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EFFECT OF THE SOLVENT ON THE FORMATION AND IONIC DISSOCIATION OF THE ADDUCTS OF ALKALI METALS WITH AROMATIC HYDROCARBONS

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I. INTRODUCTION

The chemistry of the organometallic compounds of the alkali metals is developing fairly rapidly. The adducts of alkali metals with aromatic hydrocarbons have attracted much attention because of their unusual structure [1,2] and because they have found wide application in polymer chemistry [3-7] and in synthetic organic chemistry [5,8,9]. The reactions involving the addition of alkali metals to aromatic hydrocarbons were first investigated by Schlenk [10,11], who established, in particular, that in ethyl ether sodium readily adds to anthracene and phenanthrene but not to naphthalene and biphenyl. However, Scott observed [12] that these hydrocarbons react rapidly and quantitatively with sodium when the solvent is 1,2-dimethoxyethane. Subsequently the adducts of benzene and its homologues with alkali metals were obtained in this solvent [13,14].

Scott [12] noted an appreciable electrical conductivity of the solutions of the adducts, indicating their ionic nature. Hückel and Bretschneider [15], who studied the reactions of alkali and alkaline earth metals with aromatic hydrocarbons in liquid ammonia, suggested that the hydrocarbon is converted into an anion by capturing electrons from the metal atom. Weissman and coworkers [16] showed that solutions of aromatic organosodium compounds in tetrahydrofuran exhibit strong paramagnetic absorption and concluded that the aromatic anion is at the same time a paramagnetic species; it has therefore been called a radical-anion ($Ar^{\cdot-}$). The reaction of an aromatic hydrocarbon (Ar) with an alkali metal can be represented by the equation

$$Ar + M \rightleftarrows Ar^{\cdot-}M^{+}. \quad (1)$$

Laitinen and Wawzonek [17] and Hoijtink et al. [18] obtained radical-ions in the electrolytic reduction of hydrocarbons (see also the reviews of de Boer [2] and Hoijtink [19]). The reaction with polycyclic hydrocarbons proceeds further - a second electron adds to the radical-anion and a doubly charged anion (dianion) is formed.

Measurements of the magnetic susceptibility of the solutions of the adducts of anthracene and phenanthrene with sodium [20] showed that, on more prolonged contact between the solution and the metal surface, the paramagnetic compound formed initially ($Ar^{\cdot-}M^{+}$) is converted into a diamagnetic product as a result of the reaction

$$Ar^{\cdot-}M^{+} + M \rightleftarrows Ar^{2-}2M^{+}. \quad (2)$$

Addition of the hydrocarbon to a solution of its dianions results in the appearance of paramagnetism due to the reaction

$$Ar^{2-}2M^{+} + Ar \rightleftarrows 2Ar^{\cdot-}M^{+}. \quad (3)$$

This is an equilibrium reaction and therefore the dianion can be formed not only by the reduction of the radical-anion, but also by the disproportionation of two radical-anions. Recently the possible addition of three electrons to the decacycline molecule has been observed [21].

The properties of radical-anions have been extensively studied by electron spin resonance and electron spectroscopic methods. The ESR spectra were studied by Weissman and coworkers [22-26] and other investigators [27-29]. The

principal studies on the electronic absorption spectra were carried out by Hoijtink and his school[30,31] (see also Refs. 1 and 2). The interpretation of the spectra within the framework of the molecular orbital method[32-36] leads to the conclusion that the electron in the radical-anion occupies the lowest antibonding orbital of the aromatic molecule. The bond with the metal ion is achieved by the coulombic interaction of the entire π-electron system of the radical-anion. The electronic structure of the adducts of alkali metals with aromatic hydrocarbons has been recently discussed in detail in de Boer's review[2].

The problem of the effect of the solvent and metal on the equilibria in the formation and dissociation of adducts has not so far been elucidated adequately, despite its great importance, in particular for the understanding of anionic polymerisation and other organic anionic reactions. This led us to write the present review on the above problem.

II. SOLVATION OF CATIONS IN ADDUCT FORMATION REACTIONS

The positions of equilibria (1)–(3) involving a particular hydrocarbon depend greatly not only on the nature of the metal but also on the solvent, the latter showing different effects on different metals. This was shown qualitatively by Schlenk[10,11] and Scott[12]. Thus, in contrast to lithium, sodium does not react with naphthalene and biphenyl in ethyl ether, but in methyl ether adducts are formed. Potassium interacts with naphthalene and biphenyl even in octane and toluene[37]. The equilibrium concentrations of the radical-anions of benzene[38] formed in the reaction with lithium and potassium in 1,2-diethoxyethane, are higher by approximately two powers of ten than in the reaction with sodium, and the relative concentrations of toluene radical-anions[38] are 100 in 1,2-dimethoxyethane, 30 in 1-ethoxy-2-methoxyethane, and 3 in 1,2-diethoxyethane. Pudovik and Muratova[39] showed that a red dilithium derivative of naphthalene (the solution of naphthalene radical-anions is green) forms in dimethoxymethane and in dioxan. According to Garst's data[40], the nature of the solvent and the metal is important in radical-anion disproportionation reactions.

The pronounced dependence of equilibrium (1) on the nature of the metal and solvent can be explained by an examination of the energy balance in the formation of radical-anions[4]:

$$\Delta H = L + I - E_{Ar} - S_{M^+} - S_{Ar^-} - Q, \qquad (4)$$

where ΔH is the enthalpy of the reaction, L the heat of sublimation of the metal, I its ionisation potential, E_{Ar} the electron affinity of the aromatic hydrocarbon, S_{M^+} and S_{Ar^-} are the heats of solvation of the metal cation and the radical-anion, and Q is the energy of the coulombic interaction of the ions. The electron affinity of the aromatic hydrocarbons (in electron-volts) increases in the sequence[41] benzene (-0.54), biphenyl (0.41), naphthalene (0.65), phenanthrene (0.69), anthracene (1.19). The heats of sublimation and the ionisation potentials of alkali metals and the radii (r) of their cations are presented in Table 1.

The larger is the sum $L + I$ the less vigorous should be the reaction of the metal. In fact, Table 2 shows that the yields of biphenyl radical-anions do not vary with the metal in the same way in different solvents[42]. This is due to the large contribution to the energy of reaction (1) by the heat of solvation of the cations, which is markedly influenced by the solvent.

TABLE 1. Constants of alkali metals[43].

Metal	L, kcal mole^{-1}	I, eV	r, Å
Li	32.2	5.39	0.78
Na	23.4	5.14	0.98
K	18.9	4.34	1.33
Rb	18.0	4.18	1.49
Cs	16.3	3.89	1.65

TABLE 2. Relative concentrations of biphenyl adducts.

Solvent	Li	Na	K
1,3-Dimethoxypropane	100	7	30
1,2-Diethoxyethane	45	15	65
Tetrahydrofuran	100	45	30
Tetrahydropyran	80	10	6

Approximate calculation shows[44] that the heats of solvation do indeed constitute an appreciable fraction of the heat of reaction (1), as a result of which the formation of the hydrocarbon radical-anion in electron-donor solvents is in most cases exothermic. Solodovnikov[29] estimated the heat of reaction of benzene with potassium in 1,2-dimethoxyethane from the temperature variation of the intensity of the ESR signal due to the benzene radical-anion. In the temperature range 233–273°K the heat of reaction is about 20 kcal mole^{-1}.

The temperature variation of the equilibrium constant (K) for the reaction of sodium with biphenyl in certain ethers and their mixtures with n-heptane has been investigated spectrophotometrically[42,45,46]. The enthalpies (ΔH) and entropies (ΔS) of reaction were calculated from the results by the method of least squares using the equation $\ln K = -\Delta H/RT + \Delta S/R$. The values of K_{273}, ΔH, and ΔS and also the temperature range in which these parameters were determined are listed in Table 3. The equilibrium constants were determined without taking into account the activity coefficients. However, this does not prevent a comparison of the effects of solvents (with similar dielectric constants and dipole moments — see Table 5) on the thermodynamics of the formation of the adduct.

The data in Table 3 show (cf. Nos. 1 and 19) that the variation of ΔH when the reaction is carried out in different solvents is as much as ~25 kcal mole^{-1}. This confirms what has been said above about the importance of the contribution of the heat of solvation to the energy of the reaction. The absolute values of ΔH, obtained under comparable conditions, decrease in the series dimethyl ether of diethylene glycol > 1,2-dimethoxyethane > 1-ethoxy-2-methoxyethane > 1,2-dimethoxypropane > tetrahydrofuran > 1,2-diethoxyethane > 1,3-dimethoxypropane > tetrahydropyran.

As a result of the ordering of solvent molecules in the solvation shells of the ions, the entropy of the system decreases and the entropy of reaction ΔS is negative. The degree of ordering is higher the more stable is the solvate and therefore on changing the solvent the absolute values of ΔH and ΔS vary in unison, the effects of their variation on the free energy of reaction ($\Delta F = \Delta H - T\Delta S$) cancelling out, so that the variation of the latter is 1–2 kcal mole^{-1}.

TABLE 3. Thermodynamic parameters for the formation of sodiobiphenyl in various solvents [45,46].

No.	Solvent	K_{273}	T, °K	$-\Delta H$, kcal mole^{-1}	$-\Delta S$, e.u.
1	dimethyl ether of diethylene glycol–heptane*	—	318—298	31	100
2	1,2-dimethoxyethane–heptane**	—	318—303	13.0±0.5	43±2
3	ditto	—	303—283	18.0±0.6	61±2
4	1-ethoxy-2-methoxyethane	7.2	318—273	17.4±0.5	60±2
5	1-ethoxy-2-methoxyethane–heptane**	—	303—283	12.2±0.2	46±2
6	ditto	2.1	283—268	20.0±0.8	71±3
7	1-ethoxy-2-methoxyethane–ethyl ether**	—	303—283	14	50
8	ditto	4.8	283—273	25	87
9	1,2-diethoxyethane	0.2	293—258	9.6±0.4	39±2
10	ditto	—	258—243	22.0±1	86±4
11	1,2-diethoxyethane–heptane**	0.1	283—258	7	30
12	ditto	—	258—243	16	64
13	1,2-dimethoxypropane	4.6	318—273	16.5±0.7	58±3
14	1,3-dimethoxypropane	0.04	263—238	15.5±0.3	63±1
15	tetrahydrofuran	1.4	313—263	11.2±0.5	40±2
16	tetrahydrofuran–heptane***	—	303—283	5.5	21
17	ditto	0.7	283—263	8.5	31
18	»	—	263—253	14	54
19	tetrahydropyran	0.06	273—228	6.8±0.2	31±1

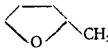
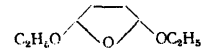
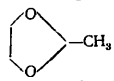
* The volume ratio of the ether and heptane in the mixture was 1:1.4.
** 4.3:1.
*** 6:1.

Thermodynamic data have also been obtained spectrophotometrically for the reaction of sodium with naphthalene in 1,2-diethoxyethane [45] and for the reaction of sodium with 4-ethylbiphenyl and *N*-ethylcarbazole in tetrahydrofuran [47].

The above thermodynamic data give an idea of the relative solvating power of a number of ethers. More detailed information about its variation with the structure of the solvent molecules can be obtained from Table 4, which gives the relative equilibrium concentrations of sodiobiphenyl (C_{sb}) and sodionaphthalene (C_{sn}) formed at room temperature in the presence of a sodium mirror of large area at the same concentrations of hydrocarbon solutions (arbitrarily defined as 100) in 31 ethers and acetals [42,48]. The values of C_{sb} were determined at the same time by electron spin resonance, the results agreeing satisfactorily with the spectrophotometric measurements (the values of C_{sb} in Table 4 are averages of the results of both methods). If biphenyl was quantitatively converted into the adduct in ethereal solution, i.e. C_{sb} = 100, the ether was diluted with n-heptane and the value of C_{sb} in Table 4 refers to an equimolar mixture of the ether and n-heptane. The last column of Table 4 lists the shifts ($\Delta\nu_{OD}$) of the stretching vibration frequency of the OD bond in the infrared spectrum of deuteriomethanol CH_3OD on formation of the hydrogen bond with the oxygen atom of the ether [49]. According to Gordy [50], $\Delta\nu_{OD}$ is a measure of the electron-donor properties (basicity) of the ethers.

The results in Table 4 may be compared with independent data on the effects of solvents on the spectra of the adducts or the electrical conductivity of their solutions, which according to a number of workers [51-54] also reflect the effect of the solvation of the alkali metal cation. According to these studies, the variation of the solvating power of the ethers (1,2-dimethoxyethane > tetrahydrofuran > tetrahydropyran, methyltetrahydrofuran > 1,4-dioxan) is the same as the sequence corresponding to the decrease of C_{sb} and C_{sn} in these solvents (Nos. 4, 23–26 in Table 4).

TABLE 4. Effect of the structure of solvent molecules on the equilibrium concentrations of the adducts of sodium with biphenyl (sb) and naphthalene (sn) and on the electron-donor properties of the ethers [48,49].

No.	Solvent	C_{sb}	C_{sn}	$\Delta\nu_{OD}$, cm^{-1}
	a. Effect of the size of the alkyl groups in ethers with one and two oxygen atoms			
1	CH_3OCH_3	2	20	—
2	$CH_3OC_2H_5$	1	3	—
3	$C_2H_5OC_2H_5$	1	2	106
4	$CH_3OC_2H_4OCH_3$	100	100	93
5	$CH_3OC_2H_4OC_2H_5$	60	100	95
6	$CH_3OC_2H_4OC_3H_7$	22	85	97
7	$CH_3OC_2H_4OC_4H_9$	20	82	95
8	$CH_3OC_2H_4OC_5H_{11}$	15	70	98
9	$C_2H_5OC_2H_4OC_2H_5$	15	60	98
10	$C_4H_9OC_2H_4OC_4H_9$	10	20	100
	b. Effect of the structure of the bridge between the oxygen atoms in glycol ethers			
11	$CH_3OCH_2OCH_3$	0	0	84
	$CH_3O(CH_2)_2OCH_3$	100	100	93
12	$CH_3O(CH_2)_3OCH_3$	7	50	100
13	$CH_3O(CH_2)_4OCH_3$	3	20	104
14	$CH_3O(CH_2)_5OCH_3$	—	6	104
	$C_2H_5O(CH_2)_2OC_2H_5$	15	60	98
15	$C_2H_5O(CH_2)_3OC_2H_5$	—	14	106
16	$C_2H_5O(CH_2)_4OC_2H_5$	—	10	106
17	$CH_3OCH(CH_3)OCH_3$	0	7	91
18	$CH_4OCH(CH_3)CH_2OCH_3$	45	90	96
19	$CH_3OCH(CH_3)CH(CH_3)OCH_3$	17	85	100
	c. Effect of the number of units and the type of alkyl substituents in poly(ethylene glycol) ethers (data for the reaction of sodium with biphenyl in mixtures of ethers with heptane)			
20	$CH_3O(C_2H_4O)_3CH_3$	100	—	90
21	$CH_3O(C_2H_4O)_2CH_3$	100	—	90
	$CH_3OC_2H_4OCH_3$	15	—	93
22	$C_2H_5O(C_2H_4O)_2C_2H_5$	35	—	98
	d. Effect of the size of the ring, the number of oxygen atoms, and the type of substituents in cyclic ethers			
23		45	85	115
24		10	50	112
25		4	35	100
26		10	55	114
27		0	5	92
	e. Effect of the size of the ring and the position of the substituents in cyclic acetals			
28		10	70	76
29		15	70	85
30		—	15	88
31		—	30	85

From this point of view, comparison of the results of Shatenshtein et al. [48] and those of Garst et al. [55] is of greatest interest. The latter worker observed that the position of the principal band in the absorption spectrum of the ketyl of sodiobenzophenone depends on the solvent. From the standpoint of the postulate of the ionic nature of ketyls [56,57],

the author explained the shifts of the absorption band by the variation of the interionic interaction due to the differences in the degree of solvation of the Na^+ cation in different solvents. According to McClelland's theoretical findings [57], the band is displaced more towards the red region of the spectrum the higher is the solvating power of the solvent. Then it follows from the data of Garst et al. [55] that the degree of solvation of the Na^+ cation decreases in parallel with C_{sb} and C_{sn} in the same solvents (Table 5).

The phenomenon of cation solvation cannot be explained if solvation is regarded as a purely electrostatic ion–dipole interaction. This is shown by the data in Table 3 on the thermodynamics of the formation of biphenyl radical-anions in different solvents taking into account their polar properties, by the absence of correlation between other parameters reflecting the differences in the solvating power of the solvents and their dielectric constants and dipole moments (see Table 5).

The results can be readily interpreted if the solvation is regarded as complex formation, i.e. a process of the donor–acceptor type. This approach enabled Izmailov [63] to explain the characteristic features of the hydration of alkali metal cations. The electron donors are oxygen atoms which have unshared electron pairs and the cation is the acceptor which provides vacant electron orbitals. The number and direction of the donor–acceptor bonds are determined by the multiplicity and type of hybridisation of the free orbitals of the cations. The probable vacant orbitals in Li^+, Na^+, and K^+ are $2s2p$, $3s3p$, and $4s4p3d$, the type of hybridisation of which is sp^3, sp^3, and sp^3d^2 respectively according to Eyring et al. [64] Thus in the solvation of Na^+ the oxygen atoms of the ligand must be located at the vertices of a tetrahedron with the cation at its centre. The greatest contribution to the heat of solvation comes from the energy of formation of the donor–acceptor bond between the cation and the solvent molecules. The secondary solvation of the cations takes place by ion–dipole interaction, whose energy makes a smaller contribution to the total solvation energy.

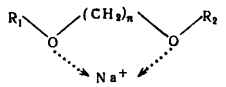
The above considerations hold also in the solvation of alkali metal cations by ethers. The more pronounced are the electron-donor properties of the oxygen atom of the given ether, the higher is the solvation energy and at the same time the stronger is the hydrogen bond formed between the ether molecules and CH_3OD. Therefore one should expect a correspondence between the relative concentrations C_{sb} and C_{sn} and $\Delta\nu_{OD}$ in the ether series. However, according to the data in Table 4 there is no such correlation. For example, the electron-donor properties of ethylene glycol ethers increase on substituting one or both CH_3 groups in 1,2-dimethoxyethane by alkyl groups with a larger number of carbon atoms, as a result of the higher inductive effect ($+I$) of such substituents, but the solvation of the Na^+ ion is then weakened. The inductive effect of the oxygen atom is of the opposite sign ($-I$) and therefore, as the methylene bridge separating the oxygen atoms in glycol ethers becomes longer, the latter become stronger bases, and yet the most stable solvate is formed by 1,2-dimethoxyethane. These discrepancies can be explained by the fact that steric factors, which play an important role in the solvation of the cation, have virtually no effect on the formation of the hydrogen bond.

TABLE 5. Comparison of the relative concentrations C_{sb} and C_{sn} with the position of the principal band (λ_{max}, nm) in the spectrum of sodiobenzophenone and the dielectric constants (DC) and dipole moments (μ) of the solvents*.

Solvent	C_{sb}	C_{sn}	λ_{max}	DC$_{25°}$	μ
Dimethyl ether of diethylene glycol	—	—	704	7.25 [58]	—
1,2-Dimethoxyethane	100	100	697	6.96 [58]	1.72 [61]
1-Ethoxy-2-methoxyethane	60	100	—	5.77 [58]	1.68 [61]
Tetrahydrofuran	45	85	675	7.31 [58]	1.87 [62]
2-Methyltetrahydrofuran	10	50	654	4.6 [59]	—
1,2-Diethoxyethane	15	60	—	4.89 [58]	1.65 [61]
Tetrahydropyran	10	50	—	5.4 [59]	1.87 [62]
1,4-Dioxan	4	35	643	2.23 [59]	0.4 [62]
Dimethylacetal	0	7	642	—	—
Ethyl ether	0	2	632	4.22 [59]	1.22 [62]
Dimethoxymethane	0	0	628	2.65 [60]	0.67 [62]

* The superscript numbers indicate the references to work from which the values of the dielectric constants and dipole moments have been taken.

The nature of the steric hindrance may be deduced using the glycol ethers as an example. Studies of the formation of complexes of titanium tetrafluoride [65] or tin tetrachloride [58] with ethers containing two oxygen atoms show that the latter are capable of forming two bonds with an acceptor. The dipole moment of the complex $SnCl_4.2C_2H_5OC_2H_4OC_2H_5$ corresponds to the octahedral model with *cis*-disposition of the oxygen atoms. It may be supposed that the reaction of the ethylene glycol ether with Na^+ ions involves the formation of a chelate complex:



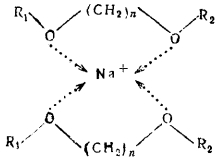
The postulate of the chelate complexes of alkali metals was put forward by Sidgwick [66] as early as the 1920's. Since then it has often been used [59,67–69] to account for the high solvating power of 1,2-dimethoxyethane in various anionic organic reactions.

The structure of the methylene bridge is of great importance for the formation of a stable solvate. The atomic grouping characteristic of ethylene glycol ethers $[-O(CH_2)_2O-]$ must be regarded as the most favourable. For example, even in 1,2-dibutoxyethane the values of C_{sb} and C_{sn} are higher than in 1,3-dimethoxypropane and other dimethyl ethers of higher glycols. This feature of the steric hindrance is associated with the stability of the *cis*-conformation of the molecule, which is necessary for the formation of the chelate. As the number of CH_2 groups freely rotating relative to one another increases, the transition of the molecule to this conformation becomes increasingly difficult. The occurrence of free rotation about all the C–C and C–O bonds in glycol ether molecules was confirmed [61] by the agreement of the experimental dipole moments with those calculated theoretically on the basis of this hypothesis. Free rotation accounts also for the decrease of the solvating power of ethylene glycol ethers with increase in the size of alkyl side-groups, since the possibility of the screening of oxygen atoms by the latter then increases. We have seen (Table 3) that steric hindrance in the solvation of the metal ion is clearly reflected in the values of the thermodynamic parameters for the formation of the adduct.

It is interesting to note that the stability of the complexes of stannic chloride with glycol ethers [58] as well as the values of C_{sb} or C_{sn} (Table 4) decrease in the following sequence when the number n of methylene groups is reduced: $2 > 3 > 4 > 1$. At the same time the change in the

length of the alkyl groups of glycol ethers affects the formation of complexes with stannic chloride less than the solvation of Na^+ ions, since the stability of the stannic chloride complexes with 1,2-diethoxyethane and 1,2-dibutoxyethane is almost the same. This is not surprising, since usually the more intense is the interaction the smaller is its sensitivity to structural factors.

The data on the thermodynamics of the reaction of sodium with biphenyl also made it possible[45,46] to arrive at certain conclusions concerning the mechanism of the solvation. Thus if the solvent is an ethylene glycol ether or its mixture with heptane, the relation between $\log K$ and $1/T$ is represented by two straight lines of different slopes, and ΔH and ΔS each have two different values, depending on the temperature range in which the reaction has been carried out in the given solvent (Table 3, Nos. 2, 3, 5–12, Fig. 1). This can be explained by a stepwise mechanism of the solvation of the sodium ion. Since its coordination number is four[63] and ethylene glycol ether molecules are capable of forming simultaneously two donor–acceptor bonds each, there are two types of chelate complex — with one (see above) and two ether molecules:



Decrease of temperature favours the formation of coordination-saturated solvates. The absolute values of ΔH and ΔS then increase. Szwarc[70] also concluded that two 1,2-dimethoxyethane or four tetrahydrofuran molecules are involved in the solvation of the sodium ion. The temperature corresponding to the break in the $\log K - 1/T$ linear plots must be regarded as the temperature corresponding to the conversion of one type of solvate into another. It falls with increasing steric hindrance in the solvation: 1,2-dimethoxyethane (303°K) > 1-ethoxy-2-methoxyethane (283°K) > 1,2-diethoxyethane (258°K). The above temperatures were determined for a mixture of ether with heptane[46].

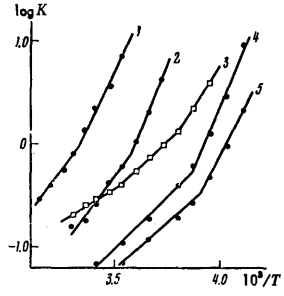


Fig. 1. Variation of $\log K$ for the formation of sodiobiphenyl with $1/T$; solvent: 1) 1,2-dimethoxyethane–heptane; 2) 1-ethoxy-2-methoxyethane–heptane; 3) tetrahydrofuran–heptane; 4) 1,2-diethoxyethane; 5) 1,2-diethoxyethane–heptane.

In contrast to glycol ethers, each tetrahydrofuran molecule can form only one donor–acceptor bond with the cation. It proved possible to demonstrate three solvation steps, of the possible four, on the basis of the temperature variation of the logarithm of the equilibrium constant for the reaction of sodium with biphenyl in a mixture of tetrahydrofuran with heptane (Table 3, Nos. 16–18, Fig. 1). The breaks in the straight line occur at 283°K and 263°K. Judging from the literature data[52] obtained by different methods, the Na^+ cation is fully solvated in tetrahydrofuran only at 200°K. The formation of the coordination-saturated complex (solvate) of the cation is accompanied by a weakening of the coulombic interaction between the ions. Therefore the increment of ΔH for the reaction when the temperature is reduced does not correspond to an additional heat of solvation but to the difference between the latter and the decrease of the coulombic interaction energy.

The hypothesis of the stepwise mechanism of solvation in tetrahydrofuran was put forward by Medvedev, Gantmakher, and coworkers[71] to explain the effect of added ethers on the frequency shift in the spectrum of diphenylalkyl-lithium. It was assumed that two stages in the solvation of the cation in the ion pair are possible — with one and two molecules[72]. The stepwise character of the solvation of lithium alkyls with ether containing one and two oxygen atoms is also reflected in the kinetics of the reaction of butyl-lithium with butyl bromide[73]. The solvation of organic anions by ethers as a result of donor–acceptor interaction is unlikely; the interaction between the solvent and the radical-anion is more probably of a coulombic type. The energy of the solvation of the radical-anion should then be approximately of the same order of magnitude as the energy of the secondary solvation of the cation. Consequently the effect of the solvent on the formation of radical-anions is determined mainly by the solvation of the cation, particularly if account is taken of the fact that differences in the polarity of ethers are only slight.

III. THE ROLE OF CATION SOLVATION IN ADDUCT IONIC DISSOCIATION EQUILIBRIA

The study of the ionic dissociation of adducts in ethereal solutions makes it possible to confirm and extend the above postulates concerning the solvation of cations. Table 6 lists the molar conductances of sodionaphthalene (I — 0.0023 M; II — 0.004 M) multiplied by the viscosity of the solvent[42,45]. Evidently $\Lambda\eta$ decreases by a factor of almost 600 on going from the dimethyl ether of diethylene glycol to tetrahydropyran, although the dielectric constants of the solvents differ little. The sequence of the values of $\Lambda\eta$

TABLE 6. Products of the viscosity and molar conductance of sodionaphthalene solutions at 293°K ($\Lambda\eta$, $cm^2\ \Omega^{-1}\ cP$).[45]

Solvent	$\Lambda\eta$ I	$\Lambda\eta$ II	$DC_{20°}$
Dimethyl ether of diethylene glycol	6.2	5.8	7.25
1,2-Dimethoxyethane	3.3	3.3	6.96
1-Ethoxy-2-methoxyethane	0.77	0.4	5.77
Tetrahydrofuran	0.59	0.44	7.31
1,2-Diethoxyethane	0.09	0.03	4.89
Tetrahydropyran	—	0.01	5.4

corresponds to the solvating power of the solvents (cf. Table 5), since a decrease of the degree of solvation favours ion association. The latter is in general pronounced in ethereal solutions and the adduct is largely present in the form of ion pairs. This follows from the determination of the approximate values of the dissociation constants K_d for the lithium, sodium, and potassium derivatives of naphthalene, calculated[42] by the method of Fuoss and Kraus[74] from measurements of the concentration dependence of the molar conductances (Table 7).

The dissociation constants of the adducts and certain other organometallic derivatives of alkali metals determined by other workers[52,75-79] in tetrahydrofuran solution are also of the order of 10^{-6}–10^{-7} M (Table 8).

The degree of dissociation of lithionaphthalene in 1,2-dimethoxyethane and tetrahydrofuran and also of sodionaphthalene in 1,2-dimethoxyethane at 293°K and a concentration of the order of 0.002 M is approximately 0.1. Under these conditions the value of $\Lambda\eta$ for sodionaphthalene solutions in the dimethyl ether of ethylene glycol is larger only by a factor of two than in 1,2-dimethoxyethane (Table 6), i.e. even in a solvent with a higher solvating power than 1,2-dimethoxyethane the concentration of ion pairs is still high. Dilution of the solution of sodionaphthalene in 1,2-dimethoxyethane to 10^{-4} M increases somewhat the degree of dissociation — approximately to 0.3.

These findings contradict Hoijtink's assertion[51] that sodionaphthalene is completely dissociated in 1,2-dimethoxyethane into free solvated ions. Hoijtink's view was shared by Weissman[52] and a number of other workers[53,54], who investigated the ESR of the radical-anions.

In the ESR spectrum of the sodionaphthalene solution in tetrahydrofuran there is additional splitting, which is absent from the spectrum of the 1,2-dimethoxyethane solution[52]. The intensity of the splitting decreases as the temperature is reduced. At 200°K it almost completely vanishes and the spectrum becomes identical with that of the solution in 1,2-dimethoxyethane. Similar observations were made for solutions of sodionaphthalene in methyltetrahydrofuran, tetrahydropyran, and dioxan[52].

The additional splitting in the ESR spectrum is due to the interaction of the unpaired electron of the radical-anion with the nucleus of the Na^+ cation. Such interaction cannot take place when the ions are free. Therefore Atherton and Weissman[52] suggested that in 1,2-dimethoxyethane the adduct is completely dissociated, while in other ethers it is present mainly in the form of ion pairs. The absence of the additional splitting from the spectrum of the tetrahydrofuran solution at 200°K and below this implies, in view of these investigations, that sodionaphthalene is also completely dissociated under these conditions. The increase of the degree of dissociation as the temperature is reduced can be explained[51] by the increase of the dielectric constant of the solvent. Rowlands and coworkers[81] also observed an additional splitting in the ESR spectra of the radical-anions

TABLE 7. Dissociation constants ($10^6 K_d$, mole litre^{-1}) of naphthalene adducts at 293°K.

Solvent	Li	Na	K
1,2-Dimethoxyethane	16	25	6.5
Tetrahydrofuran	18	1	0.5

TABLE 8. Dissociation constants of adducts in tetrahydrofuran.

Adduct	T,°K	$10^6 K_d$, mole × litre^{-1}	References	Adduct	T,°K	$10^6 K_d$, mole × litre^{-1}	References
Lithionapthalene	293	1.0	75	Sodioterphenyl	298	3.8	76
Sodionaphthalene	295	1.7	52	Sodiopyrene	298	7.0	76
»	293	1.0*	80	Sodioperylene	298	23	76
»	298	0.2*	76	Sodiotetraphenylethylene	298	2.0	77
Sodiobiphenyl	298	1.2	76	Fluorenylsodium	298	0.7	78
Sodioanthracene	298	4.6	76	»	203	40	78
Sodiotetracene	298	15	76	Sodiostyrene	298	0.15	79

* The discrepancy between the values of K_d in Refs. 76 and 80 is due to the different methods of calculation used, the results of the measurements being almost identical. In our view, there is no point in resorting to the more accurate method of calculation, as in Ref. 76, since Λ_∞ is evaluated by extrapolation over a long section of the experimental $\Lambda C - \sqrt{C}$ curve.

of pyrazine and pyridazine (obtained by reaction with sodium) in tetrahydrofuran solution, but not in 1,2-dimethoxyethane. Like Atherton and Weissman[52], they failed to observe the interaction of the unpaired electron with the nucleus of the potassium ion. According to Hush and Rowlands[36], this is due to the insufficient resolving power of the instruments, since examination of the spectroscopic data with the aid of the molecular orbital method leads to the conclusion that in tetrahydrofuran there is powerful ion association of the adducts of naphthalene and anthracene with lithium, sodium, and potassium. Later studies confirmed the validity of this view to some extent. In particular, splitting was observed in the ESR spectra of potassiobiphenyl[82] in tetrahydropyran, dihydropyran, and tetrahydrofuran (quoted in the order of decreasing degree of association) solutions, while the solution in 1,2-dimethoxyethane gave rise to the spectrum of the "free" radical-anion.

Data on the effect of the solvent and the cation on the ion association were obtained also by other investigators using the ESR method. Fraenkel and coworkers[54] showed that the degree of association of cyclo-octatetraene radical-anions with a cation decreases in the following order (the cation and the solvent are indicated): Na^+, tetrahydrofuran > Na^+, dimethoxyethane ≥ Li^+, tetrahydrofuran > Li^+, dimethoxyethane. On the basis of similar experiments, de Boer and Mackor[53] concluded that lithio-, sodio- and potassio-pyracene are completely dissociated into ions in 1,2-dimethoxyethane and completely associated in methyltetrahydrofuran at temperatures in the range between 300° and 180°K. The spectrum of the "free" radical-anion in tetrahydrofuran solution appeared at 183°K in the presence of K^+ and at 193°K in the presence of Na^+, while in the presence of Li^+ it was observed at all the temperatures. Evidently these results[52-54,81,82] are fully consistent with the postulates concerning the relative solvating power of the solvents and the variation of the degree of solvation with the radius of the cation. The contradiction between the conclusion that total dissociation of adducts in ethereal solutions is possible, which was arrived at on the basis of ESR spectroscopic studies, and the results obtained by conductimetric measurements[42,46] can be resolved by means of the hypothesis that two types of ion pairs exist — in contact (I) and separated (II)[46,76,80]. In the latter type the ions are separated by a layer of solvent molecules (Sl)[83,84]. Equilibrium in the dissociation of ion pairs into free solvated ions can be represented by

$$\underset{\text{(I)}}{Ar^-M^+} \overset{\Delta H_1}{\underset{Sl}{\rightleftharpoons}} \underset{\text{(II)}}{Ar^-|Sl|M^+} \overset{\Delta H_2}{\underset{Sl}{\rightleftharpoons}} \underset{\text{(III)}}{Ar^-_{Sl} + M^+_{Sl}} \qquad (5)$$

The position of the equilibrium depends on the type of the adduct, the solvent, and the concentration of the solution and temperature†.

Geske and Maki[86] and McClelland[57] note that the interaction of the unpaired electron with the nucleus of the cation is possible only in the ion pairs in contact, while in separated ion pairs this is prevented by the layer of solvent molecules. Hence the ESR spectra provide information about the concentration of the ion pairs in contact but not about the degree of dissociation of adducts into free ions[46,76].

The idea of the existence of two types of ion pairs has been used recently also to account for other phenomena in solutions of organometallic compounds of alkali metals. Thus Hogen-Esch and Smid[78] observed a change in the spectrum of fluorenylsodium solution in tetrahydrofuran at low temperatures. This phenomenon cannot be attributed to the formation of free ions, since the dissociation constant is very low — 4×10^{-5} M at 203°K. Therefore they concluded that a decrease of temperature is accompanied by the conversion of the ion pairs in contact into separated ion pairs, which have a different spectrum. According to Smid[75], separated ion pairs exist at room temperature in tetrahydrofuran solution of lithionaphthalene and ion pairs in contact in solution of sodionaphthalene in the same solvent.

Similar postulates were introduced recently by Szwarc[87,88] into the chemistry of living polymers to account for the effect of the solvent on the polymerisation kinetics. In his view, the active centres for the chain propagation of living polystyrene in tetrahydrofuran are separated ion pairs and in dioxan ion pairs in contact. Therefore in the first case the rate of polymerisation is about 200 times higher than in the second (the counter-ion is Li^+). Szwarc's explanation is satisfactorily consistent with McClelland's conclusion[57] that ion pairs in contact exist in solutions of metal adducts of benzophenone and anthracene in dioxan.

The mechanism of the dissociation of ion pairs represented by Eqn. (5) also explains satisfactorily[42,76,80] the shape of the curves for the temperature variation of the molar conductance of the adducts of aromatic hydrocarbons with alkali metals in ethereal solutions (Fig. 2). $\Lambda-T$ curves of similar shape were obtained by Hoijtink and coworkers[89,90] and Buschow[91] in studies on solutions of adducts of polyacenes in methyltetrahydrofuran. In particular, it was found that, as the temperature is reduced, the conductance of the lithium adducts falls rapidly, that of sodium adducts passes through a maximum, and that of potassium adducts increases slowly (in the case of potassiopentacene there is a maximum approximately about 220°K). The authors[89-91] explained these results by the increase of the dielectric constant of the solvent as the temperature is reduced, as a result of which the equilibrium in the dissociation of ion pairs is displaced towards free ions, and Λ increases. The simultaneous increase in the viscosity of the solvent lowers the mobility of the ions and results in a fall of Λ. Thus the shape of the $\Lambda-T$ curve is determined by the competing effects of two factors: the changes in the degree of dissociation and in viscosity.

† Recently Szwarc[85] examined quantitatively the problem of equilibria involving the participation of ions and ion pairs. He discussed the effect of the solvent on the degree of solvation, mobility, and association of ions, the structure of ion pairs, etc.

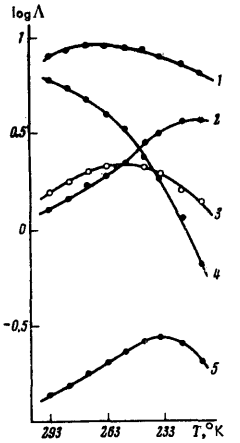


Fig. 2. Variation with T of $\log\Lambda$ for sodionaphthalene solutions; solvent: 1) 1,2-dimethoxyethane; 2) tetrahydrofuran; 3) 1-ethoxy-2-methoxyethane; 4) dimethyl ether of diethylene glycol; 5) 1,2-diethoxyethane.

In conformity with the results of spectroscopic studies, Hoijtink and Buschow concluded that the effect of viscosity begins to influence Λ when the dissociation equilibrium is almost completely displaced to the right. They assert that lithium adducts are present in solution in the form of free ions even at room temperature, while complete dissociation of sodium and potassium adducts occurs at the temperature corresponding to the maximum value of Λ. However, when the effect of viscosity is removed by multiplying Λ by η, it is found that in almost all cases the conductance, and hence the degree of dissociation, increases continuously as the temperature is reduced, down to 213°K (Fig. 3). Comparison of the quantities $\Lambda_T\eta_T$ and $\Lambda_{293}\eta_{293}$ shows that at 213°K too the degree of dissociation is still far from unity. On this basis, one may conclude[80] that below a certain temperature, determined by the properties of the system under investigation, the effect of the increase in the viscosity of the solvent begins to influence Λ more than the increase in the degree of dissociation. Thus this, at first sight unusual phenomenon, can be rationally explained by taking into account the equilibria represented in Eqn. (5).

The heat of dissociation of ion pairs in contact into free ions $\Delta H'_d = \Delta H_1 + \Delta H_2$ is higher than the heat of dissociation of separated ion pairs $\Delta H''_d = \Delta H_2$. Hence it follows that the rate of change of the logarithm of the dissociation constant with $1/T$, which is $-\Delta H_d/R$, will be higher in the dissociation of ion pairs in contact. Probably it is because of this that at relatively high temperatures, when the concentration of ion pairs in contact is much higher than that of separated ion pairs, the effect of dissociation on Λ is more pronounced than the effect of viscosity, and Λ increases as the temperature is reduced. At lower temperatures, when the concentration of ion pairs in contact becomes insignificant and the increase of K_d is slower, viscosity has the dominant effect on Λ, and the latter falls, i.e. the $\Lambda-T$ curve passes through a maximum.

The above explanation presupposes that the temperature corresponding to the maximum value of Λ is the temperature at which one type of ion pairs is converted into the

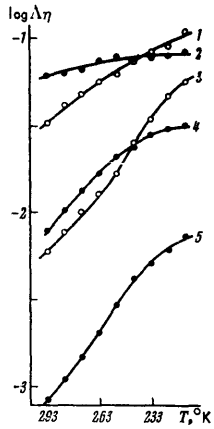


Fig. 3. Variation with T of $\log \Lambda\eta$ for sodionaphthalene solutions; solvent: 1) 1,2-dimethoxyethane; 2) dimethyl ether of diethylene glycol; 3) tetrahydrofuran; 4) 1-ethoxy-2-methoxyethane; 5) 1,2-diethoxyethane.

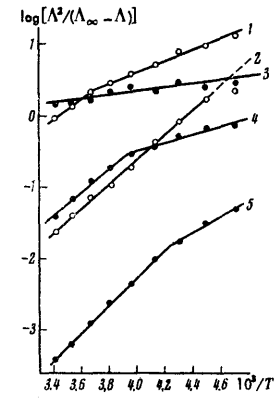


Fig. 4. Variation with $1/T$ of $\log [\Lambda^2/(\Lambda_\infty - \Lambda)]$ for sodionaphthalene solutions; solvent: 1) 1,2-dimethoxyethane; 2) tetrahydrofuran; 3) dimethyl ether of diethylene glycol; 4) 1-ethoxy-2-methoxyethane; 5) 1,2-diethoxyethane.

other. The temperature (°K) of the transition of the sodionaphthalene ion pairs in contact into separated ion pairs falls with decrease in the solvating power of the solvent: dimethyl ether of ethylene glycol (> 293°) > 1,2-dimethoxyethane (273°) > 1-ethoxy-2-methoxyethane (253°) > 1,2-diethoxyethane (235°) > tetrahydrofuran (213°). The analogy with the temperature of conversion of one type of solvate of the sodium cation into another (p. 104) is striking. Possibly the formation of a coordination-saturated solvate is accompanied by the formation of separated ion pairs.

The existence of equilibrium between ion pairs in contact and separated ion pairs is confirmed by the calculation of the heats of dissociation (ΔH_d) of the adducts[42]. If the molar conductance at infinite dilution at any one temperature and the variation of Λ and η with temperature are known, it is possible to estimate approximately the variation of K_d as the temperature is reduced. Approximate values of ΔH_d were calculated from the slopes of the linear plots of $\log K_d$ against $1/T$. In agreement with the above explanation of the shape of the $\Lambda - T$ curves, the values of ΔH_d differ, depending on whether the molar conductance Λ increases or decreases as the temperature is reduced. In the first case $\Delta H_d \simeq$ -6 – -9 kcal mole^{-1} and in the second $\Delta H_d \simeq$ -1.5 – -4 kcal mole^{-1}. The higher value of ΔH_d is due to the dissociation of the ion pairs in contact. The available literature data on the heats of dissociation of adducts are close to those given above. Weissman[52] found from ESR spectroscopic data ΔH_d = -7.6 kcal mole^{-1} for sodionaphthalene in tetrahydrofuran and Smid[78] obtained from conductivity data ΔH_d = -8 kcal mole^{-1} in the range 298–253°K (ion pairs in contact) and ΔH_d = -1.5 kcal × × mole^{-1} below 253°K (separated ion pairs) for fluorenylsodium in tetrahydrofuran. Two values of ΔH_d correspond to the $\Lambda - T$ curves which pass through a maximum, and, as was to be expected, the lower value occurs at lower temperatures, where separated ion pairs predominate. Graphically this is reflected in a break in $\log K_d - 1/T$ plots (Fig. 4). The temperatures corresponding to the breaks and to the maximum values of Λ are approximately the same[80].

Ether	Break, °K	Maximum, °K
1,2-Dimethoxyethane	~273	~273
1-Ethoxy-2-methoxyethane	253	253
1,2-Diethoxyethane	235	238

The above considerations concerning the mechanism of the dissociation and the state of the adducts of aromatic hydrocarbons with alkali metals in ethereal solutions are in good agreement with the data on the solvating power of ethers of different structures. There is also agreement between the conclusion that two types of ion pairs exist (in contact and separated) and that the solvation of cations proceeds by a stepwise mechanism. It follows from the results of the study of the electrical conductivity of the ethereal solutions of naphthalene adducts that the interionic interaction, which determines the position of the dissociation equilibrium, depends significantly on the conditions of cation solvation.

IV. THE ROLE OF THE METAL AND SOLVENT IN RADICAL-ANION DISPROPORTIONATION AND REDUCTION EQUILIBRIA

The adduct of sodium and naphthalene, which is widely used to initiate anionic polymerisation[3–7], has a green colour whatever the ether in which it is formed; the green colour (absorption maxima at 365 and 810 nm) is due to the presence of naphthalene radical-anions. The reaction of naphthalene with lithium is different. In 1,4-dioxan and 1,2-diethoxyethane[45,92] the green colour of the radical-anions is appreciable only in the first instants after the solution of naphthalene comes into contact with the metallic lithium mirror (its preparation has been described by Petrov et al.[93]). A stable red colour is then obtained due to the appearance in the spectrum of a broad band at wavelengths near 550 nm. On addition of an excess of naphthalene to the red solution in the absence of lithium, this maximum disappears and the spectrum is then characteristic of the naphthalene radical-anions (Fig. 5). The above

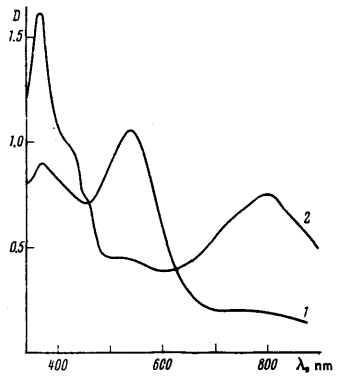


Fig. 5. Spectra of naphthalene–lithium adducts in 1,2-diethoxyethane:
1) in the presence of an excess of lithium; 2) in the presence of an excess of naphthalene.

phenomena have been interpreted[45,92] as evidence for the formation of naphthalene dianions. Their formation in the initial instants, when the solution still contains an appreciable amount of naphthalene, suggests that under these conditions they are formed as a result of the disproportionation of radical-anions [equilibrium (3)].

In tetrahydrofuran and 1,2-dimethoxyethane the green colour of the naphthalene radical-anions persists until reaction (1) involving the formation of radical-anions reaches completion. Only then does the colour of the solution change, and the broad band in the region of 550 nm appears in the spectrum. This means that in this case equilibrium (3) is displaced to the right and the dianions are produced preferentially by the reduction of radical-anions according to Eqn. (2).

Hoijtink and Buschow[94] were the first to describe the spectrum of the naphthalene dianions, which were obtained by the reaction of naphthalene with lithium in methyltetrahydrofuran. They noted that the dianions, which are very reactive, are readily protonated by the solvent at room temperature, forming the carbanions ArH^-:

$$C_5H_{10}O + Ar^{2-}2M^+ \rightarrow ArH^-M^+ + C_5H_9O^-M^+. \qquad (6)$$

For this reason, it was impossible to obtain the spectrum of the dianions without the superposition on the latter of the spectrum of the carbanions, which absorb in the wavelength range 350–500 nm.

Smid[75] quotes the spectrum of the solution of the products of the reaction of lithium with naphthalene in tetrahydrofuran (absorption maximum of the dianions at 555 nm), which is of a very similar form to that measured by Shatenshtein et al.[92]

Henrici-Olivé and Olivé[95-98] studied the properties and the preparation of solutions of naphthalene dianions in tetrahydrofuran. They investigated the reactions of lithium and sodium with naphthalene in dimethoxyethane and tetrahydrofuran by measuring the magnetic properties of the solutions of the resulting adducts. They observed that in tetrahydrofuran in the presence of an excess of lithium the concentration of the paramagnetic adduct is much lower than the initial concentration of the hydrocarbon, while the active alkalinity (determined by titration with propyl alcohol) is 1.5 times greater than the alkalinity corresponding to the complete conversion of naphthalene into radical-anions (in 1,2-dimethoxyethane and also with sodium in tetrahydrofuran such phenomena were not observed). Hence Henrici-Olivé and Olivé concluded that, in the presence of an excess of lithium in tetrahydrofuran, dianions are formed together with radical-anions. According to these investigators[96], about 90% of the naphthalene is converted into dianions in 5 h (ratio of the number of lithium gramme-atoms to the number of moles of naphthalene 4.5; concentration of naphthalene 0.15–0.2 M). The colour of the solution gradually changes from green to dark violet. As was to be expected, the addition of an excess of naphthalene to the solution of the dianions results in the restoration of the green colour and an increase in the paramagnetism of the solution.

There exists a definite relation between the state of the adduct in solution and the mode of formation of the dianions, namely the disproportionation of the radical-anions occurs more readily in those solvents where the adducts are present predominantly in the form of ion pairs in contact, since, according to Garst[77], the powerful interionic attraction in such pairs favours the disproportionation reaction, compensating the energetically unfavourable repulsion of electrons in the dianions. On the other hand, if the adduct (lithionaphthalene) is present in solution in the form of separated ion pairs, the electrostatic interaction between the ions is weaker and the disproportionation virtually does not occur. The reduction of the radical-anions as well as their formation according to Eqn. (1) are favoured by solvents with a higher solvating power, in which separated ion pairs are present.

The problem of the disproportionation reactions has been considered in greatest detail by Garst[75,79,100] from the above standpoint. In the study of the effect of the solvent on the radical-anion disproportionation equilibrium it was found that the disproportionation constant (K_{disp}) of sodiotetraphenylethylene[99] increases in the series dimethyl ether of diethylene glycol $\simeq$ 1,2-dimethoxyethane $<$ tetrahydrofuran $<$ 1,4-dioxan, ethyl ether. The following sequence of solvents as regards their effect on the disproportionation constant of sodiostilbene has been obtained[100]: tetrahydrofuran $<$ methyltetrahydrofuran $<$ 1,4-dioxan. After comparing these data with the shifts in the spectra of sodiobenzophenone ketyl as a function of the solvent[55], Garst concluded[99] that a decrease in the degree of solvation of ions (mainly the cations) favours the displacement of the equilibrium in the direction of the formation of dianions. When the temperature is reduced, the degree of solvation of the cations increases, and the interionic attraction weakens, as a result of which the equilibrium should be displaced towards the formation of radical-anions, as is observed experimentally. The increase of the constant K_{disp} for the radical-anions of tetraphenylethylene in tetrahydrofuran with increase in the radius of the cation (at room temperature) observed by Garst and Zabolotny[77] and Ewans and Tabner[101] does not contradict this explanation either, since the interionic interaction in the above solvent increases in the series of cations $Li^+ < Na^+ < K^+$. At the same time Garst et al.[99] observed that in methyltetrahydrofuran, whose solvating power is lower than that of tetrahydrofuran, K_{disp} for stilbene radical-anions decreases in the opposite sense compared with tetrahydrofuran, i.e. with increase in the radius of the cation. Garst[77] believes that this reversal of the reactivity of metals is caused by competition between interionic interaction and solvation. If the reaction is performed in a solvent which solvates cations to a high degree, then the

solvation effect predominates as the radius of the cation increases, and K_{disp} falls, while in a weakly solvating solvent the effect of interionic interaction prevails and K_{disp} increases with the radius of the cation. Thus the dianion formation reactions also convincingly demonstrate the close relation between the phenomenon of cation solvation and interionic interaction (see also Refs. 102 and 103).

It must be emphasised that the above relations involving the effect of the solvent and the nature of the alkali metal on the formation and ionic dissociation of the adducts of alkali metals with aromatic hydrocarbons are of a more general significance, since they apply to a considerable extent to the entire field of organic anionic reactions. To illustrate this postulate, one may refer to the reviews published in this journal [104,105] and to the work carried out in our laboratory [73,106-111] on a series of anionic reactions in ether solvents.

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MODERN IDEAS ON THE SUPERMOLECULAR STRUCTURE OF CELLULOSE

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According to modern ideas, cellulose macromolecules form long, unbranched, elastic threads, consisting of D-glucopyranose residues linked by β-glucoside bonds in the 1,4-position.

Since each glucopyranose residue contains alcoholic hydroxy-groups, the cellulose molecule with a degree of polymerisation of 1000 contains 3000 hydroxy-groups. These groups screen the adjacent units in the cellulose macromolecule, and are responsible for rigidity and elasticity; they also determine the nature of the bonds between the macromolecules. The way in which the cellulose macromolecules are mutually arranged in natural and synthetic fibres and in films has an important effect on the strength, stretch, elasticity, hygroscopicity, reactivity, solubility, capacity to undergo wet grinding, ability to take dyes, and many other properties of these fibres.

Unfortunately, we still know very little about the supermolecular structures that are responsible for these properties of cellulose. Nevertheless, it is in this field that we must look for an explanation of processes that lead to the preparation of ultra-strong cellulose fibres, highly reactive celluloses, and other materials of great industrial importance.