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Application of Solvation Excess Concept to Solutions of 3 : 1 and 1 : 3 Electrolytes

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Abstract—Data on water activity in solutions of a series of 3 : 1 and 1 : 3 electrolytes [$AlCl_3$, $Al(NO_3)_3$, $LaCl_3$, $La(NO_3)_3$, H_3PO_4, NaH_2PO_4] have been generalized in the frame of solvation excesses concept. Solvation excess reflects the distribution of the selected structural elements (ions or solvent particles) in the solution. The computed values have demonstrated the opposite contributions of ion association and hydration of ions and ion associates. Solvation excess concept allows determination of water molecules fraction constituting the excess at ions and their associates. The comparison of results obtained with different choice of model structural units has shown the electrolyte concentration ranges of validity of the respective models.

Keywords: electrolyte, solvation excess, hydration, association

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The existence of multi-charged ionic species in aqueous solutions is limited by hydrolysis of 3 : 1 electrolytes (single-charged cations) and 1 : 3 electrolytes. Therefore, the 1 : 3 electrolytes in aqueous solutions are generally treated as the 1 : 1 electrolytes (for instance, H_3PO_4, NaH_2PO_4, KH_2PO_4, etc.) or the 1 : 2 ones (Na_2HPO_4), and the corresponding activity coefficients are collected in the reference books. In the cases of 3 : 1 electrolytes, such model is used for calculation of the activity coefficients, even if the fraction of hydrolyzed triple-charged atomic ions is on the order of 1% of the total cationic form (Ga^{3+} [1, 2]).

The only known method to determine electrolyte activity as a function of concentration in the case of the 3 : 1 or 1 : 3 electrolytes in aqueous solution is the isopiestic approach; in this case the primary thermodynamic value is water activity in the electrolyte solution. The values of rational coefficients of water activity at certain solution molality is determined by the chosen model of the electrolyte (1 : 3, 1 : 2, 1 : 1, or non-dissociated particle) and comply with water molar fraction. The additional factor to be accounted for in the case of 3 : 1 electrolytes is the existence of a part of the solvent in the form of cation-bound (hydrate) water included into the equilibrium solid phase of the salt.

When the basic structural elements (ionic and neutral particles) are being selected in the frame of solvation excess concept, their decomposition into the constituting fragments or hydrolysis transformations are neglected, but all the equilibrium processes of their aggregation are taken into account: ion association (favoring the system phase separation) and hydration of ions and ion associates (resulting in negative deviation from ideality).

The simplest case of solvation excess concept application is that for binary system of non-electrolytes 1 and 2 with no chemical reactions occurring. Under such assumptions, dividing of the Duhem–Margules equation (1) by the Gibbs–Duhem equation (3) at T, p = const gives Eq. (3), necessary for calculation of solvation excesses.

$$x_1 d\ln f_1 = -x_2 d\ln f_2, \tag{1}$$

$$x_1 d\ln a_1 = -x_2 d\ln a_2, \tag{2}$$

$$(d\ln f_1/d\ln a_1)_{T,p} = (d\ln f_2/d\ln a_2)_{T,p}$$
$$= (d\ln f_1/d\ln x_1)_{T,p}/[1 + (d\ln f_1/d\ln x_1)_{T,p}] = -\Gamma^1_{1(2)} = -\Gamma^2_{2(1)}. \tag{3}$$

Hereinafter x are molar fractions, a are activities, and f are rational activity coefficients of the respective components; $\Gamma^1_{1(2)}$ stands for the solvation excess, the index in parentheses indicates a species altering activity of the other species.

The experimentally determined value of $(d\ln f_1/d\ln a_1)_{T,p}$ corresponds to solvation excess [3, 4], as it is ranged within (–1; +∞), identically to the range of values of function [Eq. (4)].

$$\Gamma^1_{1(2)} \equiv N_1/V\int_0^{r_c}(\rho_{1,1}-\rho_{1,2})4\pi r^2dr = [\tilde{n}_1(r_c)-(x_1/x_2)\tilde{n}_2(r_c)], \quad (4)$$

where N_1/V being average density of particles 1; $\rho_{1,1}$ and $\rho_{1,2}$ being radial distribution functions of particles 1 and 2 at the central particle 1; $\tilde{n}_1$ and $\tilde{n}_2$ being numbers of particles 1 and 2 within sphere with radius equal to that of molecular correlation r_c.

The value of –1 corresponds to strong chemical binding of the first component with the second at any stoichiometric ratio. If the solution composition complies with the stoichiometric composition of the formed compound, the system is degenerated from the two-component into the single-component one. The value of +∞ corresponds to critical phase of the system [3].

Definition of the solvation excess (4) is equivalent to several relationship equations between the excesses [3, 5]; in the cases of systems consisting of three or more components these can be written as follows.

$$\Gamma^k_{i(j)} = -(x_i/x_j)\Gamma^k_{j(i)}, \quad (5a)$$

$$\Gamma^k_{i(j)} = \Gamma^k_{i(l)} - (x_i/x_j)\Gamma^k_{j(l)}, \quad (5b)$$

$$\Sigma^l_{k=1}x_k\Gamma^k_{i(j)} = 0 \ (i \neq j), \quad (5c)$$

where l being a number of different particles (basic structural units).

Equation (5a) corresponds to Eq. (2) if the solution composition is changed only due to variation of the a_i and a_j variables, other particles activity being constant. Eq. (5b) expresses the fact that the paired distributions (i, j) can be reduced to distribution of pairs (i, l) with l corresponding to the same component, for instance, the solvent particle. Equation (5c) mathematically expresses the requirement of isotropy of the solution, as for any chosen pair of particles (i, j) sum of their excesses over the whole set of central particles including i and j should be zero.

The solvent–electrolyte binary system includes three basic structural elements, resulting in 18 different solvation excesses, 4 of which would be independent without additional requirements of charge neutrality. In the case of the system of solvent 1 and electrolyte (3 : 1 or 1 : 3) the latter is expressed in the form of Eq. (6).

$$\Gamma^1_{3+(-)} = \Gamma^1_{-(3+)} = 0; \ \Gamma^{3+}_{-(3+)} = 3; \ \Gamma^{-}_{3+(-)} = 1/3. \quad (6)$$

For the latter pair of excesses, symmetrical form is available [Eq. (7)].

$$\Gamma^{-}_{-(3+)} = \Gamma^{3+}_{3+(-)} = -1. \quad (7)$$

Equation (7) means that ions distribution around the central particle is such that the total charge of the ionic atmosphere within the radius of molecular correlations compensates for charge of the central particle.

If activities of ions as basic structural elements of aqueous solutions are introduced as intermediate variables [6], phenomenological equations will follow, allowing calculation of solvation excesses from data on water activity in the electrolyte solution. Indeed, firstly the excesses are introduced into the equations, and increments of logarithms of the cation and the anion activities thus appear in the expressions. The introduction of the mean activity coefficient $(\nu_+ + + \nu_-)d\ln a_\pm \equiv \nu_+ d\ln a_+ + \nu_- d\ln a_-$ allows retaining the only ion activity in the equation, for instance, $\ln a_+$. According to Eq. (5), sum of excesses being a factor at that small increment is always zero; this results in the equations to be discussed below.

This work aimed to compare results of calculations of solvation excesses with differently chosen structural units, constituting the electrolyte solution. To do so, basing on the reference data (molality of the electrolyte solution and corresponding water activity [7] at 25°C) we calculated water activity coefficient in the following cases: $n = 1$ (electrolyte being a single particle), $n = 2$ (electrolyte consisting of two particles, 1 : 1), $n = 3$ (electrolyte consisting of three particles, 2 : 1 or 1 : 2), and $n = 4$ (electrolyte consisting of four particles, 3 : 1 or 1 : 3). Then, using the phenomenological coupling Eqs. (8)–(11), the results obtained for solutions of certain molality were compared.

$$n = 2\text{: } (d\ln f_1/d\ln a_1)_{T,p} = -\Gamma^1_{1(+)} = -\Gamma^1_{1(-)}$$
$$= -[\Gamma^{+}_{+(1)} + \Gamma^{-}_{+(1)}] = -[\Gamma^{+}_{-(1)} + \Gamma^{-}_{-(1)}], \quad (8)$$

$$n = 3\text{: } (d\ln f_1/d\ln a_1)_{T,p} = -\Gamma^1_{1(2+)} = -\Gamma^1_{1(-)}$$
$$= -[\Gamma^{2+}_{2+(1)} + 2\Gamma^{-}_{2+(1)}] = -[1/2\Gamma^{2+}_{-(1)} + \Gamma^{-}_{-(1)}], \quad (9)$$

$$n = 4\text{: } (d\ln f_1/d\ln a_1)_{T,p} = -\Gamma^1_{1(3+)} = -\Gamma^1_{1(-)}$$
$$= -[\Gamma^{3+}_{3+(1)} + 3\Gamma^{-}_{3+(1)}] = -[1/3\Gamma^{3+}_{-(1)} + \Gamma^{-}_{-(1)}]. \quad (10)$$

In the case of 1 : 3 electrolytes, the equations were symmetrical; for example, at $n = 4$:

$$(d\ln f_1/d\ln a_1)_{T,p} = -\Gamma^1_{1(3-)} = -\Gamma^1_{1(+)} = -[\Gamma^{3-}_{3-(1)} + 3\Gamma^{+}_{3-(1)}]$$
$$= -[1/3\Gamma^{3-}_{+(1)} + \Gamma^{+}_{+(1)}]. \quad (11)$$

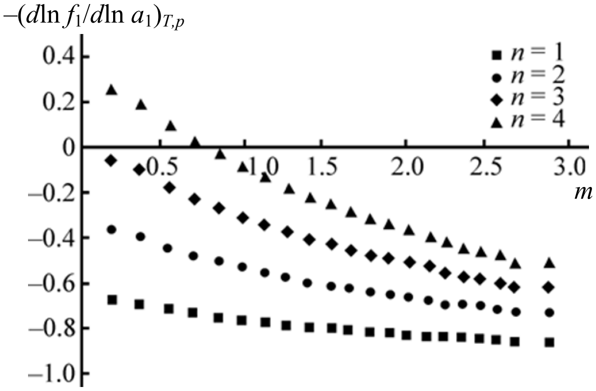

Fig. 1. Solvation excesses in the case of $La(NO_3)_3$ at n = 1, 2, 3, and 4.

Negative excesses at electrolyte ions can be transformed into positive ones via Eq. (5a). For example, if $[\Gamma^{3-}_{3-(1)} + 3\Gamma^{+}_{3-(1)}] < 0$, then $-x_1/x_{3-}[\Gamma^{3-}_{3-(1)} + 3\Gamma^{+}_{3-(1)}] = [\Gamma^{3-}_{1(3-)} + 3\Gamma^{+}_{1(3-)}] > 0$.

In the studied concentration range, hydration of the structural ionic particles and their association products prevails over the effect of ions self-association. It should be noted that contribution of the hydration factor to the excess value approaches zero with decreasing electrolyte concentration, as water becomes the major component constituting the nearest surrounding of ions or ion associates, and is not reflected in the solvation excess. In the case of the most dilute solutions, the major factor determining the excess sign is the number of particles formed by electrolyte upon dissociation, to form contact ion pairs, separated ion pairs, or Debye ion atmosphere.

In the cases of symmetric strong 1 : 1 and 2 : 2 electrolytes in their aqueous solutions the only set of basic structural elements is possible (cation, anion, and H_2O); in the majority of the studied systems of such type the $[\Gamma^{+}_{+(1)} + \Gamma^{-}_{+(1)}]$ values can be positive (dilute solutions) as well as negative (concentrated solutions) [8]. The solution composition at which sum of the

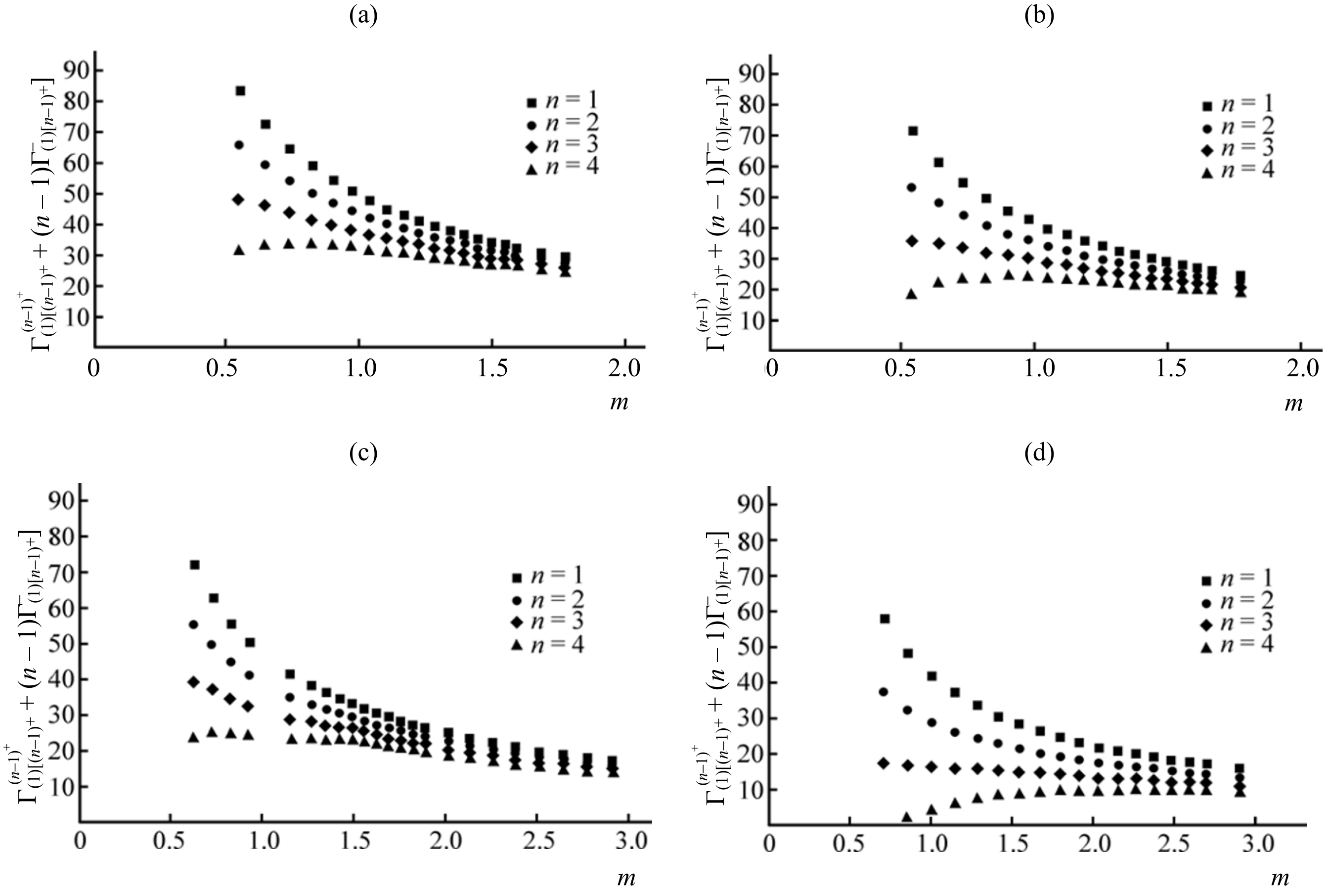

Fig. 2. Inverse solvation excesses in the cases of (a) $AlCl_3$, (b) $LaCl_3$, (c) $Al(NO_3)_3$, (d) and $La(NO_3)_3$ at n = 1, 2, 3, and 4. At n = 1 [Eq. (3)] was used for the calculation; the values of $\Gamma^{1}_{2(1)}$ are given in this case.

Table 1. Inverse solvation excesses $\Gamma^{(n-1)^+}_{1[(n-1)^+]} + (n-1)\Gamma^{-}_{1[(n-1)^+]}$ at n = 1[a], 2, 3, and 4

a_w	AlCl$_3$					Al(H$_2$O)$_6$Cl$_3$				LaCl$_3$					La(H$_2$O)$_6$Cl$_3$			
	m	n = 1	n = 2	n = 3	n = 4	n = 1	n = 2	n = 3	n = 4	m	n = 1	n = 2	n = 3	n = 4	n = 1	n = 2	n = 3	n = 4
0.98	0.312	136	94.6	53.6	13.0	128.7	85.9	43.6	1.81	0.331	124.4	81.6	39.3	–2.5	116.9	72.6	28.9	–14
0.94	0.733	64.8	54.1	43.7	33.6	57.8	46.3	35.1	24.2	0.811	57.0	45.8	35.0	24.4	49.9	37.7	25.9	14.4
0.90	1.035	47.8	42.2	36.8	31.6	41.1	34.9	28.8	23.1	1.169	41.3	35.4	29.8	24.3	34.5	27.8	21.4	15.3
0.88	1.164	43.2	39.0	34.9	30.9	36.6	31.8	27.2	22.7	1.322	37.1	32.5	28.0	23.8	30.3	24.9	19.8	15.0
0.86	1.28	39.6	35.9	32.4	29.1	33.0	28.8	24.8	21.0	1.468	33.8	30.0	26.5	23.1	27.1	22.7	18.5	14.6
0.84	1.39	36.8	33.8	30.9	28.2	30.2	26.8	23.4	20.4	1.606	31.2	27.9	24.9	22.0	24.5	20.6	17.1	13.7
0.82	1.498	34.3	31.8	29.3	27.0	27.8	24.8	21.9	19.3	1.736	29.0	26.2	23.6	21.1	22.3	19.0	15.8	12.9
0.8	1.592	32.6	30.5	28.5	26.7	26.2	23.7	21.3	19.1	1.862	27.3	24.9	22.7	20.6	20.7	17.8	15.1	12.6
0.78	1.685	30.9	29.0	27.2	25.5	24.5	22.2	20.0	18.0	1.984	25.7	23.6	21.6	19.8	19.1	16.5	14.1	11.9

[a] At n = 1 [Eq. (3)] was used for the calculation; the values of $\Gamma^{1}_{2(1)}$ are given in this case.

Table 2. Inverse $\Gamma^{(n-1)^-}_{1[(n-1)^-]} + (n-1)\Gamma^{+}_{1[(n-1)^-]}$ and direct $\Gamma^{(n-1)^-}_{[(n-1)^-](1)} + \Gamma^{+}_{[(n-1)^-](1)}$ solvation excesses in the case of H$_3$PO$_4$

a_1	m	$\Gamma^{(n-1)^-}_{1[(n-1)^-]} + (n-1)\Gamma^{+}_{1[(n-1)^-]}$				x_1/x_2	Excess of H$_2$O, %	$\Gamma^{(n-1)^-}_{[(n-1)^-](1)} + \Gamma^{+}_{[(n-1)^-](1)}$		
		n = 1	n = 2	n = 3	n = 4			n = 2	n = 3	n = 4
0.99	0.5	17.7	–73	–162	–248	111	16	0.7	1.5	2.2
0.95	2.338	7.53	–7.42	–21.3	–34.1	23.7	31.7	0.31	0.90	1.44
0.91	3.87	6.54	–0.32	–6.38	–11.8	14.3	45.6	0.02	0.44	0.82
0.89	4.56	6.04	0.77	–3.8	–7.81	12.2	49.6	–0.06	0.31	0.64
0.85	5.86	5.47	2.16	–0.61	–2.98	9.47	57.8	–0.23	0.06	0.31
0.81	7.05	4.91	2.56	0.63	–0.97	7.87	62.4	–0.33	–0.08	0.12
0.78	7.9	4.56	2.64	1.11	–0.15	7.03	64.9	–0.38	–0.16	0.02
0.74	9.04	4.12	2.59	1.4	0.44	6.14	67.1	–0.42	–0.23	–0.07
0.66	11.44	3.36	2.3	1.51	0.9	4.85	69.3	–0.47	–0.31	–0.19
0.62	12.73	3.07	2.19	1.55	1.06	4.36	70.4	–0.5	–0.36	–0.24
0.5	16.77	2.49	1.97	1.62	1.37	3.31	75.2	–0.6	–0.49	–0.41
0.4	21	1.99	1.62	1.37	1.21	2.64	75.4	–0.61	–0.52	–0.46
0.3	26.6	1.57	1.31	1.16	1.05	2.09	75.1	–0.63	–0.56	–0.5
0.2	35.7	1.14	0.96	0.86	0.79	1.55	73.6	–0.62	–0.55	–0.51
0.1	55.6	0.72	0.62	0.57	0.54	1	72.0	–0.62	–0.57	–0.54

excesses is zero corresponds to condition of mutual compensation of the two factors: ions association and hydration of ions and their associates. In even more dilute solutions, (m << 0.1 mol/kg), the factor of ions association degenerated as well: $\Gamma^{+}_{+(1)} + \Gamma^{-}_{+(1)} \xrightarrow[m\to 0]{} 0$. The marked features were further used in analysis of

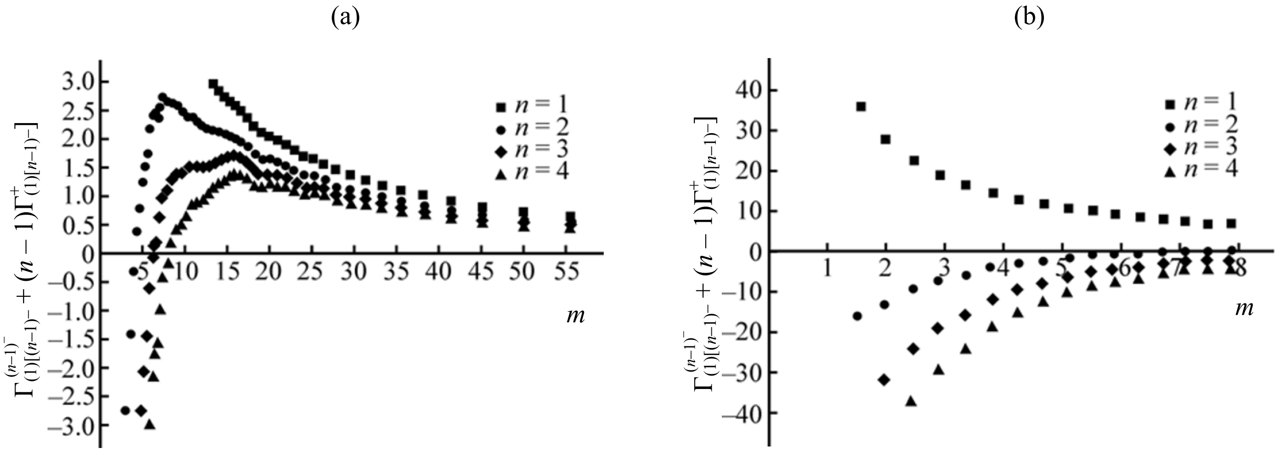

Fig. 3. Inverse solvation excesses in the cases of (a) H_3PO_4 and (b) NaH_2PO_4 at n = 1, 2, 3, and 4. At n = 1 [Eq. (3)] was used for the calculation; the values of $\Gamma^1_{2(1)}$ are given in this case.

the excesses values of aqueous solutions of $LaCl_3$, $La(NO_3)_3$, $AlCl_3$, $Al(NO_3)_3$, H_3PO_4, and NaH_2PO_4.

Noteworthily, the fraction of hydrolyzed ions $LaOH^{2+}$ and $AlOH^{2+}$ was 10^{-8} and 10^{-4}, respectively, therefore, their contribution to the excesses was negligible [2]. The differences between results of calculations at different n (Fig. 1) was smaller in the case of concentrated solutions. In all cases, excesses values revealed strong regularity of the electrolyte distribution with respect to the solvent. In the case of dilute solutions, the only branch (n = 4, 3 : 1 electrolyte) reached negative aqueous excess (the inverse excesses, those of ions over water near the ionic centers, being positive). That behavior corresponded to prevailing of ion association factor due to weakening of the hydration effect in the case of four-atomic nitrate anion.

Hence, of the four sets of basic structural elements concerned in the case of 3 : 1 electrolyte (Fig. 2), the n = 4 case was the only one satisfying the requirement of $\Gamma^{+}_{+(1)} + \Gamma^{-}_{+(1)} \xrightarrow[m\to 0]{} 0$.

The comparison of the calculated aqueous excesses of 3 : 1 electrolytes showed that aluminum salts (both chloride and nitrate) were more hydrated that the corresponding lanthanum salts; at the same time, the chlorides were hydrated stronger than the nitrates. Similar behavior was previously marked in the cases of chlorides and nitrates of singly and doubly charged cations [4, 6].

If the aluminum (lanthanum) ion solvated with six water molecules was taken as the structural element, the aqueous excesses could be confronted with the excesses at ions as structural units. From Table 1 it is seen that with such model choice the six solvating water molecules were withdrawn from the excessive water at ions. That result could be expected, as the solvation excesses concept neglected details of the components distribution in the volume corresponding to radius of molecular correlation.

Calculation results in the case of phosphoric acid and its singly substituted phosphates are shown in Table 2 and Fig. 3. The data on water vapor tension over solutions of phosphoric acid allowed for quantitative characterization of negative (related to hydration) deviations from ideality. Furthermore, we demonstrated the necessity of accounting for the first stage of association at the solution molality of 3.8 mol/kg and above; over that concentration range the solvation excess turned negative when the electrolyte was considered as the 1 : 1 one (n = 2). That result allowed estimation of degree of the first stage dissociation from positive values of the solvation excess $[\Gamma^{-}_{-(1)} + \Gamma^{+}_{-(1)}]$, increasing upon dilution but not exceeding 1. If phosphoric acid was represented as the 1 : 2 or 1 : 3 electrolyte, the excesses turned negative in the case of even more concentrated solution. Value of the inverse excess did not exceed 3 (higher values were physically meaningless in the case of tribasic acid). Assuming that in dilute solutions the non-dissociated phosphoric acid existed in the form of $[(H_3O^+)_3{\cdot}PO_4^{3-}]$, dehydrating with increasing concentration, and taking into account that at 25°C the equilibrium solid phase of phosphoric acid corresponded to the $[H_3PO_4{\cdot}0.5H_2O]$ stoichiometry [2], phosphoric acid in aqueous solution could be represented as the 1 : 3 electrolyte. In dilute solutions equilibrium of mutual distribution of the singly-charged $[H_3O]^+$ and triply-charged $[PO_4]^{3-}$ structural units of the acid was attained.

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