

## THERMAL EFFECTS OF DISSOLUTION OF ALUMINIUM HALOGENIDES IN ACETONITRILE AND TETRAHYDROFURAN

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Molar enthalpies of dissolution of aluminium chlorides, bromides, and iodides in acetonitrile and tetrahydrofuran at 295K have been determined experimentally. Results of the measurements carried out in presence of air humidity point to the fact that in both solvents preferential solvation of the solute by water molecules takes place. In an inert atmosphere, all the values obtained are negative. Molar heat of dissolution has for  $\text{AlCl}_3$  the lowest negative value:  $-181 \text{ kJ mol}^{-1}$  in acetonitrile and  $-107.8 \text{ kJ mol}^{-1}$  in tetrahydrofuran. For  $\text{AlBr}_3$  and  $\text{AlI}_3$  exothermicity of dissolution is considerably higher:  $-817$  and  $-887 \text{ kJ mol}^{-1}$  for acetonitrile, and  $-489$  and  $-713 \text{ kJ mol}^{-1}$  for tetrahydrofuran. The transfer from water into both organic solvents has an endothermic character for  $\text{AlCl}_3$  only; for  $\text{AlBr}_3$  and  $\text{AlI}_3$ , the character of transfer is unambiguously exothermic. The obtained results are interpreted as effects of interaction between the solute and the solvent.

The solutions of aluminium halogenides in nonaqueous aprotic solvents are employed in many fields. They act as catalysts in organic syntheses, as electrolytes in lithium cells and as media for electrodeposition of aluminium<sup>1-4</sup>. The latter has also been a motif for this paper which aims at investigating effects of processes which proceed during dissolution of aluminium chlorides, bromides, and iodides in acetonitrile and tetrahydrofuran. The paper is a part of a complex study on composition and electrochemical behaviour of these systems<sup>5-8</sup>.

The solvents were chosen according to the following criteria: both solvents differ in value of relative permittivity, donor ability, localisation of the residual charge, and steric properties. Both solvents can be relatively well purified and dehydrated. There are many published data on both solvents, particularly on acetonitrile, to make a comparison possible.

### THEORETICAL

The process of dissolution of a solid may be divided into two main stages comprising destruction of the crystal structure, connected with dissociation of certain bonds, and interaction of the solvent with the particles thus obtained. It follows that

$$\Delta H_{\text{sol}} = \Delta H_{\text{destr}} + \Delta H_{\text{int}}, \quad (1)$$

where  $\Delta H$  are changes in enthalpy assigned to the given process.

$\Delta H_{\text{int}}$  involves not only thermal effect of solvation, but also thermal effect of a chemical reaction between the solute and the solvent.

$$\Delta H_{\text{int}} = \Delta H_{\text{sol}} + \Delta H_{\text{reac}}. \quad (2)$$

Problems and regularities of solvation enthalpies of ions in water and some organic solvents were studied by Friedman and coworkers<sup>9,10</sup>. Factors which affect value of  $\Delta H_{\text{int}}$  may be, according to Parker and coworkers<sup>11-13</sup>, incorporated into three groups:

1) *Interaction between molecules of the solvent (solvent-solvent interaction)*. The bonds between molecules of the solvent and their configuration are destroyed when the solute enters the solvent. A rearrangement and formation of new bonds and configuration take place. A very firm three-dimensional structure based on the hydrogen bond may be seen in water. The latter is not, from this point of view, an ideal solvent since energy is again consumed to destroy the firm structure in question.

If nonaqueous aprotic solvents are involved, with absence of hydrogen bond the effect of intermolecular interaction depends on their polarity. A more polar solvent involves greater arrangement before the substance enters the solvent and this arrangement must be destroyed in the course of dissolution. Hence a paradox conclusion follows that dissolution of a substance will be more difficult if the solvent is more polar. It is true that consumption of energy needed to destroy more arranged polar solvent is higher than for the nonpolar one; on the other hand, however, the consumption is usually abundantly compensated by energy evolved during the formation of a strong solvate with ionic compounds.

2) *Solvent-solute interaction*. This effect is more complicated because it is dependent on the properties of the two corresponding substances. As for the solvent, the effect is influenced, beside polarity expressed by relative permittivity, by basicity of the solvent, that means by the capability to give away electrons, expressed by the donor number<sup>14</sup>, and finally by steric properties. As for the solute, this effect depends on the strength and kind of bonds which dissociate during the dissolution; the effect is further dependent on the electron-acceptor ability of the formed particle and again on its steric properties. Provided that combination of these factors is for both components favourable, the enthalpic effect of solute-solvent interaction is so far negative that it predominates the above mentioned effect of interaction between the solvent molecules.

3) *The third group of effects involves interaction between the solvent and the solvated ion*; owing to this fact orientation of the second and third solvate layer around the solute may take place. This effect increases exothermic character of dissolution in water in spite of the fact that more intramolecular forces must be at the same time destroyed. An analogous mechanism cannot be applied in an aprotic solvent, where sufficiently acidic hydrogens to form hydrogen bonds are absent.

Enthalpy of solvation is a quantity difficult to measure. The enthalpic change of the solute transfer from solvent A into solvent B, denoted as  $\Delta H_{tr}$ , may be obtained in a more simple way; it holds that

$$\Delta H_{trA \rightarrow B} = \Delta H_{so1B} - \Delta H_{so1A} \quad (3)$$

The quantity thus obtained allows on the one hand to ignore effect of  $\Delta H_{destr}$ , for in both cases the dissolution of the same solute is involved, provided that in both cases equal bonds dissociate. On the other hand, magnitude  $\Delta H_{tr}$  can be interpreted with greater difficulty, since both terms  $\Delta H_{so1A}$  and  $\Delta H_{so1B}$ , can comprise all the mentioned interaction effects, including specific interaction.

## EXPERIMENTAL

Values of enthalpy of dissolution were obtained in an adiabatic calorimeter which was adapted for the operation in an inert atmosphere by means of a teflon lid.

Anhydrous aluminium halogenides, except  $AlCl_3$ , were prepared by direct reaction of halogens with aluminium in an inert atmosphere. The obtained halogenide was several times distilled in vacuum. Final product of white colour was distilled directly into an ampoule which was then sealed off. The commercially available aluminium chloride of A.R. grade (Merck) was purified by multiple sublimation and was kept in sealed ampoules.

Purification and dehydration of solvents and inert gas employed has been formerly described in detail<sup>5</sup>.

The water equivalent of the calorimeter was determined using a calorifer. Seventeen measurements were made from which a mean value of  $w = 13.816 \pm 0.45 \text{ JK}^{-1}$  was achieved.

The value of specific heat of tetrahydrofuran (THF), which could not be taken from the literature, was determined by means of a known water equivalent of the calorimeter. Ten measurements were made which led to  $c_{THF} = 1.660 \pm 0.026 \text{ J g}^{-1} \text{ K}^{-1}$ .

The specific heat value for acetonitrile,  $c_{AN} = 2.261 \text{ J g}^{-1} \text{ K}^{-1}$  given in the literature<sup>15</sup>, was likewise checked. The result of  $c_{AN} = 2.274 \pm 0.075 \text{ J g}^{-1} \text{ K}^{-1}$ , obtained from ten measurements, was close to the literature data.

The experiment of measuring heats of dissolution proceeded in the following way: the solvent was distilled directly into a vessel calibrated to 200 g of the solvent; the volume was on cooling again adjusted to the mark. The calorimeter was before filling up flushed with dry nitrogen. The solvent was introduced into the calorimeter by means of a ground closure in the counter flow of inert gas. After 10 minutes bubbling through the solvent, the inlet of the inert gas was closed and the system began to be tempered. A correction for the solvent volume change, due to the gas flow, was established and taken into account in the calibration of the flask. After tempering for 20 minutes, the temperature was recorded. The transport of halogenide into the solvent was realized after a complete settling of the temperature. The weighed ampoule with appropriate

anhydrous halogenide was hung onto the lid before the tempering and by breaking it under the solvent level. The glass rests of the ampoule were dried and weighed after the experiment. The starting temperature of Beckman thermometer was set to 22°C. The temperature was recorded at 15 s intervals till a new settlement.

Relation

$$\Delta H_{\text{sol}} = (m \cdot c + W) \cdot t \cdot n^{-1} \quad (4)$$

was used to calculate molar heat of dissolution;  $n$  is number of mols of the solute,  $W$  is water equivalent of calorimeter, related to 1 K,  $t$  is measured difference in settled temperatures before and after dissolution of the solute,  $m$  and  $c$  is weight and specific heat of the solvent.

## RESULTS

Dependence of molar heats of dissolution of individual aluminium halogenides in acetonitrile, tetrahydrofuran, and for aluminium bromide also in their mixture of 1 : 1 by weight, determined in an inert atmosphere, upon molar concentration of halogenide, are presented in Figs 1 and 2. Values of molar heat of dissolution

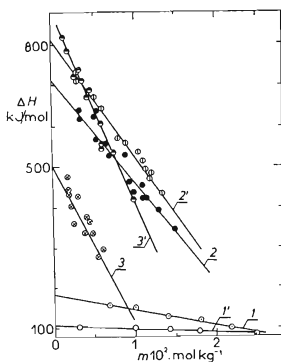


FIG. 1

Plot of Molar Heats of Dissolution of Aluminium Halogenides in Acetonitrile and Tetrahydrofuran at 295 K against Concentration of Halogenides

Curve 1  $\text{AlCl}_3$ , 2  $\text{AlBr}_3$ , 3  $\text{AlI}_3$  in tetrahydrofuran, curve 1'  $\text{AlCl}_3$ , 2'  $\text{AlBr}_3$ , 3'  $\text{AlI}_3$  in acetonitrile.

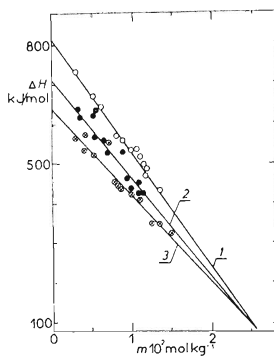


FIG. 2

Plot of Molar Heat of Dissolution of  $\text{AlBr}_3$  in Acetonitrile, Tetrahydrofuran and their Mixture of 1 : 1 at 295 K against Concentration of  $\text{AlBr}_3$

Curve 1 acetonitrile, 2 tetrahydrofuran, 3 mixture of acetonitrile and tetrahydrofuran 1 : 1 by weight.

$\Delta H_{\text{sol}}$ , achieved by extrapolation to infinite dilution, are summarized in Table I, where results of analogous measurements, obtained under air access, are likewise presented. In Table I, also tabulated values<sup>15,16</sup> are for comparison presented for molar heats of dissolution of aluminium halogenides in water. It is worth mentioning that differences in molar heats of dissolution of individual aluminium halogenides in water are by far not so distinct as in both solvents under investigation. A comparison of values of molar heats of dissolution of halogenides obtained in organic solvents in presence of air with those achieved in water show a considerable similarity of both data.

It follows from Fig. 1 that course of the dependence of molar heats of dissolution of aluminium halogenides on solute concentration (the so-called isotherms) is in both solvents very similar, in spite of their different properties. This course is quite different for aluminium chloride on one hand, and aluminium bromide and iodide on the other. Whereas the molar heat of dissolution for  $\text{AlCl}_3$  is in both solvents dependent on the concentration only very little, the molar heat of dissolution for  $\text{AlBr}_3$  and  $\text{AlI}_3$  considerably increase with decreasing concentration of the salt. In a mixed solvent consisting of 50 weight % of acetonitrile and 50 weight% of tetrahydrofuran, the molar heat of dissolution for  $\text{AlBr}_3$  is lower over the whole concentration range than in pure solvents — see Fig. 2.

Molar enthalpies of transfer,  $\Delta H_{\text{tr}}$ , from water into the organic solvent for individual halogenides, calculated according to relationship (3) from data in Table I, are presented in Table II. The latter Table comprises also values of molar enthalpy of transfer of aluminium halogenides from tetrahydrofuran into acetonitrile.

TABLE I

Molar Heat of Dissolution  $\Delta H_{\text{sol}}$  kJ mol<sup>-1</sup> of Aluminium Halogenides in Acetonitrile, Tetrahydrofuran and Water for Infinite Dilution  
Temperature 295 K.

Halogenide	AN		THF		AN + THF	H <sub>2</sub> O (ref. <sup>15</sup> )
	in the inert gas	in the air	in the inert gas	in the air	in the inert gas	
$\text{AlCl}_3$	-181.1	-310	-107.8	-319	—	-326.8
$\text{AlBr}_3$	-817.2	-249	-713.1	-440	-638.1	-357.0
$\text{AlI}_3$	-887.2	-398	-489.8	-380	—	-372.0

The transfer from water into the organic solvent, acetonitrile or tetrahydrofuran is for aluminium chloride endothermic. For  $\text{AlBr}_3$  and  $\text{AlI}_3$ ,  $\Delta H_{\text{trH}_2\text{O} \rightarrow \text{THF,AN}}$  are negative. The exothermic character is more distinct in acetonitrile than in tetrahydrofuran. In the transfer from tetrahydrofuran into acetonitrile, the change in enthalpy is for all three halogenides negative.

## DISCUSSION

The negative values of  $\Delta H_{\text{sol}}$ , obtained for all the studied halogenides in both solvents show that the enthalpy released in the interaction of the solute with solvent exceeds the enthalpy consumed for destruction of the halogenide structure. From relation (1) it must hold that

$$|\Delta H_{\text{int}}| > |\Delta H_{\text{destr}}|.$$

There is, however, a great difference between the  $\Delta H_{\text{sol}}$  values achieved in both solvents for  $\text{AlCl}_3$  and those obtained for  $\text{AlBr}_3$  and  $\text{AlI}_3$  (Table 1). This phenomenon may be due to differences in both terms,  $\Delta H_{\text{destr}}$  and  $\Delta H_{\text{int}}$ , contributing to total  $\Delta H_{\text{sol}}$  values of individual halogenides. It is therefore necessary to investigate each term separately.

Aluminium chloride has in a solid state deformed layered polymer structure of the chromium chloride type<sup>17</sup>, whereas aluminium bromide and iodide have structure of dimer molecules. Two atoms of the metal are there octahedrally coordinated by six halogen atoms. Such dimers contain two kinds of Al—X bonds of various lengths. Hence it follows that there is a qualitative difference between the polymer structure of  $\text{AlCl}_3$ , where individual polymer layers are bound with feeble van der Waals forces, and the dimer structure of the other two halogenides where the van der Waals forces act between dimers. A quantitative difference between strength of bonds of individual halogenides is expressed in values of molar enthalpies of formation and molar heats of fusion.

TABLE II  
Molar Enthalpies ( $\text{kJ mol}^{-1}$ ) of Transfer at 295 K for Aluminium Halogenides

Halogenide	$\Delta H_{\text{trH}_2\text{O} \rightarrow \text{AN}}$	$\Delta H_{\text{trH}_2\text{O} \rightarrow \text{THF}}$	$\Delta H_{\text{trTHF} \rightarrow \text{AN}}$
$\text{AlCl}_3$	+145.7	+219.0	— 73.3
$\text{AlBr}_3$	— 460.2	— 356.1	— 104.1
$\text{AlI}_3$	— 515.2	— 117.8	— 397.4

Fig. 1 shows that in spite of a different character of both solvents, the course of dependences of the molar heat of dissolution upon the halogenide concentration at the given temperature, *i.e.* the so-called isotherms in acetonitrile and tetrahydrofuran, are very similar.

The structure of  $\text{AlCl}_3$  is the strongest contribution of  $\Delta H_{\text{destr}}$  to total  $\Delta H_{\text{sol}}$  value is therefore most decisive. For the other two halogens, however, the course of isotherms and of absolute value of molar heats of dissolution cannot be assigned only to the smaller value of  $\Delta H_{\text{destr}}$ , in comparison with this value for  $\text{AlCl}_3$ , but also to a considerable effect of  $\Delta H_{\text{int}}$ .

According to the results of conductometric measurements<sup>8</sup>, electrically charged particles are being formed during the dissolution of aluminium halogenide in acetonitrile, while in tetrahydrofuran they practically do not occur. In both solvents, however, two equal, longer and hence less strong bonds dissociate in each dimer. Thus, an analogous course of the  $\text{AlBr}_3$  and  $\text{AlI}_3$  isotherms in acetonitrile and tetrahydrofuran can be essentially explained. The slope of isotherms is ascribed by Mishchenko<sup>18</sup> to the association of electrically charged particles. This explanation is not possible for tetrahydrofuran, but in the main it may be assumed that interaction of the solute particles with the solvent and contribution of  $\Delta H_{\text{int}}$  increases with decreasing concentration of solute in the solvent. This effect becomes evident on the outside in the same way, as if the association of ions decreases with decreasing concentration of ions, and their solvation increases.

It may be explained by different values of  $\Delta H_{\text{int}}$  in both solvents that  $\Delta H_{\text{sol}}$  is in acetonitrile a more negative value than in tetrahydrofuran. It is true that acetonitrile is a more polar, arranged solvent than tetrahydrofuran; from this follows a stronger interaction between molecules of the solvent and higher energy needed for destroying them. On the other hand, in acetonitrile very strong solvates are obviously formed and contribution of  $\Delta H_{\text{int}}$  to the total  $\Delta H_{\text{sol}}$  value is more negative than in tetrahydrofuran. This is in accordance with the finding that aluminium cannot be deposited from the solutions of halogenides in acetonitrile<sup>19</sup>, but it can be very well deposited from tetrahydrofuran<sup>4</sup>.

From the analysis of molar heats of dissolution,  $\Delta H_{\text{sol}}$ , for infinite dilution in various media, which are summarized in Table I, further findings follow beside the already discussed problem of higher values in acetonitrile than in tetrahydrofuran:

The  $\Delta H_{\text{sol}}$  values for the dissolution of aluminium halogenides in water are, except for  $\text{AlCl}_3$ , lower and not so different as in both solvents under investigation. The factor of a very strong structure of water, based on hydrogen bonding and bringing about a greater positive effect necessary to destroy this structure, as in aprotic solvents, contributes to this results. A decrease of total negative value of  $\Delta H_{\text{sol}}$  in water takes therefore place. In this way, also negative values  $\Delta H_{\text{trH}_2\text{O} \rightarrow \text{AN}}$  and  $\Delta H_{\text{trH}_2\text{O} \rightarrow \text{THF}}$  for  $\text{AlBr}_3$  and  $\text{AlI}_3$ , presented in Table II, may be explained. Positive values of  $\Delta H_{\text{trH}_2\text{O} \rightarrow \text{AN}}$  and  $\Delta H_{\text{trH}_2\text{O} \rightarrow \text{THF}}$  for  $\text{AlCl}_3$  may be ascribed according to (3) to a greater

specific interaction of  $\text{AlCl}_3$  with water than with aprotic solvents. On the other hand,  $\text{AlBr}_3$  and  $\text{AlI}_3$  obviously react at the given temperature with organic solvents to a greater extent than with water.

The transfer from tetrahydrofuran into acetonitrile is for all three halogenides exothermic as can be seen in Table II. This result has been discussed when investigating  $\Delta H_{\text{sol}}$  in both solvents. The exothermicity of transfer rises from  $\text{AlCl}_3$  to  $\text{AlI}_3$ . There is a possibility to explain this in two following ways: interaction  $\text{AlX}_3 - \text{AN}$  increases from chloride to iodide; or *vice versa* interaction  $\text{AlX}_3 - \text{THF}$  decreases from chloride to iodide. This second explanation is supported also by the finding that  $\text{AlCl}_3$  causes catalytic splitting of cyclic chain of tetrahydrofuran and formation of compound  $\text{AlCl}_2\text{O}(\text{CH}_2)_4\text{Cl}\cdot\text{C}_4\text{H}_8\text{O}$  (ref.<sup>20</sup>). Total thermal effect of transfer  $\text{THF} \rightarrow \text{AN}$  is very probably given by combination of both factors.

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