparent from the discussion.

To apply the Fuoss conductance equation,[5] $F/\Lambda = 1/\Lambda_0 + f^2C\Lambda/FK\Lambda_0^2$, one must have a means of estimating the limiting conductance Λ_0 with a reasonable degree of accuracy. A visual extrapolation of a Λ–$\sqrt{C}$ curve to zero concentration is not possible in our case, since the low degree of dissociation leads to an inaccurate steep extrapolation. The Λ_0 values at 25° therefore were estimated in the following way. The

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(3) D. Edelson and R. M. Fuoss, *J. Chem. Educ.*, **27**, 610 (1950).

(4) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 612 (1965).

(5) F. Accascina and R. M. Fuoss, "Electrolytic Conductance," John Wiley and Sons, Inc., New York, N. Y., 1959.

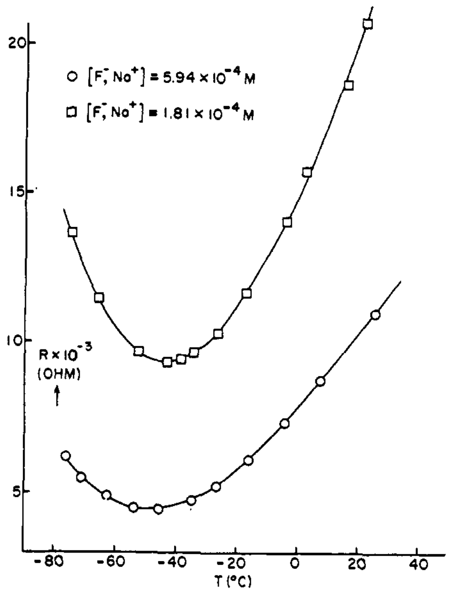

Figure 2. Change of resistance with temperature for a THF solution of fluorenylsodium.

limiting conductances for the Li, Na, and Cs ions in THF at 25° have been reported[6] to be 36.6, 48.2, and 68.4, respectively. A value of about 50 for the fluorenyl ion would seem reasonable in view of the values obtained for aromatic radical ions in the same solvent.[7] We therefore have taken $\Lambda_0(F^-,Na^+) = 100$, making λ_0^- for the fluorenyl carbanion equal to 51.8. However, even if this estimate would be wrong by 20%, which is unlikely, this would mean an error of about 10% in the over-all Λ_0. Since this is a systematic error, it would only affect the absolute values of the equilibrium constants calculated from the Fuoss plots, but would have little effect on their relative ratios.

Taking $\Lambda_0(F^-,Na^+) = 100$, one calculates $\Lambda_0(F^-,Li^+) = 88.4$ and $\Lambda_0(F^-,Cs^+) = 120$. The Walden rule, stating that the product $\Lambda_0\eta$ is a constant, was then applied to determine the Λ_0 values for these salts at other temperatures. The constancy of this product was checked for the alkali salts of tetraphenylboron in THF over the same temperature range.[8] It appears that the Walden product decreases monotonically with temperature, the total change amounting to 7% for the cesium salt and to 10% for the sodium and lithium salts between +25 and −75°. The probable cause of the decrease in the product $\Lambda_0\eta$ may be found in an enhanced cation solvation as the temperature is lowered, leading to a lower λ_0^+ value for the cations. We therefore have applied the Walden rule to the values of the fluorenyl salts at 25°, but incorporated the corresponding corrections as found for the alkali tetraphenylboron salts. We feel that this procedure will yield a set of reasonable Λ_0 values over this temperature range.

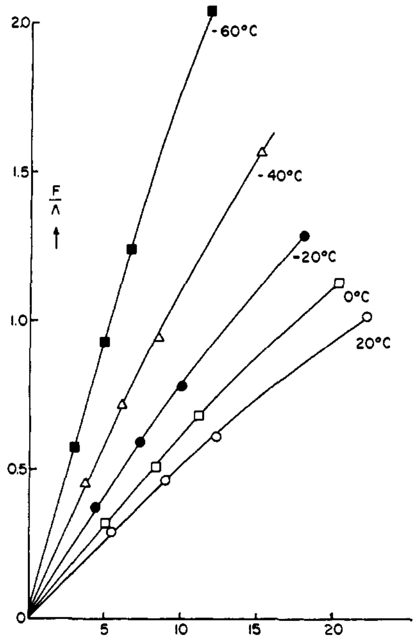

Figure 3. Fuoss conductivity plots for fluorenylcesium in THF at various temperatures.

An IBM 1622 computer was used to analyze the data and to plot F/Λ *vs.* $f^2C\Lambda/F$. Figure 3 is an illustration of some of these Fuoss plots obtained for fluorenyl cesium (for the sake of clarity, not all temperatures are shown on this graph). The lines are slightly curved at the higher concentrations, in particular for the cesium salt, indicating the onset of triple ion formation. However, the initial slopes can be determined quite accurately. The dissociation constants then were calculated from these slopes and the appropriate Λ_0 value.

All the pertinent data are collected in Tables I, II, and III, including the Λ_0 values used in the calculations. It appears that for all three salts, K_d increases with decreasing temperature.

Table I. Experimental and Calculated Dissociation Constants of Fluorenylcesium in THF over the Temperature Range +25 to −70°

Temp., °C.	$\eta \times 10^3$, mp.	Λ_0	$K_d \times 10^8$ mole/l. (exptl.)	$K_d \times 10^8$ mole/l. (calcd. a = 3.76 Å.)
25	4.60	120	1.38	. . .
20	4.84	113.5	1.53	1.67
10	5.46	100	1.81	1.87
0	6.13	88.4	2.11	2.15
−10	6.92	77.6	2.46	2.47
−20	7.94	67.1	2.81	2.84
−30	9.12	57.9	3.19	3.18
−40	10.72	48.8	3.66	3.57
−50	12.59	41.2	4.13	4.10
−60	15.49	33.2	4.90	4.60
−70	19.27	26.5	5.47	5.05

Figure 4 shows plots of log K_d *vs.* $1/T$ for the three salts. The enthalpy of dissociation, $\Delta H°_d$, can be determined from the tangent of the curve at a particular temperature. It is immediately evident that $\Delta H°_d$ becomes less negative at lower temperatures for all the three salts, with a rather drastic change seen for the sodium salt.

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(6) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J. Phys. Chem.*, **69**, 608 (1965).

(7) R. V. Slates and M. Szwarc, *ibid.*, **69**, 4124 (1965).

(8) C. Carvajal, J. K. Toelle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, 87, 5548 (1965).

Table II. Experimental and Calculated Dissociation Constants of Fluorenylsodium in THF over the Temperature Range +25 to −70°

Temp., °C.	Λ_0	$K_d \times 10^7$ mole/l. (exptl.)	K_i[a]	$K_c \times 10^7$ mole/l. (calcd.)	$K_s \times 10^5$ mole/l. (calcd.)
25	100	6.17	...	...	...
20	94.5	7.52	0.060	7.96	1.34
10	83.2	12.6	0.112	14.0	1.45
0	73.5	21.1	0.156	24.4	1.56
−10	64.5	37.0	0.250	46.2	1.85
−20	55.6	66.6	0.436	95.5	2.20
−30	47.7	118	0.795	212	2.64
−40	40.0	206	1.51	518	3.43
−50	33.7	298	3.02	1190	3.93
−60	27.0	405	6.31	2960	4.65
−70	21.5	480	...	...	...

[a] Interpolated from Figure 2 of the preceding paper.

Table III. Dissociation Constants of Fluorenyllithium in THF over the Temperature Range +25 to −70°

Temp., °C.	Λ_0	$K_d \times 10^6$ mole/l. (exptl.)
25	88.4	3.89
20	83.6	4.40
10	73.5	5.44
0	65.0	6.57
−10	56.9	7.90
−20	49.1	9.66
−30	42.2	11.6
−40	35.4	13.2
−50	29.8	15.3
−60	23.8	19.1
−70	19.0	19.9

Discussion

The simplest model of an electrolyte solution assumes the ions to be charged spheres, distributed in a continuum characterized by its macroscopic dielectric constant and viscosity. Using this "sphere in continuum" model, Fuoss[5,9] calculated that the dissociation constant, K_d, for an ion pair in such a system is given by

$$K_d = (3000/4\pi Na^3)\exp(-e^2/aDkT) \qquad (1)$$

where D is the macroscopic dielectric constant and a the center-to-center distance between the two ions in contact. The theory requires that for a particular salt a plot of log K_d *vs.* $1/D$ at constant temperature yield a straight line. The interionic distance, a, can then be simply computed from its slope. In case one of the ions contains a dipole[10] or is electrically asymetrical,[11] a charge–dipole energy term ($\mu ed^2/D$) must be added to the charge–charge energy term (e^2/aD). Here, μ is the dipole moment of the ion and d is the distance from the center of the dipole to the center of the opposite ion.

In many electrolyte systems calculations based on the sphere in continuum model appear to be in good agreement with the experimentally observed dissociation constants. This is particularly true when dealing with large ions in which the ionic charge is shielded by bulky groups, or in general when specific ion–solvent interactions are absent. In such cases the limiting conductance of an ion varies to a good approximation inversely with the solvent viscosity, as expressed in the constancy of the Walden product.

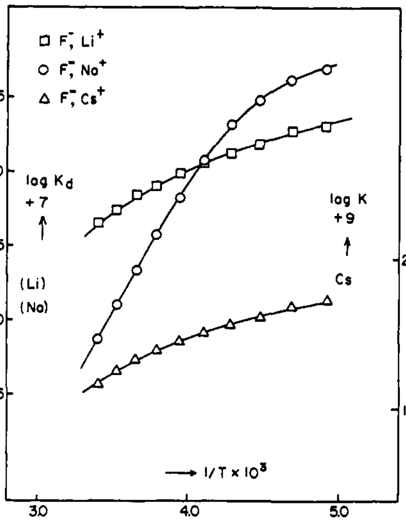

Figure 4. Temperature dependence of the dissociation constants for fluorenyllithium, -sodium, and -cesium in THF.

It was shown in the preceding paper[2] that of the three fluorenyl salts, the cesium compound does not appear to form any solvent-separated ion pairs in THF in the temperature range between 25 and −70°. This observation led to the conclusion that any specific solvation between the Cs^+ ion and the THF molecules must be small. Hence, one may therefore apply the Fuoss expression for K_d with reasonable confidence. Using the observed K_d for F^-,Cs^+ at 25°, *i.e.*, 1.38×10^{-8} mole/l., we calculate the center-to-center distance a of the F^-,Cs^+ ion pair to be 3.76 Å. Taking the ionic radius of the bare Cs^+ cation[12] as 1.66 Å., we find the electrostatic radius of the fluorenyl carbanion to be 2.1 Å., a very reasonable value.

Assuming the distance a to be independent of temperature, one may now calculate the dissociation constants at any other temperature, using the experimentally observed relationship $DT = -1.49T + 2660$. The calculated K_d values are shown in Table I. The agreement between observed and calculated K_d values is surprisingly good, the small differences being well within the experimental error.

Using a thermodynamic approach based on the Born cycle, Denison and Ramsey[13] showed the enthalpy change, $\Delta H°_d$, on dissociation of 1 mole of ion pairs into 2 moles of free ions in a medium of dielectric constant D to be equal to

$$\Delta H°_d = (Ne^2/aD)[1 + \mathrm{d}\ln D/\mathrm{d}\ln T] \qquad (2)$$

It again should be stressed that a sphere in continuum model is assumed in this treatment and specific solvent–solute interactions are neglected. Only the solvation enthalpy arising from the difference in electrostatic potential energy of an ion pair in a continuum of dielectric constant D as compared to the free ion[14] is

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(9) R. M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(10) R. M. Fuoss and C. A. Kraus, *ibid.*, **79**, 3304 (1957).

(11) F. Accascina, A. D'Aprano, and R. M. Fuoss, *ibid.*, **81**, 1058 (1959).

(12) L. Pauling, *ibid.*, **49**, 765 (1927).

(13) J. T. Denison and J. B. Ramsey, *ibid.*, **77**, 2615 (1955).

(14) M. Born, *Z. Physik.*, **1**, 45 (1920).

taken into consideration. The weakness of such a model is apparent immediately, since it cannot account for the observed differences in solvation enthalpies of cations and anions with equal radii. Several refinements of the theory have been proposed[15] taking into account solvent–solute interactions. However, in the absence of such interactions, the simplified treatment still yields reasonable results.[13] The same expression for $\Delta H°_d$ can be obtained from the thermodynamic relation $\Delta H°_d = -R\mathrm{d}\ln K_d/\mathrm{d}(1/T)$ on substituting for K_d the expression derived by Fuoss (see eq. 1).

It is apparent from eq. 2 that the dissociation of an ion pair is exothermic for $\mathrm{d}\ln D/\mathrm{d}\ln T < -1$. This derivative can be determined directly for THF from the observed empirical relationship $D = -1.49 + 2660/T$. It changes slowly with temperature and has a value of -1.20 at 25° and -1.13 at $-70°$.[16] Hence, it is not surprising that for all the salts studied in THF up to now, the dissociation into free ions was found to be exothermic.[17]

Calculating now the $\Delta H°_d$ for F^-,Cs^+ from eq. 2 and using for the distance a, the calculated value of 3.76 Å., we find $\Delta H°_{d,298} = -2.4$ kcal./mole and $\Delta H°_{d,203} = -1.0$ kcal./mole. The experimental values which can be obtained from Figure 4 by taking the tangents of the F^-,Cs^+ curve at 298 and 203°K. are $\Delta H°_{d,298} = -2.7 \pm 0.3$ kcal./mole and $\Delta H°_{d,203} = -1.0 \pm 0.2$ kcal./mole. Again the agreement is very satisfactory, and it indicates once more the lack of specific solvation of Cs^+ in THF, a conclusion already deduced from spectral data.[2]

The change in the entropy on dissociation can be calculated using the experimental K_d values of Table I. Since $\Delta S°_d = \Delta H°_d/T + 2.3R\log K_d$, we find $\Delta S°_{d,298} = -45$ e.u. and $\Delta S°_{d,203} = -38$ e.u. Obviously, the theoretical $\Delta S°_d$ values will be similar, since the experimental and calculated K_d and $\Delta H°_d$ values were shown to be the same within experimental error. The relative large decrease in entropy shows that the entropy increase expected on dissociation of a nonsolvated ion pair into two free nonsolvated ions is more than compensated by the decrease of the entropy of the solvent. The latter is due to the ordering effect of free ions exerted on the solvent molecules relative to that of the ion pairs. The values found for $\Delta S°_d$ for F^-,Cs^+ are lower than those found by Denison and Ramsey[13] for substituted phenyltrimethylammonium perchlorates. This should be the case, since the K_d values for these perchlorates are substantially higher than for the fluorenyl cesium salt which has a much lower interionic distance.

Turning now to the data obtained for F^-,Na^+, it is immediately clear that for this salt the simple expression for K_d based on the sphere in continuum model will fail. Since $a(F^-,Na)$ should be smaller than $a(F^-,Cs^+)$, one would expect $K_d(F^-,Na) < K_d(F^-,Cs^+)$. However, the data show the K_d for F^-,Na^+ at 25° to be about 45 times larger than that for F^-,Cs^+.

It has been pointed out frequently that the sphere in continuum model fails to describe the experimental observations in many electrolyte systems.[18] In particular, when small ions are involved, or in mixtures of solvents containing a strongly solvating component, large deviations have been observed.[19] In such cases, the interionic distance a, for example, may depend on the solvent composition, and so will the Walden product $\Lambda_0\eta$. One then must consider the detailed molecular structure of the solvent in the immediate vicinity of the ions, which is obviously different from its macroscopic structure.

It has been suggested by Sadek and Fuoss[20] that in such systems ion-pair formation may be described as follows. A solvent-separated ion pair is assumed to be described by the sphere in continuum model, with the distance a being the center-to-center distance between the ions in the solvent-separated ion pair. The expulsion of the last solvent molecules to form the contact ion pair constitutes a discrete stepwise process described by the equilibrium constant between the two chemically distinct ion pairs. In this last step the use of the macroscopic dielectric constant must fail in calculating the potential energy, due to dielectric saturation by the extremely strong field in the vicinity of the ion and the absence of solvent between the ions. As Sadek and Fuoss pointed out, it is precisely these small distances which contribute most to the Coulombic interaction energy. This factor becomes more important as smaller ions are involved.

The picture described above is similar to Grunwald's description[2,21] of the contact and solvent-separated ion pair and may therefore be applicable to the sodium and lithium salts of the fluorenyl carbanion in THF. The following equilibria were shown[2] to describe the behavior of these salts in THF.

$$\begin{tikzcd}
F^-M^+ \arrow[rr, shift left, "(K_i)"] \arrow[dr, shift left] & & F^-||M^+ \arrow[ll, shift left] \arrow[dl, shift left, "(K_s)"] \\
& F^- + M^+ \arrow[ul, shift left, "(K_c)"] \arrow[ur, shift left] &
\end{tikzcd} \qquad (3)$$

The ratio $[F^-||M^+]/[F^-M^+] = K_i$ is constant, assuming the solvent concentration does not change. In mixtures of solvents containing small quantities of powerful solvating agents (*e.g.*, dimethyl sulfoxide), this assumption may not be justified and the change in solvent composition must be taken into account.[2] K_c and K_d are the dissociation constants for the contact and solvent-separated ion pair, respectively. As pointed out, eq. 1 describing the sphere in continuum model may be applicable to a solvent-separated ion pair. The spectral studies reported in the preceding paper[2a] show that both F^-,Li^+ and F^-,Na^+ exist as solvent-separated ion pairs at $-70°$, and their K_d values at this temperature therefore may be used to calculate the ion-pair distance a. For $F^-||Li^+$, K_d at $-70°$ is 2.0×10^{-5} mole/l. yielding a value for $a =$

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(15) W. R. Gilkerson, *J. Chem. Phys.*, **25**, 1199 (1956); A. D. Buckingham, *Discussions Faraday Soc.*, **24**, 151 (1957).

(16) A good linear relationship is also obtained from a plot of ln D *vs.* ln T, d ln D/d ln T being -1.16. Whether this coefficient is constant or slightly temperature dependent is difficult to decide. We have chosen the D *vs.* $1/T$ plot, since in that case the calculated ΔH values agree somewhat better with the observed values. Taking d ln D/d ln T equal to -1.16 would change our ΔH values by about 20%.

(17) (a) Results (to be published) of conductance studies on solutions of radical ions, living polymers, and tetraphenylborons from this laboratory; see also (b) J. Dieleman, Thesis, Free University, Amsterdam, 1962; (c) K. H. J. Buschow, Thesis, Free University, Amsterdam, 1963.

(18) F. M. Sacks and R. M. Fuoss, *J. Am. Chem. Soc.*, **75**, 5172 (1953); H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5897 (1954).

(19) A. D'Aprano and R. M. Fuoss, *J. Phys. Chem.*, **67**, 1722 (1963); T. L. Fabry and R. M. Fuoss, *ibid.*, **68**, 907 (1964); J. B. Hyne, *J. Am. Chem. Soc.*, **85**, 304 (1963).

(20) H. Sadek and R. M. Fuoss, *ibid.*, **76**, 5905 (1954).

(21) E. Grunwald, *Anal. Chem.*, **26**, 1696 (1954).

6.3 Å. Models for a solvent-separated ion pair with a THF molecule located above the plane of the fluorene ring between the two ions show that this is a most reasonable value for the center-to-center distance in such an ion pair, accepting the 2.1 Å. for the radius of the carbanion.[22] A similar calculation for $F^-||Na^+$ ($K_d = 4.8 \times 10^{-5}$ mole/l. at −70°) gives $a = 7$ Å. A larger distance for the Na salt is to be expected.

On dissociation of the solvent-separated ion pair, the counterion carries its solvation shell with it. Any specific solvation enthalpy therefore is small in this process, and the $\Delta H°_s$ of dissociation may be calculated by applying eq. 2. For $F^-||Li^+$ and $F^-||Na^+$ this leads to $\Delta H°_s$ values of −0.6 and −0.5 kcal./mole, respectively, using the calculated a values found for the respective fluorenyl salts at −70°. The experimental values, determined from the tangents of the log K_d–$1/T$ plots are −1.3 ± 0.4 and −1.4 ± 0.4 kcal./mole, respectively. The agreement is fair in view of the experimental uncertainties in the K_d values and in the slopes of the plots of Figure 4. However, the slightly larger negative value of $\Delta H°_s$ in both cases may be genuine and could be an indication that additional specific solvation occurs on dissociation of the solvent-separated ion pair.

It can be easily shown that the dissociation constants of the equilibria 3 are related as follows (assuming activity coefficients equal unity)

$$1/K_d = 1/K_c + 1/K_s \qquad (4)$$

and

$$K_d = K_s K_i [1 + K_i]^{-1} \qquad (5)$$

where K_d is the dissociation constant calculated from the Fuoss conductance equation. Also, the enthalpy of dissociation, $\Delta H°_d$, as measured from the log K_d–$1/T$ plot, is related to the enthalpy of dissociation, $\Delta H°_s$, of the solvent-separated ion pair and to the enthalpy change, $\Delta H°_i$, of the equilibrium $F^-,Na^+ \rightleftarrows F^-||Na^+$, in the following way.

$$\Delta H°_d = \Delta H°_s + \Delta H°_i (1 + K_i)^{-1} \qquad (6)$$

Since, for F^-,Na^+, the constants K_d and K_i are known over the entire temperature range from 25 to −70°, one may calculate K_s and K_c using the relationships 4 and 5. Their values are reported in Table II, including the experimental K_d and K_i data. In Figure 5, log K_s and log K_c are plotted *vs.* $1/T$ and for comparison the experimental log K_d–$1/T$ plot is added. The intersection of the two calculated curves represents the temperature (−34 for F^-,Na^+ in THF) at which the concentrations of the two ion pairs are equal, since $K_c = K_s$, or $K_i = 1$. From the log K_c–$1/T$ plot (which depicts the behavior of the contact ion pair over this temperature range) we calculate $\Delta H°_c = -9.5$ kcal./mole, its value being nearly constant over the entire temperature range. For F^-,Cs^+ the change of $\Delta H°_d$ with T could be described by the simple relationship derived from the sphere in continuum model. For F^-,Na^+, this would require a change of $\Delta H°_c$ of almost −6 kcal./mole. Obviously, a contact ion pair does not follow the simple model when strong specific solvation effects are present. Since $\Delta H°_c = \Delta H°_s + \Delta H°_i$, it is clear that the large negative value for the enthalpy of dissociation of such a contact ion pair is to a large extent caused by the strong gain in solvation enthalpy on formation of the solvent-separated ion pair. In this process, the solvating power of the solvent rather than its macroscopic dielectric constant is of prime importance, and the change of D with temperature apparently affects $\Delta H°_c$ very little. In fact, since at low temperature ΔH_s becomes less negative, $\Delta H°_i$ will be even more negative. It was pointed out in the preceding paper that this is plausible, since at lower temperature the average (not necessarily integral) number of solvent molecules in the solvation shell around the cation in the $F^-||Na^+$ ion pair may increase, thereby increasing $\Delta H°_i$. This is also reflected in the slight decrease in the Walden product, indicating a decrease in Λ_0 at lower temperatures. This would be the case if the average size of the solvation shell of the cation is enlarged.

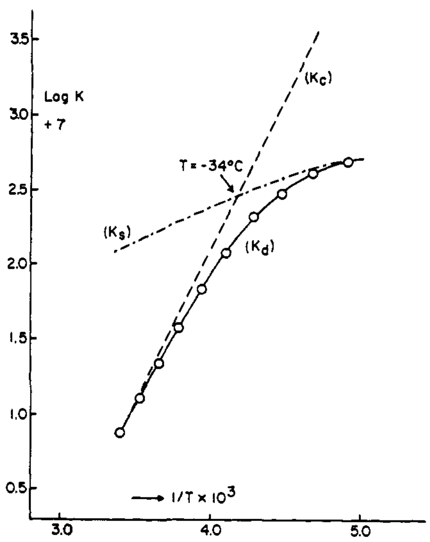

Figure 5. Temperature dependence of the dissociation constants for the contact (K_c) and solvent-separated ion pair (K_s), calculated from the experimental values of K_d and K_i (see text).

The entropy change $\Delta S°_c$, as determined from Figure 5, is found to be −60 e.u. This is substantially more than the −45 e.u. found for F^-,Cs^+ at 25°, and indicates again the ability of the Na ion to immobilize the solvent molecules once it becomes separated from the carbanion.

The slope of the log K_s *vs.* $1/T$ curve follows the expected change with temperature. Application of eq. 2 yields value of $\Delta H°_s$ of −0.5 kcal./mole at −70° and −1.2 kcal./mole at +25°, assuming that $a = 7$ Å. and independent of temperature. The corresponding experimental values are −1.4 and −1.9 kcal./mole. This small discrepancy, as indicated before, may be experimental error or it could be due to a small amount of specific solvation enthalpy on dissociation of the solvent-separated ion pair. For example, the average number of solvent molecules in the solvation shell of the free Na^+ ion may be slightly higher than that in the solvated ion pair. This is also indicated by the entropy change $\Delta S°_s$ of $F^-||Na^+$ at −70°. Its value

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[22] Dixon, Gwinner, and Lini (*J. Am. Chem. Soc.*, 87, 1379 (1965)), have also concluded from n.m.r. data on complexes of fluorenyllithium with THF and DME in benzene, that the Li ion is located above the plane of the fluorenyl carbanion. The data in benzene most likely refer to contact ion pairs, but their data in pure THF must refer to predominantly solvent-separated ion pairs, at least for fluorenyllithium.

(from the experimental ΔH°_d and K_d at $-70°$) is found to be -27 e.u., while calculated by means of the Denison–Ramsay treatment it is -23 e.u.

The difference, $\Delta S^\circ_c - \Delta S^\circ_s$, amounts to about -33 e.u., and represents the entropy change, ΔS°_i, of the equilibrium $F^-,Na^+ + n\text{THF} \rightleftarrows F^-||Na^+$. The magnitude of this entropy change may indicate that about two to three additional solvent molecules are immobilized on formation of the solvent-separated ion pair. This point has been elaborated on in the preceding paper.[2a]

For fluorenyllithium, $K_i = 2.9$ at 25°. Hence, for this salt most ion pairs are solvent separated at room temperature. This is immediately apparent from the behavior of the log K_d *vs.* $1/T$ plot (Figure 4), the $\Delta H^\circ_{d,298}$ being -3.2 ± 0.3 kcal./mole. Calculated from eq. 6 we find -3.2 kcal./mole (using the previously[2a] determined $\Delta H^\circ_i = -7$ kcal./mole and computing ΔH°_s from eq. 2, assuming $a = 6.3$ Å.).

The fluorenyl carbanion is probably very little specifically solvated, and this may be true generally for most carbanions and radical ions in THF. One would expect, therefore, the contact ion pairs of the sodium salt of these species (in so far they are derived from aromatic hydrocarbons) to have a heat of dissociation, ΔH°_c, of about -8 to -10 kcal./mole at 25° in this solvent, and an entropy of dissociation, ΔS°_c, of about -60 e.u. The formation of the solvation shell around the Na^+ ion is the main driving force of the dissociation and determines the magnitude of the thermodynamic quantities involved in the dissociation. As long as the center-to-center distance does not change much, these quantities therefore will depend mainly on the type of cation and on the solvent. It is therefore instructive to look at some conductivity data that have recently been reported in the literature. For the sodium salt of the biphenyl mononegative ion in THF a value for the enthalpy of dissociation of -8.1 kcal./mole at 20° was found,[17b] together with a ΔS°_d of about -50 e.u. These values make it improbable that in THF this salt is associated to a solvent-separated ion pair at this temperature as was deduced from a quantum mechanical interpretation of the observed spectral shift of this compound at lower temperature.[17b] A ΔH°_d value of about -1 to -2 kcal./mole would be more likely in that case. Similarly, a value of -7.5 kcal./mole was reported[23] for the ΔH°_d of the sodium naphthalene mononegative ion in THF at 25°. The dissociation constant at this temperature[7] is 2×10^{-7} mole/l., and both values indicate that this salt again is present as a contact ion pair, a supposition which is strongly supported by the observed spectral shift found on cooling the solution.[2a] The observed K_d value for the lithium salt of the naphthalene anion[24] in THF is about 2.5×10^{-6} mole/l. at 25°, very close to the K_d value of F^-,Li^+ under similar conditions. This is not surprising, since the N^-,Li^+ spectrum in THF indicates about 60 to 80% solvent-separated ion pairs for this salt at this temperature, similar to what is found[2a] for F^-,Li^+.

Garst and Zabolotny[25] have reported a ΔH°_d value of -11.6 kcal./mole for the mononegative ion of sodium tetraphenylethylene. The data were obtained indirectly from spectral measurements of the disproportionation equilibrium of this anion into the monomer and the dianion. The thermodynamic quantities for this latter equilibrium, however, seem to indicate that the mononegative anion is solvent separated at room temperature.[2] A ΔH°_d value of -11.6 kcal. for this ion appears therefore unreasonable, and conductance measurements carried out by Roberts and Szwarc[26] show that its actual value is close to that expected for a solvent-separated ion pair.

Finally, let us compare the dissociation constants of the fluorenyl salts with those previously obtained for the polystyryl salts[4] and the tetraphenylboron salts[4,6] in the same solvent. At room temperature the respective K values for the Na salts are 6.17×10^{-7}, 1.52×10^{-7}, and 8.52×10^{-5} *M;* and for the Cs salts, 1.38×10^{-8}, 2.8×10^{-9}, and 1.87×10^{-6} *M.* The ratios $K[\text{Na}]/K[\text{Cs}]$ for the three salts are 44.7 (F^-), 54.3 ($\sim\!\!\sim S^-$), and 45.6 (B^-Ph_4). The similarity in these values, despite the different anions, is evidence that the anions are very little specifically solvated by the THF. The consistently higher value for the sodium salts again shows the strong specific solvation of Na by THF as compared to the larger Cs ion. The ratios of $K[\text{Li}]/K[\text{Cs}]$ for the three salts are, of course, not the same, since F^-,Li^+ is predominantly a solvent-separated ion pair at 25°, while $\sim\!\!\sim S^-,Li^+$ appears to be a contact ion pair.

The dissociation constant of the sodium and cesium fluorenyl salts are higher by a factor of 4 to 4.5 as compared to those of the corresponding polystyryl salts. The greater charge delocalization in the fluorenyl salts, leading to a slightly higher center-to-center distance in the contact ion pair, is the probable reason for this.

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(23) N. M. Atherton and S. I. Weissman, *J. Am. Chem. Soc.*, **83**, 1330 (1961). This result was obtained from an e.s.r. technique, and the authors may have measured the equilibrium between the contact and solvent-separated ion pair.[2] In this case, the actual ΔH°_d of free ion formation would be slightly more negative.

(24) J. Smid, unpublished results.

(25) J. F. Garst and E. R. Zabolotny, *J. Am. Chem. Soc.*, **87**, 495 (1965).

(26) R. C. Roberts and M. Szwarc, *ibid.*, **87**, 5542 (1965).