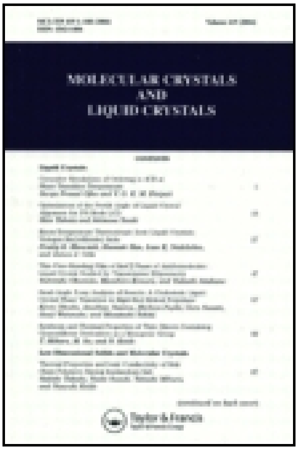

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Reactions Occurring in Gels of Lithium Tetraalkyl Borates Promoted by Supermolecular Structure of Complexes

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REACTIONS OCCURRING IN GELS OF LITHIUM TETRAALKYL BORATES PROMOTED BY SUPERMOLECULAR STRUCTURE OF COMPLEXES

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As $Li[BOR'(OR)_3]$ and $Li[B(OR)_4]$ complexes, where R' and R are alkyls of iso- and normal structure, are formed from boron alkoxides and lithium in solutions of low dielectric permittivity, they are involved in autocatalytic polyassociation to give viscoelastic systems (gels) possessing a mechanical memory [1]. For gels subjected to shear stress flow at activation heat values, ΔH_a of 15 to 35 kJ/mol and temperatures of 293 to 333 K, relaxation rates exhibited by the supermolecular structure of complexes subjected to deformation are $16 \cdot 10^8$ mol/s. Restitution of the structure of gels subjected to the mechanical destruction causes no changes in the viscoelasticity. The viscoelasticity of gels is entropic in nature. Certain solutions of complexes are in a liquid-crystalline state. The complexes possess an ionic structure. They are associated at the Li...O coordination bond as well as by means of alkyl groups with forces of dispersive interaction involved [2-4]. The lithium cation of complexes is in a four-coordination state. It has two available bonds. Therefore the coordination saturation is incomplete and the complexes are capable of being solvated by electron-donating compounds. In the presence of aliphatic alcohols, (ROH), $Li[t\text{-}C_4H_9OB(OR)_3]$ complexes cause an increase in the viscosity of hydrocarbon solutions relative to solutions of non-solvated complexes [5]. The changes occurring in the structural

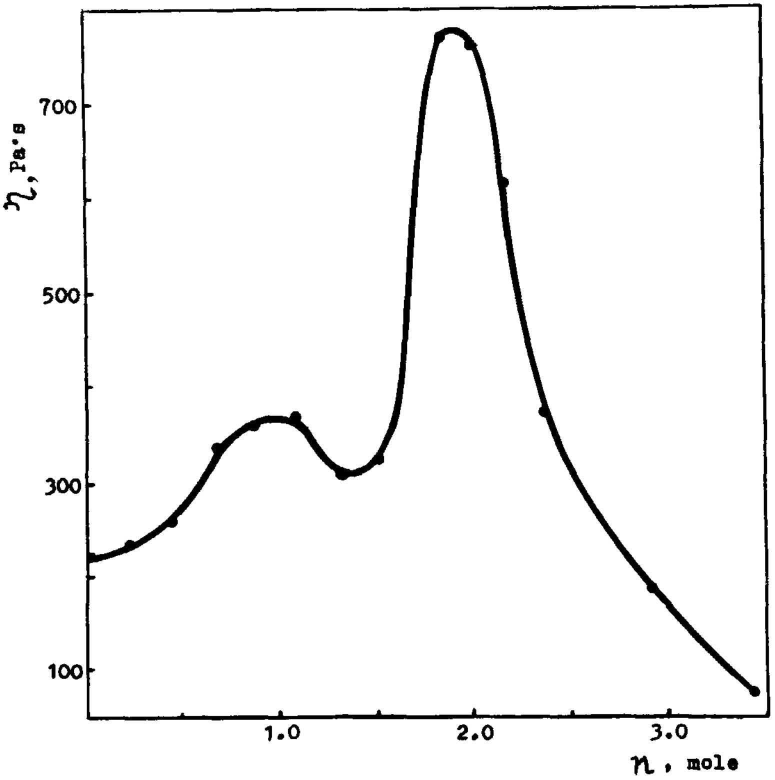
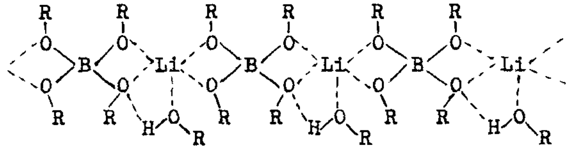


Figure 1. The effect of the content of $C_7H_{15}OH$ at 293 K, of the deformation rate (0.1667 s^{-1}) and of the concentration of the complex (0.03 mol/l) on the viscosity of the gel of $[t\text{-}C_4H_9OB(OC_7H_{15})_3]Li$ in heptane solution.

viscosity of gels of solvated complexes are a function of the complex:alcohol ratio (C:A = 1:n). They are extreme in character (see Fig. 1). The solvation of complexes by alcohols occurs in structured solutions (gels) as a two-stage process to give mono- and disolvates, $[t\text{-}C_4H_9OB(OR)_3]Li \cdot nHOR$. The effective viscosity maxima of gels in an equilibrium state occur at C:A molar ratios of 1:10 and 1:1.8 for the first and the second maximum in the rheologram, respectively (see Fig. 1). The structuring occurring in solutions and gels is accelerated by the solvation of complexes of lithium tert-butyl borates (see Table 1). Since the viscosity of structured solutions of solvated complexes depends on the electron- and proton-donating properties of a solvating reagent, such a "burst" of the solution viscosity observed in the presence of alcohols can be accounted for by the solvation of the complexes with increasing coordination number of Li as well as by the formation of a hydrogen bond in the associated solvate [5, 6]:



The increase in the solution viscosity observed in the presence of alcohols at a given molar ratio is probably due to the increasing free energy of intermolecular donor-acceptor Li...O, H...O and dispersive R...R interactions. Associations of complexes remain stable and the supermolecular structure of gels retains orderliness due to interdependency interrelationship of interactions of the both types. The energy of the H-bond should be proportional to that of the Li...O interaction while its very existence should testify to the formation of a solvated complex coordinated at a

Table 1. The Kinetic Parameters Obtained for Structured Solutions of $[t\text{-}C_4H_9OB(OR)_3]Li\cdot nROH^*$

R	T,K	n = 0		n = 1		n = 1.8	
		a**	b***	a	b	a	b
1	2	3	4	5	6	7	8
C_4H_9	293	9.70	83.21	55.56	78.76	95.23	77.44
	303	11.49	85.50	58.82	81.38	133.33	79.32
	313	25.64	86.32	74.07	83.56	125.00	82.19
	323	20.83	89.72	54.05	87.16	95.24	86.64
	333	29.41	91.62	55.56	89.86	90.91	88.50
	343	52.63	92.80	52.63	92.80	133.33	90.15
	353	71.43	94.69	54.05	95.51	55.56	78.76
C_5H_{11}	293	8.37	83.37	34.48	79.92	117.65	76.93
	303	14.70	84.88	45.45	82.03	86.96	80.40
	313	20.41	86.91	68.97	83.74	105.26	82.64
	323	41.67	87.85	57.97	89.97	200.00	83.64
	333	20.00	92.69	68.90	89.26	129.03	87.53
	343	100.00	90.97	133.33	90.08	125.00	90.33
	353	66.67	94.90	129.03	92.96	76.92	94.48
C_6H_{13}	293	10.99	82.70	82.55	79.41	76.92	77.98
	303	12.42	85.30	46.51	81.98	83.33	80.51
	313	26.32	86.25	62.50	84.00	100.00	82.77
	323	23.81	89.36	58.82	86.93	181.82	83.90
	333	35.71	91.85	76.92	88.96	153.85	87.04
	343	25.00	94.92	86.96	91.37	133.33	90.15
	353	41.67	96.27	58.82	95.26	108.10	93.48
C_7H_{15}	293	3.36	85.59	27.39	80.48	100.00	77.33
	303	6.90	86.78	57.14	81.46	111.11	79.78
	313	8.55	89.17	72.73	83.60	200.00	80.90

Table 1 (Continued)

1	2	3	4	5	6	7	8
	323	10.00	91.69	90.91	85.76	181.82	83.90
	333	33.33	91.28	100.00	88.23	200.00	86.32
	343	52.63	92.80	333.33	87.54	60.61	92.40
	353	133.33	92.86	125.00	93.05	285.71	90.62
C_8H_{17}	293	5.81	84.26	54.05	78.82	74.07	78.06
	303	6.27	87.02	35.71	82.64	76.92	80.71
	313	7.87	89.39	55.56	84.30	153.85	81.65
	323	14.49	90.69	57.14	87.01	86.96	85.88
	333	31.25	91.45	68.97	89.26	142.90	87.27
	343	58.82	92.48	86.96	91.37	166.67	89.51
	353	66.67	94.90	166.67	92.21	125.00	93.05
$C_{10}H_{21}$	293	-	-	20.41	81.20	71.42	78.14
	303	-	-	40.00	82.36	52.63	81.66
	313	-	-	41.67	85.05	55.56	84.30
	323	6.06	93.03	58.82	86.93	62.50	86.77
	333	7.14	95.54	50.00	90.15	125.00	87.62
	343	7.69	98.28	58.82	92.48	125.00	90.33
	353	-	-	64.52	94.99	-	-

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[*] The concentration of the complex in heptane solution is 0.02 mol/l. The relative error is ± 2%.

[**] $k_\eta \cdot 10^3$, Pa s/s. [***] ΔG, kJ/mol.

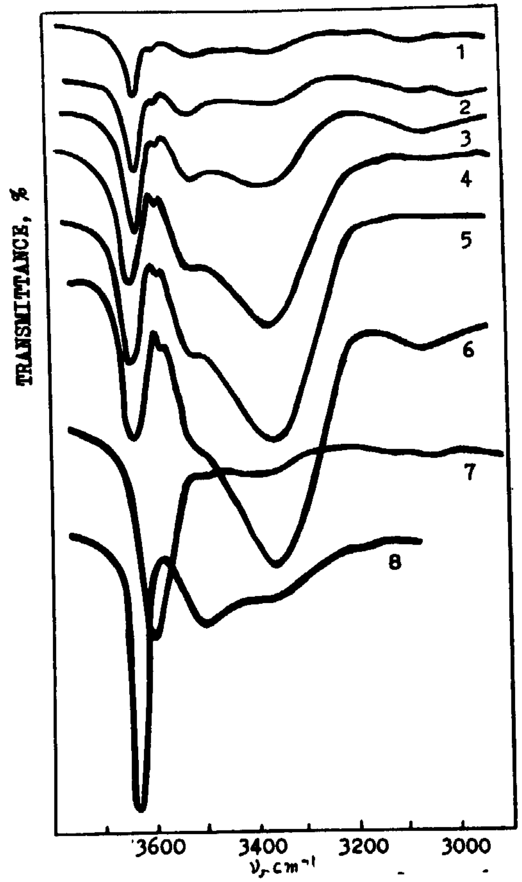
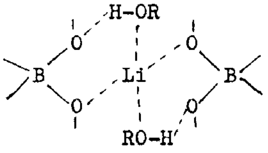


Figure 2. IR spectra obtained for the gels of $[t\text{-}C_4H_9OB(OR)_3]Li\cdot$ $\cdot nHOR$, R = C_5H_{11}, n: 1 - 0.5; 2 - 0.7; 3 - 1.0; 4 - 1.3; 5 - 1.7; 6 - 2.0; 7 - R = $H(CF_2\text{-}CF_2)_2$, n = 2.0; 8 - $C_5H_{11}OH$ in CCl_4; (1-6) - in heptane; 7 - in toluene.

lithium cation. The probability of the H-bond formation by interaction of $[t\text{-}C_4H_9OB(OR)_3]Li$ and $H(CF_2\text{-}CF_2)_2OH$, $H(CF_2\text{-}CF_2)_3OH$, $(C_5H_{11})_2O$, and ROH (R = $n\text{-}C_4H_9$ to $n\text{-}C_7H_{15}$) occurring in heptane, toluene and CCl_4 (0.02-0.08 mol/l) was studied using IR spectroscopy. The IR spectra obtained for structured solutions of gels of $[t\text{-}C_4H_9OB(OR)_3]Li$ complexes and those of ether solvates, $[t\text{-}C_4H_9OB(OR)_3]Li\cdot nOR_2$, show no absorption bands in the 3700-3000 cm^{-1} region. On addition of alcohols to the solutions of complexes ($n = 0.5 \div 2.0$) a redistribution of the intensities of $\nu_{OH\ free}$ (3648-3632 cm^{-1}) and $\nu_{OH\ bonded}$ (3365-3380 cm^{-1}) absorption bands is observed. The intensity of $\nu_{OH\ bonded}$ increases considerably in time, while that of $\nu_{OH\ free}$ decreases. A similar effect is observed on increasing the molar fraction of alcohol in a solution. The spectra obtained for all gels of solvated complexes are different from those of alcohols in that they show two new bands of low intensity: a narrow one at 3588 cm^{-1} and a broad one at 3095-3065 cm^{-1} (see Fig. 2). The intensity of the broad band changes as a function of the molar ratio C:A = 1:n. A similar trend is observed for viscosity values (see Fig. 1). The greatest intensity of absorption in this region is observed at n= = 1-2 (spectra 3 and 6). The intensity of the 3095-3065 cm^{-1} band becomes greater than that of the 3380-3365 cm^{-1} band with increasing length of the alkyl substituent of $[t\text{-}C_4H_9OB(OR)_3]Li\cdot nHOR$ (R = $n\text{-}C_6H_{13}$, $n\text{-}C_7H_{15}$) for n = 1-2. The spectra taken in the 3600-3200 cm^{-1} region for alcoholic solvates of complexes are typical for the hydroxyl involved in hydrogen bond formation[7]. However, $\nu_{OH\ bonded}$ bands characteristic of gels of solvated lithium tert-butyltrialkyl borates exhibit more significant shifts to the low-frequency region relative to those of aminoalcohols containing intermolecular hydrogen bonds[7,8]. The fact that spectra of the solvated complexes show several $\nu_{\text{OH bonded}}$ bands is evidence for the existence of H-bonds of varying strength, which is probably due to the equilibrium state of the system:

$$[t\text{-}C_4H_9OB(OR)_3]Li + nROH \rightleftarrows [t\text{-}C_4H_9OB(OR)_3]Li\cdot nROH$$

The electron-donating Li...O interaction affects the relative intensity and ν_{O-H} frequency shift characteristic of the H-bond as well as the viscosity of gels of solvated complexes [5]. The band assigned to the bonded hydroxyl is known to be shifted to the low-frequency region with increasing size of the cycle formed by the H-bond [9, 10]. Therefore, the 3095-3065 cm^{-1} band should be assigned to the H-bonds of types I, II, a set of transitional interactions with concomitant and continuous energy variations probably preceding the H-bond formation.



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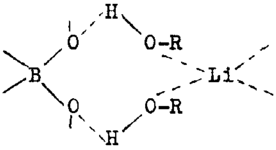
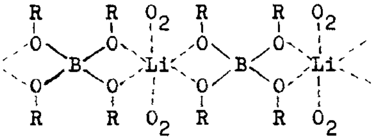


II

The results obtained in the study of solvation of complexes [1] suggest that lithium tetraalkyl borates are capable of activating small n-donor molecules of gases such as oxygen and of transporting them onto the relaxation sites of other molecules.



A study was made of the kinetic properties exhibited by Li[t-C_4H_9-

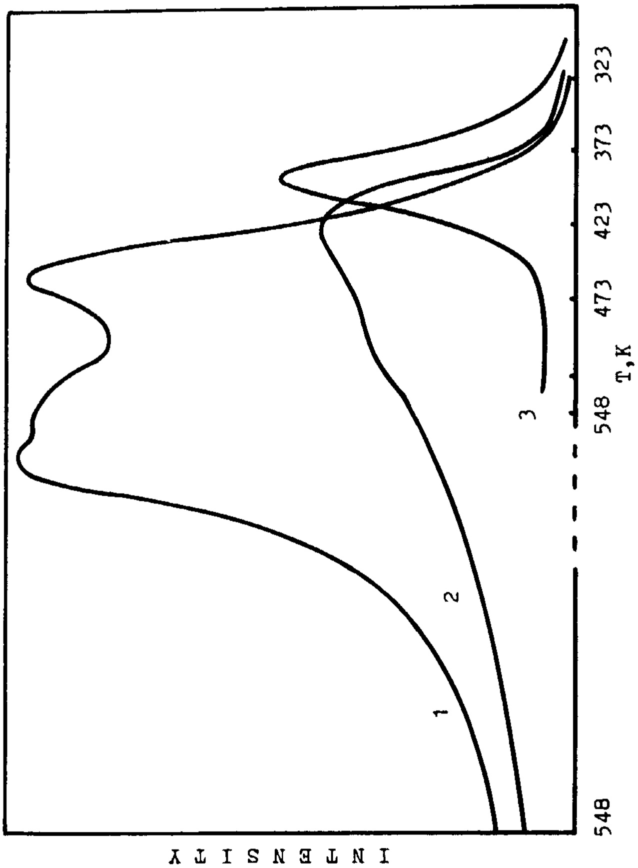


Figure 3. Chromatograms obtained for O_2 desorbed from the following solvates of complexes: 1 - $[t\text{-}C_4H_9OB(OC_4H_9)_3]Li\cdot 2.13\ O_2$; 2 - $[t\text{-}C_4H_9OB(OC_7H_{15})_3]Li\cdot 1.39\ O_2$; 3 - $[t\text{-}C_4H_9OB(OC_{10}H_{21})_3]Li\cdot 1.98\ O_2$.

$OB(OR)_3]$ ($R = n\text{-}C_4H_9$, $n\text{-}C_7H_{15}$, $n\text{-}C_{10}H_{21}$) during oxygen adsorption-desorption occurring at 298–548 K (see Table 2). The activation energies for the thermal desorption of oxygen from the complexes were determined from equations (1) and (2) for the first- and the second-order reactions, respectively:

$$\ln \frac{\ln(Q_0/Q)}{T^2} = \ln \frac{\nu R}{\beta E} - \frac{E}{RT} \qquad (1)$$

$$\ln \frac{(1/Q - 1/Q_0)}{T^2} = \ln \frac{\nu R}{\beta E} - \frac{E}{RT} \qquad (2)$$

Q_0 is the total amount of oxygen desorbed; Q is the amount of oxygen adsorbed on a complex at time τ; ν is the frequency factor; β is the temperature coefficient for the linear dependence of temperature versus time. The reaction rate constant was obtained using a graphical solution of eq. (3):

$$-dC/d\tau = kC^m, \quad C = nO_2/nLi[t\text{-}C_4H_9OB(OR)_3] \qquad (3)$$

The complexes are solvated by oxygen at a molar ratio of $nO_2/$ $/nLi[t\text{-}C_4H_9OB(OR)_3] \cong 2$ irrespective of the length of the alkyl substituent. The kinetic parameters of the thermal desorption of oxygen from disolvates depend on the structure of the complexes as well as on thermal treatment conditions. Under isothermal conditions (423 K) as well as under temperature scanning conditions (up to 548 K) oxygen desorbs from $[t\text{-}C_4H_9OB(OC_4H_9)_3]Li\cdot nO_2$ solvate in two clearly defined stages, while from the $[t\text{-}C_4H_9\text{-}OB(OC_{10}H_{21})_3]Li\cdot nO_2$ complex it desorbs in one stage (see Fig. 3). The solvate of $[t\text{-}C_4H_9OB(OC_7H_{15})_3]Li\cdot nO_2$ complex occupies an intermediate position with respect to the desorption behaviour of oxygen. Chromatogram 2 as distinct from chromatograms 1 and 3 shows neither any clearcut division of the process into two sta-

Table 2. The Kinetic Parameters Obtained for the Thermal Desorption of Oxygen Occurring from $[t\text{-}C_4H_9OB(OR)_3]Li \cdot nO_2$ Complexes

R	C	First stage		Second stage		ΔE_{act}, kJ/mol		ΔH_{act}, kJ/mol	
		a*	b**	a	b	a	b	a	b
		k, s^{-1}	k,mol/mol·s	k, s^{-1}	k,mol/mol·s				
C_4H_9	2.1	2.31 10^{-3}	8.76 10^{-4}	7.44 10^{-3}	1.72 10^{-2}	48.90	52.42	45.30	45.22
	1.68	3.09 10^{-3}	1.18 10^{-3}	-	3.46 10^{-3}	57.28	56.40	53.68	46.48
	2.13	7.03 10^{-4}	2.67 10^{-4}	1.85 10^{-3}	2.33 10^{-3}	48.69	47.98	45.09	37.89
C_7H_{15}	1.39	6.25 10^{-4}	5.40 10^{-4}	1.13 10^{-3}	1.55 10^{-3}	68.71	56.35	65.19	49.31
$C_{10}H_{21}$	1.98	total stage, 1st order				56.31	70.92	53.00	64.30
	0.13		1.06 10^{-2}			-	124.01	-	117.38

*1st order; **2nd order

ges nor any complete coincidence of the both stages in time. The mass of oxygen desorbed from $[t\text{-}C_4H_9OB(OC_{10}H_{21})_3]Li\cdot nO_2$ changes with temperature and time. This dependence is described by a Gaussian curve (see curve 3). The temperature of the beginning of the process rises as the length of the alkyl substituent of the complex decreases. A greater activation energy for $Li...O_2$ bond scission is required for a disolvate compared to a monosolvate for deformation and disruption of the symmetric coordinatively saturated solvate shell of a lithium cation to occur. Therefore, the first stage of thermal desorption of oxygen from $[t\text{-}C_4H_9OB(OC_4H_9)_3]Li\cdot nO_2$ and $[t\text{-}C_4H_9OB(OC_7H_{15})_3]Li\cdot nO_2$ disolvates proceeds more slowly relative to the second one. The total process of the thermal desorption of oxygen occurring from $[t\text{-}C_4H_9OB(OC_{10}H_{21})_3]Li\cdot nO_2$ at $n \cong 2$ is equally well described by equations of the first- (1) and second-order (2) reactions, the activation energies being 56.31 and 70.92 kJ/mol, respectively. However, the following function $\ln \frac{\ln(Q_o/Q)}{T^2} = f(1/T)$ becomes nonlinear as the degree of solvation of a complex decreases and n becomes equal to 0.13. The activation energy increases to 124 kJ/mol and the reaction proceeds according to the second-order reaction law. The two-stage process of the thermal desorption of oxygen occurring from $[t\text{-}C_4H_9OB(OC_7H_{15})_3]Li\cdot nO_2$ at $n = 0.088$ cannot be described by straight line equations. The following relationships: $\ln \frac{\ln(Q_o/Q)}{T^2} = f\ (1/T)$, $\ln \frac{(1/Q-1/Q_o}{T^2} = f\ (1/T)$ become nonlinear. The results of the study show that the kinetic parameters of the process are affected by the structure of lithium tetraalkyl borates to a greater extent than by the thermal treatment conditions (see Table 2). With lengthening of the alkyl substituent of a complex, the two-stage desorption process becomes a one-stage process and suffers no further changes with rising temperature. The thermal desorption of oxygen proceeds less readily as the organic mass of a complex increases. However, a low activation heat observed for the process testifies to the high capacity for the activation of oxygen exhibited by complexes of lithium tetraalkyl borates.

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