Influence of water on conductivity of aluminium halide solutions in acetonitrile

L. LUX

Department of Chemistry, Faculty of Metallurgy, Technical University,
CS-043 85 Košice

Equilibria of the substitution and association reactions of AlCl₃ and AlBr₃ with acetonitrile were investigated by measuring the conductivity of solutions at varying concentrations of AlCl₃, AlBr₃, and water in the acetonitrile solution. Both halides behave in acetonitrile in the absence of water as relatively strong electrolytes. It has been revealed that water displaces acetonitrile from the solvate sphere of cation of both halides. As for AlBr₃, the bromide ion is also displaced from the coordination sphere of aluminium and replaced by a neutral water molecule, which simultaneously results in an increased number of ionized particles in solution. The hydrate $AlX_3 \cdot 6H_2O$ was identified as final product which separates from the solution by adding water.

Изучены равновесия реакций замещения и ассоциации AlCl₃ и AlBr₃ с ацетонитрилом посредством измерения электропроводности раствора в зависимости от концентрации AlCl₃, AlBr₃, как и в зависимости от концентрации воды в растворе ацетонитрила. Оба галогенида ведут себя в ацетонитриле как сравнительно сильные электролиты в отсутствии воды. Обнаружено, что вода вытесняет ацетонитрил из сольватной оболочки катиона у обоих галогенидов. У AlBr₃ доходит и к вытеснению иона брома из координационной сферы алюминия и его замещению нейтральной молекулой воды, что одновременно приводит к увеличению числа ионизированных частиц в растворе. Конечным продуктом, выделенным из раствора при добавлении воды был идентифицированный гидрат $AlX_3 \cdot 6H_2O$.

Acetonitrile is a typical aprotic solvent which is widely used in electrochemical research because of its profitable properties, *i.e.* rather high value of relative permittivity ($\varepsilon_r = 36.1$), low boiling point (81.6 °C), and low value of viscosity (0.3409×10^{-3} Pa s) at 20 °C [1, 2]. Aluminium halides are well soluble in aprotic solvents owing to their character of Lewis acid [3]. In solvents with sufficiently high value of relative permittivity such as acetonitrile, a ionization of aluminium halide

which may be formally regarded as disproportionation takes place

$$Al_2X_6 \rightleftharpoons AlX_2^+ + AlX_4^- \qquad\qquad (A)$$
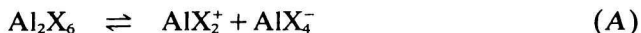
As the particle X^- is not stable in aprotic solvents, but forms a complex anion AlX_4^- with the electroneutral particle AlX_3 [4], the dissociation in acetonitrile does not follow the scheme

$$AlX_3 \rightleftharpoons AlX_2^+ + X^- \qquad\qquad (B)$$

$$Al_2X_6 \rightleftharpoons Al_2X_5^+ + X^- \qquad\qquad (C)$$

The particle AlX_2^+ in solution also contains solvent molecules in the coordination sphere. During dissolution, the coordination number of aluminium changes and reaches the value of six: $[AlX_2(AN)_4]^+$ [3].

Libus and *Puchalska* [5] have ascertained that a disproportionation of aluminium chloride according to scheme (A) takes place in solution of acetonitrile. Irrespective of this statement, the existence of the particle $AlCl_4^-$ was proved in the solution of acetonitrile as well as in the solid phase by means of infrared absorption spectroscopy [6]. The solutions of aluminium chloride and bromide were subjected to polarographic investigations [7] either in pure state or in the presence of excess halides added into solution in the form of LiCl and tetraethylammonium chloride [8] as well as in the presence of water [9]. The major aim of these experiments was to reveal the substitution equilibria in acetonitrile solutions of aluminium halides. These experiments completed by the measurements of the heat of dissolution of aluminium chloride and bromide in acetonitrile [10] and the results obtained by the conductometric method give a complex view on the properties and electrochemical behaviour of these solutions.

Experimental

All measurements were carried out in the atmosphere of dry nitrogen or argon without access of air humidity. The purification of the aluminium halides used, solvent, and inert gas was described earlier [7]. All measuring vessels were adapted to inert atmosphere and made possible to supply the inert gas into or over the solution.

The conductivities of solutions were measured with a conductometer OK 102/1 (Radelkis, Budapest) equipped with a platinum measuring cell OK 902. The used conductivity cell and measuring electrode were adapted for the conditions of air exclusion. The cell was equipped with a side tube which enabled us to add the solution into the cell during measurement without any opening. The whole system was thermostatted to (25 ± 0.1) °C. The solution of water in acetonitrile with exactly defined content of water was used as titrating agent for conductometric titrations with water (Figs. 3 and 4).

The dependence of molar conductivity on square root of electrolyte concentration was subjected to analysis according to the method of *Fuoss* and *Kraus* [11] by using the equations

$$\frac{F(z)}{\lambda} = \frac{1}{\lambda_0} + \frac{K_A}{\lambda_0^2} \cdot \frac{c f_\pm^2 \lambda}{F(z)} \tag{1}$$

where $F(z)$ is the tabulated function of the variable z

$$z = S\lambda^{1/2} c^{1/2} \lambda_0^{-3/2} \tag{2}$$

$$F(z) = 1 - z[1 - z(1 - ...)^{-1/2}]^{-1/2} \tag{3}$$

$$S = A + B\lambda_0 \tag{4}$$

The meaning of other symbols is as follows:

λ_0	— limiting molar conductivity	S cm^2 mol^{-1}
K_A	— association constant of eqn (A)	mol^{-1} dm^3
$f_\pm$	— mean activity coefficient	
A	— constant	S mol$^{-3/2}$ dm$^{7/2}$
B	— constant	mol$^{-1/2}$ dm$^{3/2}$

The values of constants A and B which are dependent on solvent properties are tabulated in paper [12].

This kind of calculation is limited to the region of low concentrations. The authors of paper [11] give an empirical formula for estimating the concentration of electrolyte for which this procedure may be used. It results from this formula that the lower the value of relative permittivity of solvent, the lower concentration of electrolyte must be used for measuring the dependence of molar conductivity on concentration.

If we graphically represent the dependence of numerical value of the quantity $F(z)/\lambda$ on numerical value of the quantity $c f_\pm^2 \lambda / F(z)$, we obtain a straight line the slope of which gives the value K_A/λ_0^2 while the section cut out by this straight line on the axis of coordinates is equal to $1/\lambda_0$. The procedure of calculation is iterative and was performed by means of a computer. The values of λ_0 and K_A thus calculated are given in Table 1.

Table 1

Values of limiting molar conductivity, association constant, and Onsager slope (theoretical and experimental) for the solutions of aluminium chloride and bromide in acetonitrile

Al_2X_6	$\lambda_0 \cdot 10^2$	K_A	$S \cdot 10^2$	
	S dm^2 mol^{-1}	mol^{-1} dm^3	S dm$^{7/2}$ mol$^{-3/2}$	
			Theor.	Exp.
Al_2Cl_6	165.3	4.52	− 139.6	− 152.7
Al_2Br_6	153.4	4.18	− 131.0	− 160.0

Results and discussion

The variation of the value of molar conductivity with the square root of concentration of Al_2Cl_6 and Al_2Br_6 is represented in Figs. 1 and 2. In both cases, the curves designated by No. *1* correspond to waterless solvent, *i.e.* the solvent which was dried by available laboratory procedure. Curves *2*, *3*, *4* represent this dependence in the presence of different amounts of water in acetonitrile. The concentrations of water in acetonitrile were 0.1 volume % (curve *2*), 0.5 volume % (curve *3*), and 1 volume % (curve *4*).

The results of measurements in waterless acetonitrile (curves *1* in Figs. 1 and 2) were treated by the above-mentioned method according to *Fuoss* and *Kraus* [11]. The calculated values of λ_0 and K_A are given in Table 1. This table also contains the theoretical values of S obtained by means of eqn (*4*) and experimental values of S obtained from experimental data plotted in Figs. 1 and 2. The numerical values of the constant K_A may be loaded by an error because a deviation from linear course of the relationship $\lambda = f(c^{1/2})$ appears even in waterless acetonitrile, which brings about a decrease in accuracy of measurements just in that region of electrolyte concentration where the greatest number of experimental points should be obtained. Though we cannot take the numerical values of the constant K_A for precise, they indicate that both aluminium chloride and bromide dissolved in
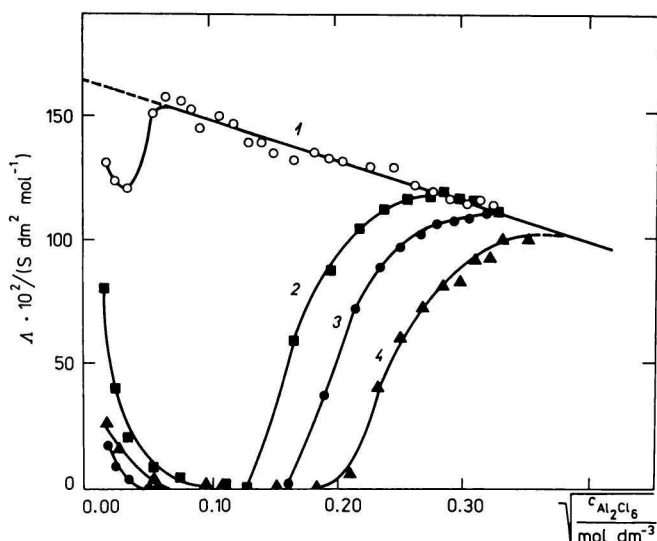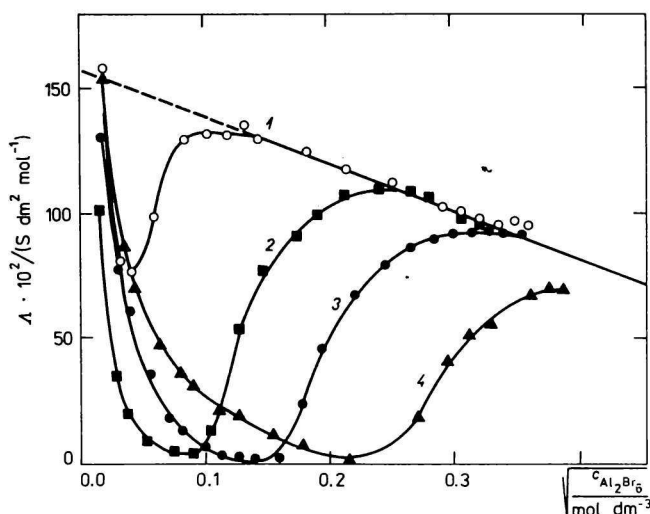

Fig. 1. Variation of molar conductivity with square root of Al_2Cl_6 concentration in acetonitrile.
1. "Waterless" acetonitrile (AN); *2*. AN containing 0.1 volume % of H_2O; *3*. AN containing 0.5 volume % of H_2O; *4*. AN containing 1.0 volume % of H_2O.

Fig. 2. Variation of molar conductivity with square root of Al_2Br_6 concentration in acetonitrile.
1. "Waterless" acetonitrile (AN); 2. AN containing 0.1 volume % of H_2O; 3. AN containing 0.5 volume % of H_2O; 4. AN containing 1.0 volume % of H_2O.

acetonitrile may be regarded as slightly associated and relatively strong electrolytes [13]. The negative deviation of experimental slope of the relation $\lambda = f(c^{1/2})$ from the theoretical value calculated according to the Debye—Hückel—Onsager limiting law is due just to the association of ions which is not respected in this law.

Influence of water

The deviation from linear course of the relation $\lambda = f(c^{1/2})$ which appears in Figs. 1 and 2 even for waterless solvent (curves 1) was also observed by other authors for solutions of aluminium halides in other solvents and was differently interpreted. *Libus* and *Puchalska* [5] attribute the observed deviation from linearity in the region of low concentrations of aluminium chloride in acetonitrile unambiguously to the presence of small amount of water in solvent. *Jorné* and *Tobias* [14] observed the deviation from linear course by measuring the conductivity of mixed solutions of aluminium chloride and alkaline chlorides in propylene carbonate and attributed it to the change in type of dissociation in solution which sets in owing to the change in concentration of aluminium chloride. *Breivogel* and *Eisenberg* [15] who investigated similar mixed solutions in propylene carbonate and γ-butyrolactone attributed the observed deviation from linearity of the conductivity dependence to the formation of multi-nucleus complexes in the given

region of aluminium chloride concentration. *Dubois et al.* [16] ascribe the deviation from linearity of the conductivity dependence to the presence of water in the system aluminium bromide—acetonitrile.

The results obtained in our laboratory unambiguously evidence that the discussed deviation from linearity of the relation $\lambda = f(c^{1/2})$ is a consequence of the presence of water in solution. The deviation from linear course increases with concentration of water in the solution of aluminium chloride and bromide in acetonitrile at low concentrations of these substances and simultaneously extends the concentration region in which the deviation from linearity of the relation $\lambda = f(c^{1/2})$ occurs (Figs. 1 and 2). We may observe the existence of turbidity in the conductivity cell at low concentrations of water whereas this precipitate separates at higher concentrations of water. This phenomenon indicates the fact that the presence of water in the solutions of aluminium halides in acetonitrile not only changes the properties of solvent such as relative permittivity, density, and viscosity, but also gives rise to specific interaction with the dissolved substance. It is
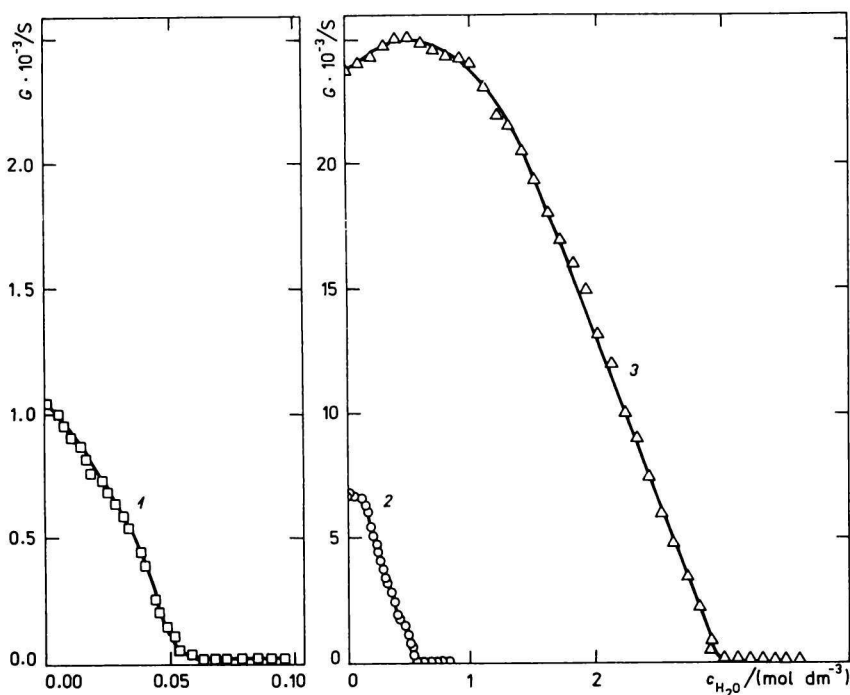

Fig. 3. Conductometric titration of a solution of AlCl$_3$ in acetonitrile with a solution of water in acetonitrile ($G = f(c_{H_2O})$).

1. Concentration of AlCl$_3$ = 0.013 mol dm^{-3}; *2.* concentration of AlCl$_3$ = 0.094 mol dm^{-3}; *3.* concentration of AlCl$_3$ = 0.516 mol dm^{-3}.

worth of noticing that water occurs even in a solution prepared with the so-called waterless solvent in spite of careful purification and dehydration. We estimate that this quantity of water amounts to 10—30 µg of water per 1 g of solvent and it does not occur in the original purified solvent. It is brought into the solution with dissolved substance or in the course of subsequent manipulation with the solution.

A clearer image of the effect of water on solutions of aluminium halides is obtained by investigating the course of conductivity of solution as a function of water concentration at constant content of aluminium chloride and bromide in acetonitrile [16]. These relationships are represented in Figs. 3 and 4. A conducto-metric titration of aluminium chloride in acetonitrile with the solution of water in acetonitrile is represented in Fig. 3 while a conductometric titration of aluminium bromide in acetonitrile with the solution of water in acetonitrile is represented in Fig. 4. The conductivity of solution almost linearly decreases with increasing concentration of water. At the value of the ratio $x(H_2O)/x(AlX_3) \approx 6$ a marked break appears on the titration curve. It is the equivalence point. Afterwards, the conductivity of solution does not change any more. The difference between conductivities of $AlCl_3$ and $AlBr_3$ in acetonitrile is equal for both types of experiments. Whether the value of molar conductivity is investigated as a function
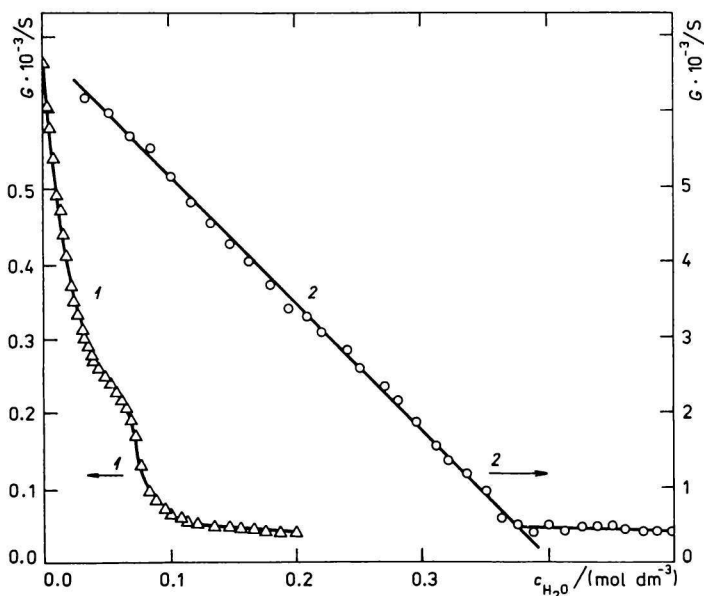

Fig. 4. Conductometric titration of a solution of $AlBr_3$ in acetonitrile with a solution of water in acetonitrile ($G = f(c_{H_2O})$).
1. Concentration of $AlBr_3 = 0.01$ mol dm^{-3}; 2. concentration of $AlBr_3 = 0.1$ mol dm^{-3}.

of concentration of aluminium halide or the solutions of aluminium chloride and bromide are estimated by conductometric titration, the conductivity of the solutions of aluminium bromide in the presence of water is always higher than the conductivity of the solutions of aluminium chloride at equal concentrations of this compound and water in acetonitrile. While the conductivity of the solution of aluminium chloride falls after addition of water down to zero (Figs. 1 and 3), the decrease in conductivity of the solutions of aluminium bromide down to zero is not to be observed even at higher concentrations of water (Figs. 2 and 4).

The precipitate which separated from the solution owing to addition of water into the solutions of aluminium chloride and bromide in acetonitrile was isolated and subjected to chemical as well as DTA analysis. It was unambiguously ascertained that it was a compound of the composition $AlX_3 \cdot 6H_2O$ [17].

The observed effects due to the presence of water in the acetonitrile solutions of aluminium halides may be explained on the basis of the following system of chemical processes.

In the presence of water, acetonitrile in the solvate sphere of the cation formed by reaction (A) is gradually replaced by stronger bonded water according to the scheme

$$[AlX_2(AN)_4]^+ + 4H_2O \quad \rightarrow \quad [AlX_2(H_2O)_4]^+ + 4AN \qquad (D)$$

This effect may produce a slight increase in conductivity of the system at low concentrations of water which manifests itself on curves 2 and 3 in Fig. 3. It is a consequence of increased mobility of the hydrated ion in comparison with the ion which is solvated by acetonitrile.

Further substitution of halide ions for water sets in only in weaker bonded $AlBr_3$, but not $AlCl_3$
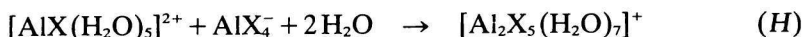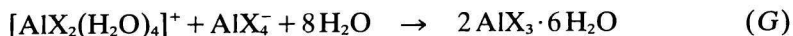
$$[AlBr_2(H_2O)_4]^+ + H_2O \quad \rightarrow \quad [AlBr(H_2O)_5]^{2+} + Br^- \qquad (E)$$

This substitution is responsible for the difference between conductivities of the $AlCl_3$ and $AlBr_3$ solutions. The formation of the bivalent cation $[AlBr(H_2O)_5]^{2+}$ brings about a higher conductivity of the acetonitrile solutions of $AlBr_3$ when compared with the solutions of $AlCl_3$ of equal concentration of halide (curves 2, 3, and 4 in Figs. 1 and 2). The bromide ion arising in reaction (E) reacts with a molecule of $AlBr_3$ to give a complex

$$AlBr_3 + Br^- \quad \rightarrow \quad AlBr_4^- \qquad (F)$$
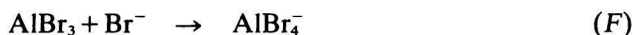
owing to which the high mobility of Br^- is eliminated. The presence of this ion should manifest itself by a considerably higher conductivity than the observed one. Anyway, we must take into consideration an increased concentration of ions due to reaction (E).

A different behaviour of aluminium chloride and bromide in acetonitrile towards addition of water was also observed in polarographic investigation of these systems [9]. While the polarographic record of $AlBr_3$ entirely changed in the presence of water in acetonitrile, no substantial change in polarographic record of $AlCl_3$ due to the presence of water in acetonitrile was observed.

Further decrease in conductivity accompanied by formation of turbidity or precipitate at water concentrations corresponding to the ratio $x(H_2O)/x(AlX_3) = 6$ or more is caused by association of ionic complexes and formation of hydrates insoluble in acetonitrile

$$[AlX_2(H_2O)_4]^+ + AlX_4^- + 8H_2O \rightarrow 2AlX_3 \cdot 6H_2O \qquad (G)$$

$$[AlX(H_2O)_5]^{2+} + AlX_4^- + 2H_2O \rightarrow [Al_2X_5(H_2O)_7]^+ \qquad (H)$$

The reaction described by eqn (H) implies that conducting particles may remain in the acetonitrile solution of aluminium bromide even in the presence of fairly high concentration of water, which is evident from Fig. 4.

The process described by eqn (G) results in the decrease of conductivity of the acetonitrile solutions of aluminium chloride and bromide, which may be observed in Figs. 3 and 4. On the other hand, the value of molar conductivity at constant content of water may with increasing concentration of aluminium halide reach the value of molar conductivity characteristic of the solution in waterless acetonitrile provided the concentration of water in solution gets negligible with respect to the concentration of aluminium halide. The rise of the value of molar conductivity towards this value is to be observed in Figs. 1 and 2.

The character of the curves corresponding to titration of aluminium chloride and bromide with water indicates that the conductivity of solution measured as a function of water concentration decreases and after reaching $x(H_2O)/x(AlX_3) = 6$ (see eqn (G)) no further change in conductivity of solution appears because the whole quantity of aluminium halide is in the form of $AlX_3 \cdot 6H_2O$ which is insoluble in acetonitrile.

On the basis of the above and other published results [18], we may state that the anomalies in conductivity of the solutions of aluminium halides in aprotic solvents are due to specific interaction between water and anhydrous aluminium halides.

References

1. Geary, W. J., *Coord. Chem. Rev.* 7, 81 (1971).
2. Covington, A. K. and Dickinson, T., *Physical Chemistry of Organic Solvent Systems.* Plenum Press, New York, 1973.
3. Akitt, J. W., Duncan, R. H., Beattie, I. R., and Jones, P. J., *J. Magn. Resonance 34*, 435 (1979).
4. Gutmann, V., *Coordination Chemistry in Non-Aqueous Solutions.* Springer-Verlag, Vienna, 1968.

5. Libus, W. and Puchalska, D., *J. Phys. Chem. 71,* 3549 (1967).
6. Jones, D. E. H. and Wood, J. L., *J. Chem. Soc. A1971,* 3132.
7. Gálová, M. and Lux, L., *Chem. Zvesti 29,* 279 (1975).
8. Gálová, M. and Lux, L., *Chem. Zvesti 30,* 599 (1976).
9. Gálová, M. and Lux, L., *Chem. Zvesti 30,* 604 (1976).
10. Gálová, M. and Kladeková, D., *Collect. Czech. Chem. Commun. 45,* 2300 (1980).
11. Fuoss, R. M. and Kraus, C. A., *J. Amer. Chem. Soc. 55,* 476 (1933).
12. Bockris, J. O'M. and Reddy, A. K. N., *Modern Electrochemistry,* p. 436. Plenum Press, New York, 1972.
13. Gálová, M. and Lux, L., *Extended Abstracts of the 28th Meeting of ISE,* p. 621. Varna, 1977.
14. Jorné, J. and Tobias, W., *J. Phys. Chem. 78,* 2521 (1974).
15. Breivogel, F. W. and Eisenberg, M., *Electrochim. Acta 14,* 459 (1969).
16. Dubois, B., Lancelin, G., and Vandorpe, B., *Rev. Chim. Miner. 17,* 65 (1980).
17. Lux, L., *CSc. Thesis.* Technical University, Košice, 1978.
18. Gálová, M., Lux, L., and Eckert, J., *Z. Phys. Chem.* (Leipzig) *263,* 377 (1982).

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