The research of nitrates hydratation by ultraacoustic method

V.Janёnas

Lithuanian Agricultural Academy, Department of Physics.
4324 Kaunas-Akademija

The speed of water and binary system water-nitrate is being measured by ultrasonic interferometer. Density is being measured by picknometer in this system, the adiabatic compressibility, being in concentration of 0,5 m of salt and 25°C temperature, is being calculated from the values of density and ultrasonic velocity.

From the values of adiabatic compressibility and according the theory of Debye, and the fact that silver nitrate has a minimal hydratation, the thickness of the various nitrates the first polar layer and of cation non - compressive volume the second hydration layer is being counted. The hydratation of nitrates if valued by ton - compressive volume of the second layer of cation.

The layer of the water molecules, which is near a ion is considered to be a non - compressive one. If the volume of solution is V, and the non - compressive volume in it is V_1, it means that the non - compressive part in a colution is equal to:

$$\alpha = \frac{V_1}{V} \qquad (1)$$

One can find the non - compressive part (α) from the adiabatic compression coefficients of water and solution, which are β_0 and β. [1-6],

$$\alpha = \frac{\Delta\beta}{\beta_0} \qquad (2)$$

here $\Delta\beta = \beta_0 - \beta$.

The influence of anions upon water's structure is a little one [1-7]. Cations are surrounded by two water molecules layers with different structure [7-8].

The non - compressive volume in water solutions of nitrates consists of ions volume and cations non - compressive volume of the first and the second layer.

The non - compressive part of the solution's volume can be expressed this way [17-19]:

$$\alpha = \frac{V_1}{V} = \frac{\Delta\beta}{\beta_0} = \frac{NV_a}{V} = nV_a \qquad (3)$$

here N - a number of dissolved salt molecules in a colution, V_a - the non - compressive volume of one dehydrated salt molecule, n - a number of salt molecules in a unit of the solution's volume

$$n = \frac{N}{V} = \frac{\dfrac{m_0}{\mu} N_A}{V} = \frac{m_0 \rho N_A}{\mu m}$$

here m_0 - a mass of dissolved salt, ρ - density of the solution, N_A - Avogadro number.

μ - a molecular mass of salt, m - a mass of the solution.

As we see from the formula (3), the non - compressive volume of one hydrated molecule is equal to:

$$V_a = \frac{\Delta\beta}{\beta_0 n} \qquad (4)$$

It is established that in a process of researching salting and unsalting phenomena [6,11,12,13], these ones depend on hydratation of dissolved salts. The other [6] affirms, that the phenomena of salting and unsalting depends only upon the hydratation of the second layer. It is established [14] that $AgNO_3$ neither salts nor unsalts the water solutions of nitric acid, it means that there is not any hydratation in $AgNO_3$. The water molecules which are surrounding silver ion can only polarize and form the first layer of cation.

The non - compressive volume of one molecule of silver nitrate is equal to:

$$V_a = \frac{\Delta\beta}{\beta_0 n} = \frac{4}{3}\pi r^3_{+ef} + V_- \qquad (5)$$

here r_{ef} - an effective ray of silver cation with the first polarizing layer of molecules, V_- - the volume of ion $NO_3 \cdot V_a = 24,8 \, Å^3$ [15].

The coefficient of adiabatic compression of solution is being counted from the formula $\beta = 1/\rho r^2$ [1-6]; here ρ - density of solution, v - ultrasonic speed in the solution. Ultrasonic speed of the solution is being measured by ultrasonic interferometer, the frequency of which

is 10 MHz to within 0,01%. The constant temperature in a camera of interferometer is maintained by ultrathermostat to within ±0,1° C. Density is measured by picknometer, the volume of which is 50 cm^3 to within ± 0,001%. Only chemically fresh nitrates are used. Solutions and salts have been weighted by scales, the exactness of which to within ±0,05 milligram. The double destilated water has been used for the production of solution.

The results of ultrasonic speed (v), density (ρ) and adiabatic compression (β) of various nitrates are given in table 1.

It can be seen from the table, that for silver nitrate $\Delta\beta/\beta_0$ = 0,048, n = 3,10 -4 molec./ $Å^3$. By the means of these results, an effective ray r_{+ef} = 3,2 Å silver cation is counted. Its crystallographical ray r_+ = 1,13 Å, and the thickness of the first polarizing layer of cation is equal to d=3,2 - 1,13 = 2,07 Å.

Considering the molecule of H_2O a sphere, the ray of the water molecule is r_{H_2O}=1,93 Å. It means, that the thickness of polarizing the water molecules layer, which cations are surrounded by, is more or less equal to the ray of the water molecule.

The thickness of polarizing water molecules layer surrounding all cations, is equal. It means that the non - compressive volume in the second layer is counted using the formula:

$$V = \frac{\Delta\beta}{\beta_0} - \frac{4}{3}\pi(r_+ d)^3 - n_0 V_- \qquad (6)$$

here n_0 a number of anions in a salt molecule, r_+ - a crystallographic ray of cation, d - thickness of a polarizing layer of cations, d is equal to 2 for 1 - valency cations. The polarizing layer is twice less for 2 - valency cations. According to Debye theory [16] the ray of ions screening is twice less for 2 - valency ions. The screening ray is three times less for 3 - valency cations, and that is why the thickness of polarizing layer is three times less.

The meanings of the second layer of the non - compressive volume in the various cations of nitrates (concentration is 0,5 m and temperature is 25°C) are given in the table 1. In the picture No 1 dependance of non-compressive volume ΔV from cation crystalographical radius is shown graphically. Having in mind that the density of a cation's superficial charge is $\rho = \frac{z \cdot e}{4\pi r^2}$ (there z is valency of a cation, e is elementary charge, r is crystalographical radius of a cation), the $\rho \approx 1/r^2$.

It is seen, that there is a straight line dependence upon 1 - valency, 2 - valency, and 3 - valency cations and between ΔV and the cation's charge density. It means that this hydratation model for nitrates is right, and all magnitudes characterizing hydratation are valued depending upon charge density of salts' cations.

The water molecules are changed in form in the polarizing layer of 1 - valency cations, the crystallographical rays of which are bigger than the ray of Ag+ ion.

Table 1. Meanings of the ultrasonic speed (v), density (ρ), adiabatical compression (β) and the non - compressive volume of the cation's second layer (Δv). Temperature - 25°C. Concentration - 0,5 m.

No	Nitrates	Cations crystalogr.Ray A	V, m/s	$\rho \times 10^3$, kg/m	$\beta \times 10^{11}$ m^2/N	ΔV, $Å^3$
1	$NaNO_3$	0.98	1517.8	1.0236	42.41	38.40
2	KNO_3	1.33	1513.2	1.0296	42.53	-14.15
3	$RbNO_3$	1.48	1497.5	1.0472	42.48	-40.80
4	$CsNO_3$	1.65	1488.1	1.0667	42.62	-69.45
5	$AgNO_3$	1.13	1483.8	1.0662	42.60	-0.00
6	$Mg(NO_3)_2$	0.78	1533.3	1.0495	40.53	243.80
7	$Ca(NO_3)_2$	1.06	1522.8	1.0552	40.85	204.83
8	$Sr(NO_3)_2$	1.27	1518.9	1.0776	40.22	239.44
9	$Mn(NO_3)_2$	0.91	1522.3	1.0601	40.70	220.83
10	$Co(NO_3)_2$	0.82	1523.0	1.0686	40.29	258.46
11	$Ni(NO_3)_2$	0.78	1524.6	1.0699	40.20	293.89
12	$Cu(NO_3)_2$	0.79	1517.3	1.0735	40.47	248.39
13	$Zn(NO_3)_2$	0.83	1520.1	1.0717	40.34	251.24
14	$Cd(NO_3)_2$	1.03	1504.4	1.0894	40.56	228.97

15	Al(NO$_3$)$_3$	0.57	1554.8	1.0756	38.46	368,25
16	Ga(NO$_3$)$_3$	0.62	1535.4	1.0930	38.81	358.98
17	In(NO$_3$)$_3$	0.92	1531.3	1.1091	39.40	306.57
18	Y(NO$_3$)$_3$	1.06	1535.3	1.1029	38.46	372.34
19	La(NO$_3$)$_3$	1.22	1512.6	1.1256	38,85	336,95
20	Ce(NO$_3$)$_3$	1.18	1508.7	1.1256	39.03	325.22
21	Fe(NO$_3$)$_3$	0.67	1536.1	1.0843	39.09	336.90
22	Cr(NO$_3$)$_3$	0.64	1542.0	1.0856	38.74	363.95
23	H$_2$O		1497.0	0.9971	44.75	

The specific forces of Van der Waals appear, the effect of which weaken hydrogen combines between water molecules in the second layer. Water compression increasses in this layer. Hydratation is negative then. The water molecules are deformed when crystalographical rays are less than Ag$^+$ion in 1 - valency cations polarization layer.

The specific Van der Waals forces appear then. They are quite opposite than in a case of a negative hydratation. These forces increase hydrogen combines between the water molecules in a solution. The compression of water in that layer is being reduced, and the positive hydratation appears then. The 2 - valency and 3 - valency cations have the positive hydratation only.

The deformation of polarizated water molecules depends upon the factor where an oxygen atom of polarizated molecule is.If an oxygen atom of polarizated water molecule is in a sphere of Debye screening, we have negative hydratation, if it is behind the screening sphere the hydratation is positive.

References

1.Ïàñêèíêèé Ô.Ã. Ñæèìàåìîñòü è ñêîëüâàòàöèÿ ýëåêòðîëèòîâ. "ÆÔÕ". 1938. ò.II. â.5. 606-628.

2.Äóáèíîâ Ó.Ó., Êóôäÿöåâ Á.Á. Ñêîðîñòü ðàñïðîñòðàíåíèÿ óëüòðàçâóêà è ãèäðàòàöèÿ ðàñòâîðîâ "ÆÔÕ" 1957. ò.31, â. 10. 2191-2199.

3.Ìèõàéëîâ È.Ã., Ñîëîâúåâ Â.À., Ñûðíèêîâ Þ.Ï. Îñíîâû ìîëåêóëÿðíîé àêóñòèêè. Èçä. "Íàóêà", Ì., 1964.

4.Ñòþð Äæ., Åããåð Å. Ñâåñòñîâà àãàçêîíòà, æèäêîñòåé è ðàñòâîðîâ. Ïîä ðåä.Ó.Ìýçîíà. Èçä. "Ìèð". Ì., 1969 2Ô. 375-397.

5.Ïîäíèííí Ð., Ñòîêñ Ð. Ðàñòâîðû ýëåêòðîëèòîâ. Èçäàòèíèç., Ì., 1963.

6.Íàáèíòîâûã ïðîöåïñû ñîñáâàííîíé ýëåê-òðîíèêè. Ïåð. ñ àíãë., ïîà ðåä. Äæ.Áíðêíñà. Èçäàòèíèç., Ì., 1958.

7.Ìèõàéëîâ È.Ã., Ñàâêîâ Ë.È. è äð. Ñêîðîñòü çâóêà è ñêæèìàåìîñòü êîìïîíåíðèâàííûõ ðàñòâîðîâ ñèëüíûõ ýëåêòðîëèòîâ. "Âåñòí. ËÃÓ". 1957, â.22. 25-42.

8.Ãëàçèäîâà È.È. Óðàíèè è åãî ñîáäèíåíèÿ. Èçä. ÀÍ ÑÑÑÐ. Ì., 1959. 250-254.

9.Ñàìîéëîâ Î.ß. Ñòðóêòóðà âîäíûõ ðàñòâîðîâ ýëåêòðîëèòîâ è ãèäðàòàöèÿ èîíîâ. Èçä. ÀÍ ÑÑÑÐ. Ì., 1957.

10.Êðåñòîâ Ã.À. Òåðìîäèíàìèêà èîííûõ ïðî-öåññîâ â ðàñòâîðàõ. Èçä. "Õèìèÿ". Ë., 1973.

11.Ìèùåíî Ê.Ï., Ñàìîéëîâ Î.ß. Ñá. "Ðàçêèòèå ôèçè÷åñêîé õèìèè â ÑÑÑÐ. Èçä. "Íàóêà". Ì., 1967. 177-222.

12.Ñàìîéëîâ Î.ß. Ê òåîðèè âûñàëèâàíèÿ èç âîäíûõ ðàñòâîðîâ. Æ.ñòðóêò.õèì., 1966. ò.7 N 1. 15-23; 1970. ò.II. N 6. 990-993.

13.Êîïïî Â.Å., Ìàçóòîâ Ð.Ê., Ñàìîéëîâ Î.ß. Çàâèñèìîñòü ãåäëàæíâê ãèäðàòàöèè âûñàëèâàåèåìîíî êàòèîíà îò ãèäðàòàöèè êàòèîíîâ âûñàëèâàòåëÿ ïî äàííûì ßÌÐ. "Æ.ñòðóê.õèìèè" 1969. ò.10, N 3. 407-410.

14.×åðíóøåâ À.Å., Çàè÷êî Í.Ä. Òðóäû Âñîñóàäðàñôàññîííîãî íáî-ñÿ-èññëåäîâàòåùèíêîìïêÿ è ïðîáëåìíîó êîîòèòóòà àçîíîé ïðîìûøëåííîñòè è ïðîäóêòîâ ðãàíè÷åñêîé ñèíòåçà. Õèìèÿ è òåõíîëîãèÿ àçîòíûõ óäîáðåíèé. Ì. 1973. â.19. ñ.19.

15.Janz J., James D.W. Electrochim. Acta, 1962, vol.7. p.427.

16.Èçìàéëîâ Í.À. Ýëåêòðîõèòèÿ ðàñòâîðîâ. Èçä. "Õèìèÿ", Ì., 1976.

17.Áîáàíîâ À.Ê. Èññëåäâàíèå ãèäðàòàöèè ýëåêòðèëèòîâ óëüäàåðàêóñòîò÷åñêèì ìåòîïîì. "ÆÔÕ", 1979. ò.53. N 4. 963-65.

18.Áîáàíîâ Â.Ê. Ïðåìîíïîíêè óëüòðàåêóñòîñ÷åñêîé è êêèôàòî÷åñêîì ìåòîäàìè äëÿ èçó÷åíèÿ ãèäðàòàöèè ýëåêòðîèòîâ. "ÆÔÕ". ò. 52. N 6. 1462-1465.

19.Áîáàíîâ Â.Ê. Îîðåäåëåíèåê ÷èñëè ãèäðàòàöèè èîíîâ ïî êîýôôèöèåíòàì ñæèìàåìîñòè è âÿçêîñòè. Õèìèÿ è õèìè÷åñêàÿ òåõíîëîãèÿ. ò.21. â.6. 1978. 826-830.

V.Janėnas

Nitratø hidratacijos tyrimas ultraakustiniu metodu

Santrauka

Ultraakustiniu interferometru iðmatuotas binarinës sistemos vanduo - nitratas ir vandens ultragarso greitis, o piknometru - tankis. Ið ultragarso greièio ir tankio reikðmiø apskaièiuotas tirpalø adiabatinis spûdumas, esant 0,5 m druskos ir 25° C temperatûroje.

Ið adiabatinio spûdumo reikðmiø, remiantis Debajaus teorija ir tuo, kad sidabro nitratas turi minimalià hidratacijà, apskaièiuotas ávairiø nitratø katijonø pirmojo poliarizacinio sluoksnio storis ir katijonø antrojo hidratacinio sluoksnio nespûdus tûris. Ið katijonø antrojo sluoksnio nespûdaus tûrio ávertinama nitratø hidratacija

Â.Ê.Áîáàíñ

Èññëåäîâàíèå ãèäðàòàöèè íèòðàòîâ óëüòðàêóñòè÷åñêèì ìåòîäîì

Ðåçþìå

Óëüòðàãàóôêîíûé èíòåðôåðìåòðîì èçìåðûëàñ êîðîñòü óëüòðàçãóôêà â áèíàðíûõ ñèñòåìàõ âîäà-íèòðàò. Ïëîòíîíòü ðàñòâîðà èçìåðÿëàñ ïèêíîìåòì÷åñêèì ìåòîäàì.Èçìåðÿëèñ ïðîèçâåäåíèÿ ïðè òåìïåðàòóðîò 25° Ñ, êîíöåíòðàöèÿ íèòðàòà àáåà 0.5 ì. Ïî çíà÷åíèÿ êîðîñòè è ïëîòíîñòè ðàññ-èòàíî àäèàáàòè÷åñÿ ñæèìàåìîíòü ðàñòâîðîâ. Ïðèòåðÿñ ñà òåîðèþ Äåáàÿ, è, ïðèíèìàÿ, ÷òî íèòðàòî ñåðåáðà ìèíèìàëíî ãèäðàòèðàâà, ïî çíà÷åíÿì àäèàáàòè÷åíêî ñæèìàåìîñòè âû÷èëÿåìèñ òîùùèíà ïåðâîãî ãèäðàòîíîî ñëîÿ êàòèîíîâ. Çàòåì ðàññ÷èòûâàåíûé íåñæèìàåìûé íáúåì âòîðîãî ñëîÿ êàòèîíîâ, èç êîòîðîãî îöåáâ ãèäðàòàöèÿ íèòðàòîâ.