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UV-Spectra of Fluorenyl Salts in the Binary Mixtures of DME and Benzene

Katsuhiko Takaya and Norio Ise
Department of Polymer Chemistry, Kyoto University, Kyoto 606

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The temperature dependence of UV spectra of fluorenyl lithium and sodium was investigated in 30, 40, and 50 vol% dimethoxyethane (DME)–benzene mixtures. The lithium salt had two absorption peaks at 352 and 373 nm, and the sodium salt at 358 and 373 nm. The fraction of solvent-separated ion pairs for the sodium salt was much lower than that of the lithium salt, and the heat of conversion ($-\Delta H_i$) of contact-ion pairs to solvent-separated ion pairs was larger (9—11 kcal/mol) for the sodium salt than that (1—4 kcal/mol) for the lithium salt.

In our laboratory living anionic polymerizations of styrene with alkali metal gegenions were investigated in the binary mixtures of 1,2-dimethoxyethane (DME) and benzene[1–3] and in triglyme–benzene mixtures.[4] The reactivity of ion pairs in DME–benzene mixtures was higher[1–4] than that in other ethereal solvents in general.[5–9] The dissociation constants of polystyryl ion pairs in DME–benzene systems were not larger than those in other solvent systems. These tendencies suggest that the higher reactivity of the ion pair (even for the caesium salt) should be attributed to the contribution of the solvent-separated ion pairs. This is supported by the fact that lithium and sodium salts have a larger inter-charge distance a in the ion pair (6—10.5 and 9.3 Å, respectively),[2] calculated by the Fuoss equation,[10] than in THF (4.5 and 4.4 Å, respectively) and in MeTHF (3.3—3.4 Å) and in THP (3.5—3.7 Å)

$$K_{\mathrm{d}} = \frac{3000}{4\pi Na^3}\cdot\exp\left(-\frac{e^2}{a\varepsilon kT}\right), \qquad (1)$$

where K_{d}, N, ε, and k are the dissociation constant of ion pair, the Avogadro number, the dielectric constant, and the Boltzmann constant, respectively.

It must, however, be taken into consideration in the present systems that the formation of the "cybotactic region" [11] of DME molecules or a different composition of the solvent in the vicinity of the ions and ion pairs from that in the bulk solvent system might be probable as one of the reasons for the larger a values.

It was also a question why the sodium ion pair was most reactive among the polystyryl salts in DME–benzene (50 vol%) mixture. To obtain information about the solvation of the ion pairs, we investigated UV spectra of lithium and sodium salts of fluorene as model compounds in the binary mixtures of DME and benzene between 0 and 25 °C. Smid *et al.* studied the UV spectra of the same salts in ethereal solvents.[12]

Experimental

Commercial fluorene was recrystallized several times using alcohol and dried under a high vacuum. DME, preliminarily dehydrated by metal sodium, were refluxed over CaH_2 for a week and distilled onto Na–K alloy. Then DME was subjected to deaeration-dehydration treatment on a vacuum line by cooling and degassing with stirring in the presence of Na–K alloy dispersion. Benzene, contacted with concentrated sulfuric acid for a few weeks, was fully washed with concentrated sulfuric acid, aqueous sodium hydroxide solution, and water to be neutral, then dehydrated with $CaCl_2$ and thereafter with CaH_2. This benzene was then treated in the same manner as DME.

The fluorenyl salts were prepared from solutions of the corresponding polystyryl salts in tetrahydrofuran (THF) under a high vacuum. The THF of the fluorenyl salt solution was substituted with DME–benzene mixtures.

The fluorenyl salt solutions directly prepared in the DME–benzene mixture by treating fluorene with sodium mirror did not show different spectra from those of the salts prepared from polystyryl salts. The salt solutions were stored in a freezer or in an ice-box.

Results and Discussion

In Fig. 1, the UV spectra of fluorenyl lithium in the binary mixture of DME and benzene (at DME contents of 30, 40, and 50 vol%) between 0 and 25 °C are given. The carbanions had absorption bands at 350 and 373 nm, and the absorption peak at 350 nm decreased and that at 373 nm increased when the temperature was lowered.

In Fig. 2, the UV spectra of fluorenyl sodium in the 30, 40, and 50 vol% DME–benzene mixtures between 0 and 25 °C are shown. Two peaks were observed and maxima were at 358 and 373 nm in addition to the absorptions in the visible regions.

In both salts, absorption peaks were the same as those observed in other solvent systems.[12] As new

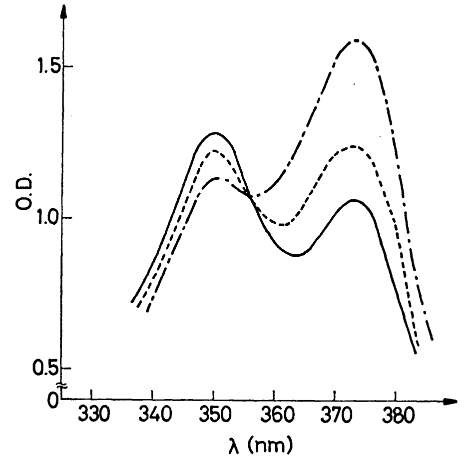

Fig. 1(a). Absorption spectra of fluorenyl lithium in DME–benzene (30: 70) mixture.
——: 25 °C, ----: 14.5 °C, -·-·-: 0 °C.

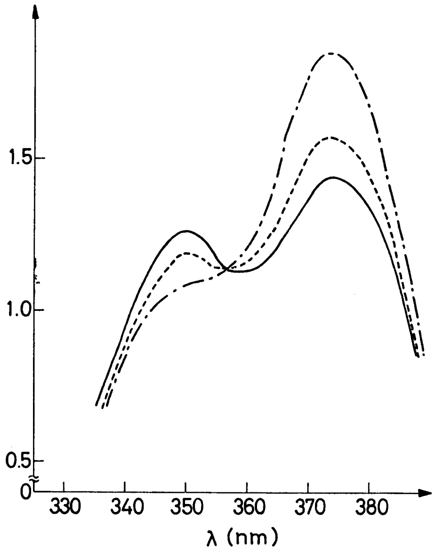

Fig. 1(b). Absorption spectra of fluorenyl lithium in DME–benzene (40: 60) mixture.
——: 25.0 °C, ----: 15.0 °C, —·—: 0 °C

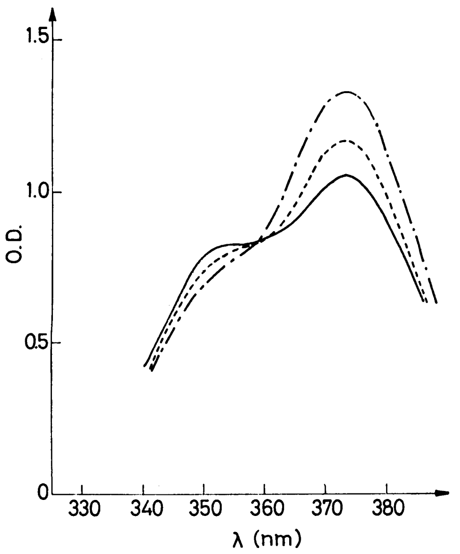

Fig. 1(c). Absorption spectra of fluorenyl lithium in DME–benzene (50: 50) mixture.
——: 25.0 °C, ----: 15.6 °C, —·—: 0 °C

peaks were not observed, the presence of higher aggregates in these salts than ion pairs remained unknown.[4]

The isosbestic points were observed for all cases and the relative heights of the two peaks were not affected by addition of highly dissociable tetraphenylboride as common ion salt. These facts indicate that the observed changes correspond to an equilibrium between contact ion pairs and solvent-separated ion pairs, which is sensitive to solvent, temperature, and gegenions. The peaks, which were predominant at high temperatures, are dependent on cations (*viz.* 350, and 358 nm for lithium and sodium salts, respectively, in the present system), but the peaks at 373 nm were independent of cations, as was shown by Smid *et al.*[12] The formation of the cybotactic region in the present system was suggested by the fact that the absorption peaks of the contact-ion pairs of lithium and sodium salts (F^-, M^+) were most bathochromically shifted in DME–benzene systems among the ethereal solvents and close to those in pure DME.

In Table 1, the fraction of solvent-separated ion pair $F^-//M^+$ was calculated according to Smid's method and is summarized together with other relevant data. The fraction of $F^-//M^+$ for both the lithium and sodium salts was larger than in other ethereal solvents with a similar polarity. Comparing the lithium and sodium ion pairs, the former is much richer in $F^-//Li^+$ than the latter. So the fraction of the solvent-separated ion pairs in the sodium salt of living polystyrene should be expected to be smaller than that of lithium salt, when we assume that the polystyryl anions have a structure

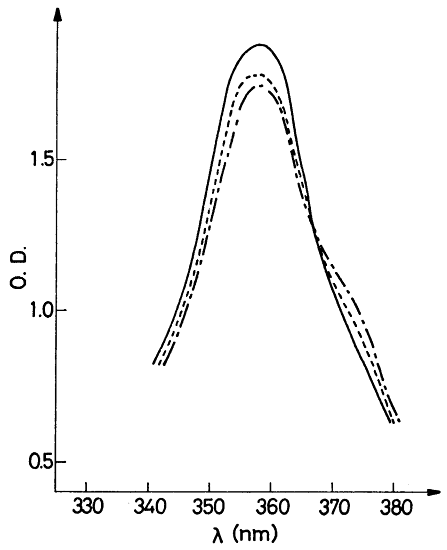

Fig. 2(a). Absorption spectra of fluorenyl sodium in DME–benzene (30: 70) mixture.
——: 25.0 °C, ----: 13.5 °C, —·—: 0 °C

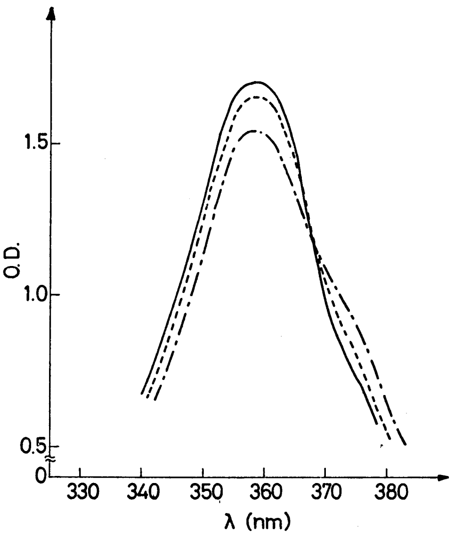

Fig. 2(b). Absorption spectra of fluorenyl sodium in DME–benzene (40: 60) mixture.
——: 24.5 °C, ----: 13.0 °C, —·—: 0 °C

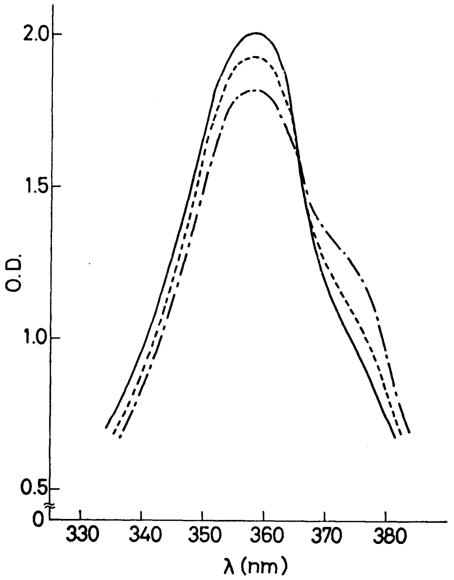

Fig. 2(c). Absorption spectra of fluorenyl sodium in DME–benzene (50: 50) mixture.
——: 24.7 °C, ----: 15.5 °C, -·-·-: 0 °C

Table 1. Absorption maxima of contact and solvent-separated fluorenyl ion pairs in DME–benzene mixtures

Gegen-ion	Fraction of DME (vol%)	Temp. (°C)	Dielectric constant ε	λ_{max} F^-,M^+ (nm)	λ_{max} $F^-//M^+$ (nm)	Fraction of $F^-//M^+$
Li^+	30	25	3.38	350	373	0.45
		0	3.60	350	373	0.60
	40	25	3.81	350	373	0.54
		0	4.07	350	373	0.64
	50	25	4.33	350	373	0.63
		0	4.67	350	373	0.72
Na^+	30	25	3.38	358	373	0
		0	3.60	358	373	0.07
	40	25	3.81	358	373	0.04
		0	4.07	358	373	0.17
	50	25	4.33	358	373	0.06
		0	4.67	358	373	0.21

relatively similar to fluorenyl anions. Therefore the difference of the ion-pair rate constant k_p' between the lithium and sodium salts in the DME–benzene systems should be attributed to the difference of the structure of the solvent-separated ion pairs of the both salts.

The equilibrium constant K between the two kinds of ion pairs should be written as

$$F^-, M^+ + n\cdot DME \overset{K}{\rightleftarrows} F^-//M^+ \quad (2)$$

$$K = \frac{[F^-//M^+]}{[F^-, M^+]\cdot[DME]} \quad (3)$$

If the solvent is in a large excess, the ratio $[F^-//M^+]/[F^-, M^+](\equiv K_i)$ should be proportional to K. So the K_i value should be constant at a fixed temperature. The K_i values for the fluorenyl salts in the DME–benzene systems were calculated by the method by Smid *et al.*[12,13] and are given in Table 2. From the slope of $\log K_i$ *vs.* $1/T$ plot, the $-\Delta H_i$ values were given as 1.3—3.8 kcal/mol and 9.2—11 kcal/mol for the lithium and sodium ion pairs, respectively. The ΔH_i and ΔS_i values in the present systems are summarized in Table 3, together with the results in other solvents.

Table 2. Equilibrium constant K_i for fluorenyl salts in DME–benzene mixtures

Gegenion	Solvent	Temp. (°C)	K_i
	DME–benzene		
Li^+	30:70	0	1.5
		14.5	1.1
		25.5	0.8
	40:60	0	1.8
		15.0	1.4
		25.0	1.2
	50:50	0	3.5
		15.6	3.0
		24.6	2.8
	DME–benzene		
Na^+	30:70	0	0.070
		13.5	0.025
		25.0	0
	40:60	0	0.21
		13.0	0.092
		24.5	0.040
	50:50	0	0.26
		15.5	0.11
		24.7	0.06

Table 3. Thermodynamic quantities of the conversion of F^-,M^+ to $F^-//M^+$ in various solvents

Group	Gegen-ion	Solvent (ε)	$-\Delta H_i$ (kcal/mol)	$-\Delta S_i$ (e.u.)
DME–Benzene				
(I)	Li^+	50:50 (4.3)	1.3±1	1.0±2
		40:60 (3.8)	2.7±1	6.0±2
		30:70 (3.6)	3.8±1	13 ±2
	Na^+	50:50 (4.3)	9.2±2	38 ±8
		40:60 (3.8)	11 ±2	44 ±8
		30:70 (3.6)	(11)	(50)
(II)[a]	Na^+	THF (7.4)	7.1	33
	Li^+	THF	7.6	22
	Li^+	THP (5.6)	6.6	28
	Li^+	MeTHF (6.2)	7.5	27

a) Taken from Ref. 12.

The $-\Delta H_i$ values should be determined by a competition between the Coulombic energy between electric charges in the ion pairs and the solvation energy; the former is endothermic and the latter exothermic. If we assume that the solvation energy for ion pairs of fluorenyl lithium and sodium is nearly the same, as seen from the fact that the absorption peaks of solvent-separated ion pairs are independent of solvent, gegenions and temperature, and if we assume that the degrees of solvation in solvent-separated ion pairs and those in free ions should differ from each other, the trends of

$-\Delta H_i$ in Table 3 will be understood as follows. The smaller $-\Delta H_i$ values for the lithium salt in DME–benzene systems is reasonable because Coulombic forces in the lithium contact ion pairs are stronger than in the sodium ion pairs. In this respect, the sodium salt of 4,5-dimethyl-phenanthrene anion[14)] has larger $-\Delta H_i$ and $-\Delta S_i$ values than the lithium salt (namely, $-\Delta H_i=5.0$ and 12.6 kcal/mol and $-\Delta S_i=17.0$ and 51.6 e.u. for the lithium and sodium salts, respectively, in THF, and $-\Delta H_i=3.7$ and 19.1 kcal/mol and $-\Delta S_i=10.9$ and 61.2 e.u. for the lithium and sodium salts, respectively, in DME). When we compare these values for the lithium salt between the DME–benzene system and the THF system, the larger $-\Delta H_i$ value in the latter should be attributed to the lack of the external solvation towards contact-ion pairs. The fact that the increase of DME content decreased the $-\Delta H_i$ value might be due to solvation towards the contact-ion pairs.

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