Studies of Ion Pairs. Isomerization of Ion Pairs Possessing a Solvated Agent on Their Periphery into the Agent-Separated Pairs

R. V. Slates and M. Szwarc

Contribution from the Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse, New York 13210.

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Abstract: The equilibrium between metallic sodium and biphenyl on one hand and sodium biphenyl on the other was investigated in 2-methyltetrahydrofuran (MeTHF) and in tetrahydropyran (THP). The investigation covered the temperature range −40 to +25°, and it was shown that the van't Hoff plots were linear for both systems. Conductance studies indicated that the dissociation of $B\cdot^-,Na^+$ ion pair in MeTHF is negligible and it is even lower in THP. The heat of dissociation of $B\cdot^-,Na^+$ into free ions is −3.4 kcal/mole in MeTHF, corresponding to $\Delta S = -56$ eu. The salt, $B\cdot^-,Na^+$, becomes coordinated with glyme-3 or glyme-4 if these polyethers are added to the system. It was shown that the coordination is stoichiometric, giving $B\cdot^-,Na^+$:glyme = 1:1. Equilibrium constants of coordination were determined for glyme-3 and glyme-4 over the whole investigated temperature range, and the respective ΔH and ΔS of coordination were derived. The coordinating agent may serve as a probe which reveals the structure of the original ion pair in the investigated solvent. The pairs $B\cdot^-,Na^+$ are of the contact type in MeTHF and in THP. The pairs coordinated with glyme-3 are still of contact type, indicating that the glyme is attached to the periphery of the pair. However, two isomeric ion pairs are formed when glyme-4 is coordinated with $B\cdot^-,Na^+$. In one the glyme is attached to the periphery of the pair, whereas the glyme separates the ions in the other. This seems to be the first example of isomerism arising from different location of the coordinating (solvating) agent in an ion pair. The heat and entropy of isomerization were determined.

The pioneering studies of Schlenk[1] demonstrated that sodium metal reacts with aromatic hydrocarbons giving the respective radical ions. The nature of solvent is extremely important, and the degree of conversion greatly depends on its choice.[2] Obviously, the solvation of the product provides much of the driving force of the reaction.

Subsequent studies of Hoijtink[3] proved that these reactions are exothermic and, hence, the equilibrium constant of a process such as

$$\text{Na(metal)} + \text{biphenyl(soln)} \rightleftharpoons \text{Na}^+,\text{biphenyl}\cdot^-\text{(soln)} \qquad \text{(I)}$$

increases with decreasing temperature. Equilibria of this type have been extensively studied by Shatenstein and his colleagues.[4,5] It appears from their work that steric factors are often even more important than the polarity of the solvent; *e.g.*, at 0° the equilibrium constant for reaction I is 5.0 for 1,2-dimethoxypropane but only 0.04 for 1,3-dimethoxypropane.[4] This indicates that the *specific* coordination of the solvent with the cation of an ion pair is of paramount significance in determining the position of the equilibrium.

Studies of system I have been carried out in our laboratory. Our intention was (1) to reexamine the dependence of the heat of reaction on temperature; (2) to determine to what extent the dissociation of ion pairs

$$\text{Na}^+,\text{biphenyl}\cdot^- \rightleftharpoons \text{Na}^+ + \text{biphenyl}\cdot^- \qquad \text{(II)}$$

contributes to the over-all equilibrium constant; and (3) to use the system for studies of ion-pair interaction with suitable coordinating agents added to the solvent. In our present work three solvents were examined: tetrahydrofuran (THF), 2-methyltetrahydrofuran (MeTHF), and tetrahydropyran (THP). Glyme-3 ($CH_3OCH_2CH_2OCH_2CH_2OCH_3$) and glyme-4 ($CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$) were chosen as the coordinating agents.

Experimental Section

After some preliminary work, the apparatus shown in Figure 1 was designed. It permitted reliable studies of the equilibrium over a wide temperature range. The apparatus consisted of a 300-ml round flask (A), an all-glass, magnetically driven centrifugal pump (B), and a 2-mm optical cell (C). Thermometer pockets (T_1 and T_2) were provided at the cell and in the flask to permit accurate temperature measurements. Flask A and the pump were immersed in a large dewar filled with a suitable liquid maintained at the desired temperature. The optical cell was placed in the cell compartment of a Cary-14 spectrophotometer, and this permitted the spectrum to be recorded with the liquid circulating.

The solvents, acquired commercially, were refluxed twice with liquid potassium and fractionated. The purified liquid was contacted with sodium and sodium benzophenone, and, after being deaerated, it was distilled under high vacuum into a calibrated receiver equipped with a break-seal and an optical cell. Purified biphenyl had been previously sublimed under vacuum into the same container before the distillation of the solvent. The concentration of the biphenyl solution was then determined spectrophotometrically. Thereafter, the container was attached at point D to flask A of the flow apparatus, an ampoule with metallic sodium was connected at point E, and the unit was evacuated through the outlet F. After flaming out the whole apparatus, sodium was distilled into A to form a thick film on its wall. The sodium ampoule was then removed, and the apparatus was detached from the vacuum line by sealing it off at point F. The break-seal on the container of the biphenyl solution was crushed, the solution transferred into A and chilled, and the container removed by sealing it off.

It was found that the centrifugal pump operates well if a small pressure of an inert gas is maintained in the unit. This was done by having an ampoule (G) filled with purified helium attached to

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[1] W. Schlenk, J. Appenrodt, A. Michael, and A. Thal, *Ber.*, **47**, 43 (1914).

[2] D. N. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

[3] G. J. Hoijtink, E. de Boer, P. H. van der Meij, and W. P. Weijland, *Rec. Trav. Chim.*, **75**, 487 (1956).

[4] A. I. Shatenstein, E. S. Petrov, and M. I. Belousava, "Organic Reactivity," Vol. 1, Tartus State University, Estonia, USSR, 1964, p 191.

[5] A. I. Shatenstein, E. S. Petrov, and E. A. Yakovleva, Preprint, I.U.P.A.C. Meeting on Macromolecules, Prague, 1965, p 163.

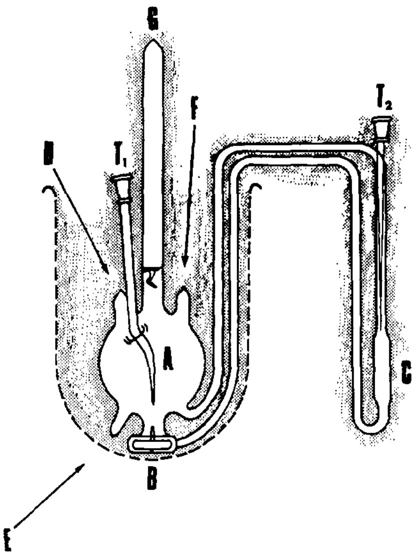

Figure 1. The apparatus developed for studies of equilibrium between sodium and sodium biphenyl.

the flask, and eventually the helium was introduced into the unit by crushing the respective break-seal. In experiments involving glymes, the ampoules containing determined quantities of the required reagent were attached to G through break-seals. The glymes were purified by our standard procedure using alkali metals.

Equilibrium was established first at the lowest temperature. A 3-pentanone slush bath was used in THP studies to maintain the circulating solution at about $-45°$ without freezing the solvent. The approach to equilibrium is very slow at low temperature and, therefore, the solution was kept overnight in the cooling bath. It was found impractical to reach equilibrium at temperatures much lower than $-50°$. To avoid heat losses, the connecting tubes were thermally insulated. The spectrum was determined and the optical density measured at λ_{max} 400 mμ.[6] Condensation on the walls of the optical cell was prevented by inserting a Petri dish containing isopropyl alcohol into the cell compartment. The system was assumed to be at equilibrium when the optical density remained constant for one-half hour. After recording the spectrum of the equilibrated solution, the temperature of the bath was slowly raised by a few degrees, and the spectrum recorded again when the system attained its new equilibrium. This procedure was repeated until eventually the temperature reached 25°

As the temperature rises sodium is deposited. It is essential to avoid the formation of colloidal sodium which could scatter the light of the spectrophotometer beam. Moreover, the chemical potential of colloidal sodium may differ from that of the bulk and this may distort the investigated equilibrium. The presence of a heavy sodium film and the circulation of the solution, coupled with the slow rise of temperature, led to the deposition of the excess sodium on the film, preventing erroneous measurements of optical density.

Our conventional technique[7] was used in conductance studies. All the experimental details pertinent for this work are given in the above reference.

Results

The dissociation constants of $Na^+,B\cdot^-$ ion pairs in MeTHF were determined conductometrically over a temperature range of -70 to $+25°$. The relevant K_{Diss}'s were calculated from the respective Fuoss lines and Λ_0's, the latter being computed from the Λ_0's determined in THF[6] by accepting the validity of the Walden rule. The reliability of this rule may be questioned; nevertheless, any reasonable deviations from it applicability could not affect the final K_{Diss} by more than 50%. The plot of log K_{Diss} *vs.* $1/T$ is shown in Figure 2. The heat of dissociation was found to be -3.4 kcal/mole (ΔH in THF is -7.3 kcal/mole) and the corresponding $\Delta S = -56$ eu. The interaction of the free Na^+ ion with MeTHF is apparently weaker than that with THF. Nevertheless, the free sodium cations are probably coordinated with the same number of solvent molecules in either medium, because ΔS in THF (-52 eu) differs insignificantly from that found in MeTHF.

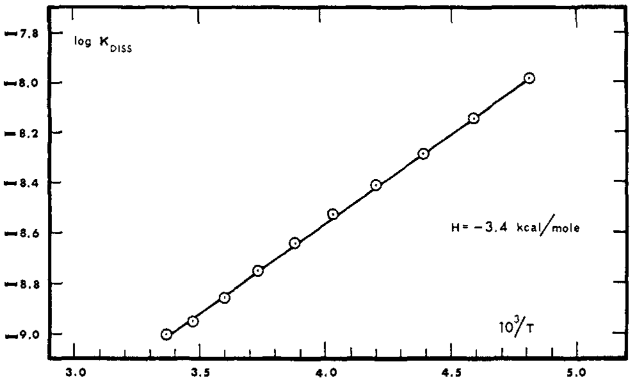

Figure 2. The dissociation constant of $B\cdot^-,Na^+$ ion pairs in MeTHF as a function of T.

The fraction of free ions in the investigated solutions may now be estimated. At the lowest concentration of $Na^+,B\cdot^-$ it amounts to not more than 1–2% and, therefore, the equilibrium constants, K_I, may be calculated

$$\text{Na(metal)} + \text{B(sol)} \overset{K_I}{\rightleftharpoons} \text{B}\cdot^-\text{Na}^+\text{(soln)}$$

from the spectrophotometric data without introducing corrections to account for the presence of the free ions.

Sodium biphenyl in MeTHF and in THP absorbs at λ_{max} 400 mμ. Neither the addition of glyme-3 nor variation of temperature affected the position of the absorption maximum, although the extinction coefficient increased by 4% as the solution was cooled from 25 to $-40°$ (of course, the volume contraction was accounted for in the calculation). However, some changes in spectrum were observed in the presence of glyme-4, the λ_{max} being again 400 mμ at 25° but 406 or 407 mμ at $-40°$. In fact, two overlapping bands, one corresponding to λ_{max} 400 mμ the other to 406 mμ, appeared at intermediate temperatures, and for each concentration of glyme-4 it was possible to determine the temperature at which both bands had equal intensity. The broadening of the spectrum resulting from this phenomenon was small, and consequently the optical density was insignificantly affected.

The experimental K_I values in MeTHF are listed in Table I. The plot of log K_I *vs.* $1/T$, shown in Figure 3, is linear over the whole investigated temperature range. The agreement with the single value reported by Shatenstein, *et al.*,[5] is excellent. The reaction is exothermic, $-\Delta H \sim 9.9$ kcal/mole and $\Delta S \sim -43$ eu. The substantial decrease in entropy of the over-all reaction is expected; it reflects the degree of orientation of the neighboring solvent molecules by the ion pair.

Addition of glyme-4 substantially increased the total concentration of radical ions which coexist with metallic sodium. Conductance studies indicated only a

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(6) In the presence of glyme-4 the absorption maximum shifts from 400 to 406 or 407 mμ. The optical density is then determined at the maximum of the absorption curve.

(7) P. Chang, R. V. Slates, and M. Szwarc, *J. Phys. Chem.*, 70, 3180 (1966).

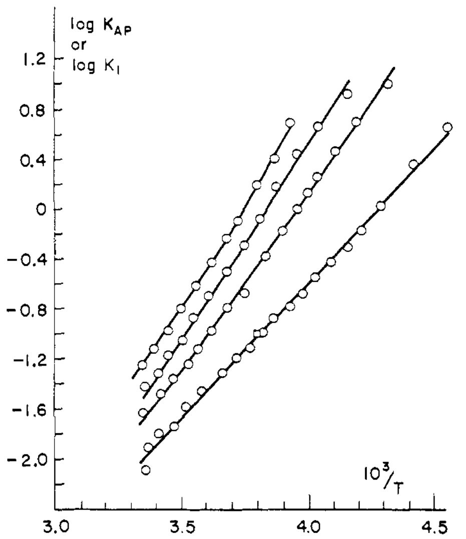

Figure 3. Equilibrium constants K_I and K_{AP} for the system $B\cdot^-,Na^+$ in MeTHF in the absence or presence of glyme-4 as function of temperature. The □ is the single result of Shatenstein.

slight change in the fraction of free ions (less than 4%), and therefore the increase in the observed optical density must be attributed to the participation of another equilibrium, *viz.*

$$B\cdot^-,Na^+ + (\text{glyme}) \underset{}{\overset{K_E}{\rightleftarrows}} B\cdot^-,Na^+(\text{glyme})_n$$

which, together with equilibrium I, was responsible for the formation of the additional radical ions.

Table I. Equilibrium between Sodium Metal, Biphenyl, and Sodium Biphenyl in MeTHF

Temp, °C	$B\cdot^- \times 10^4\ M^a$	$B \times 10^4\ M^a$	K_I
24.9	0.029	3.49	0.0082
20.0	0.057	3.48	0.016
15.0	0.064	3.50	0.018
11.2	0.091	3.48	0.026
5.9	0.119	3.48	0.034
0.4	0.167	3.45	0.048
−4.0	0.214	3.42	0.063
−7.6	0.262	3.39	0.077
−11.3	0.34	3.33	0.101 (0.11)[b]
−14.3	0.42	3.25	0.130
−18.6	0.525	3.17	0.166
−21.5	0.64	3.07	0.208
−24.8	0.81	2.91	0.280
−28.6	1.01	2.72	0.37
−32.5	1.25	2.50	0.50
−35.3	1.52	2.25	0.68
−40.0	1.95	1.84	1.06
−47.0	2.66	1.16	2.28
−53.2	3.15	0.695	4.53

[a] Temperature corrected. Due to contraction of the volume, the total concentration of B + B^- increases with decreasing temperature. [b] The value of K in parenthesis was reported by Shatenstein, *et al.*[5] The actual number of optical density determinations is much greater than those listed in the table. The temperature intervals between the measurements were indeed very small.

Let us denote by $B\cdot^-$ the concentration of $B\cdot^-,Na^+$ in equilibrium with sodium in the absence of glyme, by $B_1\cdot^-$ its concentration in the presence of glyme, and by $(B\cdot^-,E)$ the concentration of the complex, $B\cdot^-,Na^+(\text{glyme})_n$. The initial concentration of biphenyl is denoted by B_0 and the concentration of glyme by E.

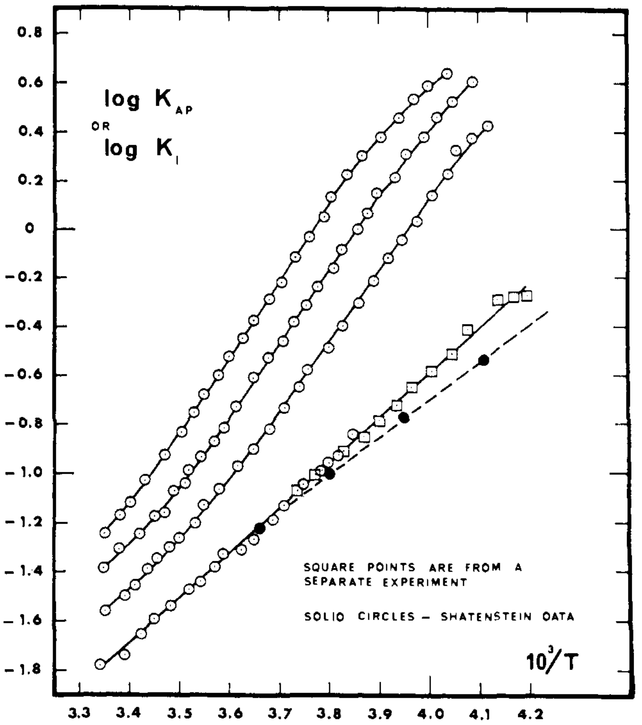

Figure 4. Equilibrium constants K_I and K_{AP} for the system $B\cdot^-,Na^+$ in THP in the absence and presence of glyme-4.

The following relations are then established if the system is at equilibrium with respect to both reactions

$$K_I = B\cdot^-/[B_0 - B\cdot^-] = B_1\cdot^-/[B_0 - B_1\cdot^- - (B\cdot^-,E)]$$

$$K_E = (B\cdot^-,E)/B_1\cdot^-(E)^n$$

The apparent equilibrium constant, K_{AP}, is defined as the ratio

$$K_{AP} = [B_1\cdot^- + (B\cdot^-,E)]/[B_0 - B_1\cdot^- - (B\cdot^-,E)]$$

and its value is obtained directly from the experimental spectrophotometric data given in Table II (see also Figures 3 and 4). It follows that

$$(K_{AP} - K_I)/K_I = K_E E^n$$

The value of n is given by the slope of the line obtained by plotting log $(K_{AP} - K_I)$ *vs.* log E. Such lines are shown in Figure 5 and since their slopes are unity, $n = 1$; *i.e.*, the complex involves only one molecule of glyme.

The complexing constant K_E could be determined by plotting $(K_{AP} - K_I)/K_I$ *vs.* E, but this method is most susceptible to small experimental errors. To improve the reliability of the data log $[(K_{AP} - K_I)/K_I F]$ was plotted *vs.* $1/T$. The factor F accounts for the volume contraction and corrects the result to a constant, temperature-independent concentration of glyme. Since

$$\log [(K_{AP} - K_I)/K_I F] = \log K_E + \log E_{\text{const}}$$

the left-hand side is most probably a linear function of $1/T$. This plot permits us to average the experimental fluctuations and gives the data from which reliable values of K_E are calculated.

Similar investigations were performed in THP using glyme-3 or glyme-4 as the complexing agents. Approximate conductance studies indicated that K_{Diss} of sodium biphenyl in THP is less than 5×10^{-11} M at 20°,

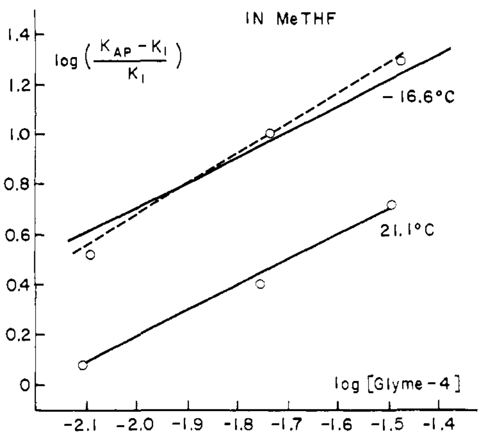

Figure 5. Plot of log $(K_{AP} - K_I)/K_I$ *vs.* log [glyme-4]. The dotted line is the least-squares one; the solid line is the "best" line having slope 1.

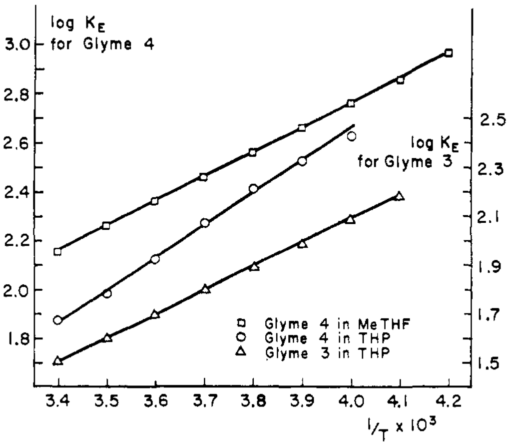

Figure 6. Plot of log K_E *vs.* $1/T$.

increasing perhaps to 1×10^{-10} *M* at −23°. Addition of glyme, far in excess of the highest concentration used in the equilibrium experiments, raised these values only by a factor of 2–3. Hence, the concentration of free ions was again negligible, even in the experiments performed at the lowest temperatures and in the presence of the largest amounts of glyme. Therefore, the equilibrium constants K_I and K_E could be determined in both THP and MeTHF, with no corrections being necessary to account for the presence of free ions.

The equilibrium constants K_I in THP are given in Table III and presented graphically in Figure 4. The agreement with Shatenstein's data[4] is again satisfactory, although we suspect that his solutions did not reach the ultimate equilibrium at lower temperatures (see Figure 4). The data leading to K_{AP} for both glyme-3 and glyme-4 are collected in Table IV and the latter are also presented graphically in Figure 4. It was shown again that only one molecule of glyme-3 or glyme-4 participates in the complex formed in THP.

The equilibrium constants, K_E, of the reaction

$$B\cdot^-,Na^+ + \text{glyme} \rightleftarrows B\cdot^-,Na^+(\text{glyme})$$

are calculated for MeTHF and THP and for glyme-4 and glyme-3. The final results are collected in Table V and presented graphically in Figure 6.

A few experiments were performed in THF. The conversion is rather high and ionization not negligible. Consequently, the system was not suitable for our studies. Generally, a satisfactory agreement with Shatenstein's data[4] was again observed.

Table II. Equilibrium between Sodium Metal, Biphenyl, and Sodium Biphenyl in MeTHF in the Presence of Glyme-4

Temp, °C	$B\cdot^- \times 10^4$ *M* (total)[a]	$B \times 10^4$ *M*[a]	K_{AP}
Total [Glyme-4] = 77.8×10^{-4} *M* at 20°			
25.4	0.08	3.44	0.023
19.6	0.11	3.43	0.033
14.9	0.15	3.41	0.043
10.6	0.19	3.39	0.056
6.9	0.25	3.34	0.075
3.0	0.34	3.27	0.105
−1.7	0.51	3.12	0.162
−6.4	0.63	3.01	0.211
−12.0	1.08	2.58	0.419
−16.5	1.47	2.21	0.667
−20.4	1.86	1.84	1.01
−23.0	2.13	1.58	1.35
−25.5	2.40	1.32	1.81
−30.0	2.80	0.95	2.95
−34.5	3.14	0.63	5.01
−41.8	3.45	0.34	10.0
Total [Glyme-4] = 176×10^{-4} *M* at 20°			
24.6	0.13	3.39	0.038
20.4	0.16	3.38	0.048
17.0	0.23	3.32	0.068
12.1	0.29	3.28	0.088
8.3	0.41	3.17	0.130
3.8	0.60	3.00	0.200
−1.2	0.87	2.76	0.314
−6.3	1.23	2.41	0.512
−10.4	1.69	1.97	0.856
−15.4	2.22	1.47	1.51
−20.2	2.72	0.98	2.77
−25.8	3.07	0.65	4.71
−32.9	3.36	0.40	8.42
−37.8	3.48	0.29	11.8
Total [Glyme-4] = 322×10^{-4} *M* at 20°			
25.6	0.185	3.33	0.056
21.6	0.25	3.28	0.076
16.7	0.34	3.21	0.106
12.3	0.49	3.08	0.158
7.6	0.69	2.90	0.239
3.4	0.97	2.64	0.368
−1.0	1.33	2.29	0.581
−4.0	1.62	2.02	0.80
−9.9	2.24	1.42	1.58
−14.4	2.65	1.03	2.56
−18.9	2.94	0.76	3.89
−23.7	3.19	0.53	6.07
−28.8	3.33	0.41	8.07
−34.5	3.43	0.33	10.4

[a] Temperature corrected.

Discussion

The results of Scott, *et al.*,[2] demonstrated that the extent of reaction I is greatly affected by the nature of solvent. The subsequent extensive investigations by Shatenstein and his colleagues[4,5] revealed how the heat and entropy of these processes are affected by the solvation of ion pairs. The problem of interactions between solvent and ion pairs has been recently reviewed.[8] Such interactions may be treated under two headings: (1) in a purely physical interaction the ion pair is visualized as a dipole immersed in a solvent which is treated as a continuum characterized by its dielectric constant; and (2) in a chemical interaction

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(8) M. Szwarc, *Makromol. Chem.*, **89**, 44 (1965).

Table III. Equilibrium between Sodium Metal, Biphenyl, and Sodium Biphenyl in THP[a]

Temp, °C	$B\cdot^- \times 10^4$ M[b]	$B \times 10^4$ M[b]	K_I[c]
26.0	0.064	3.91	0.016
19.5	0.085	3.92	0.022
14.0	0.113	3.91	0.029
9.1	0.140	3.91	0.036
5.2	0.182	3.88	0.047
0.8	0.209	3.88	0.054
−3.7	0.283	3.82	0.074 (0.068)
−8.8	0.385	3.74	0.103
−9.9	0.34[d]	3.04[d]	0.111 (0.10)
−14.4	0.42[d]	2.97[d]	0.143
−19.1	0.54[d]	2.87[d]	0.190 (0.12)
−23.7	0.72[d]	2.71[d]	0.265
−27.9	0.97[d]	2.48[d]	0.390 (0.27)
$\Delta H = -8.6$ kcal/mole; $\Delta S = -37$ eu			

[a] Three series of experiments were performed. Identical results were obtained, indicating that all the impurities which distort the results, particularly at higher temperatures, have been successfully removed. The actual number of optical density determinations is much greater than those listed in the table (see Figure 4). The temperature intervals between the measurements were indeed very small. [b] Temperature corrected. [c] The values of K in parentheses are those reported by Shatenstein, *et al.*,[4] interpolated to the closest temperatures given in the table. [d] Second series of experiments with different initial concentrations of biphenyl.

the solvent acts as a reagent and forms stoichiometric complexes with the ion pairs. In the case of ethereal solvents, which are our main concern, the complexing involves predominantly the cation.

The physical electrostatic interaction depends on the dielectric constant of the medium. It should be recalled, however, that the local dielectric constant differs from the bulk dielectric constant. This complicates considerably any treatment based on the Born's approach. In addition, van der Waals forces should not be neglected.[9]

The problem of chemical complexing is vexed because it is not always possible to distinguish, in an unequivocal way, between a "bonded" and "nonbonded" solvent molecule. In many systems more than one type of ion pair may exist in a solution. The various types are distinguished by the specific geometry and the degree of their complexing with the molecules of solvent. This conclusion was visualized by Fuoss[10] who approached the problem of structure of ion pairs by considering their formation resulting from recombination of free ions coordinated with solvent molecules. The necessity of expulsion of the last sheath of solvent molecules before the ions come into physical contact leads to a barrier and, therefore, permits one to visualize at least two types of ion pairs, *i.e.*, those separated and the others nonseparated by solvent molecules.

Winstein[11] was first to suggest that equilibrium between contact and solvent-separated ion pairs may be established in solution, and this idea was developed further by Grunwald.[12] Since then the existence of two (or more) types of ion pairs was demonstrated by various physico-chemical studies. For example, in some systems, notably sodium and lithium salts of fluorenyl carbanions, these species may be differentiated, because their optical spectra are distinct.[13] A wealth of new and intriguing information shedding much light on this subject has been provided recently by the esr studies of salts of radical anions.[14] We hope that our present work provides still another avenue for studying the structure of ion pairs in solution.

The reaction of metallic sodium with a biphenyl solution giving a solution of $B\cdot^-,Na^+$ leads to a decrease in the entropy of the system which is approximately equal to the entropy of solvation of gaseous $B\cdot^-,Na^+$ ion pairs. It is interesting to note that for both, MeTHF and THP, the plots of log K_I *vs.* $1/T$ are linear over the investigated temperature range, indicating that only *one* type of $B\cdot^-,Na^+$ ion pair, presumably the contact one, exists under these conditions. This conclusion is supported by spectral observations; the λ_{max} is identical for both solutions and not affected by temperature. The situation is different in THF where a similar plot might be curved, and a shift of λ_{max} toward longer wavelength is observed on lowering the temperature of solution.

It should be noted that $-\Delta H_I$ and $-\Delta S_I$ are nearly identical for the reaction in THP and MeTHF (in THP $-\Delta H = 8.6$ kcal/mole and $-\Delta S = 37$ eu; in MeTHF the respective values are 9.9 kcal/mole and 43 eu). The differences are small and may be within experimental errors. Even more striking is the similarity between the respective K_I's (see Tables I and III). This may not be surprising since the two ethers are isomeric and strikingly similar in their behavior, although the dielectric constant of THP is lower than that of MeTHF (at 25° $\epsilon = 5.61$ for THP and 6.24 for 2-MeTHF: unpublished data from this laboratory). The ion pair is of a contact type (judging from spectral and conductance evidence), and therefore a small change in the dielectric constant of the ethers affects insignificantly the equilibrium constant of their formation.

Association of ion pairs with various complexing agents, particularly with those which act as polydentate species, permits us to investigate two problems: (a) how the nature of the complexing agent affects the equilibrium of the adduct formation, and especially to what extent the heat and the entropy of association are influenced by its structure; (b) how the complexing agent may be treated as a probe with the aid of which the structure of the original ion pair may be studied. The latter approach will be discussed now.

To clarify our ideas let us consider a few hypothetical cases of interaction between an ion pair and a complexing agent. The original ion pair may be of contact type or solvent separated.

(1) A contact ion pair may interact strongly with the surrounding solvent molecules to form on its periphery a relatively rigid coordination shell. A coordinating polydentate agent added to such a solution would then replace two or more solvent molecules in the shell. Such a process should lead to an *increase* in the entropy of the system. The reaction is expected to be exothermic and to leave unaltered the absorption spectrum of the ion pair. Such findings are, therefore, diagnostic for the proposed structure of the original ion pair.

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(9) E. Grunwald and E. Price, *J. Am. Chem. Soc.*, **86**, 4517 (1964).

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

(11) S. Winstein, E. Clippinger, A. H. Fainberg, and G. C. Robinson, *ibid.*, **76**, 2597 (1954).

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Table IV. Equilibrium between Sodium Metal, Biphenyl, and Sodium Biphenyl in THP in the Presence of Glyme-4 or Glyme-3

Temp, °C	$B\cdot^- \times 10^4$ *M* (total)[a]	$B \times 10^4$ *M*[a]	K_{AP}	Temp, °C	$B \times 10^4$ *M* (total)	$B \times 10^4$ *M*	K_{AP}
Total [Glyme-4] = 94.5 × 10^{-4} *M* at 20°				Total [Glyme-3] = 105 × 10^{-4} *M* at 20°			
25.2	0.11	3.87	0.028	25.2	0.12	4.31	0.028
20.2	0.13	3.86	0.035	20.7	0.14	4.31	0.033
16.4	0.17	3.85	0.044	17.1	0.17	4.30	0.040
12.5	0.21	3.82	0.055	12.3	0.22	4.28	0.051
8.3	0.28	3.77	0.074	8.8	0.25	4.26	0.059
3.5	0.39	3.68	0.106	5.4	0.31	4.22	0.073
−1.5	0.54	3.55	0.152	1.6	0.40	4.15	0.096
−5.5	0.75	3.37	0.221	−2.0	0.55	4.01	0.138
−9.7	1.02	3.12	0.327	−5.4	0.61	3.97	0.155
−14.0	1.38	2.77	0 499	−9.2	0.83	3.78	0.218
−17.9	1.81	2.36	0.769	−12.6	1.00	3.62	0.276
−20.0	1.99	2.19	0.907	−16.5	1.20	3.44	0.349
−23.6	2.44	1.75	1.39	−21.8	1.73	2.94	0.587
−26.9	2.87	1.34	2.14	−25.7	2.10	2.59	0.810
−30.5	3.11	1.12	2.76	−28.2	2.37	2.34	1.01
				−31.5	2.68	2.04	1.32
Total [Glyme-4] = 208.4 × 10^{-4} *M* at 20°				Total [Glyme-3] = 233 × 10^{-4} *M* at 20°			
25.7	0.16	3.82	0.041	25.5	0.16	4.27	0.038
19.5	0.21	3.79	0.056	22.3	0.19	4.26	0.043
14.9	0.26	3.76	0.069	18.0	0.21	4.26	0.050
10.7	0.37	3.67	0.102	13.9	0.26	4.23	0.062
5.7	0.53	3.53	0.150	10.0	0.32	4.19	0.075
0.8	0.81	3.28	0.246	5.7	0.40	4.13	0.096
−3.3	1.05	3.05	0.344	2.5	0.49	4.05	0.122
−6.8	1.35	2.77	0.488	−1.0	0.61	3.95	0.154
−10.4	1.69	2.45	0.690	−4.2	0.78	3.80	0.206
−14.0	2.07	2.08	0.992	−8.3	1.02	3.58	0.284
−16.8	2.44	1.72	1.42	−12.1	1.29	3.33	0.387
−20.7	2.81	1.37	2.06	−15.9	1.64	3.00	0.546
−24.4	3.12	1.08	2.88	−19.1	1.96	2.70	0.727
−28.4	3.37	0.85	3.95	−23.4	2.42	2.26	1.07
−30.5	3.46	0.77	4.47	−27.6	2.83	1.87	1.51
				−30.4	3.11	1.61	1.93
				−32.8	3.34	1.39	2.41
Total [Glyme-4] = 364 × 10^{-4} *M* at 20°				Total [Glyme-3] = 418 × 10^{-4} *M* at 20°			
25.4	0.21	3.76	0.057	24.9	0.24	4.19	0.058
21.0	0.28	3.71	0.077	20.0	0.28	4.18	0.068
14.8	0.42	3.60	0.118	15.4	0.34	4.14	0.082
10.2	0.60	3.44	0.176	10.5	0.45	4.06	0.111
6.4	0.81	3.25	0.250	5.7	0.59	3.94	0.149
2.6	1.07	3.00	0.357	1.6	0.77	3.78	0.202
−1.2	1.39	2.71	0.512	−2.8	1.01	3.56	0.284
−5.3	1.80	2.32	0.775	−7.4	1.36	3.23	0.422
−8.9	2.19	1.94	1.125	−11.5	1.72	2.90	0.592
−12.7	2.61	1.54	1.69	−16.2	2.17	2.47	0.879
−17.0	2.94	1.23	2.39	−20.0	2.60	2.06	1.26
−21.3	3.24	0.95	3.40	−24.0	3.04	1.64	1.85
−25.3	3.42	0.79	4.33	−27.1	3.26	1.44	2.26
−30.0	3.57	0.66	5.38	−31.2	3.51	1.21	2.89

[a] Temperature corrected.

(2) A contact ion pair may interact weakly with solvent introducing, nevertheless, some degree of orientation in its surrounding. In such a case the peripherial complexing with the added agent should decrease the entropy of the system only slightly (probably by 2–6 eu), and again it would leave the optical spectrum unaltered.

(3) A contact ion pair may become coordinated with a complexing agent which inserts itself between the ions. Such a process increases the dipole moment of the pair, and therefore it decreases substantially the entropy of the system (by approximately 10–30 eu). The insertion should cause a bathochromic shift in the absorption spectrum of the relevant colored anion.[13,15]

(4) Finally, a reaction of the coordinating agent with an ion pair separated by solvent may result in

Table V. K_E Values (M^{-1}) for

$B\cdot^-,Na^+ + \text{glyme} \rightleftarrows B\cdot^-,Na^+(\text{glyme})$

Temp, °C	MeTHF-glyme-4	THP-glyme-4	THP-glyme-3
21.1	145	75	32
12.7	182	97	40
4.8	229	132	50
−2.7	288	187	62
−9.9	363	260	78
−16.6	460	335	98
−23.0	580	405	120
−29.0	742	. . .	150
−34.9	934	. . .	. . .
	$\Delta H = -4.6$ kcal/mole $\Delta S = -5.7$ eu	$\Delta H = -6.0$ kcal/mole $\Delta S = -11.8$ eu	$\Delta H = -4.5$ kcal/mole $\Delta S = -8.6$ eu

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Table VI. The Isomeric Solvation of Ion Pairs by Glyme-4[a]

	In THP			In MeTHF		
Temp, °C, at which both maxima have equal intensity	−5	−11	−20	−1	−8.4	−20.4
[Glyme-4] × 10^2 *M*	3.6	2.1	0.95	3.2	1.76	0.8
K_E[glyme]	8.4	5.3	3.5	9.06	6.30	4.27
Fraction of all the glyme-coordinated ion pairs	0.89	0.845	0.775	0.90	0.86	0.81
Fraction of glyme-separated pairs	0.5	0.5	0.5	0.5	0.5	0.5
% of glyme-coordinated pairs separated by glyme ($B\cdot^-$,E,Na^+)	56	59	64.5	56	58	62
% of glyme-coordinated pairs having glyme on their periphery ($B\cdot^-$,Na^+,E)	44	41	35.5	44	42	38

[a] Nonseparated pair absorbs at 400 mμ. Separated pair absorbs at 406 mμ in THP and at 408 mμ in MeTHF.

Table VII. Formation of Isomeric, Glyme-Coordinated Ion Pairs

$$B\cdot^-,Na^+ + E \rightleftarrows B\cdot^-,Na^+,E \quad K_{E,C}$$

$$B\cdot^-,Na^+ + E \rightleftarrows B\cdot^- E,Na^+ \quad K_{E,S}$$

	THP			MeTHF		
	$B\cdot^-$,Na^+,E	$B\cdot^-$,E,Na^+	Over-all	$B\cdot^-$,Na^+,E	$B\cdot^-$,E,Na^+	Over-all
E = glyme-4						
Δ*H*, kcal/mole	−4.6	−7.0	−6	−3.6	−5.4	−4.6
Δ*S*, eu	−8.4	−17	−12	−3.6	−9.7	−5.7
E = glyme-3						
Δ*H*, kcal/mole	−4.5	Non detectable	−4.5			
Δ*S*, eu	−8.6		−8.6			

replacement of some of the coordinated solvent molecules by a complexing polydentate agent. This process is expected to increase the entropy of the system and, as in case 1, it should not alter the spectrum of the anion.

Having explained the merits of the "probe" method, we may consider our present results. The results presented in the preceding graphs and tables prove that the complex of sodium biphenyl and glyme-3 or glyme-4 corresponds to well-defined stoichiometry, *viz.*, 1:1. Hence, such a "solvation" should be classified as a chemical coordination and not as a physical interaction. The complexing capacities of glyme-3 and glyme-4 with sodium biphenyl in THP are compared in Table V. The association constant is two to three times larger for the latter agent than for the former.

Isomeric Ion Pairs

The spectra of the $B\cdot^-$,Na^+ and of its complexes with glyme-3 or glyme-4 were scrutinized over the whole investigated temperature range. It was pointed out that in the absence of glyme, the spectrum of $B\cdot^-$,Na^+ shows a sharp peak at 400 mμ, its position being unaffected by the temperature. The same absorption peak was observed in the solutions containing glyme-3, but a definite variation was observed in the solutions containing glyme-4. On lowering the solution temperature a shoulder developed at higher wavelength and at some intermediate temperatures two close peaks could be discerned. At −40° again only one sharp peak was seen at 406 mμ in THP and at 408 mμ in MeTHF. The analogy with the behavior of the fluorenyl salts[12] implies that the two peaks belong to two distinct species, namely, the contact ion pair, coordinated or not with the glyme, and the separated pair, most probably separated by glyme. In Table VI we report the temperatures, and the respective concentrations of glyme-4, at which both peaks are of equal intensity. Assuming identical extinction coefficients for all the ion pairs (this assumption will be justified), we conclude that under the conditions listed in Table VI the separated ion pairs form one-half of all the pairs. On the other hand, the calculations based on the determined values of K_E give us the fraction of *all* the glyme-complexed ion pairs (see fourth line of Table VI). It is obvious, therefore, that only a fraction of the glyme-complexed pairs are separated, the remaining being coordinated with the glyme attached to their periphery. This, therefore, is the first reported case of isomeric ion pairs in which the isomerism arises from a different position of the coordinating agent.

The data given in Table VI permit us to calculate $K_{E,C}$ and $K_{E,S}$ for three temperatures; the *K*'s denote the equilibrium constants of $B\cdot^-$,Na^+ complexing to form the peripherally glymated (contact) and glyme-separated ion pairs. Plots of log $K_{E,C}$ and log $K_{E,S}$ *vs.* 1/*T* are shown in Figure 7, and the respective ΔH_C, ΔS_C, ΔH_S, and ΔS_S are listed in Table VII. The heat

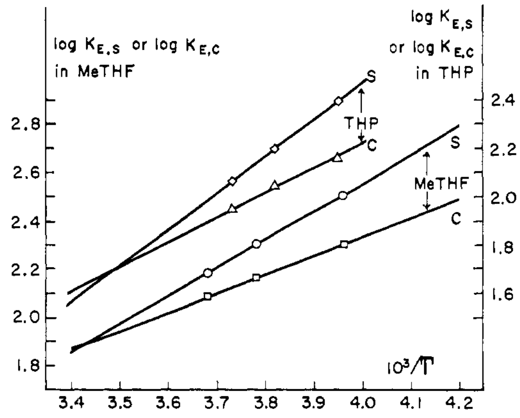

Figure 7. Plots of log $K_{E,S}$ and log $K_{E,C}$ *vs.* 1/*T* for the isomeric ion pairs coordinated with glyme-4.

Table VIII. Comparison of ΔH and ΔS in Reactions of Ion Pairs[a]

	Formation of $B\cdot^-,Na^+$ from Metallic Sodium and Biphenyl Solution			
Solvent	MeTHF	THP	THF	
ΔH, kcal/mole	−9.9	−8.6	−11.2	
ΔS, eu	−43	−37	−40	
	Dissociation of Contact Ion-Pairs into Coordinated Ions			
Ion pair	$B\cdot^-,Na^+$(MeTHF)	$B\cdot^-,Na^+$(THF)	$N\cdot^-,Na^+$(THF)	$\sim S^-,Na^+$(THF)
ΔH, kcal/mole	−3.4	−7.3	−8.2	−8.2
ΔS, eu	−56	−52	−58	−59
	Dissociation of Solvent-Separated Ion-Pairs into Ions			
Ion pair	$Pe\cdot^-,Na^+$(THF)	$Pe\cdot^-,Na^+$(DME)	$B\cdot^-,Na^+$(DME)	$Triph\cdot^-,Na^+$(DME)
ΔH, kcal/mole	−2.2	−2.5	−2.1	−2.4
ΔS, eu	−29	−32.5	−31.5	−32.5

[a] $B\cdot^-,Na^+$ = sodium biphenyl; $N\cdot^-,Na^+$ = sodium naphthalene; $\sim S^-,Na^+$ = sodium salt of living polystyrene; $Pe\cdot^-,Na^+$ = sodium perylene; $Triph\cdot^-,Na^+$ = sodium triphenylene.

and entropy of coordination of $B\cdot^-,Na^+$ for the peripherally glymated (contact) ion pairs seem to be the same for glyme-4 and glyme-3. However, only glyme-4 forms any appreciable fraction of the glyme-separated pairs, whereas the fraction formed by glyme-3, if any, is too small to be detected. The heat of isomerization of peripherally glymated pair into a glyme-separated pair is −2.4 kcal/mole in THP and −1.8 kcal/mole in MeTHF; *i.e.*, within the experimental uncertainties both values are virtually identical. The entropies of isomerization are again similar in both solvents, namely, −8.6 and −6.1 eu, respectively. The negative entropy of isomerization is caused by increase in the dipole moment of the pair when transformed from a contact to glyme-separated one.

The existence of the two isomers raises the question of how rapidly they are interconverted. We hope that future esr studies of this subject may provide the answer to this question.

One may raise an objection to our assumption of equal extinction coefficients for both species. The alternative assumption, *viz.*, that *all* the complexed ion pairs form the separated pairs, leads to inconsistent extinction coefficients and to some other implausible conclusions, whereas the results based on the assumption of equal extinction coefficients are self-consistent. Finally, let us stress that the 1:1 complex of $B\cdot^-,Na^+$ with glyme-3 is observed but its spectrum proves that it is a contact pair. Therefore, the corollary that complexing may produce either a contact or a separated ion pair is undeniable.

Conclusion

It was demonstrated that stoichiometric complexes (1:1) are formed on addition of glyme-3 or glyme-4 to sodium biphenyl ion pairs in THP or MeTHF. The method leading to the determination of the equilibrium constants remains valid whether the complexing agent separates the ions of the pair or whether it does not. This technique is therefore more powerful than the spectrophotometric method[13,15] which is only capable of revealing the separated ion pairs. The results show that two isomeric complexes are formed when $B\cdot^-,Na^+$ associates with glyme-4 in THP or in MeTHF, one with the glyme peripherially bonded, the other having it inserted between the ions of the pair.

The change in the entropy of the process involving ion pairs is diagnostic for the type of reaction. The data collected in Table VIII illustrate this point. One may, therefore, deduce the structure of ion pair by examining the entropies of processes involving such a specie. For example, using the glymes as probes, we demonstrated that $B\cdot^-,Na^+$ in MeTHF or THP forms tight contact pairs weakly coordinated with the solvent.

It should be stressed that the concept of discrete types of ion pairs such, *e.g.*, as the contact and the solvent-separated, does not apply to all systems. The interaction energy between the two ions of a pair involves contribution arising from the *average* force field of the surrounding solvent molecules.[7,16] The *average* force field is temperature dependent, and therefore the potential energy curve giving the energy of the pair as a function of their separation is also temperature dependent. It is possible, therefore, that the two minima determining the positions for the contact and solvent-separated pairs may merge at some temperatures, while only one or the other appears in the high- and low-temperature regions, respectively. In such a case, only one maximum is seen in the absorption spectrum, its position being, however, shifted with temperature. Such a case was described recently by Nicholls and Szwarc.[16] The spectrum of the lithium salt of dihydroanthracene anion (and of its 10-substituted derivatives) in THF shows two distinct peaks, one at 400 mμ, the other at 450 mμ. The changes in their intensities and the effect of added glyme-4 identify them unequivocally as the contact and solvent-separated pairs. On the other hand, the spectrum of the sodium salt shows only one peak. Its absorption maximum shifts from 425 mμ at 25° to 455 mμ at −70°, although the half-width remains virtually constant. Since we demonstrated here that the spectra of two species may be resolved into two peaks, even if their separation is as low as 6 mμ, it is likely that the single peak observed for the sodium salt cannot represent an overlap of two peaks separated by 30 mμ. Hence, this is a case when the average force field due to the surrounding solvent varies sufficiently with temperature to afford a shift of the energy minimum from that representing a contact pair to that corresponding to a solvent separated-pair. Thermodynamic distinction of two species is then not justified.

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