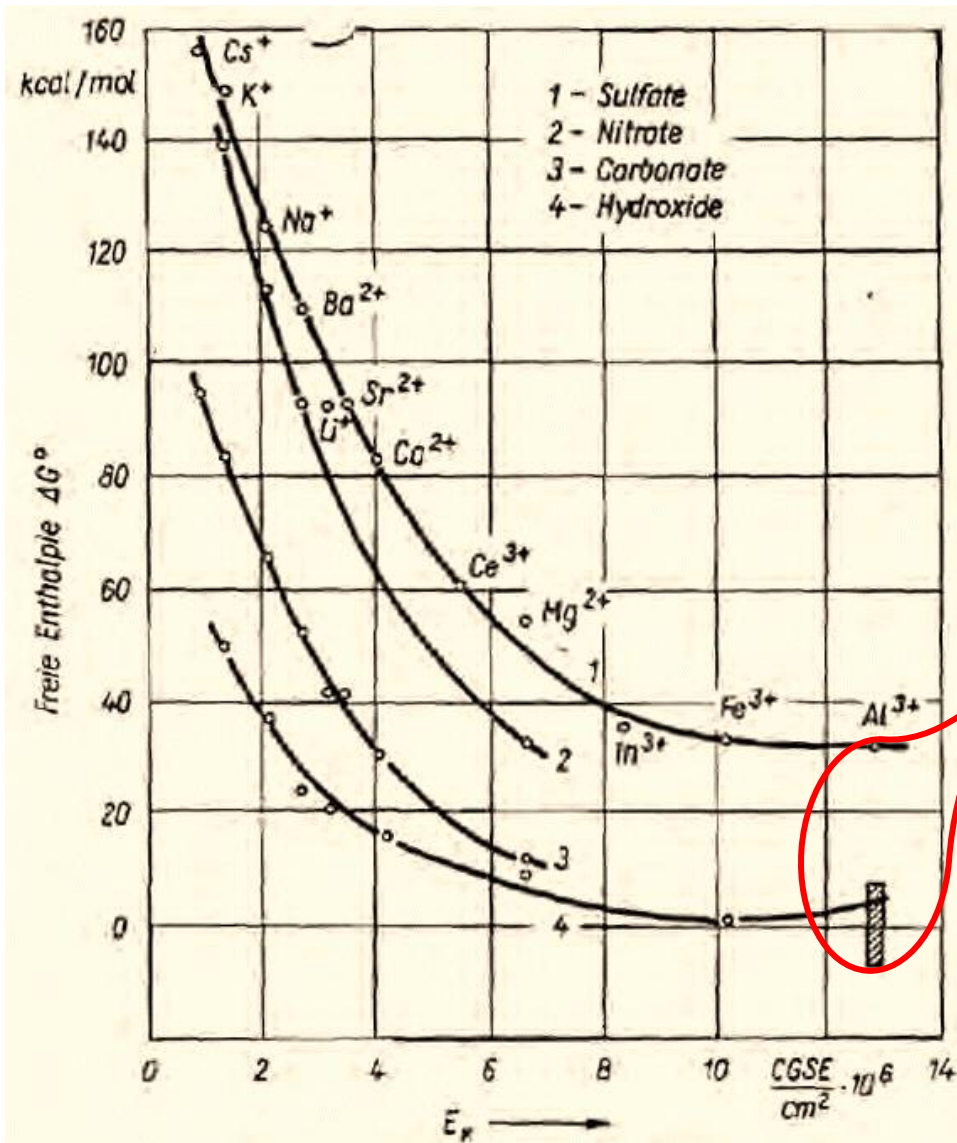


# water soluble aluminum salts

H. Dobrev

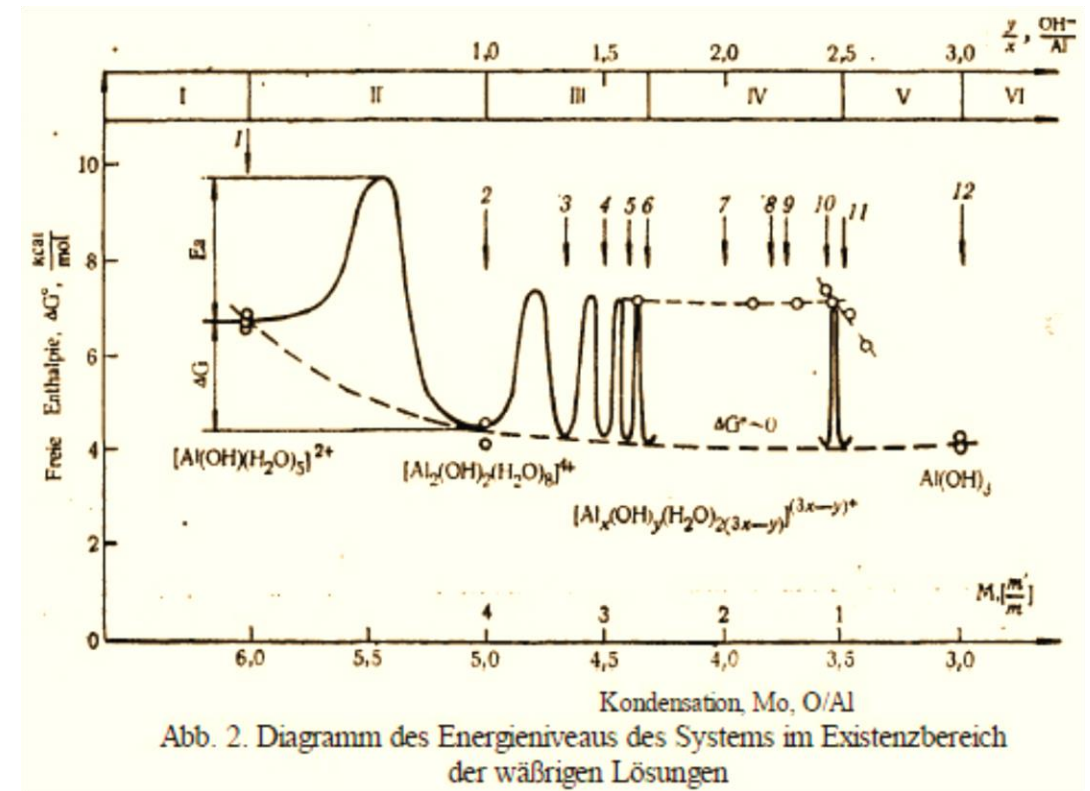


The low energy level of aluminum compounds and the proximity of their thermodynamic potentials is the fundamental cause of their diversity. This is also the reason for many contradicting results in the numerous conducted studies of aluminum compounds.

In an acid (alkaline) environment, aluminum is thermodynamically unstable and transforms into a water solution. Because of the significant hydration energy of  $\text{Al}^{3+}$  ions in the water solution, they switch into hexaaquaaluminum ions:  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ . The polycondensation results in the formation of various poly nuclear aquahydroxyaluminium complex ions:



The energy level diagram of  $\text{Al}_2\text{O}_3$ -HA- $\text{H}_2\text{O}$  (where HA-mineral acid) type Systems is plotted based on equilibrium data of the dissociation of aquahydroxyaluminium cations and the values of electroconductivity activation energy and viscosity. The driving force of condensation processes of aluminium-oxygen octahedra is expressed by the thermodynamic potentials per mole of water liberated during condensation. The simultaneous existence of various polycondensation products in aqueous solutions of basic aluminium salts, the discrepancies in literature data available, as well as some peculiarities of the Systems discussed are explained by the small driving force and the presence of product transition activation energy.



# basicity

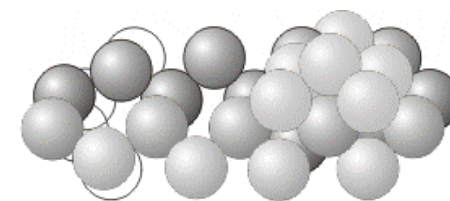


Table 1

№		Al %	Al <sub>2</sub> O <sub>3</sub> %	xAl <sub>2</sub> O <sub>3</sub> yHClzH <sub>2</sub> O x=1; 0,9<y<2; 4<z<85 Al <sub>2</sub> O <sub>3</sub> .MHCl.M <sub>2</sub> H <sub>2</sub> SO <sub>4</sub> .zH <sub>2</sub> O	TC2006-95 (solvo)		Basicity, %		БДС EN 883		Basicity, a	
					M	M <sub>2</sub>	(6-M)/6*100	a/3*100	Al(OH) <sub>a</sub> Cl <sub>b</sub>	Al(OH) <sub>a</sub> Cl <sub>b</sub> (SO <sub>4</sub> ) <sub>c</sub>	a>1,05	
					HCl/Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	%	%	a+b=3; b=M/2	a+b+2c=3; c=M <sub>2</sub> /2	(6-M)/2	3-M/2-M <sub>2</sub>
1	AH	34,6	65,4	Al <sub>2</sub> O <sub>3</sub> 3H <sub>2</sub> O	0		100		Al(OH) <sub>3</sub>		3	
2	ACH	5,8	11,0	Al <sub>2</sub> O <sub>3</sub> 1,044HCl140,55H <sub>2</sub> O	1,04			82,60	Al(OH) <sub>2,48</sub> Cl <sub>0,52</sub>		2,48	
3	<b>CFS10AI</b>	<b>9,9</b>	<b>18,8</b>	<b>Al<sub>2</sub>O<sub>3</sub>.1,4HCl.0,05H<sub>2</sub>SO<sub>4</sub>.21,4H<sub>2</sub>O</b>	<b>1,40</b>	<b>0,05</b>	<b>75,00</b>		<b>Al(OH)<sub>2,25</sub>Cl<sub>0,7</sub>(SO<sub>4</sub>)<sub>0,025</sub></b>			<b>2,25</b>
4	CFS10AI	10,1	19,0	Al <sub>2</sub> O <sub>3</sub> .HCl.0,16H <sub>2</sub> SO <sub>4</sub> .21,29H <sub>2</sub> O	1,00	0,16	78,00		Al(OH) <sub>2,34</sub> Cl <sub>0,50</sub> (SO <sub>4</sub> ) <sub>0,08</sub>			2,34
5	CFS10AI	10,5	19,8	Al <sub>2</sub> O <sub>3</sub> .0,95HCl.0,1H <sub>2</sub> SO <sub>4</sub> .20,8H <sub>2</sub> O	0,80	0,09	80,83		Al(OH) <sub>2,43</sub> Cl <sub>0,48</sub> (SO <sub>4</sub> ) <sub>0,05</sub>			2,43
6	CFS	5,3	10,0	Al <sub>2</sub> O <sub>3</sub> .0,91HCl.0,61H <sub>2</sub> SO <sub>4</sub> .45,79H <sub>2</sub> O	0,91	0,61	63,33		Al(OH) <sub>1,90</sub> Cl <sub>0,46</sub> (SO <sub>4</sub> ) <sub>0,30</sub>			1,94
7	CFS	3,3	6,3	Al <sub>2</sub> O <sub>3</sub> .0,78HCl.1,49H <sub>2</sub> SO <sub>4</sub> .79,2H <sub>2</sub> O	0,78	1,49	37,33		Al(OH) <sub>1,12</sub> Cl <sub>0,39</sub> (SO <sub>4</sub> ) <sub>0,74</sub>			1,12
8	PAC	13,2	24,9	Al <sub>2</sub> O <sub>3</sub> .4HCl.9H <sub>2</sub> O	4	0	33,33		Al(OH) <sub>1</sub> Cl <sub>2</sub>		1	
9	PAS	12,2	23,1	Al <sub>2</sub> O <sub>3</sub> .2H <sub>2</sub> SO <sub>4</sub> 8H <sub>2</sub> O		2	33,33		Al(OH) <sub>1</sub> (SO <sub>4</sub> ) <sub>1</sub>			1
10	AC	11,2	21,1	Al <sub>2</sub> O <sub>3</sub> 6HCl9H <sub>2</sub> O	6		0		AlCl <sub>3</sub> 6H <sub>2</sub> O		0	
11	AS	8,6	16,2	Al <sub>2</sub> O <sub>3</sub> 3H <sub>2</sub> SO <sub>4</sub> 13H <sub>2</sub> O		3		0		Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> 16H <sub>2</sub> O		0

Note: AH- Aluminium hydroxide,  
AC- Aluminium chloride,  
AS- Aluminium sulfate

# equilibria

The interaction between aluminum, hydrochloric acid and water is complex, complicated, perplexing and as yet debated, but various stages have been recorded and agreed upon. In this paper (Dobrev 1983 ENERGETISCHE CHARAKTERISTIK ...) some data are summarized about the hydrolysis of  $Al^{3+}$ :

Table 2

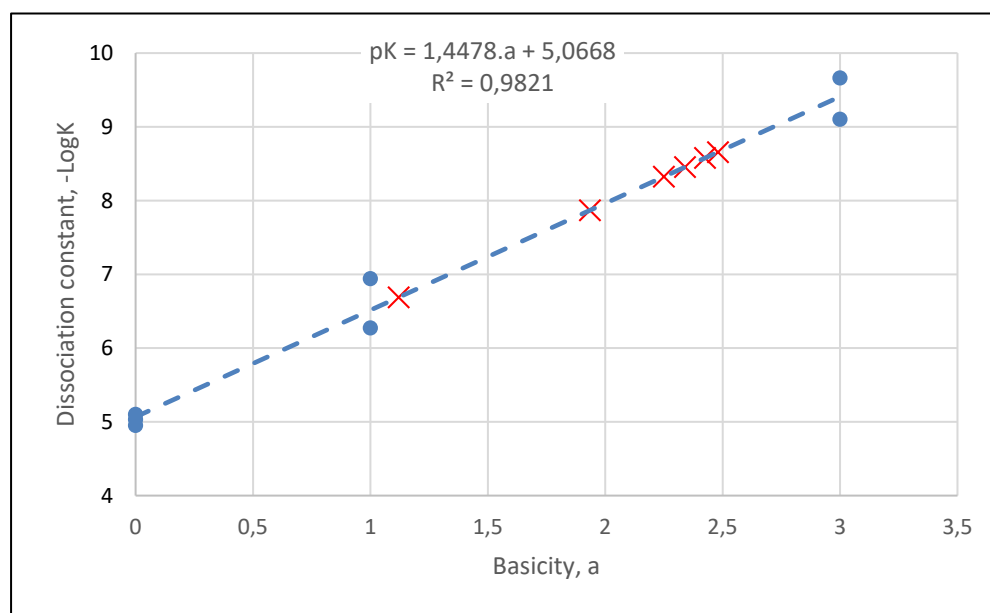
Stadium	$\frac{Mo}{Al}$	Reaktion	pK -lgK	$\frac{\Delta G^0,}{mol}$ Kcal	n	$\frac{\Delta G^0,}{mol}$ Kcal	Lit.
I	6	$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(OH)(H_2O)_5]^{2+} + H_3O^+$	4,95	6,747	1	6,747	17
		$\{Al^{3+} + H_2O \rightleftharpoons [Al(OH)]^+ + H^+\}$	5,03	6,856		6,856	7
		$\{Al(H_2O)_6^{3+} \rightleftharpoons [Al(H_2O)_5OH]^{2+} + H^+\}$	5,10	6,953		6,953	18
II	5	$2Al^{3+} + 2H_2O \rightleftharpoons [Al_2(OH)_2]^{4+} + 2H^+$	6,27	8,550	2	4,273	7
		$\{[Al(H_2O)_6]^{3+} \rightleftharpoons [Al_2(OH)_2(H_2O)_8]^{4+} + 2H^+ + 2H_2O\}$	6,94	9,46		4,726	18
		$\{[Al(OH)(H_2O)_5]^{2+} + [Al(H_2O)_6]^{3+} \rightleftharpoons [Al_2(OH)_2(H_2O)_8]^{4+} + H_3O^+ + H_2O\}$ $\{[Al(OH)(H_2O)_5]^{2+} + [Al(H_2O)_6]^{3+} \rightleftharpoons [Al_2(OH)_2(H_2O)_8]^{4+} + H^+ + 2H_2O\}$					
III	5	$[Al_x(OH)_{(2x-2)}(H_2O)_{(2x+4)}]^{(x+2)+}$ $[Al_x(OH)_y(H_2O)_{2(3x-y)}]^{(3x-y)+}$					
IV	3						
V	3	$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+$	9,1	12,4	3	4,134	7
		$\{[Al(H_2O)_6]^{3+} \rightleftharpoons Al(OH)_3 + 3H^+ + 3H_2O\}$	9,66	13,17		4,367	20
		$\{[Al(OH)(H_2O)_5]^{2+} \rightleftharpoons Al(OH)_3 + 2H^+ + 2H_2O\}$					
VI	1,5	$Al_2O_3 \cdot 3H_2O \rightleftharpoons Al_2O_3 \cdot H_2O + 2H_2O$		1,56	2	5,030	21
		$\{Al(OH)_3 \rightleftharpoons AlOOH + H_2O\}$		0,78	1	5,030	21
		$Al_2O_3 \cdot 3H_2O \rightleftharpoons Al_2O_3 + 3H_2O$		4,243	3	5,665	21

1) Die Werte der freien Enthalpie der Bildung von Verbindungen aus Elementen ( $G_f^0$ ) sind nach [21] bestimmt:

	$Al_2O_3$	$Al_2O_3 \cdot H_2O$	$Al_2O_3 \cdot 3H_2O$	$H_2O$
$G_f^0, \frac{kcal}{mol}$ (298°K)	-104,030	-484,018	-628,188	-71,305

Table 3

№		Al %	Al <sub>2</sub> O <sub>3</sub> %	xAl <sub>2</sub> O <sub>3</sub> yHClzH <sub>2</sub> O x=1; 0,9<y<2; 4<z<85 Al <sub>2</sub> O <sub>3</sub> .MHCl.M <sub>2</sub> H <sub>2</sub> SO <sub>4</sub> .zH <sub>2</sub> O	TC2006-95 (solvo)			Basicity, a			
					M	M <sub>2</sub>	M <sub>0</sub>	a>1,05			-LogK
					HCl/Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	[O/Al]=6-a	(6-M)/2	3-M/2-M <sub>2</sub>	a	pKa
0							3			3	9,66
1	AH	34,6	65,4	Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O	0		3	3		3	9,10
2	ACH	5,8	11,0	Al <sub>2</sub> O <sub>3</sub> ·1,044HCl·0,55H <sub>2</sub> O	1,04		3,52	2,48		2,48	8,66
3	<b>CFS10AI</b>	<b>9,9</b>	<b>18,8</b>	<b>Al<sub>2</sub>O<sub>3</sub>·1,4HCl·0,05H<sub>2</sub>SO<sub>4</sub>·21,4H<sub>2</sub>O</b>	<b>1,40</b>	<b>0,05</b>	<b>3,75</b>		<b>2,25</b>	<b>2,25</b>	<b>8,32</b>
4	CFS10AI	10,1	19,0	Al <sub>2</sub> O <sub>3</sub> ·HCl·0,16H <sub>2</sub> SO <sub>4</sub> ·21,29H <sub>2</sub> O	1,00	0,16	3,66		2,34	2,34	8,45
5	CFS10AI	10,5	19,8	Al <sub>2</sub> O <sub>3</sub> ·0,95HCl·0,1H <sub>2</sub> SO <sub>4</sub> ·20,8H <sub>2</sub> O	0,80	0,09	3,58		2,43	2,43	8,58
6	CFS	5,3	10,0	Al <sub>2</sub> O <sub>3</sub> ·0,91HCl·0,61H <sub>2</sub> SO <sub>4</sub> ·45,79H <sub>2</sub> O	0,91	0,61	4,07		1,94	1,94	7,87
7	CFS	3,2	6,0	Al <sub>2</sub> O <sub>3</sub> ·0,78HCl·1,49H <sub>2</sub> SO <sub>4</sub> ·79,2H <sub>2</sub> O	0,78	1,49	4,88		1,12	1,12	6,69
8	PAC	13,2	24,9	Al <sub>2</sub> O <sub>3</sub> ·4HCl·9H <sub>2</sub> O	4		5	1		1	6,27
9	PAS	12,2	23,1	Al <sub>2</sub> O <sub>3</sub> ·2H <sub>2</sub> SO <sub>4</sub> ·8H <sub>2</sub> O		2	5		1	1	6,94
10	AC	11,2	21,1	Al <sub>2</sub> O <sub>3</sub> ·6HCl·9H <sub>2</sub> O	6		6	0		0	5,10
11	AS	8,6	16,2	Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> SO <sub>4</sub> ·13H <sub>2</sub> O		3	6		0	0	5,03
12							6			0	4,95



The depicted dependence reflects the relations between the data in Table 2 (in blue) and products synthesized by us with numbers 2 to 7 in Table 3. As we have shown, the basicity of the solutions under study can easily be calculated from the analytical data of the composition.

Found dependency:  $pK = 1,4478.a + 5,0668$  or  $pK = -1,4478.M_0 + 13,753$   
( $R^2 = 0,9821$ )

**This is an opportunity to determine the value of the dissociation constant with sufficient confidence.**

**This is particularly useful in the case of high basicity and highly concentrated polyaluminum salt solutions for which standard potentiometric titration methods is not applicable.**