DISSOCIATION OF ALUMINIUM BROMIDE IN NONPOLAR MEDIA

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Dissociation constants of aluminium bromide in n-heptane and benzene ($7{\cdot}24 \cdot 10^{-23}$; $7{\cdot}53 \cdot 10^{-17}$) have been calculated from the measurements of the dependence of electric conductivities of aluminium bromide solutions upon concentration. It follows from the measurements that in the given media, aluminium bromide is dissociated to dibromo-aluminium cation and tetrabromo-aluminium anion. Addition of a third component-isoprene-to the given systems shifts the dissociation equilibrium towards free cations. The dissociation constants could not be measured, for these systems are in a non-steady state when cationic polymerization takes place.

Aluminium bromide is a common catalyst for cationic polymerizations[1]. Its catalytic activity is extraordinarily sensitive to experimental conditions as, for example, presence of trace amounts of certain substances, primarily water, kind of solvent, *etc.* For that reason, character of elementary processes of polymerization with this catalyst is unknown in most cases. An open problem remains initiation, when the role of free ions and ionic pairs or higher aggregates in terms of active particles, their solvatation, and formation of complexes with monomers has not been elucidated hitherto. The present paper aims at obtaining more detailed data on the concentration of ions and dissociation relations in aluminium bromide solutions of very low relative permittivity, such as n-heptane and benzene have. Particular attention has been paid to thorough purification and drying of all the reagents used, since aluminium bromide forms with protogenic substances complex acids whose presence considerably distorts the conductivity values.

Longworth and Plesch[2] estimated value of the dissociation constant in the alkyl bromide medium on the basis of results of other authors, and Wendt[3] measured the dissociation constants in nitrobenzene. A number of papers presents measurements of electric conductivities of aluminium bromide solutions in solvents having relative permittivity 5 and higher[4,5] (chlorinated hydrocarbons, pyridine, nitrobenzene, acetonitrile, *etc.*) predominantly to study formation of aluminium bromide complexes; however, electric conductivities in solvents having very low value of relative permittivity have not been up to now systematically measured, except for some informative data[4,6].

EXPERIMENTAL

Reagents. Isoprene, n-heptane, benzene, and aluminium bromide were purified as described previously[7]. In addition, benzene and n-heptane were for experiments in a circulating apparatus finally purified in a vacuum apparatus with crystalline aluminium bromide by gradual triple condensation of the solvent from an ampule containing aluminium bromide into another one. The solvent distilled away from the third ampule with bromide into the storage ampule was then used for the experiments.

Apparatus with glass-ground joints. Electric measurements and polymerization were mostly studied in an all-glass apparatus described previously[7]. All manipulations with the solvents and monomer were carried out in vacuum. For dosing the solvent as well as aluminium bromide, ampules with a tip were used which was broken by means of a magnet on inserting the ampule into the apparatus. As reactor, a vessel was employed, into which demountable conductivity cell[8] had been inserted.

Circulating apparatus. In order to study electric conductivities of aluminium bromide solutions and isoprene polymerization under strictly waterless conditions, an all-glass vacuum apparatus without ground joints was employed. Residual humidity and impurities on the walls were removed by washing with a pure, continually dried solvent. Fig. 1 presents diagram of the apparatus in question. The solvent (n-heptane, benzene) with sodium hydride was heated in flask B by heating tape T. The vapours passed through part N filled with glass-wool or porcelain bodies to retain sodium hydride, and condensed in condenser C. From here, the solvent refluxed into flask B through electromagnetic valves E_1 and E_2 and trap S. Glass valve V prevented penetrating of the solvent and its vapours from flask B into trap S. On pouring into sodium hydride, the feeding tube P was sealed. Through the side tube furnished with metallic vacuum stopcock K_1 the solvent was distilled into flask B and the apparatus was evacuated. Flask Z with metallic vacuum stopcock K_2 served to keep the stock solvent. To this drying part of the apparatus, reaction vessel A was connected at places D and D′ over and under valve E_2. A calibrated vessel (burette) or, as graphically presented in Fig. 1, tube of a glass spiral pressure gauge M was sealed to vessel A. The pressure gauge glass spiral was placed in a flask, where a compensating pressure (measured by mercury pressure gauge R) was set by evacuating or admitting air with use

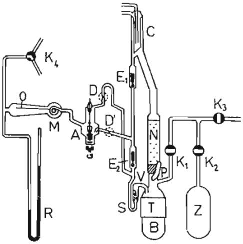


FIG. 1

Vacuum Circulating Apparatus
For specification see the text.

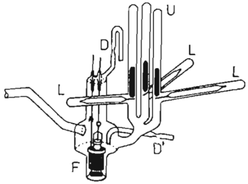


FIG. 2

Reaction Vessel with Conductivity Cell
For specification see the text.

of stopcock K_4. Deflections of the indicator end O, measured by a cathetometer, were then proportional to the difference between the compensating pressure and that present in vessel A (deflection of 0·0474 mm/Torr). In the reaction vessel A, a demountable conductivity cell[8,9] (resistivity constant $C = 6{\cdot}752 . 10^{-3}\,\mathrm{cm}^{-1}$) made of teflon and platinum–iridium alloy was suspended. A detailed view of vessel A is given in Fig. 2. To the vessel itself, containing conductivity cell F, a dosing systems was sealed consisting of 3 perpendicular tubes U with magnetic bodies, and of three oblique tubes L with aluminium bromide ampules *etc.* The magnetic bodies served then for breaking tips of the ampules. The vessel content was agitated by magnetic stirrer.

Procedure. After the circulating apparatus having been assembled, the solvent was degased by repeated cooling with liquid nitrogen, evacuating and defrosting, and afterwards, the apparatus was evacuated definitively. Finally, the whole apparatus was continuously washed with pure solvent dried in flask B. Electromagnetic valves E_1 and E_2 served to control flow rate of the circulating solvent. After several days of circulation, the apparatus was again evacuated, thereby small amount of hydrogen, produced from sodium hydride by water traces, being removed. The specific conductivity measurement of the solvent served as rough indicator of purity during the circulation. Prior to the measurement itself, the solvent was let to circulate more than 30 hours. Valve E_2 was then opened and excess of the solvent flew out from vessel A down to a volume given by the level of the side outlet tube (approx. 30 ml). The solvent in vessel A as well as in flask B was cooled down with liquid nitrogen and vessel A was sealed off from the apparatus at narrow places of inlet tubes D and D′. After tempering the content of vessel A in the bath, specific conductivity of pure solvent was first measured. The measurement itself was started after breaking the ampules and dissolving their content. The aluminium bromide concentration was additionally determined by gravimetric analysis. When measuring the concentration dependence of specific conductivity of the solutions in the circulating apparatus, the technique of gradual diluting a fraction of the basic solution by the solvent distilled off from the residue of the solution poured off[10] was employed. From vessel A (Fig. 1) always an exact amount (approx. 1/2 of the solution volume) was poured off into the burette sealed to vessel A instead of the spiral pressure gauge M. Then, a certain amount of the solvent was distilled from the burette back to vessel A, thus a solution of lower concentration being prepared. Individual concentrations were calculated from dilution ratios and initial concentration. During the polymerization of isoprene in the circulating apparatus, also the ampule with isoprene together with the ampule containing aluminium bromide were present in the dosing system. The time dependence of the conversion degree was followed

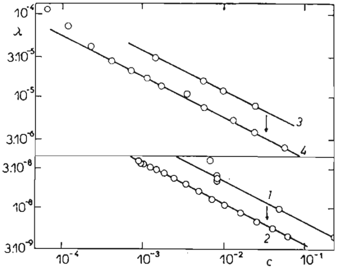


FIG. 3

Plot of Equivalent Conductivity λ [$\Omega^{-1}\,\mathrm{cm}^2 . \mathrm{mol}^{-1}$] of Al_2Br_6 Solutions against Molar Concentration *c* in n-Heptane and Benzene Media at 21°C

1, *2* n-Heptane, *3*, *4* benzene. *1*, *3* measurements in the glass-ground apparatus, *2*, *4* measurements in the circulating apparatus.

by measuring decrease of the partial pressure of isoprene in the system. The spiral pressure gauge was employed for the pressure measurements.

The electric conductivity measurement was carried out in an apparatus the parts of which, the demountable conductivity cell including, were described earlier[8]. The reactor with the conductivity cell was placed in a bath whose temperature amounted to 21 ± 0·05°C. The specific conductivity ($\varkappa$) of pure solvent (it was lower than $10^{-16}\,\Omega^{-1}\,\text{cm}^{-1}$ for n-heptane, for benzene about $10^{-14}\,\Omega^{-1}\,\text{cm}^{-1}$) was always negligible when compared with conductivities of individual solutions.

RESULTS AND DISCUSSION

The electric conductivities were studied in the glass-ground apparatus as well as in the circulating one, both as dependent on the dilution of the aluminium bromide solution and also during cationic isoprene polymerization initiated with Al_2Br_6. The dependence of equivalent conductivity λ on aluminium bromide concentration c is graphically presented in Fig. 3. When leading curve *1* through the points plotted, the point corresponding to the concentration of $6{\cdot}85 \,.\, 10^{-3}$ mol/l was omitted, because the error due to impurities in the solution (mainly water) increases with the decreasing concentration. Contrary to this, the point corresponding to the concentration of $8{\cdot}25 \,.\, 10^{-3}$ mol/l was obtained from three experiments in the circulating apparatus with a nearly consistent result. In these three experiments, however, the ampule with concentrated Al_2Br_6 solution prepared in the same way as for the experiments in the glass-ground apparatus, was employed. In order to remove also impurities introduced into the basic aluminium bromide solution in the ampules, likewise the measurements of the concentration dependence of electric conductivity were made in the circulating vacuum apparatus by preparing the basic solution directly in the reactor made of crystalline aluminium bromide. The data in Fig. 3, curve *2*, correspond to this experiment. It can be seen that the equivalent conductivities obtained in the circulating apparatus are by approx. 50% lower. Both curves have tangent $-1/2$ in logarithmic coordinates. For further calculations, the results were taken from the circulating apparatus (curve *2*), where higher purity was achieved.

Experimental results in benzene are presented also in Fig. 3 (curves *3* and *4*). It is obvious that also tangents of curves *3* and *4* are equal $(-1/2)$ and the equivalent conductivity is in the circulating apparatus again by approx. 50% lower. Value $(-1/2)$ of the tangent of the plot of $\log \lambda$ against $\log c$ shows that even at high concentrations the equivalent conductivity obeys the Onsager equation and beside molecules and free ions, ionic pairs[11] only are present in the solution (*e.g.* in benzene, the ionic pair is formed by a pair of opposite ions distant up to about 120 Å from each other), but not higher ionic aggregates, as for example, triple ions, quadrupols, *etc.* In the solvents having low permittivity, the curves of $\log \lambda$ against $\log c$ shall pass the minimum[12] at which concentration $c_{\min}$ of the solute is usually between 10^{-3} to 10^{-5} mol/l. Relation used in the literature[13] approximately indicates the position of minimum $c_{\text{min}} \approx 3 \cdot 10^{-7}\varepsilon^3$. For benzene solutions, c_{min} should be about $4 \cdot 10^{-6}$ mol/l, but for very low relative permittivity values ε, (as in our case) this relation no longer satisfies for the most part. For example, minimum of the equivalent conductivity is with the benzene solution of tetra-n-butylammonium salts[12] achieved for the concentrations of 10^{-4} to 10^{-5} mol/l. As the conductivity minima did not appear in our case either at concentrations of the order of magnitude 0·1 mol/l, it is evident that aluminium bromide is very slightly dissociated so that even at higher concentrations, the concentration of its ionized form is lower than c_{min}. In order to calculate dissociation constant K corresponding to the assumed dissociation $Al_2Br_6 \rightleftarrows AlBr_2^+ + AlBr_4^-$, equation

$$1/\lambda = 1/\lambda_0 + c\lambda/K\lambda_0^2 \tag{1}$$

can be applied. Here, λ_0 is the limiting equivalent conductivity and c is the Al_2Br_6 concentration [mol/l]. In this equation, $10^3\varkappa$ may be introduced instead of $c\lambda$ using relation $c\lambda = 10^3\varkappa$.

In Fig. 4, results of the electric conductivity measurements in the circulating apparatus in n-heptane and benzene are plotted. It can be seen that section on axis $1/\lambda$, which shall be equal to $1/\lambda_0$, cannot be read out and the straight lines point towards origin. In Table I, $K\lambda_0^2$ are then reciprocal values of the tangent of the curves presented in Fig. 4. To determine values $K\lambda_0^2$ the Fuoss method was not employed, since the Fuoss function F(z) attained values of 0·9995 to 1·0 and activity coefficients of 0·95 to 1·0, respectively, whereas relative error of individual measurements was as much as ±10%.

The value of the limiting equivalent conductivity λ_0 cannot be then determined experimentally and their approximate values were therefore calculated with use of the Stokes law (Table I) under the following assumptions[14]: *1)* Dissociation of aluminium bromide produces $AlBr_2^+$ and $AlBr_4^-$ ions in n-heptane, and $[AlBr_2(C_6H_6)_2]^+$ and $AlBr_4^-$ ions in benzene[4,7] media. *2)* In order to calculate the equivalent Stokes

TABLE I

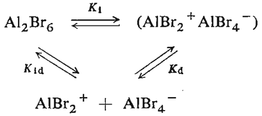
Value of Dissociation Constant K of Aluminium Bromide Dissociated to $AlBr_2^+$ and $AlBr_4^-$ Ions

Medium	η cP	a^a Å	λ_0 Ω^{-1} cm^2 mol^{-1}	$K\lambda_0^2$	K
n-Heptane	0·410	6·3	129	$1{\cdot}21 \cdot 10^{-18}$	$7{\cdot}24 \cdot 10^{-23}$
Benzene	0·649	7·8^b	66	$3{\cdot}28 \cdot 10^{-13}$	$7{\cdot}53 \cdot 10^{-17}$

[a] Distance of the minimum approach; [b] Ion $[AlBr_2(C_6H_6)_2]^+$ is assumed as cation.

radii of the ions, the volumes of molecules[15] of 269 Å^3 and 127 Å^3 for Al_2Br_6 and C_6H_6, respectively, were taken into account. The ratio of volumes of the $AlBr_2^+$ and $AlBr_4^-$ ions was equal to the ratio of sums of their atomic weights. *3)* The influence of the formation of solvated complexes upon the value of the equivalent Stokes radius was neglected. *4)* For the calculation, values of macroscopic viscosity η of the medium were used. The sum of the Stokes radii of appropriate cations and anions a is likewise summarized in Table I. The value a represents distance of a minimum approach of opposite-charged ions without the solvate envelope. From the λ_0 values calculated and $K\lambda_0^2$ values measured, dissociation constants K were established. These constants are therefore subject to an error which results not only from the measurements themselves, but also from the calculation of ionic radii a, and hence also from λ_0.

The dissociation of aluminium bromide can be expressed by



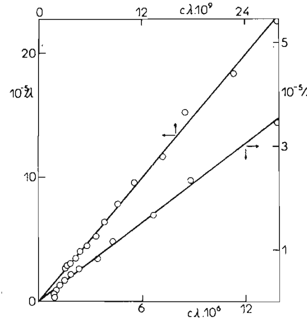


FIG. 4

Plot of Equivalent Conductivity λ [Ω^{-1} cm^2 . . mol^{-1}] of Al_2Br_6 Solutions of Molar Concentrations c against Product $c\lambda$ at 21°C

Upper line n-Heptane, lower line benzene.

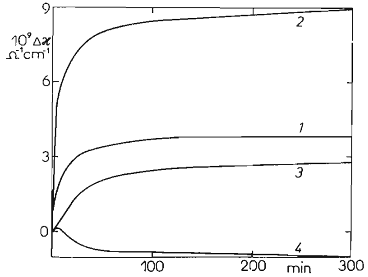


FIG. 5

Changes in Specific Conductivity ($\Delta\varkappa$) due to Isoprene Additions in the Polymerization under Constant Volume

50 ml Benzene, $[Al_2Br_6] = 1{\cdot}0 \cdot 10^{-2}$ mol/l, 21°C. Addition of: *1* 3·8 mmol of isoprene; 2—4 10 mmol of isoprene.

Constant K_i denotes the ionization (self-ionization, autodissociation) of aluminium bromide to the ionized form, *i.e.* ionic pair with a minimum distance between the ions. K_d is the constant of the dissociation of ionic pairs to free ions and K_{id} is constant of direct dissociation of the molecules to free ions. The measured values of the dissociation constants K represent then effective constants which are associated with the constants of single processes, given in the diagram, by relationship

$$K = \frac{[\mathrm{AlBr}_2^+]\,[\mathrm{AlBr}_4^-]}{[\mathrm{Al}_2\mathrm{Br}_6] + [\mathrm{AlBr}_2^+ + \mathrm{AlBr}_4^-]} = \frac{K_i K_d}{1 + K_i} \approx K_i K_d\,, \tag{2}$$

while from the dependence of the equivalent conductivity upon the concentration, discussed above, follows that $K_i \ll 1$.

In all the electric conductivity measurements in question, content of water in the system plays a great role. Whereas the π-complex of aluminium bromide with benzene is little dissociated and hence little electrically conductive, in presence of water the opposite takes place.

The σ-complexes[16] produced are strongly conductive and moreover, they are responsible for a series of isomerization, alkylation, and polymerization reactions, which produce from the original inert solvent a great number of various compounds[17,18] which form electrically very conductive "red oil" on the bottom and walls of the vessels, even in n-heptane. For that reason, absolute conductivity values as well as those of the dissociation constants calculated can be changed by no more measurable traces of impurities, mainly water. This is demonstrated also by differences in the conductivities, obtained in experiments with use of the glass-ground as well as circulating apparatus. Many papers concerned with the measurements of the aluminium bromide dipole moment in benzene similarly show that instead of the original values of the dipole moments measured (3·3 to 6·3 D (ref.[19])), lower values (2·6 D (ref.[20]) and 1 D (ref.[21])) of the dipole moments were later measured under very pure conditions.

For the quantitative determination of the concentration of active centres during the polymerization it would be necessary to know the dissociation constants in the three-component system $\mathrm{Al_2Br_6}$–solvent–monomer. The monomer (*e.g.* isoprene), namely, considerably rises degree of the aluminium bromide dissociation, due to the formation of complexes, the monomer or even solvent[7] being involved. On adding isoprene to the bromide solution, however, simultaneously at once the polymerization begins which is not stable and during which electric conductivity of the system considerably changes with time. The course of conductivity is under certain concentration conditions not even monotonic. Fig. 5 shows the course of electric conductivities during polymerization under constant volume in benzene. Individual additions of isoprene are 3·8 and four times 10 mmol always after 300 min of the polymerization. Prior to the isoprene addition, the specific conductivity was $1{\cdot}16 \,.\, 10^{-12}\,\Omega^{-1}\,\mathrm{cm}^{-1}$.

In the graph, differences ($\Delta\varkappa$) between specific conductivity and the conductivity before the addition of isoprene are plotted. Total course of the specified conductivity is formed by a stepwise curve on which origin of the course after further addition of isoprene lies in the point of the preceding curve after 300 min of the polymerization. Owing to the time changes in the conductivity during the polymerization, dependence of the electric conductivities on stoichiometric composition of the reaction mixture and hence either the dissociation constants of aluminium bromide in this system cannot be therefore determined. The higher activity of bromide in benzene than in n-heptane[22] is in agreement with the dissociation degree measured; this agreement, however, is qualitative only. The comparison of the polymerization activities, mutual roles of the solvent and isoprene in the formation of complexes, and effect of impurities (water) are demonstrated in Table II. The polymerization of isoprene (30 ml of the solvent; $[Al_2Br_6] = 8{\cdot}25 \,.\, 10^{-3}$ mol/l; initial concentration of monomer 0·33 mol/l; 21°C) in small conversions satisfies the second-order reaction $-\mathrm{d}p_i/\mathrm{d}t = kp_i^2$, where t is time, p_i the partial pressure of isoprene, and k the rate factor. Values of the rate factors in Table II then indicate the polymerization activity. In the same way in which the ability of the solvent to produce complexes with aluminium bromide and its ionic products as well as its solvation ability increases, the competitive effect of isoprene in terms of a solvatation and complex-forming partner decreases. This is illustrated in Table II by the ratio of the specific conductivity $\varkappa$ of the polymerization mixture after 50 min of the polymerization to the initial specific conductivity $\varkappa_0$ (system in time $t = 0$, without isoprene). The $\varkappa/\varkappa_0$ ratio is lower in benzene, while the polymerization activity is, in contrast, higher.

The effect of impurities is demonstrated by a small addition of water to the polymerization system in n-heptane. A more dissociated Brönsted acid is produced in the system so that both the polymerization activity and initial specific conductivity

TABLE II

Changes in Specific Conductivities and Rate Factors k in the Polymerization of Isoprene under Constant Volume

$\varkappa_0$ Initial specific conductivity (system without isoprene), $\varkappa$ specific conductivity after 50 min of polymerization. 30 ml of the solvent, $[Al_2Br_6] = 8{\cdot}25 \,.\, 10^{-3}$ mol/l, initial concentration of isoprene 0·33 mol/l, 21°C.

Medium	n-Heptane	n-Heptane H_2O^a	Benzene
$10^3\,k$, Torr^{-1} min^{-1}	1·2	4·5	17·6
$\varkappa/\varkappa_0$	91·7	13·2	65·6

[a] $[H_2O] : [Al_2Br_6] = 2 \,.\, 10^{-2}$.

are increased in comparison with the anhydrous system, but the value $\varkappa$ obtained after 50 min is with respect to the system without the addition of water lower and the $\varkappa/\varkappa_0$ ratio is then approximately seven times smaller.

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