Study of complex formation between aluminum bromide and benzene by ^{27}Al NMR spectroscopy

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The reaction of aluminum bromide with benzene in *n*-hexane was studied by ^{27}Al NMR spectroscopy in the temperature range from −80 to +20 °C. The formation of $C_6H_6 \cdot Al_2Br_6$ (1 : 2) complexes is accompanied by broadening of the resonance line with δ 178. No peak splitting following a decrease in the temperature was observed but the temperature dependence of the line width passed through a maximum near −60 °C. A procedure for determination of the constant *K* for the formation of 1 : 2 complexes at −20, 0, and +20 °C based on the line broadening with an increase in the C_6H_6 : Al_2Br_6 molar ratio was proposed. The thermodynamic parameters of complex formation, Δ*G*, Δ*H*, and Δ*S*, were calculated.

Key words: benzene, aluminum bromide, complexes, ^{27}Al NMR spectroscopy.

In a study of the influence of various factors on the low-temperature cationic polymerization of isobutylene in *n*-hexane, we found that, when the aluminum bromide—MeOH and aluminum bromide—Bu^{t}Cl systems used as initiators are prepared under certain conditions, minor additives of aromatic compounds such as benzene and chlorobenzene ensure a quite substantial increase in the process rate. The observed acceleration of the polymerization is mainly due to the increase in the activity of the initiating system. In our opinion, this may be due to the involvement of aluminum bromide complexes with arenes in the formation of the active sites of polymerization. These complexes have been known for a fairly long period and characterized using various methods.[1] However, the data obtained by different researchers are often contradictory. In particular, this refers to the color of complexes, which is sometimes observed and is attributed either to the appearance of additional absorption bands upon complex formation[2] or to the formation of secondary products (ternary complexes) with participation of proton-generating admixtures including moisture.[1,3] The presence of traces of water often results in poor agreement between the data obtained at low (up to 10 mmol L^{-1}) and high concentrations of aluminum bromide, in particular, by dielectrometric measurements.[4]

This disagreement stimulated us to study the formation of aluminum bromide—PhH complexes with thorough drying of components, similar to that employed in polymerization experiments in a high-vacuum system (see Experimental). The complex formation was monitored by ^{27}Al NMR spectroscopy, which permits one, in principle, to follow the variation of the environment of aluminum atoms depending on the amount of benzene and the temperature. It should be noted that the use of ^{1}H NMR[5] or IR spectroscopy[6] proved to be useless for the analysis of aluminum bromide and gallium chloride complexes with arenes because the spectra recorded were virtually identical to the spectra of the initial arenes.

Experimental

Hydrocarbons (*n*-hexane, benzene) were shaken with concentrated H_2SO_4, washed with water, with a 10% solution of $NaHCO_3$, and again with water, dried with $CaCl_2$, distilled, dried additionally over 4 Å molecular sieves, deaerated by three "freezing—evacuation—thawing" cycles, refluxed over a potassium—sodium alloy, and recondensed *in vacuo.*

Dry aluminum bromide (analytically pure grade) was additionally heated at 150 °C for 1 h in a flow of dry argon and then twice sublimed *in vacuo.*[7] Solutions of benzene and aluminum bromide in hexane were prepared by mixing the components in all-welded setups and then distributed into thin-walled glass beads or into tubes with thin-walled partitions. The solutions were mixed in similar vessels and the resulting mixture was poured into an NMR tube welded to the setup. The fact that the solution mixtures were colorless indicated a high degree of drying of the components.[1] ^{27}Al NMR spectra were recorded on a Bruker WP-100 spectrometer (23.45 MHz) in the temperature range from −80 to +20 °C. A 0.15 *M* aqueous solution of $Al(NO_3)_3$ served as the external standard.

Results and Discussion

In our investigations, we relied on the published data that were, in our opinion, the most reliable and substantiated[1,8]; according to these data, in solutions in hydrocarbon solvents that are not highly dilute, aluminum bromide exists mainly as the dimer Al_2Br_6. The enthalpy of dimerization is −(111 to 121) kJ mol^{-1} (see Refs 9, 10). The dimeric structure of the bromide is also retained in its complexes with benzene, although in this case, the

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bonds between aluminum and the bridging bromine atom might be somewhat bent.[11] These compounds have the composition $C_6H_6 \cdot Al_2Br_6$ (with a formal ratio of 1 : 2) and, according to the Mulliken classification, they are πv-type complexes. They are normally classified as weak complexes with an enthalpy of formation of about 1—10 kJ mol^{-1}; benzene can be regarded as a weak electron donor with respect to Al_2Br_6.

The ^{27}Al NMR spectra of hexane solutions of mixtures of Al_2Br_6 with benzene recorded at temperatures from −80 to +20 °C and Al_2Br_6 : C_6H_6 molar ratios of 1 : 2, 1 : 4, and 1 : 16 exhibited only one signal with a maximum at δ 178±1 and with a variable observed width at the half-height s_{obs}.

The s_{obs} values found for the spectra of mixtures with benzene, the corresponding parameters s_{Al} of the spectra of hexane solutions of Al_2Br_6 (with the same Al_2Br_6 concentrations), and the differences between these two parameters $s_{obs}-s_{Al}$ are listed in Table 1. It can be seen from the data given in the Table that the dependences of $s_{obs} - s_{Al}$ on temperature for different Al_2Br_6 : C_6H_6 ratios pass through a maximum at about −60 °C. Dependences of this type are typical of the NMR spectra of systems in which different forms of the compound analyzed occur in equilibrium.[12] In the high-temperature region, the two states of Al_2Br_6 molecules, *i.e.*, free molecules and those bound in the complex, undergo fast (on the NMR time scale) exchange. In the low-temperature region, the exchange is slow, and the vicinity of the maximum (−60 °C) represents the region of medium exchange. In this case, it is especially important to estimate the relative exchange rates from these dependences because splitting of signals into separate resonances on passing to slow exchange, typical of the NMR spectroscopy in the case of stronger complexes, does not show itself for the system in question. In all probability, complexation involving arenes results only in a slight perturbation of the electron distribution in the Lewis acid molecule and, hence, it does not shift the Al signal.

Table 1. Effect of temperature and the $[Al_2Br_6]_0/[C_6H_6]_0$ molar ratio on the resonance line width (*s*/Hz) in the ^{27}Al NMR spectrum

T/°C	s_{Al}	s_{obs}			$s_{obs} - s_{Al}$		
		I[a]	II[b]	III[c]	I[a]	II[b]	III[c]
−80	4836	5317	4951	4863	481	115	27
−60	2075	4713	3585	2736	2638	1510	661
−40	1361	2353	2745	3092	992	1384	1731
−20	895	1119	1323	1553	224	428	658
0	545	640	713	882	95	168	337
+20	415	468	495	697	53	80	282

Note. $[Al_2Br_6]_0$ = 0.09 mol L^{-1}.

[a] $[C_6H_6]_0$ = 0.18 mol L^{-1}, $[Al_2Br_6]_0/[C_6H_6]_0$ = 1 : 2.

[b] $[C_6H_6]_0$ = 0.36 mol L^{-1}, $[Al_2Br_6]_0/[C_6H_6]_0$ = 1 : 4.

[c] $[C_6H_6]_0$ = 1.44 mol L^{-1}, $[Al_2Br_6]_0/[C_6H_6]_0$ = 1 : 16.

The reversible exchange between the two states of Al_2Br_6 can be represented in the following way

$$Al_2Br_6 + C_6H_6 \overset{K}{\rightleftharpoons} [C_6H_6 \cdot Al_2Br_6],$$

where *K* is the equilibrium constant given by the relation

$$K = \frac{[C_6H_6 \cdot Al_2Br_6]}{([Al_2Br_6]_0 - [C_6H_6 \cdot Al_2Br_6])([C_6H_6]_0 - [C_6H_6 \cdot Al_2Br_6])}. \quad (1)$$

Here $[C_6H_6 \cdot Al_2Br_6]$ is the equilibrium concentration of the complex and $[Al_2Br_6]_0$ and $[C_6H_6]_0$ are the initial concentrations of the components.

In a previous publication,[13] characteristics of complexes formed by triethylaluminum with a series of nitrogen-, oxygen-, and sulfur-containing compounds were studied by analyzing the effect of the type of electron donor on the width of the resonance line at room temperature (in the fast exchange region) using the following relation of additivity:

$$s_{obs} = s_{Al}p_{Al} + s_c p_c, \quad (2)$$

where p_{Al} and p_c are the mole fractions of free and complexed Et_3Al and s_{Al} and s_c are the line widths for the two forms. Our results comply with the criterion[12] of fast exchange between the two states in a temperature range not lower than −20 °C. Therefore, we used Eq. (2) to calculate the equilibrium constants *K* for the $C_6H_6 \cdot Al_2Br_6$ complex at temperatures of −20, 0, and +20 °C. In this case, the s_c value also needed to be determined. When strong electron donors are used and stable complexes with high equilibrium constants are formed, s_c can be estimated with a sufficient accuracy from the spectrum recorded in the presence of excess donor.[13] Since benzene, as noted above, forms rather weak complexes with Al_2Br_6, the maximum binding of Al_2Br_6 would be attained if the spectra of solutions of $AlBr_3$ are recorded in pure benzene. However, high freezing temperature of benzene sharply restricts the temperature range of experiments; therefore we determined s_c using other procedures, which are considered below.

Combination of Eqs. (1) and (2) makes it possible to obtain the following equation:

$$1/K = \frac{s_c - s_{obs}}{s_{obs} - s_{Al}}[C_6H_6]_0 - \frac{s_c - s_{obs}}{s_c - s_{Al}}[Al_2Br_6]_0. \quad (3)$$

The two unknowns present in this equation, *K* and s_c, can be found in two ways. One, more complex procedure implies pairwise combination of the results of experiments carried out at a constant temperature and different $[C_6H_6]_0$: $[Al_2Br_6]_0$ ratios. If the data for each experiment are substituted into equations of type (3), the right-hand parts of the equations would be equal because the left-hand parts are equal by definition. This expedient allows one to get rid of one unknown, *K*. Subsequent transformations result in a quadratic equation having the required s_c value as one of its roots. When several pairwise combinations are available, the mean s_c value and, hence, the mean K value can be calculated. This method is actually a modification of the method of elimination of one unknown described in a monograph.[1]

It is clear that high validity of the results obtained by this procedure can be ensured when a vast set of experimental data are available. It should be borne in mind that the formation of some equilibrium amount of 1 : 1 complexes $C_6H_6 \cdot AlBr_3$ and/or 2 : 2 complexes $(C_6H_6)_2 \cdot Al_2Br_6$,[14] able to influence both the main equilibrium and the s_c value, also cannot be ruled out for the system in question. Although, according to published data,[15] the proportion of these complexes appears to be relatively low under these conditions, highly accurate or adequate results can hardly be expected as long as the calculation procedure employed is so cumbersome and the number of experimental points is limited.

The other approximate but markedly simpler procedure for determination of the K and s_c values was developed relying on the assumption that one term in the right-hand member of Eq. (3) is, in this case, much smaller than the other term and, therefore, it can be neglected. To verify this assumption, one should determine approximate s_c values for each temperature and then calculate the ratio of these two terms. The s_c value can be estimated based on the following general views on the factors influencing the width of the resonance line in the ^{27}Al NMR spectra.

It is believed[16] that line broadening in the spectra of complexes formed from aluminum compounds is due to the high gradient of the molecular electric field, having a symmetry lower than cubic, around the ^{27}Al nucleus, interacting with the nuclear-electric quadrupole moment of this nucleus. Broadening also takes place in the absence of complexation as the size of molecules of the aluminum compound increases, for example, on passing from triethylaluminum to tripropyl-, tributyl-, and trihexylaluminum.[17] In low-viscosity systems (which probably include the systems studied here), quadrupole relaxation through molecular rotation is likely to be the predominant relaxation mechanism.[17—19]

From the Debye equation,

$$\tau = 4\pi\eta\alpha^3/3kT, \tag{4}$$

where τ is the correlation time, η is the system viscosity, α is the effective radius of the particle, k is the Boltzmann constant, T is the absolute temperature, it can be seen that the correlation time should increase proportionally to the effective radius cubed. The increase in the line width s would follow a similar pattern.[17,20] This dependence was shown to hold rather well for the increase in the size of alkyl substituents R in trialkylaluminum compounds AlR_3.[17] Therefore, the line broadening observed on passing from the spectrum of Al_2Br_6 to the spectra of its complexes can be estimated, as the first approximation, from the ratio of molar volumes V_m of the dimeric bromide and the complex $C_6H_6 \cdot Al_2Br_6$.[20]

To calculate V_m of the complex using the formulas

$$V_m(i) = M(i)/d(i)$$

and

$$V_m(\text{complex}) \approx \Sigma V_m(i),$$

where $M(i)$ and $d(i)$ are the molecular weight and the density of an ith component, the following data were used: (benzene) M = 78.11 g mol^{-1}, d = 0.88 g cm^{-3} (see Ref. 21); (Al_2Br_6) M = 533.39 g mol^{-1}, d = 3.01 g cm^{-3} (see Ref. 22). The use of the additivity rule for determining the molar volume of the complex is quite justified in this case because complexes of this type are weak and, hence, the contraction accompanying their formation should be insignificant. The calculated V_m values for Al_2Br_6 and $C_6H_6 \cdot Al_2Br_6$ were 177.20 and 265.96 cm^3 mol^{-1}, respectively; the ratio $V_m(C_6H_6 \cdot Al_2Br_6) : V_m(Al_2Br_6) = 1.50$. Thus, s_c should exceed s_{Al} by a factor of at least 1.5. With allowance made for the complex asymmetry and the change in the quadrupole coupling constant upon the complex formation, the real broadening factor should be even greater.[20] This can be confirmed by the data obtained at −20 °C for a benzene concentration of 1.44 mol L^{-1} (see Table 1); in this case, s_{obs} is 1.74 times greater than s_{Al}. In view of these facts, we took 1.9 as the minimum value for the broadening coefficient s_c/s_{Al} used to calculate the ratio of the second and first terms in the right-hand part of Eq. (3). For experiments performed at temperatures from −20 to +20 °C, the following ranges for the ratios $[Al_2Br_6] \cdot [(s_c - s_{obs})/(s_c - s_{Al})]/\{[C_6H_6]_0 \cdot [(s_c - s_{obs})/(s_{obs} - s_{Al})]\}$ were found: 0.047—0.071 at 20 °C, 0.043—0.096 at 0 °C, and 0.031—0.139 at −20 °C.

Thus, under conditions of our expreriments, the magnitude of the second term is not more than 14% of the first term. At higher s_c values, the relative magnitude of the second term should be even smaller. Thus, to simplify the subsequent calculations, the second term can be neglected and Eq. (3) can be written in the approximate form

$$1/K \approx [(s_c - s_{obs})/(s_{obs} - s_{Al})] \cdot [C_6H_6]_0. \tag{5}$$

For subsequent operations, Eq. (5) was converted into an equation describing a straight line

$$\frac{1}{s_{obs} - s_{Al}} \approx \frac{1}{s_c - s_{Al}} + \frac{1}{K(s_c - s_{Al})} \cdot \frac{1}{[C_6H_6]_0}. \tag{6}$$

Now the values under interest can be found from the plot constructed in the $1/(s_{obs} - s_{Al})$—$1/[C_6H_6]_0$ coordinates. The intercept is equal to $1/(s_c - s_{Al})$, while the slope corresponds to $1/K(s_c - s_{Al})$. Calculation by the least-squares method is also applicable. We chose the second variant; the s_c and K values found for the three temperatures are listed in Table 2.

Equation (6) is similar in form to the Ketelaar and Beneshi—Hildebrand equations and to other equations,[1,23,24] which are often used in spectrophotometry

Table 2. Line widths for the $C_6H_6 \cdot Al_2Br_6$ complexes (s_c), equilibrium constants (K), and thermodynamic parameters of complex formation calculated using the least-squares method

T/K	s_c/Hz	K /L mol^{-1}	ln$K$	ΔG /kJ mol^{-1}
193	—	8.55±0.64[a]	2.146	−3.45
213	—	4.38±0.33[a]	1.478	−2.63
233	—	2.54±0.19[a]	0.932	−1.81
253	1970	1.520±0.11	0.418	−0.99
273	1085 (1104)[b]	1.200±0.09 (1.210)[c]	0.182	−0.17
293	860	0.721±0.055	−0.327	0.65

[a] Calculated from the equation $\ln K = \Delta S/R - \Delta H/(RT)$

[b] The mean value of the three s_c values (1220, 1057, and 1036 Hz) calculated by the method of elimination of one unknown (see the text).

[c] The mean value of the three K values (1.244, 1.290, and 1.095 L mol^{-1}) calculated from Eq. (3) using the mean s_c value (1104 Hz).

of molecular complexes; hence, it possesses both the merits and the drawbacks peculiar to these equations. In accordance with the results of determination of the error for the minimum broadening factor, the relative error increases with a decrease in the benzene concentration and with a decrease in temperature. This should be taken into account when using this equation for other conditions of measurements.

The fact that, under these particular conditions, the simplified calculation procedure we used provides quite a satisfactory accuracy was confirmed by comparing the s_c and K values calculated in this way for 0 °C with the corresponding values determined using the procedure of elimination of one unknown described above (see Table 2, in which these values are given in parentheses). One can easily make sure that the values calculated using the two procedures are virtually equal.

Then the equations

$$\Delta G = \Delta H - T\Delta S$$

and

$$\Delta G = -RT\ln K,$$

where R is the gas constant and T is the absolute temperature, were used to calculate the change in the thermodynamic characteristics upon complexation, namely, free energy ΔG, enthalpy ΔH, and entropy ΔS. These parameters were also calculated by the least-squares method. This gave the following values: $\Delta H = -11.4$ kJ mol^{-1}; $\Delta S = -40.9$ J K^{-1} mol^{-1}. The equation

$$\ln K = \Delta S/R - \Delta H/(RT)$$

was employed to calculate the equilibrium constants for lower temperatures. The spectral data that we obtained in the temperature range below −20 °C cannot be used directly to calculate thermodynamic or kinetic characteristics of the complexes. This is due to the fact that methods[12] proposed for these calculations in the regions of slow or medium exchange require that the differences between the chemical shifts of free and complexed compounds be known. As noted above, these differences cannot be detected for weak complexes such as $C_6H_6 \cdot Al_2Br_6$. However, since no evidence for changes in the composition or structure of these complexes following a decrease in the temperature are available from the literature, extrapolation of the K values to lower temperatures appears quite justified provided that the system remains homogeneous.

It was of interest to compare the thermodynamic parameters obtained with the published data for systems of this type and for other complexes formed by Lewis acids with aromatic hydrocarbons or alkenes. Thus it has been found[25] that the heat of dissolution of aluminum bromide in benzene (ΔH) is 18.4 kJ mol^{-1} (according to another publication,[26] 19.2±0.4 kJ mol^{-1}; the calculation was carried out for 1 mole of Al_2Br_6). This result was obtained for relatively high bromide concentrations; dissolution of the first portions of the bromide was accompanied by substantial evolution of heat, apparently, due to the interaction with the residual moisture. The heat of dissolution in cyclohexane was found to be 24.3 kJ mol^{-1}. The lower endothermicity of dissolution in benzene must be largely due to complex formation.

In a study of the dependence of the vapor pressure above aluminum bromide—aromatic hydrocarbon systems on the composition,[15] the heat of dissociation of the solid 1 : 2 benzene—aluminum bromide complex at 0 °C was found to be 44.4 kJ mol^{-1}, while the change in the entropy term upon dissociation was determined to be 125 J K^{-1} mol^{-1}. However, in this case, the additional stability of the complex and a higher entropy effect of dissociation are, apparently, due to the crystal structure of the complex. For benzene complexes with titanium and carbon halides, the K values are normally close to unity or somewhat lower. However, in this case, an additional factor related to the tendency of these halides to form associates should also be taken into account.[1] The constants of association found by spectrophotometry at 193 K for complexes of relatively weak Lewis acids such as $TiCl_4$, VCl_4, and $SnCl_4$ with several olefins, cycloolefins, and dienes were in the range from 0.06 to 0.40 L mol^{-1}; $-\Delta H$ were from 1.87 to 3.93 kJ mol^{-1}; and $-\Delta S$ were from 16.5 to 38.2 cal K^{-1} mol^{-1} (see Ref. 27). In general, the thermodynamic characteristics of $C_6H_6 \cdot Al_2Br_6$ found here are in satisfactory agreement with the data of other researchers who studied πv-type complexes.

The legitimacy of the results could be additionally confirmed by agreement with the Debye equation (4)[17]: as the temperature changes, the $s_c \cdot T/\eta$ and $s_{Al} \cdot T/\eta$ ratios should remain approximately constant. It should be borne in mind that τ is a rough characteristics for the velocity of molecular re-orientations; in reality, a more complex correlation function $\varphi_z(\tau)$ should have been used.[20,28] However, the concept of the correlation time τ and the Debye equation are employed quite often and successfully to estimate the rate of molecular re-orientations.

Table 3. Ratios $s_{Al} \cdot T/\eta$ and $s_c \cdot T/\eta$ in the temperature range from +20 to −20 °C

T/K	η_{hexane}[29]	s_{Al}	s_c	$s_{Al} \cdot T/\eta$*	$s_c \cdot T/\eta$*	s_c/s_{Al}
	/cP	kHz				
253	0.479	0.895	1.970	1.19	2.62	2.20
273	0.381	0.545	1.085	0.99	1.96	1.99
293	0.307	0.415	0.860	1.00	2.07	2.07

* Normalized value.

The results of our calculations are shown in Table 3. It was assumed that at the low concentrations employed in this work, the difference between the viscosities of the solvent and solutions can be neglected. For clearness, the obtained ratios were normalized to the $s_{Al} \cdot T/\eta$ value at +20 °C, which was taken to be unity.[29] The data reported here, with allowance for the above remarks concerning the applicability of the Debye equation, can be regarded as attesting to a regular pattern of variation of the spectral characteristics and to satisfactory correctness of the calculations. Although the $s_c \cdot T/\eta$ value at −20 °C seems somewhat overestimated, it should be taken into account that the $s_{Al} \cdot T/\eta$ value increases to some extent at this temperature, and, as a consequence, the s_c/s_{Al} ratio remains approximately constant over the whole temperature range in question. (However, some influence of the equilibrium between the dimeric and monomeric forms of aluminum bromide, which is also temperature-dependent, also cannot be ruled out.) The average value of the s_c/s_{Al} ratio is equal to 2.1±0.1 (recall that it should amount to 1.5 due to an increase in the molar volume). The observed difference between these two parameters is apparently caused by the additional contributions of the complex asymmetry and the change in the quadrupole interaction constant[20] to the line width.

Thus, the data reported here demonstrate that the method based on the measurement of the line width in the ^{27}Al NMR spectrum makes it possible to gain quite reliable information on weak complexes of the πv-type involving aluminum compounds. This fact is of special interest because most of other spectral methods are hardly applicable to the investigaton of these complexes[5,6,30] and the information content of some other methods (for example, NQR[31]) is limited due to the specific aggregation state of the samples.

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