

Electrostatic Catalysis by Ionic Aggregates. 7. Interactions of Dipolar Indicator Molecules with Ionic Clusters¹

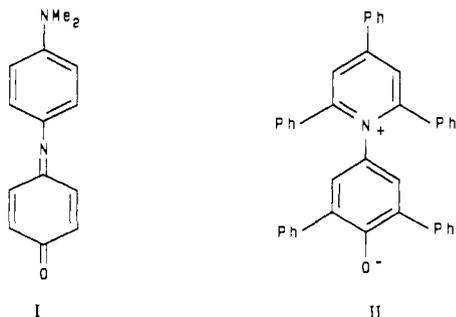
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Abstract: The spectral changes that lithium perchlorate ions in ether solution impart upon various dipolar molecules have been explored at 25.0 °C. The molecules studied in this investigation all display UV-visible spectra, which are highly sensitive to solvent polarity (solvatochromism). Of the three types of molecules chosen for the present study, only *N,N*-dimethylinindoaniline (phenol blue) displays UV-visible spectra that vary over the entire range of lithium perchlorate concentrations. For phenol blue, a change in the low-energy absorbance band of 104 nm is observed upon changing the solvent from pure diethyl ether to 5.05 M lithium perchlorate in ether. This corresponds to a stabilization of 8.01 kcal/mol for this transition. With the other indicator molecules, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye) and 8,9-diacylsesquifulvalenes, the lithium ion forms 1:1 complexes. The exceptional sensitivity of Reichardt's dye to solvent polarity makes it an extremely discriminating probe for minute amounts of lithium ions in solution. An equilibrium expression was deduced that agrees well with the experimental data and leads to the following equilibrium constants for these molecules. The values for the Reichardt's dye are $5 \times 10^6 \text{ M}^{-1}$ in diethyl ether solutions and $1 \times 10^5 \text{ M}^{-1}$ in tetrahydrofuran solutions. The values for the 8,9-diacylsesquifulvalenes are 2.39, 5.44, 7.31, and 9.35 M^{-1} for the dibenzoyl-, diformyl-, dicarbomethoxy-, and diacetyl-substituted compounds, respectively, in lithium perchlorate-tetrahydrofuran solutions and 15.8, 16.8, and 18.2 M^{-1} for the dibenzoyl-, diformyl-, and diacetyl-substituted compounds, respectively, in lithium perchlorate-diethyl ether solution. The order of participation of lithium perchlorate in the equilibrium expression indicates that 1:1 complexes are formed between dipolar molecules and lithium ions. Indeed, an order of 1 is displayed for all compounds, with the exception of 8,9-diacetyl- and 8,9-dibenzoyl-sesquifulvalene at low concentrations and 8,9-(dicarbomethoxy)sesquifulvalene at all concentrations of lithium perchlorate in diethyl ether, which form 2:1 complexes with lithium ions.

It is of fundamental importance to be able to predict the course of a chemical process. At least as important as the reactants, for this prediction, are the conditions under which the reaction is carried out. In solution, substantial control is provided by the solvent system in which the reaction is run. A large number of reactions are sensitive to the polarity of the solvent; consequently, the determination of solvent polarity is essential in order to predict, with any accuracy, the course of these and related reactions.

Many empirical models and systems have been developed in an attempt to provide a criterion of solvent polarity. These criteria have been based on various experimental techniques.² Gutmann used the molar enthalpy value for the reaction of SbCl_5 and donor compounds in CH_2Cl_2 solvent to establish a solvent-independent representation for the donor ability (Lewis basicity) of these compounds.³ From kinetic measurements of the $\text{S}_{\text{N}}1$ reaction of *tert*-butyl chloride, Grunwald and Winstein defined a scale, *Y*, which measures the ionizing power of a solvent.⁴ However, the technique of interest in the present paper was recommended by Brooker et al.,⁵ who suggested the use of a spectroscopic technique, which employs the solvent dependence of UV-visible spectra of certain indicators, such as phenol blue (I).⁶ Since then,



(1) Previous paper in this series: Pocker, Y.; Ciula, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 2904-09.

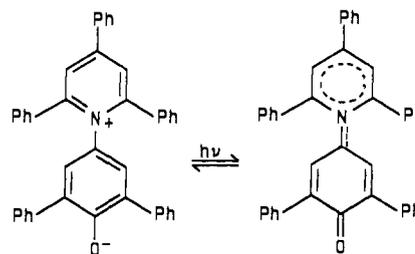
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Scheme I



many other substances have been proposed as spectroscopic solvent polarity indicators.^{7,8} The compound that exhibits the largest dependence on solvent polarity was reported by Dimroth and Reichardt (II).⁹ The dye, 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye), displays a 357-nm shift upon changing the solvent from diphenyl ether to water. This indicator has been widely used for the determination of polarity for many solvent systems. A possible drawback of using a single indicator, such as Reichardt's dye, to determine the polarity of a solvent system is that a specific solvent-indicator interaction or spectral anomaly could be built into the polarity scale. To overcome this difficulty, Taft and co-workers¹⁰ devised a scale based on the $\pi \rightarrow \pi^*$ transition of seven indicators whose spectral shifts are then averaged to give the polarity parameter for the solvent.

For these dyes to show a dependence on the medium, there must be a difference between the solvent-induced dipole moment of the ground state and the excited state. From the Franck-Condon

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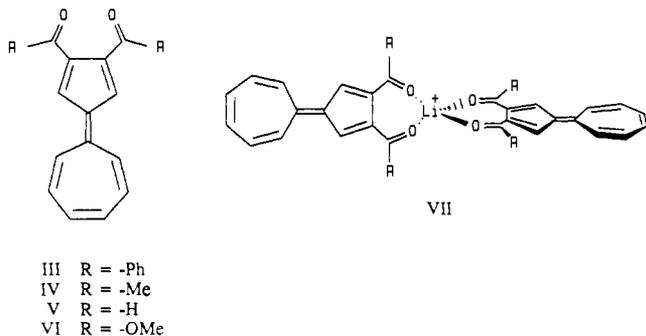
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principle, it can be assumed that the solvent molecules do not have time to reorganize when the dye molecule is excited, so that the excited state is in the same solvent cage as the ground state.¹¹ If the excited-state dipole moment is less than that of the ground state, a hypsochromic shift (blue shift) is observed as solvent polarity is increased. The opposite occurs, a bathochromic shift (red shift), if the excited-state dipole moment becomes greater than that of the ground state.

An excellent example of this solvent dependence is Reichardt's dye. In the ground state it has a large dipole moment, aligned from the pyridine ring to the phenoxide (Scheme I). Upon excitation, the charge separation is reduced, and the dipole moment with it, so this dye displays a hypsochromic shift in more polar media.¹² The opposite effect is displayed by phenol blue. This dye becomes more polar in the excited state, so this state is better stabilized by more polar solvent than the ground state; thus it exhibits a bathochromic shift upon increasing the polarity of the solvent.⁷

Trityl chloride was used as a sensitive probe to measure the polarity of the ionic media, lithium perchlorate dissolved into diethyl ether. The equilibrium constant of the ionization reaction increases 10⁹-fold upon changing the solvent from pure diethyl ether to 5.05 M lithium perchlorate in diethyl ether.¹³ Pocker and Buchholz¹⁴ were able to relate the ionizing capacity of lithium perchlorate–diethyl ether solutions with the formal *Y* values by using the respective first-order rate constants for the ionization of *tert*-butyl chloride in these media. This solvent system was also shown to catalyze the rearrangement of phenylallyl chloride¹⁵ and to dramatically increase the equilibrium constant of the proton-transfer reactions between hydroxylic acids and neutral amines.^{1,16} In all these cases, the products or intermediates produced involved a separation of charges. The resulting clusters produced on dissolving lithium perchlorate in media of low polarity have been shown to be very effective in stabilizing ionic transition states and products.

The indicators discussed above all possess charge separation in the ground or excited state. It was thought that compounds that contain charge separation could be used as probes of the polarity of solutions of lithium perchlorate in media of low dielectric constant and could furthermore be used to examine the patterns of interaction of ionic clusters with dipolar molecules in such ionic media. In this work, phenol blue (I), Reichardt's dye (II), and 8,9-diacetyl-substituted sesquifulvalenes (III–VI) were all



used as indicators of the polarity of lithium perchlorate solutions in diethyl ether and tetrahydrofuran. It was discovered that the lithium ion appears to act as a Lewis acid with respect to Reichardt's dye and sesquifulvalenes. As a consequence, Reichardt's

dye displays extreme sensitivity to minute amounts of lithium ion in solution. An apparent equilibrium constant can be used to describe the reaction of lithium ions with these indicators. The low-energy absorbance band for phenol blue exhibits a dependence upon the lithium perchlorate concentration throughout the entire solubility range of the salt in both diethyl ether (up to 6 M) and tetrahydrofuran (up to 7 M) solvents, which continued to shift to higher wavelengths with increasing salt concentration. The outstanding sensitivity of the absorption spectrum of phenol blue to the structures, properties, and dynamics of ionic clusters make it a useful polarity indicator dye.

Experimental Section

General Procedures. All UV-visible spectra were recorded on a Cary Varian Model 210 spectrophotometer interfaced to an Apple IIe computer attached through a parallel connector. The spectra were stored on 5¹/₄-in. floppy diskettes for later determinations of the appropriate wavelength maxima and equilibrium constants, where applicable. Temperature was regulated by a Forma-Temp Junior constant-temperature bath at a temperature of 25.0 ± 0.1 °C. ¹³C and ¹H NMR were recorded on a Varian VXR-300 300-MHz spectrometer. The chemical shifts are referenced to the solvent peak (CHCl₃ δ 7.25) for proton and to external TMS for ¹³C.

Reagent-grade anhydrous LiClO₄ (GFS Chemicals) was recrystallized twice from distilled water in the form LiClO₄·3H₂O and then dried at 150 °C (0.5 mmHg) for at least 16 h. The salt was stored in a sealed bottle in a desiccator until used.

Reagent-grade anhydrous diethyl ether and tetrahydrofuran (Allied Chemical Co.) were distilled over LiAlH₄ (Metal Hydrides Inc.) under a nitrogen atmosphere, just prior to use.

Reichardt's dye and phenol blue (Aldrich Chemical Co.) were used as purchased. Stock solutions of these compounds were made in dichloromethane so that 5–15 μL added to 3.00 mL of solvent would produce a concentration of approximately 5 × 10⁻⁵ M. The various solvents used in the measurements were purified and dried before use.

8,9-Dibenzoyl- (III), 8,9-Diacetyl- (IV), 8,9-Diformylsesquifulvalene (V).¹⁷ To 0.1 g of the disubstituted cyclopentadiene^{18,19} and 1.9 equiv of tropylium tetrafluoroborate (Pfaltz and Bauer, recrystallized from acetonitrile) was added 10 mL of acetonitrile. After 4 h of stirring, 0.2 g of Na₂CO₃ was added. The reaction was stirred for another h, at which time 10 mL of CH₂Cl₂ was added and the precipitated salts were removed by filtration. The solvent was then removed, and the residue was chromatographed on silica gel (50% hexane–50% ethyl acetate) to give approximately a 50% yield. The NMR spectra matched those previously reported¹⁶ for the 8,9-dibenzoyl- and 8,9-diacetylsesquifulvalene. NMR (300 MHz): (III) δ 6.68 (4 H, m, protons on 7-membered ring), 6.97 (2 H, s, protons on 5-membered ring), 7.3 (8 H, m, includes aromatic and protons from 7-membered ring), 7.75 (4 H, m, aromatic protons); (IV) δ 2.46 (6 H, s, methyl groups), 6.80 (4 H, m, protons of the 7-membered ring), 7.06 (2 H, s, protons of 5-membered ring), 7.5 (2 H, m, 7-membered ring protons); (V) δ 7.04 (4 H, m, 7-membered ring protons), 7.37 (2 H, s, 5-membered ring protons), 7.80 (2 H, m, 7-membered ring protons), 9.98 (2 H, s, aldehydic protons).

8,9-(Dicarbomethoxy)sesquifulvalene (VI). To 0.1 g of sodium 1,2-(dicarbomethoxy)cyclopentadienide²⁰ and 0.18 g of tropylium tetrafluoroborate (Pfaltz and Bauer, recrystallized from acetonitrile) was added 10 mL of freshly distilled acetonitrile at 0 °C, under an argon atmosphere. The reaction was allowed to warm to room temperature over 1 h, and the reaction was stirred 2 h longer. A total of 0.2 g of Na₂CO₃ was added, and the mixture was stirred 0.5 h. The reaction mixture was filtered to remove the precipitated salts. The solvent was removed and the residue chromatographed on silica gel (50% hexane–50% ethyl acetate). The dark red band was the product (25% yield). NMR (300 MHz): δ 3.82 (6 H, s, two methoxy groups), 6.65 (4 H, m, 7-membered ring protons), 7.06 (2 H, s, protons of the 5-membered ring), 7.37 (2 H, m, protons of 7-membered ring).

Molar Transition Energy, E_T. Kosower⁷ used the molar transition energy to define the solvent polarity scale, *Z*. Since then, this quantity has been employed as a measure of the interaction of indicator molecules with solvent systems. The molar transition energy will be used in the

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Table I. Dependence of Wavelength of Maximum Absorbance on the Species Present in Solution at 25.0 °C

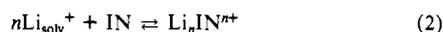
indicator	wavelength ^a of max abs				ΔE_T , ^b kcal/ mol
	in ether	in LPDE	$\Delta\lambda$ ^c	in H ₂ O	
diacetylsesquifulvalene	432.7	499.2 ^d	66.5	498	8.80
dibenzoylsesquifulvalene	456.1	504.9 ^d	48.8	505	6.06
diformylsesquifulvalene	467.5	491.0 ^d	23.5	490	2.93
(dicarbomethoxy)- sesquifulvalene	443.5	486.5 ^d	43.0	485	5.70
phenol blue	559.5	663.5 ^e	104.0	656	8.01
Reichardt's dye	826.4	555.0 ^f	-271.4	453	-16.9

^a Wavelength given in nanometers. ^b Difference in the molar energy of transition for the low-energy visible band in between diethyl ether and lithium perchlorate solutions. Calculated from eq 1. ^c $\Delta\lambda$ is the difference of the absorbance maxima in diethyl ether and that in LPDE. ^d $[\text{LiClO}_4] > 3 \text{ M}$, concentration of lithium complex is greater than 95%. ^e $[\text{LiClO}_4] = 5.9 \text{ M}$, λ_{max} continued to change with $[\text{LiClO}_4]$. ^f $[\text{LiClO}_4] = 0.1 \text{ M}$, concentration of lithium complex is greater than 99%.

present paper to compare various indicator-solvent media interactions. It can be calculated from eq 1.

$$E_T = hcN/\lambda = 28\,593 \text{ kcal mol}^{-1} \text{ nm}/\lambda \quad (1)$$

Equilibrium Constants. For the interaction of Reichardt's dye and the various substituted sesquifulvalenes with lithium perchlorate in diethyl ether and tetrahydrofuran, equilibrium constants were calculated by eq 2, with n equal to the minimum order of participation of lithium ion in the equilibrium.



From the change in the spectra between the "free" indicator and the lithium-indicator (IN) complex (Table I), assuming Beer's law behavior, it is possible to calculate the ratio of concentrations of the lithium complex and free species in solution, using eq 3.

$$\frac{[\text{Li}_n\text{IN}^{n+}]}{[\text{IN}]} = \frac{A(\lambda_1)\epsilon_F(\lambda_2) - A(\lambda_2)\epsilon_F(\lambda_1)}{A(\lambda_2)\epsilon_L(\lambda_1) - A(\lambda_1)\epsilon_L(\lambda_2)} \quad (3)$$

In this equation, $\epsilon_F(\lambda_i)$ is the molar absorptivity of the free indicator at wavelength λ_i , $\epsilon_L(\lambda_i)$ is the molar absorptivity of the lithium-indicator complex at wavelength λ_i , and $A(\lambda_i)$ is the absorbance at wavelength λ_i of the sample for which the ratio is to be measured. Wavelength λ_1 is the lowest energy absorbance band of the free indicator, and wavelength λ_2 is the band of the lithium-indicator complex. From this ratio, and the solvent lithium perchlorate concentration (eq 4), an apparent equilibrium constant, K_{eq}' can be calculated. For the diacetylsesquifulvalenes, the stoichiometric lithium concentration ($[\text{Li}^+]_{\text{stoich}}$) was used, since this concentration was at least 100 times that of the indicator concentration.

$$[\text{Li}(\text{ether})_m^+] = [\text{Li}^+]_{\text{stoich}} - [\text{Li}_n\text{IN}^{n+}] \quad (4)$$

$$K_{\text{eq}}' = \frac{[\text{Li}_n\text{IN}^{n+}]}{[\text{Li}(\text{ether})_m^+]^n [\text{IN}]} \quad (5)$$

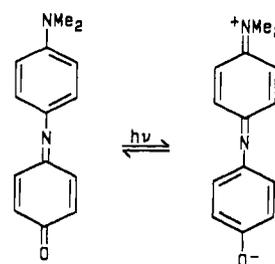
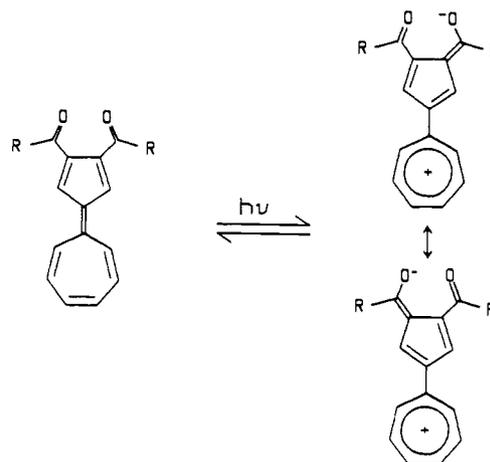
$$\log [\text{Li}_n\text{IN}^{n+}]/[\text{IN}] = \log (K_{\text{eq}}') + n \log [\text{Li}(\text{ether})_m^+] \quad (6)$$

This equilibrium constant is found by plotting the log of the ratio of lithium complex to free indicator versus the log of the lithium perchlorate concentration. The slope will give the minimum order of participation of lithium perchlorate in this reaction, and the intercept will give the apparent equilibrium constant.

An alternate method was also used to calculate the equilibrium constant for the interaction of lithium ion with these indicators. Rearrangement of the equilibrium expression (eq 5) will give

$$\frac{[\text{Li}_n\text{IN}^{n+}]}{[\text{IN}]_{\text{total}}} = \frac{K_{\text{eq}}'[\text{Li}^+]^n}{1 + K_{\text{eq}}'[\text{Li}^+]^n} \quad (7)$$

One can plot the fraction of the indicator complexed to lithium versus the negative log of the lithium ion concentration (pLi) to produce a sigmoidal curve. An equilibrium constant was determined by computing the least-squares line for the experimental data that best fit eq 7. To check for consistency, the equilibrium constant can also be deduced by determining the lithium ion concentration at the inflection point of the curve. This inflection point can be located by plotting the log of the fraction complexed versus pLi. The intersection of a line of unit slope,

Scheme II**Scheme III**

drawn from the limiting slope of the curve through the data points, with the line of slope zero drawn through 0 (fraction of indicator complexed = 1) gives this inflection point, and hence the negative log of the equilibrium constant ($\text{p}K_{\text{eq}}'$).

Results and Discussion

Compounds in which there is a change in dipole moment upon transition to an excited state will display solvent-dependent UV-visible spectra. This alteration of a UV-visible absorbance band by the medium is called *solvatochromism*. The larger the difference in the dipole moment between ground and excited state, the larger the effect that solvent polarity will play on the long wavelength absorbance bands of the UV-visible spectrum. The compounds used in this study all display solvatochromism. That is, the excited state is more polar in the cases of the 8,9-disubstituted sesquifulvalenes^{21,22} and phenol blue,²³ and the excited state is far less polar for Reichardt's dye.¹² All of these compounds were measured in a variety of solvents, and in solutions of lithium perchlorate in diethyl ether and tetrahydrofuran.

Compounds in Pure Solvents. Phenol blue and the sesquifulvalenes were measured in a variety of solvents of different polarity, from hexane to water. These indicators, along with Reichardt's dye, showed similar behavior with solvents of different polarity. From Figure 1, the two curves, one for 8,9-dibenzoylsesquifulvalene and the other for phenol blue, show similar shapes and slopes when plotted against the transition energy of the Reichardt's dye ($E_T(30)$) for the particular solvent. This would imply that these indicators are similarly solvated in pure solvents. This is not totally unexpected, because of the structural similarities that exist between these compounds (I, III-VI). In the sesquifulvalenes and phenol blue, the lowest energy electronic spectral band results from a charge-transfer transition to produce a dipolar compound. In the sesquifulvalenes, the charge transfer takes place from the 7-membered ring to the 5-membered ring (Scheme II),^{21,22} and for phenol blue the transition occurs from the quinone moiety to the dimethylaniline group (Scheme III).²³ The positive charge in phenol blue is located mainly on the quaternary nitrogen

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Table II. Energy of Transition and Wavelength Maxima for the Lowest Energy Absorbance Band of Reichardt's Dye $E_T(30)$, 8,9-Dibenzoylsesquifulvalene $E_T(\text{III})$ and Phenol Blue $E_T(\text{I})$ at 25.0 °C

solvent ^a	ϵ^b	$E_T(30)^{c,d}$	λ_{max}^e	$\Delta E_T(30)^f$	$E_T(\text{III})^d$	λ_{max}^e	$-\Delta E_T(\text{III})^f$	$E_T(\text{I})^d$	λ_{max}^e	$-\Delta E_T(\text{I})^f$
hexane (1)	1.89	30.9	925.3	0.0	64.5	443.3	0.0	52.5	544.6	0.0
carbon tetrachloride (2)	2.24	32.5	879.7	1.6	63.1	453.1	1.4	50.8	562.8	1.7
toluene (3)	2.38	33.9	843.4	3.0	61.8	462.6	2.7	50.3	568.4	2.2
triethylamine (4)	2.42	33.3	858.6	2.4	63.8	448.1	0.7	52.0	549.8	0.5
diethyl ether (5)	4.34	34.6	826.3	3.6	63.0	453.8	1.5	51.1	559.5	1.4
chloroform (6)	4.81	39.1	731.2	8.1	61.1	467.9	3.4	48.2	593.2	4.3
ethyl acetate (7)	6.02	38.1	750.4	7.1	62.0	461.1	2.5	50.1	570.7	2.4
tetrahydrofuran (8)	7.58	37.4	764.5	6.5	61.8	462.6	2.7	49.7	575.3	2.8
methylene chloride (9)	9.08	41.1	695.6	10.2	60.8	470.2	3.7	48.6	588.3	3.9
pyridine (10)	12.3	40.2	711.2	9.3	59.7	478.9	4.8	48.1	594.4	4.4
isopropyl alcohol (11)	18.3	48.6	588.3	17.7	59.9	477.3	4.6	47.7	599.4	4.8
acetone (12)	20.7	42.2	677.5	11.3	61.2	467.2	3.3	49.4	578.8	3.1
ethanol (13)	24.3	51.9	550.9	21.0	59.4	481.3	5.0	46.9	609.6	5.6
methanol (14)	32.6	55.5	515.1	24.6	59.2	482.9	5.3	46.1	620.2	6.4
dimethylformamide (15)	37.0	43.8	652.8	12.9	59.6	479.7	4.9	48.3	591.9	4.2
acetonitrile (16)	37.5	46.0	621.5	15.1	59.6	479.7	4.9	48.9	584.7	3.6
ethylene glycol (17)	37.7	56.3	507.8	25.4	57.2	499.8	7.3	45.1	633.9	7.4
dimethyl sulfoxide (18)	46.7	45.0	635.4	14.1	58.7	487.1	5.8	47.5	601.9	5.0
water (19)	78.5	63.1	453.1	32.2	56.6	505.1	7.9	43.6	655.8	8.9
<i>N</i> -methylacetamide (20)	191.3	52.0	549.8	21.1	58.8	486.2	5.7	47.0	608.3	5.5

^aNumber after the solvent name corresponds to the numerical labels in Figures 1 and 2. ^bDielectric constant of the solvent taken from ref 24. ^cTransition energy values for Reichardt's dye taken from ref 24. ^dTransition energy values given in kilocalories per mole. ^eWavelength of maximum absorbance of the lowest energy band given in nanometers. ^fChange in the transition energy defined as $\Delta E_T = E_T(\text{in pure solvent}) - E_T(\text{in hexane, as reference solvent})$.

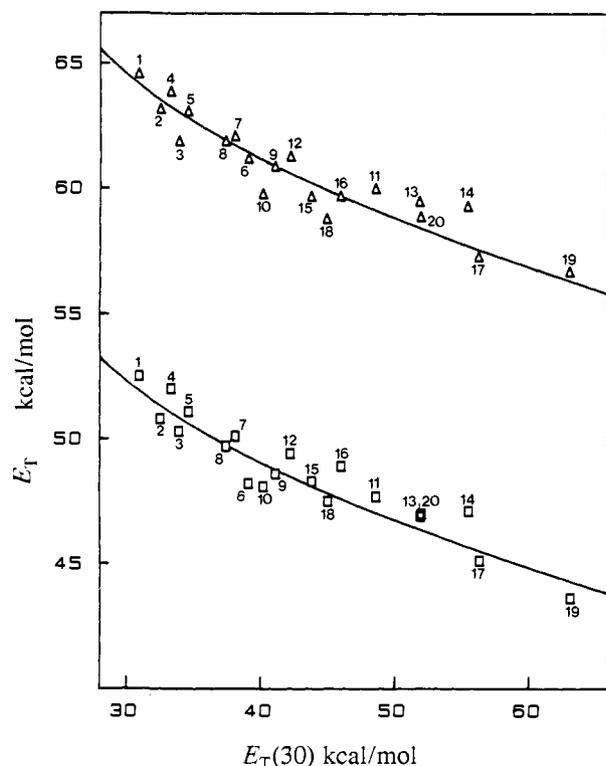


Figure 1. Plot of the transition energy of the lowest energy UV-visible band of phenol blue (\square) and 8,9-dibenzoylsesquifulvalene (Δ) versus the transition energy of Reichardt's dye in various pure solvents. Solvents listed in order of increasing dielectric constant: (1) hexane, (2) carbon tetrachloride, (3) toluene, (4) triethylamine, (5) diethyl ether, (6) chloroform, (7) ethyl acetate, (8) tetrahydrofuran, (9) dichloromethane, (10) pyridine, (11) isopropyl alcohol, (12) acetone, (13) ethanol, (14) methanol, (15) *N,N*-dimethylformamide, (16) acetonitrile, (17) ethylene glycol, (18) dimethyl sulfoxide, (19) water, and (20) *N*-methylacetamide.

of the nitrogen quinone-like moiety. In the sesquifulvalenes, the positive charge is dispersed about the tropylium group. The positive charge of both indicator structures is "hidden" within the molecule and is not available for any specific solvation interaction. The negative charge resides mainly upon oxygen atoms of the carbonyl groups in these compounds (Schemes II and III), so that the primary solvation interaction would occur through these

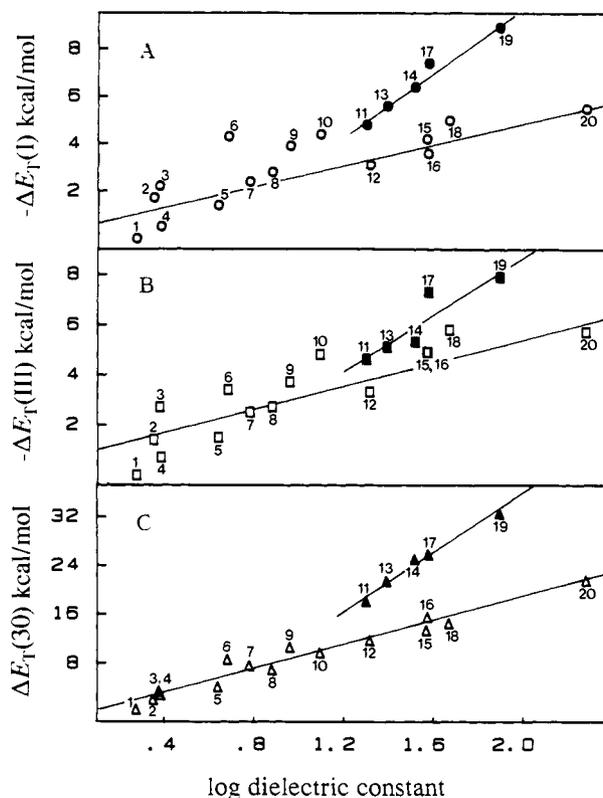


Figure 2. Dependency of the low-energy visible band, plotted as ΔE_T [$\Delta E_T = E_T(\text{in pure solvent}) - E_T(\text{in hexane, as reference})$], for (A) phenol blue, (B) 8,9-dibenzoylsesquifulvalene, and (C) Reichardt's dye, versus the log of the dielectric constant for the pure solvents used. Open symbols indicate aprotic solvents, shaded symbols indicate protic solvents. Larger values of ΔE_T for protic solvents as compared to aprotic solvent of similar dielectric constant indicate an additional interaction through hydrogen bonding to the solvent: (1) hexane, (2) carbon tetrachloride, (3) toluene, (4) triethylamine, (5) diethyl ether, (6) chloroform, (7) ethyl acetate, (8) tetrahydrofuran, (9) dichloromethane, (10) pyridine, (11) isopropyl alcohol, (12) acetone, (13) ethanol, (14) methanol, (15) *N,N*-dimethylformamide, (16) acetonitrile, (17) ethylene glycol, (18) dimethyl sulfoxide, (19) water, and (20) *N*-methylacetamide.

negatively charged carbonyl oxygens. This is evident from the fact that hydroxylic solvents, which can hydrogen bond, cause larger shifts in the low-energy spectral band than aprotic solvents

Table III. Concentrations and Ratios Used To Determine the Equilibrium Constant for Reichardt's Dye with Lithium Ion in Tetrahydrofuran Solution at 25 °C

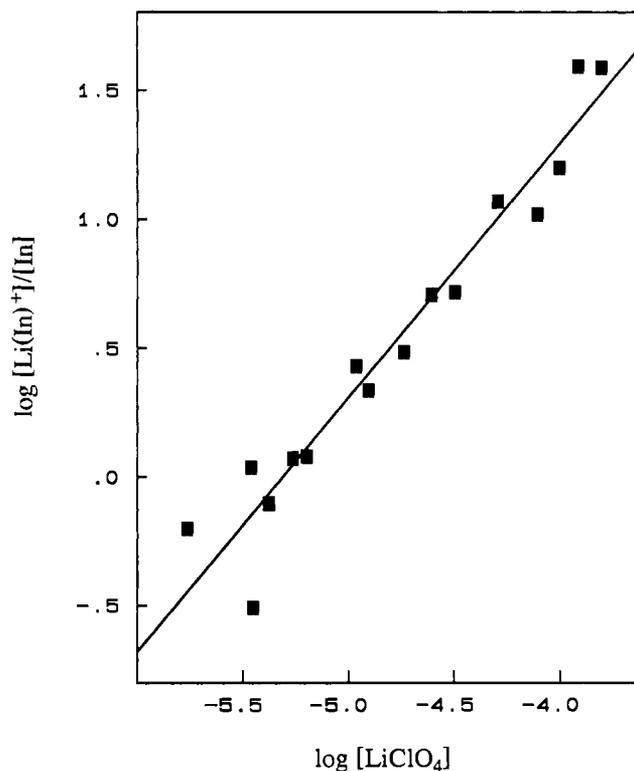
$[\text{Li}^+]_{\text{solv}},^a$ $\times 10^5$ M	$[\text{IN}],^b$ $\times 10^5$ M	$[\text{Li}(\text{IN})^+],^c$ $\times 10^5$ M	$K_{\text{eq}}^{\text{obs } d}$	\log $[\text{Li}^+]_{\text{solv}}$	\log $K_{\text{eq}}^{\text{obs}}$
0.177	4.211	2.645	0.62	-5.75	-0.20
0.349	2.275	2.473	1.08	-5.45	0.03
0.354	3.393	1.057	0.31	-5.45	-0.50
0.422	1.248	0.989	0.79	-5.37	-0.10
0.547	1.033	1.217	1.17	-5.26	0.07
0.641	2.993	3.592	1.20	-5.19	0.07
1.089	0.648	1.733	2.67	-4.96	0.42
1.257	1.380	2.976	2.15	-4.90	0.33
1.839	1.723	5.216	3.02	-4.73	0.48
2.474	0.349	1.759	5.05	-4.60	0.70
3.194	0.752	3.861	5.13	-4.49	0.71
5.090	0.172	1.965	11.42	-4.29	1.05
7.849	0.613	6.261	10.21	-4.10	1.00
9.946	0.272	4.164	15.30	-4.00	1.18
12.20	0.0526	1.909	36.29	-3.91	1.55
15.79	0.0514	1.849	35.97	-3.80	1.55

^a Concentration of lithium solvated by tetrahydrofuran.^b Concentration of uncomplexed Reichardt's dye (free indicator).^c Concentration of Reichardt's dye complexed to lithium ion (indicator-lithium complex). ^d The ratio of indicator-lithium complex concentration over free indicator concentration.of equal dielectric constant (Table II and Figure 2).^{24,25}

Compounds in Solutions of Lithium Perchlorate in Diethyl Ether and Tetrahydrofuran. The electronic spectra of phenol blue, Reichardt's dye, and the four sesquifulvalenes were recorded as a function of the lithium perchlorate concentration in both diethyl ether and tetrahydrofuran. The concentration of lithium perchlorate ranged from 0 to 6.2 M in tetrahydrofuran and from 0 to 6.0 M in diethyl ether. All indicators displayed UV-visible spectral dependence upon the concentration of salt. It is apparent from Table I that lithium perchlorate in solution causes a large change in the property of the solution. A large shift is observed with the indicators. Phenol blue is especially interesting in the fact that the wavelength band shifts to a higher wavelength than that for the dye in water. From this, one could reason that the very concentrated solutions of lithium perchlorate in diethyl ether or tetrahydrofuran (>5 M) are "more polar" than water.²⁶

Reichardt's dye has successfully been employed as an indicator of the polarity of nonacidic media.²⁷ The low-wavelength maxima decreases from 810 nm in diphenyl ether to 453 nm in water. This corresponds to an increase in the molar transition energy of 27.8 kcal/mol. Since this indicator is so very sensitive to the polarity of the environment, it was thought that it could be employed as a probe of the polarity of the ionic solutions of the lithium perchlorate in ether solvents.

The solvent-dependent behavior of these indicators comes from a change in dipole moment upon excitation of the dye. For Reichardt's dye, the ground state contains a large dipole, because of a charge separation between the negative charge on a phenoxide group and positive charge on a pyridinium moiety. This charge separation is removed upon excitation, so that the excited state is much less polar than the ground state (Scheme I).¹² In light of this, and the fact that lithium perchlorate-ether solutions can stabilize ionic systems, one would expect Reichardt's dye to be sensitive to the concentration of ions in solution. However, little change in the spectra of Reichardt's dye is observed when more than 1 equiv of lithium perchlorate is present. At very low concentrations of lithium perchlorate, an equilibrium between two forms of the dye molecule in solution could be observed. As small amounts of salt were added, the long-wavelength band at 826 nm decreased, and a new band at 555 nm appeared. This indicates

**Figure 3.** Plot to determine the equilibrium constant for Reichardt's dye with lithium ion in tetrahydrofuran: log of the ratio of the lithium ion-indicator complex concentration over the "free" indicator concentration versus the log of the lithium perchlorate concentration in tetrahydrofuran. The slope of the line is 1.**Table IV.** Equilibrium Constants for the Association of Lithium Ion with Dipolar Indicator Molecules in Diethyl Ether and Tetrahydrofuran Solutions^a

indicator	equilibrium constant DE ^b	THF ^c
Reichardt's dye	5.0×10^6	1.6×10^5
diacetylsesquifulvalene	7.10 ^d	
	18.2 ^e	9.35
dibenzoylsesquifulvalene	7.77 ^d	
	15.8 ^e	2.39
diformylsesquifulvalene	16.8 ^e	5.44
(dicarbomethoxy)sesquifulvalene	7.39 ^d	7.31

^a Measured at 25.0 °C, the equilibrium constants were calculated using eq 6. ^b Equilibrium constants measured in LiClO₄-diethyl ether solutions. ^c Equilibrium constants measured in LiClO₄-tetrahydrofuran solutions. ^d Equilibrium constant from the region of concentration of lithium perchlorate where the slope of the plot of $\log K_{\text{eq}}$ versus $\log [\text{LiClO}_4] = 0.5$. ^e Equilibrium constant from the region of concentration of lithium perchlorate where the slope of the plot of $\log K_{\text{eq}}$ versus $\log [\text{LiClO}_4] = 1.0$.

that Reichardt's dye is interacting strongly with the lithium ions present and forming a complex that is no longer sensitive to polarity changes of the environment. This is very similar to the behavior of Reichardt's dye in the presence of acids.¹⁰

Assuming the equilibrium was between free Reichardt's dye and lithium-indicator complex (eq 2), an apparent constant for this equilibrium can be calculated using eq 5 and plotting the log of ratio of lithium-indicator complex to free dye versus the log of the lithium perchlorate concentration in each solvent used (Figure 3 and Table III for the data in THF); similar results were achieved in diethyl ether as well. The equilibrium constant calculated from these graphs are 1.6×10^5 for tetrahydrofuran and 5×10^6 for diethyl ether (Table IV). The Reichardt's dye-lithium perchlorate complex was minimally soluble in diethyl ether, so that the error associated with the constants in diethyl ether are larger than those measured in tetrahydrofuran. In both cases, the slope of the graph was 1.0 ± 0.1 , indicating that a 1:1

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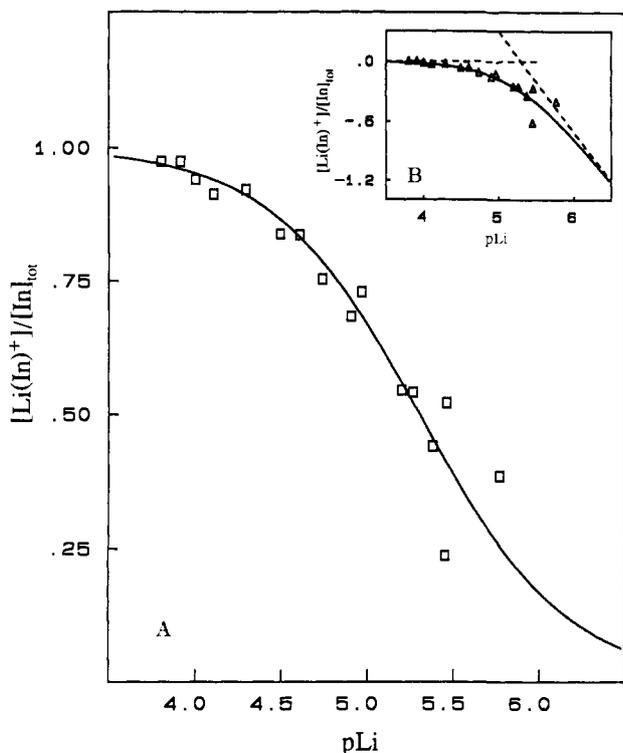


Figure 4. (A) Graph of the fraction of Reichardt's dye complexed to lithium versus negative log of the lithium ion concentration (pLi) in tetrahydrofuran solution. Points are experimental data, and the solid line is the least-squares line calculated using eq 7. (B) Graph of the log of the fraction of Reichardt's dye complexed to lithium ion versus pLi in tetrahydrofuran. The points are experimental data, and the solid curve is calculated from eq 7. The two lines are drawn tangent to the limiting slopes of the calculated curve. The intersection of these two lines, at 5.3, is the pK_{eq}' for the system.

Table V. Equilibrium Constants for the Association of Lithium Ion with Dipolar Indicator Molecules in Diethyl Ether and Tetrahydrofuran Solutions^a

indicator	equilibrium constant DE ^b	THF ^c
Reichardt's dye	1.0×10^6	2.0×10^5
diacetylsesquifulvalene		9.33
dibenzoylsesquifulvalene		2.35
diformylsesquifulvalene	17.4	5.37
(dicarbomethoxy)sesquifulvalene	7.24	7.28

^a Measured at 25.0 °C, the equilibrium constants were calculated by doing a least-squares fit of the experimental data to eq 7.

^b Equilibrium constants measured in LiClO₄-diethyl ether solutions.

^c Equilibrium constants measured in LiClO₄-tetrahydrofuran solutions.

complex of lithium ions to Reichardt's dye forms. With these large apparent equilibrium constants, and a 1:1 interaction, one could consider the lithium ion essentially titrating the indicator in solution at concentrations on the order of 5 mg/L (5 ppm). Thus, Reichardt's dye is very sensitive to the amount of lithium ion present but is not a good indicator of the polarity of more concentrated ionic solutions.

A similar equilibrium constant was arrived at by a different method of treating the data. Assuming the lithium interaction with the indicator molecules is equivalent to the proton interaction with a weak base, one can use eq 7 and plot the fraction of indicator complexed versus the pLi and the log of the fraction complexed against the pLi (Figure 4, a similar figure in diethyl ether solvent was also produced) to arrive at the equilibrium constants (Table V). This treatment was applied to Reichardt's dye in diethyl ether and tetrahydrofuran, with good agreement with the previously listed equilibrium values.

For the 8,9-diacetylsesquifulvalenes, the low-energy transition shifted to a maximum value, and further increase in lithium perchlorate concentration produced no further change in the

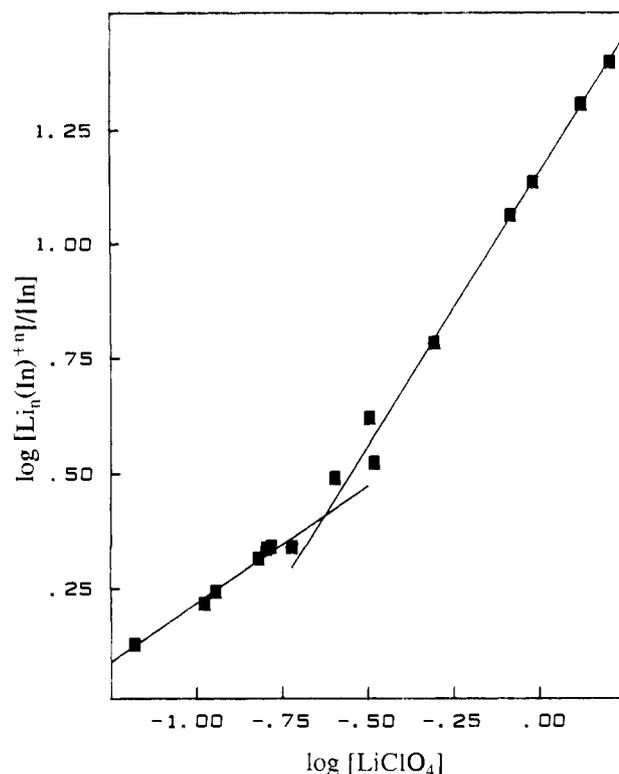


Figure 5. Plot to determine the equilibrium constant for 8,9-diacetylsesquifulvalene with lithium ion in diethyl ether: log of the ratio of the lithium ion-indicator complex concentration over the free indicator concentration versus the log of the lithium perchlorate concentration in diethyl ether. The slope of the line below 0.3 M is 0.5, and the slope above 0.3 M is 1.

spectrum. The same process was used as in the case of Reichardt's dye to calculate the equilibrium constants. The slopes of the graphs give the minimum order of participation by lithium perchlorate in the equilibrium expression. Two of the graphs displayed some dependence of the order of participation with respect to the lithium perchlorate concentration in diethyl ether solution. At low concentrations, below 0.3 M, for the 8,9-diacetyl- and 8,9-dibenzoylsesquifulvalene, the slope was 0.5, implying that a complex of two indicator molecules and one lithium ion could be forming. The slope then increased to 1.0 at higher levels of lithium perchlorate, suggesting the indicator molecule to lithium ion ratio changed to 1:1 (Figure 5, graphs of similar quality were produced for the other indicators in both diethyl ether and tetrahydrofuran solvents). 8,9-Diformylsesquifulvalene displayed a slope of unity, while the carbomethoxy-substituted sesquifulvalene exhibited a slope of 1/2, for the concentration of salt investigated in diethyl ether. For the three indicators that displayed a dye molecule to lithium ion ratio of 2:1, it can be envisioned that two indicator molecules are interacting with the lithium ion to produce a tetrahedral complex (VII).²⁸ Equilibrium constants were calculated for each linear section of the graph for each sesquifulvalene, in the solvents used (Table IV). The order of lithium perchlorate in tetrahydrofuran solvents appears to be concentration independent and equal to 1 for all the sesquifulvalene dyes investigated (Figure 6). The equilibrium constants parallel the values determined in diethyl ether solution but are smaller (Table IV). This indicates that tetrahydrofuran complexes lithium ions better than does diethyl ether.²⁹

As with Reichardt's dye, the same alternate method was used to calculate the equilibrium constants for the sesquifulvalenes, assuming lithium ion interaction with these indicators mimics that of a proton with a weak base. However, this technique was only

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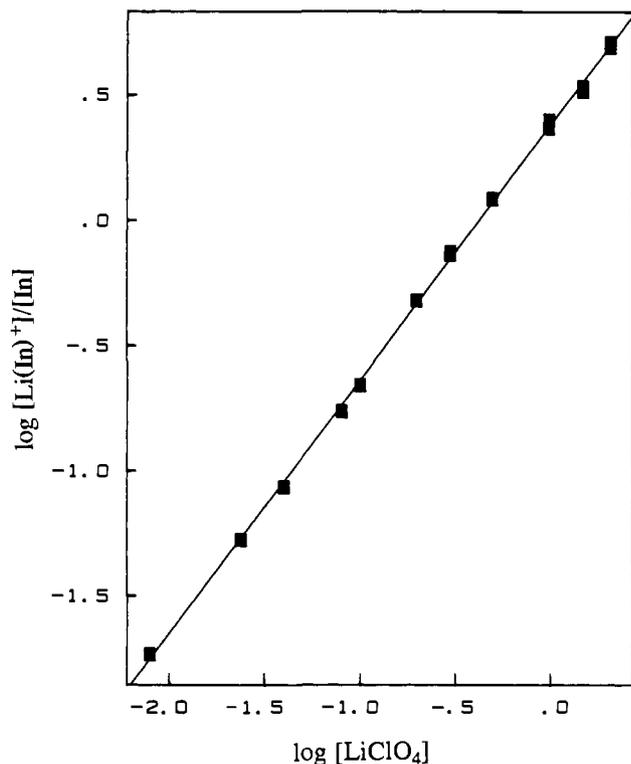


Figure 6. Plot to determine the equilibrium constant for 8,9-dibenzoylsesquifulvalene with lithium ion in tetrahydrofuran: log of the ratio of the lithium ion-indicator complex concentration over the free indicator concentration versus the log of the lithium perchlorate concentration in tetrahydrofuran. The slope of the line is 1.

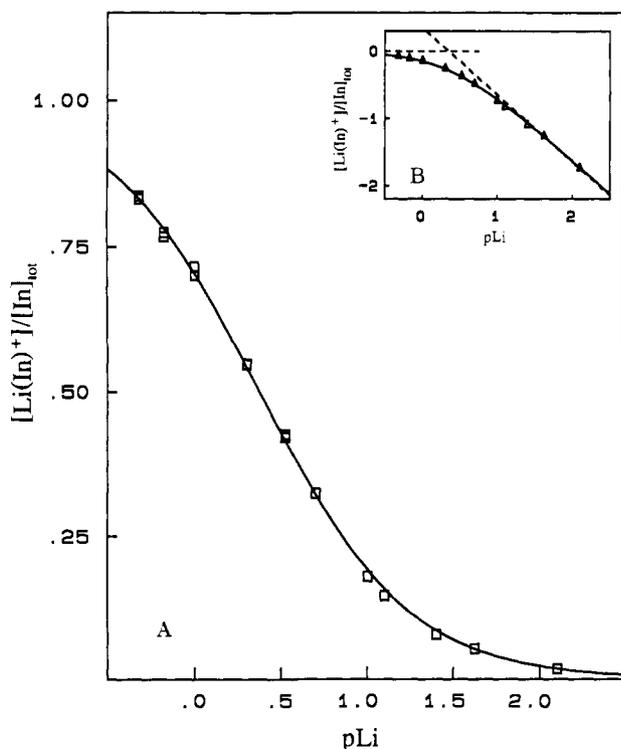


Figure 7. (A) Graph of the fraction of 8,9-dibenzoylsesquifulvalene complexed to lithium versus negative log of the lithium ion concentration (pLi) in tetrahydrofuran solution. Points are experimental data, and the solid line is the least-squares line calculated using eq 7. (B) Graph of the log of the fraction of 8,9-dibenzoylsesquifulvalene complexed to lithium ion versus pLi in tetrahydrofuran. The points are experimental data, and the solid curve is calculated from eq 7. The two lines are drawn tangent to the limiting slopes of the calculated curve. The intersection of these two lines, at 0.358, is the pK_{eq}' for the system.

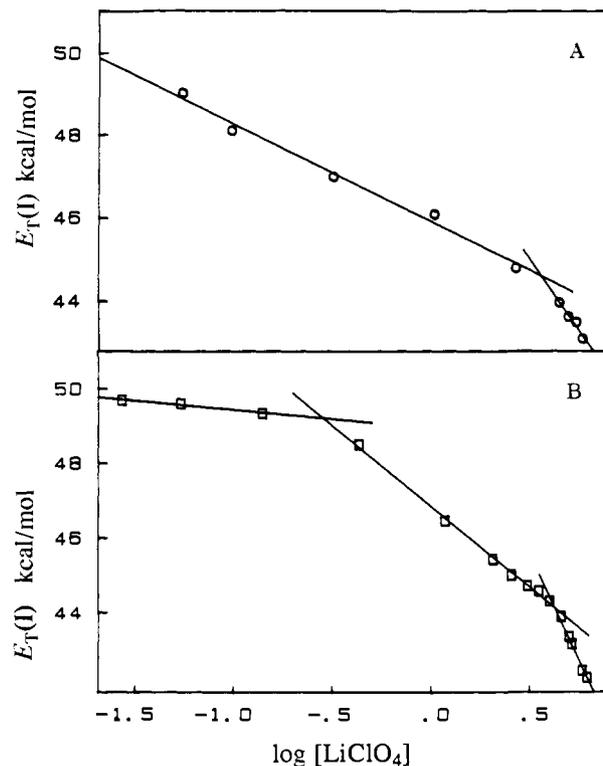


Figure 8. (A) Dependence of the low-energy transition ($E_T(I)$), plotted in kilocalories per mole) of phenol blue versus the concentrations of lithium perchlorate in diethyl ether (O). The break in the line occurs near 4.2 M. (B) Dependence of the low-energy transition ($E_T(I)$), plotted in kilocalories per mole) of phenol blue versus the concentration of lithium perchlorate in tetrahydrofuran (\square). The breaks occur near 0.3 and 4 M.

applied to those indicators that displayed equilibrium constants not dependent on the lithium ion concentrations, i.e. not the 8,9-diacetyl- or 8,9-dibenzoylsesquifulvalenes in diethyl ether. A representative plot that was used to calculate the equilibrium constant is displayed in Figure 7 for 8,9-dibenzoylsesquifulvalene in tetrahydrofuran solution. Other graphs of equal quality were produced for the other sesquifulvalenes. The equilibrium constants calculated in this way, agree well with the previously calculated equilibrium constants (Table V).

The sesquifulvalene compounds are also interesting from a theoretical point of view. As the charge-separated state becomes more important in the ground state, one could consider these compounds becoming aromatic (in Scheme III, the charge-separated resonance structure is becoming more important). This separation of charge can be detected in the ^{13}C NMR spectra of these compounds.^{30,31} The π -electron density of a carbon in the monocyclic aromatic compounds has been related to the chemical shift in the ^{13}C NMR spectra. Upon the addition of LiClO_4 to a solution of 8,9-(dicarbomethoxy)sesquifulvalene in tetrahydrofuran- d_8 , to produce a 2 M solution, a shift of 4 ppm was observed for the carbon atoms between the 7- and 5-membered rings. This result indicates a greater separation of charge is occurring in the salt solution than in pure THF. This greater charge separation in the ground state can be accounted for by the atomic resonance structure becoming more important. One could imply that these solutions of salt can help stabilize the charge-separated state of a dipolar molecule.

An attempt to fit the experimental data of the phenol blue in solutions of lithium perchlorate in diethyl ether and tetrahydrofuran to an equilibrium equation failed, so that a calculated constant for this system could not be achieved. The long-wavelength absorption band continued to shift to higher wavelengths

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with increasing lithium perchlorate concentrations (Figure 8). The molar transition energy was calculated for each concentration of lithium perchlorate in both diethyl ether and tetrahydrofuran solvents so that the change in the transition energy could be monitored. This change would be indicative of the increased interactions between phenol blue and the ionic clusters in solution as the concentration of salt is increased. The molar transition energy, in kilocalories per mole, was plotted versus the log of the lithium perchlorate concentration. For diethyl ether solutions, the transition energy was linearly dependent on the log $[\text{Li}^+, \text{ClO}_4^-]$, with a break occurring near 4.2 M (Figure 8a) corresponding to the transition from lithium dietherate, $\text{Li}(\text{OEt}_2)_2^+ \text{ClO}_4^-$, to lithium monoetherate, $\text{Li}(\text{OEt}_2)^+ \text{ClO}_4^-$ clusters.¹³ Near this point, the slope decreased from -2.35 to -6.8. The same behavior was observed in tetrahydrofuran solution, but two breaks occurred, one at 0.3 M, with the slope decreasing from -0.49 to -4.37, and the second near 4 M, with the slope decreasing further to -12.5 (Figure 8b). This second break near 4 M, similar to the diethyl ether case, represents a transition from disolvent-coordinated lithium ion, $\text{Li}(\text{THF})_2^+ \text{ClO}_4^-$ to the monocoordinated ion, $\text{Li}(\text{THF})^+ \text{ClO}_4^-$.³²

The low-energy absorbance band of phenol blue continued to change with increasing salt concentration unlike the other indicators used in this study. Thus, this dye could be used as indicator of the polarity of these solutions of ionic clusters.

Conclusion

The search for simple and useful indicators of solvent polarity continues. Here, we have presented work that shows that some indicators, which work well in pure and mixed-solvent systems,

(32) Pocker, Y.; Ciula, J. C., unpublished results.

will not behave as expected in highly ionic media, such as lithium perchlorate in diethyl ether and tetrahydrofuran. In such ionic media, the lithium ions of the media act like Lewis acids toward indicators such as Reichardt's dye, making this indicator extremely sensitive to low concentrations of lithium ion. It is possible that this indicator could be used to determine the concentration of lithium ions at the parts per million level (1×10^{-5} M) in non-aqueous solutions.

On the other hand, phenol blue can detect differences in polarity of ionic systems throughout the usable concentration range of salt, up to 6 M in diethyl ether and 7 M in tetrahydrofuran. Using this dye as a polarity indicator, we discover that at above 5.0 M lithium perchlorate in diethyl ether, this ionic system is "more polar" than water.²⁶

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Registry No. I, 2150-58-5; II, 10081-39-7; III, 120060-19-7; IV, 15310-43-7; V, 120060-20-0; VI, 120060-21-1; sodium 1,2-(dicarbomethoxy)cyclopentadienide, 68348-90-3; tropylium tetrafluoroborate, 27081-10-3; lithium, 7439-93-2; lithium perchlorate, 7791-03-9; hexane, 110-54-3; carbon tetrachloride, 56-23-5; toluene, 108-88-3; triethylamine, 121-44-8; diethyl ether, 60-29-7; chloroform, 67-66-3; ethyl acetate, 141-78-6; tetrahydrofuran, 109-99-9; methylene chloride, 75-09-2; pyridine, 110-86-1; isopropyl alcohol, 67-63-0; acetone, 67-64-1; ethanol, 64-17-5; methanol, 67-56-1; dimethylformamide, 68-12-2; acetonitrile, 75-05-8; ethylene glycol, 107-21-1; dimethyl sulfoxide, 67-68-5; water, 7732-18-5; *N*-methylacetamide, 79-16-3.

Affinities of Racemic and Meso Forms of *N,N'*-Ethylenebis[2-(*o*-hydroxyphenyl)glycine] for Divalent and Trivalent Metal Ions

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Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received August 17, 1988

Abstract: The commercially available multidentate ligand *N,N'*-ethylenebis[2-(*o*-hydroxyphenyl)glycine] (EHPG) contains a mixture of racemic and meso forms of the ligand. Theoretical work has addressed the differences in the stabilities of the meso and racemic isomers, which until the current study have not been measured. In this study the commercial ligand has been separated into a racemic mixture and meso isomer, and potentiometric and spectrophotometric stability measurements have been made of each. Reported here for both forms at 25.0 °C and $\mu = 0.10$ M (KCl) are ligand protonation constants as well as chelate protonation, stability, and hydrolysis constants with the divalent metal ions Ni(II), Cu(II), and Zn(II) and the trivalent metal ions Fe(III), Ga(III), and In(III). In all cases *rac*-EHPG forms the more stable complexes. Since the basicities of the two ligands are essentially the same (*rac*-EHPG, 38.0; *meso*-EHPG, 37.9), these ligands provide an interesting example whereby the differences observed in the stabilities of their complexes are due to differences in coordination geometry. A comparison of the equilibrium distribution of metal ion between each form of EHPG and the iron transport protein transferrin indicates that while the racemic and meso forms of the ligand may compete successfully *in vivo* for Fe(III) and Ga(III), the In(III) complexes are decidedly weaker and may be converted completely to the transferrin complexes, provided that the exchange kinetics are sufficiently rapid.

Interest in the multidentate ligand *N,N'*-ethylenebis[2-(*o*-hydroxyphenyl)glycine] (EHPG) has been long and varied. Initially this interest focused on the ability of its extremely stable iron chelate to alleviate iron chlorosis in plants caused by alkaline soil conditions.¹ Much later EHPG was used as an active site

model of the iron transport protein transferrin.²⁻⁷ Most recently work has focused on the unique vanadium coordination chemistry

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