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Abstract

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N. Ya. Turova, A. I. Grigor' ev, Corresponding Member of the Academy of Sciences of the USSR A. V. Novoselova, I. G. Arzamanova, E. N. Gur' yanova

On the Structure and Properties of the Complex Compound

$BeCl_2 \cdot AlCl_3 \cdot 3(C_2H_5)_2O$

In studying the interaction in a system consisting of etherates of beryllium and aluminum chlorides, the coexistence was discovered of a congruently melting compound of composition $BeCl_2 \cdot AlCl_3 \cdot 3(C_2H_5)_2O$, to which a sharp maximum corresponds on the phase diagram. In organic solvents this complex shows no signs of dissociation into components: even at the greatest dilution $BeCl_2 \cdot AlCl_3 \cdot 3(C_2H_5)_2O$ forms, with ether or benzene, separating two-phase systems, the complex itself being practically completely concentrated in the lower layer. Thus, in contrast to the etherates that form it, $BeCl_2 \cdot AlCl_3 \cdot 3(C_2H_5)_2O$ is almost insoluble in nonpolar organic solvents (only the solubility of benzene and ether in its melts is appreciable). The compound under consideration is a considerably stronger electrolyte than the etherates that form it—its specific electrical conductivity in benzene solution exceeds the corresponding value for $BeCl_2 \cdot 2(C_2H_5)_2O$ by 3 orders of magnitude ([1]). All these facts make it possible to assume an ionic structure for the double compound of the etherates of beryllium and aluminum chlorides and to regard it as a salt with a complex cation and anion of the type

$$[BeCl_n(R_2O)_{4-n}]^{+(2-n)}[AlCl_{5-n}(R_2O)_{n-1}]^{-(2-n)},$$

where $1 \leq n \leq 4$. Let us note at once that $n \neq 2$, since this case corresponds to nonionized molecules of simple etherates. Then the following variants are possible:

$$\begin{aligned} &\text{for } n = 1: && [BeCl(R_2O)_3]^+[AlCl_4]^-, && \text{(I)} \\ &\text{for } n = 3: && [BeCl_3(R_2O)]^-[AlCl_2(R_2O)_2]^+, && \text{(II)} \\ &\text{for } n = 4: && [BeCl_4]^{2-}[AlCl(R_2O)_3]^{2+}. && \text{(III)} \end{aligned}$$

In order to choose among the three indicated formulas, we used the method of IR spectroscopy. Measurements were carried out on a two-beam IKS-14 spec-

Fig. 1. IR spectra of etherates of beryllium and aluminum halides, chloroberyllates, and aluminates (in the KBr-prism region)

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trometer in the region 650-400 cm^{-1} (KBr prism), where the absorption bands caused by the stretching vibrations of the Be–O, Al–O, Be–Cl, and Al–Cl bonds are located. For the correct assignment of frequencies in the spectrum of the double etherate, spectra were recorded in the region under consideration for a series of simple etherates of beryllium and aluminum halides, sodium chloroaluminate, and also aluminum acetate (in the form of suspensions in Vaseline oil, melts, or benzene solutions) (Fig. 1, Table 1). The etherates of beryllium and aluminum halides were synthesized by interaction of the anhydrous halides with the corresponding ether. The data of their analyses agreed well with the calculated values, and the constants with literature data ([2,3]).

In view of the complete identity of the IR spectra of $BeCl_2 \cdot 2(C_2H_5)_2O$* and

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* A detailed investigation of compounds of the type $MeCl_n \cdot x(C_2H_5)_2O$ showed that in the region 1000-700 cm^{-1} the IR spectra of the etherates of Be and Al chlorides are identical. Therefore, the previously made ([4]) assignment of the Be–O stretching-vibration frequencies (in the region 860-900 cm^{-1}) should be recognized as erroneous.

$BeBr_2 \cdot 2(C_2H_5)_2O$, a broad intense absorption band in the region 650–550 cm^{-1} (in benzene solution it corresponds to a maximum at $\sim$ 600 cm^{-1}), as well as weaker bands in the region 500–400 cm^{-1} (Fig. 1), may with a high degree of probability be assigned to Be–O vibrations in the group $[BeO_2Cl_2]$. The stretching vibrations of the Be–Cl bonds in this case evidently lie below 400 cm^{-1}.

When comparing the IR spectra of the etherates of aluminum chloride and bromide, attention is drawn to the shift of only one of the three bands present in the spectrum

Fig. 1. IR spectra of etherates of beryllium and aluminum halides, chloroberyllates, and aluminates (in the KBr-prism region)

(492 cm^{-1} for $AlCl_3 \cdot (C_2H_5)_2O$ and 444–435 cm^{-1} for $AlBr_3 \cdot (C_2H_5)_2O$), which should be assigned to the doubly degenerate vibration of the AlF_3 group. The band at $\sim$ 540 cm^{-1} does not change its position on going from the etherate of aluminum chloride to the etherate of aluminum bromide, and is absent from the spectrum of $AlCl_3 \cdot NH_3$ (instead of it a new band appears at 570 cm^{-1}, corresponding to νAl—N). All this makes it possible to assign it to the stretching vibration of the Al–O bond. It should be noted that the pattern observed in the case of $AlCl_3 \cdot 2(CH_3)_2O$ is completely analogous to the complex with diethyl

ether (however, in the spectrum of solid $AlCl_3 \cdot 2(CH_3)_2O$ there is splitting of the 538 maximum into 549 and 531 cm^{-1}, which is apparently connected with the addition of two ether molecules*). According to Cook' s data ([6]), in the IR spectra of solid $AlCl_3 \cdot CH_3COCl$ and of a solution of $AlCl_3$ in acetone there are also intense bands at 540 and 485 cm^{-1}, which, on the basis of the foregoing, should be assigned respectively to the stretching vibrations of the Al—O and Al —Cl bonds in the tetrahedron $[AlCl_3O]$. In the indicated interval, absorption bands of Al—O stretching vibrations are observed also when only oxygen atoms are present in the coordination sphere of aluminum. Thus, according to our measurements, in the spectrum of aluminum acetate $Al(OCOCH)_3$ in the KBr region there is only one band at 555 cm^{-1}, assigned to triply degenerate Al—O stretching vibrations.

When considering the IR spectrum of $BeCl_2 \cdot AlCl_3 \cdot 3(C_2H_5)_2O$, attention is drawn first of all to the presence of two very intense and broad absorption bands with maxima at $\sim$ 600 and 495 cm^{-1}. The first of these, in its character and position in the spectrum, is close to the corresponding band of the etherate of beryllium chloride. It may therefore be assumed that it is due to stretching vibrations of the Be—O bond and indicates the presence of such a bond in the molecule of the double etherate. Bands also appear

* Earlier, Rossmy and Stamm ([5]) observed the double structure of the band of the symmetric C—O—C stretching vibration in the molecules $ZrCl_4 \cdot 2(CH_3)_2O$ and $AlCl_3 \cdot 2(CH_3)_2O$ and the presence of one maximum on going to the corresponding monoetherates. According to our observations, in the spectrum of $AlCl_3 \cdot 2(CH_3)_2O$ the splitting of the antisymmetric COC stretching vibration band is even more sharply expressed (1024 and 1000 cm^{-1}).

of lower intensity, present in the spectra of etherates of beryllium halides: 435 and 409 cm^{-1}. At the same time, the absence in the spectrum of $BeCl_2 \cdot AlCl_3 \cdot 3(C_2H_5)_2O$ of an intense band of Al—O stretching vibrations in the region of 540 cm^{-1} gives grounds for rejecting formulas (II) and (III). Then only formula (I) remains for consideration, representing the double etherate as a chloroaluminate of the cation $\{BeCl[(C_2H_5)_2O]_3\}^+$.

The correctness of this conclusion is also confirmed by the spectral picture reflecting the structure of the anion. According to data (7), the triply degenerate vibration of the tetrahedron $[BeCl_4]$ corresponds to a frequency of 540 cm^{-1} in K_2BeCl_4

Table 1

IR absorption spectra in the KBr-prism region

Compound	State / medium	Absorption bands and assignments
$BeCl_2 \cdot 2(CH_3)_2O$	solid	625 very strong; 460 weak

Compound	State / medium	Absorption bands and assignments
$BeCl_2 \cdot 2(C_2H_5)_2O$	solid	650–550 very strong; ν(B)Be—O; 479 very strong; 460 broad, 437 medium; 411 weak
$BeCl_2 \cdot 2(C_2H_5)_2O$	benzene solution	602 very strong; ν(B)Be—O; 496 medium; 473, 459, 442; –*
$BeBr_2 \cdot 2(C_2H_5)_2O$	solid	620–560 very strong; ν(B)Be—O; 484 strong; 459 strong, 443 medium; 411 weak
$BeBr_2 \cdot 2(C_2H_5)_2O$	benzene solution	590 very strong; ν(B)Be—O; 488; 460 broad, 437; –
$BeCl_2 \cdot AlCl_3 \cdot 3(C_2H_5)_2O$	solid	649–616 very strong; ν(B)Be—O; 495 very strong, $\nu(F_2)$Al—Cl; 435 broad; 409 weak
$AlCl_3 \cdot 2(CH_3)_2O$	solid	549, 531 very strong; νAl—O; 494 strong; ν(E)Al—Cl; 403 weak
$AlCl_3 \cdot 2(CH_3)_2O$	benzene solution	538 very strong; νAl—O; 494 strong; ν(E)Al—Cl; –
$AlCl_3 \cdot (C_2H_5)_2O$	melt	535 strong; νAl—O; 495 strong; ν(E)Al—Cl; 402 medium
$AlCl_3 \cdot (C_2H_5)_2O$	benzene solution	540 strong; νAl—O; 492 medium; ν(E)Al—Cl; –
crystalline $AlCl_3 \cdot (C_2H_5)_2O$ (11)	solid	536 (0); νAl—O; 409 (10)
$AlBr_3 \cdot (C_2H_5)_2O$	solid	550 very strong, 544 broad; 444–435 very strong, [ν(E)Al—Br]; 403–400 very strong
$Al(OCOCH_3)_3$	solid	555 strong
$NaAlCl_4$	solid	492, 479 very strong, 465 broad; [$\nu(F_2)$Al—Cl]

* Below 430 cm^{-1} lies an intense absorption band of benzene.

(in the case of Na_2BeCl_4 it is split into 565 and 520 cm^{-1}). In the indicated region, $BeCl_2 \cdot AlCl_3 \cdot 3(C_2H_5)_2O$ is completely transparent; therefore one may confidently conclude that the anion $[BeCl_4]^{2-}$ is absent from its structure.

The spectral characteristics of the $[AlCl_4]$ group are at present given quite fully (mainly in the works of Gerding (8) and Miller (9)). The triply degenerate vibration of the tetrahedron $[AlCl_4]$ in the IR spectrum corresponds to a strong broad band with an absorption maximum at about 500 cm^{-1} (9, 10). In the spectrum of $NaAlCl_4$, according to our measurements, weak splitting occurs with the formation of two maxima—492 and 479 cm^{-1}—and a shoulder at 465 cm^{-1}. The presence in the IR spectrum of crystalline $BeCl_2 \cdot AlCl_3 \cdot 3(C_2H_5)_2O$ of a broad absorption band with a maximum at 495 cm^{-1} (in benzene solution, a sharper maximum at 493 cm^{-1}) may be regarded as proof of the existence in the crystal lattice (and also in the melt and in solutions) of the double etherate of $[AlCl_4]$ groups.

Thus, the spectral data presented make it possible to conclude that in the molecule $BeCl_2 \cdot AlCl_3 \cdot 3(C_2H_5)_2O$ there is an anion of aluminum chlorohydric acid and beryllium—oxygen bonds (in the cation). The structure of the compound under consideration may be represented by formula (I): $[BeCl(R_2O)_3]^+[AlCl_4]^-$.

In order to study in more detail the behavior of the double etherate of Be and Al in solution, we undertook measurements of electrical conductivity in the system $[BeCl(R_2O)_3][AlCl_4]$—benzene at 20°. The concentration interval investigated extended from the composition of the complex (supercooled melt) to the beginning of the heterogeneous region ("lower layer").

As is seen from the data of Table 2, the specific and molar electrical conductivities of these highly concentrated solutions increase upon dilution, with μ rising practically rectilinearly up to values of $v \sim 750$ ml. At this concentration there is a sharp rise in viscosity; as a result, the corrected molar electrical conductivity already exhibits anomalous behavior. The phenomenon described is quite analogous to the behavior

···the behavior of etherates of beryllium halides [12] and aluminum [13], as well as complex haloaluminates (for example, $CuBr \cdot 2AlBr_3$ [14]) in solutions of diethyl ether or aromatic hydrocarbons. Thus, the observed pattern of change in electrical conductivity is characteristic of systems formed by a complex compound possessing a considerable dipole moment (of the order of 5—7 D) and by a nonpolar or weakly polar solvent.

The dipole moment of $[BeCl(R_2O)_3][AlCl_4]$, found by the method of dielectrometric titration in benzene solution [15], proved to be equal to

Table 2

Electrical conductivity in the system $BeCl_2 \cdot AlCl_3 \cdot 3(C_2H_5)_2O$—benzene at 20°

Complex concentration, wt. %	d, g/ml	v, ml	$\chi \cdot 10^3$, $\text{ohm}^{-1} \cdot \text{cm}^{-1}$	μ, $\text{ohm}^{-1} \cdot \text{cm}^2$	η/η_0	μ_{corr}, $\text{ohm}^{-1} \cdot \text{cm}^2$
100.0	1.26	346	0.42	0.145	–	–
85.2	1.21	421	2.28	0.958	44	42.4
76.6	1.17	486	3.92	1.905	20	38.5
74.5	1.16	504	3.86	1.945	19	36.9
70.7	1.15	536	4.63	2.481	14	34.7
66.2	1.13	582	4.74	2.760	11	30.3
64.0	1.12	608	5.03	3.060	9.5	29.1
58.3	1.10	680	5.79	3.935	6.8	26.7
55.9	1.09	715	5.95	4.255	6.1	25.9
54.7	1.09	730	5.95	4.340	6.0	26.0
53.7	1.08	752	5.86	4.420	5.9	26.2
52.9	1.08	762	5.79	4.411	5.7	25.2
50.6	1.07	804	5.63	4.550	5.6	25.5

6.29 D. It is highly interesting that formation of an ionic complex in the system $BeCl_2 \cdot 2(C_2H_5)_2O$–$AlCl_3 \cdot (C_2H_5)_2O$ does not lead to any appreciable increase in the dipole moment. According to our measurements,

$$\mu AlCl_3 \cdot (C_2H_5)_2O = 6.51\,D, \qquad \mu BeCl_2 \cdot 2(C_2H_5)_2O = 6.23\,D,$$

i.e., somewhat lower than the values previously found by Nespital [16]. Without dwelling here on the presumed mechanism of this phenomenon, we shall merely point out that it apparently is generally characteristic of complex aluminum halides: according to data [17], the dipole moments of numerous salts of the type $Me^I Al_2Br_7$ (measured in benzene solution) practically do not differ from the moments of the alkali halides included in their composition.

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Moscow State University
named after M. V. Lomonosov

Scientific-Research Physicochemical
Institute named after L. Ya. Karpov

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Note: Figure translations are in progress. See original paper for figures.