Non-ideal properties of the TRIS—TRIS • HCl—NaCl—H_2O buffer system in the 0—40 °C temperature interval. Application of the Pitzer equations

P. Ya. Tishchenko

Pacific Oceanological Institute, Far-Eastern Branch of the Russian Academy of Sciences,
43 ul. Baltiiskaya, 690041 Vladivostok, Russian Federation.
Fax: +7 (423 2) 31 2573. E-mail: t_pavel%dan55@marine.su

The buffer solution TRIS—TRIS · HCl—NaCl—H_2O was studied in the 0—40 °C temperature region and ionic strength interval of (0.1—4)*m* (*m* is molality) by the e.m.f. method using two types of cells without liquid junction composed of platinum-hydrogen, silver-chloride, and sodium-glass electrodes. For temperatures of 5 and 15 °C and the (1—4)*m* concentration region, the osmotic coefficients of the TRIS · HCl—H_2O solutions were measured by the isopiestic method. The results were processed in the framework of the Pitzer method, and the parameters of interaction of the components of the buffer system were calculated. The associative character of the interactions in the TRIS · HCl—H_2O solution was shown.

Key words: acid-base equilibrium, Pitzer method, activity coefficients of TRIS—TRIS · HCl—NaCl, osmotic coefficient.

The theory of ion interaction (the Pitzer method) has recently been proposed[1—5] as the theoretical basis for a new pH scale. The Pitzer method makes it possible to determine self-consistent pH values for buffer solutions in a wide range of the ionic strength by the ion interaction parameters of the components of the acid-base equilibrium. In this work, for the TRIS—TRIS · HCl—NaCl—H_2O buffer system (TRIS is 2-amino-2-(hydroxymethyl)propane-1,3-diol), these parameters were obtained by the e.m.f. and isopiestic methods for the temperature range of 0—40 °C.

Experimental

A detailed description of the equipment and procedure of measurements has been published previously[6]; therefore, here we mention only some specific features. All reagents used had ACS grade (Sigma). Recrystallized TRIS and TRIS · HCl were ground in an agate mortar and dried for 3—4 days at 65 °C. Recrystallized NaCl was calcined at 500 °C prior to use. Solutions were prepared by weighing. The density of the solutions was additionally measured at room temperature. The corrections for reducing the weight to the value in a vacuum were applied in the calculation of concentrations.

The everyday monitoring of the electric zero of the measuring apparatus showed that the deviations did not exceed 0.05 mV. Two parallel measurements were carried out for each concentration: for the temperature variation from 0 to 40 °C and, *vice versa*, from 40 to 0 °C. The results of the parallel experiments differed, as a rule, by less than 0.1 mV. The standard deviation of the single measurement of the e.m.f. of the cells (*A* and *B*) was 0.07 mV.

The osmotic coefficients of aqueous solutions of TRIS · HCl were measured by the isopiestic method, and NaCl was used as the standard. An exact amount (~200 g) of a solution of NaCl with the known concentration was placed in a ~500-mL glass vacuum desiccator. Three platinum crucibles with a known amount (~1.2 g) of a solution of TRIS · HCl were arranged above the desiccator. For better thermal equilibration, the crucibles were immersed into a solution of NaCl to 1/3 of the height. The crucibles remained dry at the outer side, because a 60-μm fluorocarbon film was placed between them and the NaCl solution. To avoid spitting, the desiccator was evacuated through a flask containing water. After evacuation, the desiccator was placed in a U-15 thermostat. The specified temperature was maintained with an accuracy of ±0.01 °C. Equilibration was reached within 3—4 days. The deviations of the concentrations of three parallel solutions relative to the average value did not exceed ±0.1%. The isopiestic molalities of TRIS · HCl and NaCl at 5 and 15 °C are presented in Table 1 along with the osmotic coefficients; in

Table 1. Isopiestic molalities (*m*) of NaCl and TRIS · HCl solutions and osmotic coefficients (ϕ) of TRIS · HCl at 5 and 15 °C

T/°C	*m*		ϕ
	NaCl	TRIS · HCl	
5	0.9585	0.9987	0.8841
	1.4135	1.4983	0.8822
	1.8534	1.9986	0.8839
	2.2763	2.4871	0.8914
	2.6663	2.9824	0.8903
	3.0554	3.4785	0.8958
	3.4549	3.9947	0.9054
15	0.9594	1.0081	0.8844
	1.4121	1.5174	0.8804
	1.8335	1.9932	0.8881
	2.2496	2.4897	0.8922
	2.6505	2.9821	0.8984
	3.0245	3.4919	0.8959
	3.3878	3.9965	0.8974

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their calculation the thermodynamic properties of a solution of NaCl were used (see Ref. 7).

Measurements in cells *A* and *B* were performed in the 0—40 °C temperature range with an interval of 5 °C.

It is impossible to find all interaction parameters of the conjugated acid-base pairs by the e.m.f. method[8]; therefore, the osmotic coefficients of TRIS · HCl—H_2O solutions were also measured by the isopiestic method. Based on the experimental data, we obtained the interaction parameters of all components of the TRIS—TRIS · HCl—NaCl—H_2O buffer system for the 0—40 °C temperature range.

Results and Discussion

The equations for e.m.f. of cells *A* and *B* have the form

$$E_A = E_A^{0'} + \frac{RT}{2F}\ln\left(1 - P^0_{H_2O}a_{H_2O}\right) + \frac{RT}{F}\ln\left(\frac{m_B}{m_{Cl}m_{BH}}\right) + \frac{RT}{F}\ln\left(\frac{\gamma_B}{\gamma_{Cl}\gamma_{BH}}\right), \quad (1)$$

$$E_B = E_B^{0'} + \frac{RT}{2F}\ln\left(1 - P^0_{H_2O}a_{H_2O}\right) + \frac{RT}{F}\ln\left(\frac{m_{Na}m_B}{m_{BH}}\right) + \frac{RT}{F}\ln\left(\frac{\gamma_{Na}\gamma_B}{\gamma_{BH}}\right). \quad (2)$$

Along with the commonly accepted designations of the Nernst equation, we used m_B and m_{BH}, which are the molalities of TRIS and TRIS · H^+, respectively; γ_B, γ_{BH}, γ_{Na}, and γ_{Cl}, the activity coefficients of TRIS, TRIS · H^+, Na^+, and Cl^-; $P^0_{H_2O}$, the pressure of water vapor at a specified temperature; and a_{H_2O}, the activity of water. According to the theory of ion interaction,[9] Eqs. (1) and (2) can be written in the form

$$\frac{FE_A}{2RT} - 0.25\cdot\ln(1 - P^0_{H_2O}a_{H_2O}) + 0.5\cdot\ln\left(\frac{m_{Cl}m_{BH}}{m_B}\right) + f^{\gamma} = \frac{FE_A^{0'}}{2RT} + m_B(\lambda_{B.B} - L_{B.BH.Cl}) + m_{BH}(L_{B.BH.Cl} - 2\beta^{(0)}_{BH.Cl}) - 3m^2_{BH}C_{BH.Cl} - m_{BH}(2g + m_{BH}g')\beta^{(1)}_{BH.Cl} + 1.5m^2_B\mu_{B.B.B}, \quad (3)$$

$$\frac{FE_B}{2RT} - 0.25\cdot\ln(1 - P^0_{H_2O}a_{H_2O}) + 0.5\cdot\ln\left(\frac{m_{BH}}{m_{Na}m_B}\right) - m_{Cl}(B_{Na.Cl} + m_{Cl}C_{Na,Cl}) + m_{Cl}(B_{BH.Cl} + m_{Cl}C_{BH.Cl}) + (m_{Na} - m_{BH})\theta_{Na.BH} + 0.5m_{Cl}(m_{Na} - m_{BH})\psi_{Na.BH.Cl} + (m_B - m_{BH})L_{B.BH.Cl} = \frac{FE_B^{0'}}{2RT} + m_B(\lambda_{B.B} + L_{B.Na.Cl}) + m_{Na}L_{B.Na.Cl} + 1.5m^2_B\mu_{B.B.B}, \quad (4a)$$

$$\frac{FE_B}{2RT} - 0.25\cdot\ln(1 - P^0_{H_2O}a_{H_2O}) + 0.5\cdot\ln\left(\frac{m_{BH}}{m_{Na}m_B}\right) - m_{Cl}(B_{Na.Cl} + m_{Cl}C_{Na,Cl}) + m_{Cl}(B_{BH.Cl} + m_{Cl}C_{BH.Cl}) + m_B(\lambda_{B.B} + L_{B.Na.Cl}) + m_{Na}L_{B.Na.Cl} + 1.5m^2_B\mu_{B.B.B} + (m_B - m_{BH})L_{B.BH.Cl} = \frac{FE_B^{0'}}{2RT} + (m_{Na} - m_{BH})\theta_{Na.BH} + 0.5m_{Cl}(m_{Na} - m_{BH})\psi_{Na.BH.Cl}. \quad (4b)$$

The designations accepted in the Pitzer method[9] were used in Eqs. (3)—(4b), except for the description of the interaction of ions with a neutral molecule. This interaction can be taken into account most rigidly by electroneutral combination of the second virial coefficients of the interaction of ions with a neutral molecule:

$$L_{n.M.X} = |z_X|\lambda_{n.M} + z_M\lambda_{n.X}.$$

Equations (3)—(4b) are written in such a way that the left part contains the parameters whose values are known from measurements and the experimental conditions, and the right part contains the sought constants. Equations (4a) and (4b) are attributed to the first and second series of experiments with cell *B*, respectively. The method of determination of the constants from the results of measurements of e.m.f. and osmotic coefficients has been published previously.[6] Note that the published data on the osmotic coefficients[10] were used along with our experimental data.

The thermodynamic properties of the TRIS buffer have previously[11,12] been studied by the e.m.f. method using cell *A*:

$$\text{Pt, } H_2 \mid \text{TRIS} + \text{TRIS}\cdot\text{HCl} + H_2O \mid \text{AgCl, Ag}. \quad (A)$$

For the determination of the thermodynamic and concentration constants, all experiments were carried out[11,12] under conditions where the solutions under study contained insignificant concentrations of the acid-base forms. Since the ion interaction parameters of all components cannot be obtained from these data, in our experiments the concentrations of the components of the buffer system were varied in a broader interval. Using cell *A*, we studied 42 solutions of TRIS—TRIS · HCl—H_2O in which the molality of TRIS · HCl varied from 0.0075 to 4 and the concentrations of the basic form of TRIS ranged within (0.0075—0.1)*m*. Cell *A* cannot be used for studying solutions with a high concentration of TRIS, because this base forms a complex with the silver ion TRIS · Ag^+ and, thus, dissolves the silver-chloride electrode,[11] resulting in distorted e.m.f. values of cell *A*. Therefore, we also carried out

Table 2. Parameters of ion interaction in the TRIS—TRIS · HCl—NaCl—H_2O system in the 0—40 °C temperature region

T	$E_A{}^{0'}$	$\beta^{(0)}{}_{BH,Cl}$	$\beta^{(1)}{}_{BH,Cl}$	$C_{BH,Cl}$	$L_{B,BH,Cl}$	$L_{B,Na,Cl}$	$\lambda_{B,B}$	$\mu_{B,B,B}$	$\theta_{Na,BH}$	$\psi_{Na,BH,Cl}$	pK_B	σ_A	σ_{Ba}	σ_{Bb}
/°C	/mV												mV	
0	716.182	0.03789	0.14537	−0.001567	−0.03830	0.01933	0.01054	−0.001706	0.01696	−0.008723	8.8491	0.18	0.08	0.14
5	713.215	0.03909	0.15350	−0.001545	−0.03546	0.01984	0.01440	−0.002103	0.01635	−0.008487	8.6818	0.17	0.08	0.14
10	710.062	0.04029	0.16052	−0.001547	−0.03321	0.01979	0.01842	−0.002508	0.01381	−0.006797	8.5201	0.16	0.10	0.15
15	706.809	0.04149	0.16688	−0.001515	−0.03001	0.02010	0.02242	−0.002919	0.00826	−0.004510	8.3650	0.17	0.11	0.14
20	703.465	0.04269	0.17156	−0.001468	−0.02656	0.02063	0.02551	−0.003204	0.00481	−0.003810	8.2164	0.18	0.11	0.11
25	700.034	0.04389	0.17395	−0.001501	−0.02445	0.02106	0.02707	−0.003433	−0.00017	−0.001455	8.0739	0.19	0.12	0.09
30	696.474	0.04509	0.17516	−0.001527	−0.02229	0.02062	0.02927	−0.003541	−0.00421	−0.000952	7.9365	0.18	0.13	0.09
35	692.826	0.04629	0.17586	−0.001594	−0.02035	0.02042	0.03079	−0.003655	−0.00575	−0.000100	7.8044	0.19	0.13	0.10
40	689.119	0.04749	0.17831	−0.001668	−0.01821	0.01983	0.03304	−0.003762	−0.00824	0.001092	7.6779	0.20	0.13	0.10

two series of measurements of the e.m.f. of cell *B* in solutions of TRIS—TRIS · HCl—NaCl—H_2O:

Pt, H_2 | TRIS + TRIS · HCl + NaCl + H_2O | Na^+-GE (*B*)

(GE is the glass electrode).

In the first series, we studied 30 solutions with equimolar ratios of TRIS · HCl to NaCl. The concentrations of these salts were varied in the (0.05—2)*m* range, and the concentrations of TRIS were (0.025—4)*m*. These concentration ratios allow one to determine the interaction parameters that take into account the non-ideal behavior of TRIS molecules. In the second series of measurements with cell *B*, we studied 28 solutions with unchanged concentrations of TRIS and TRIS · HCl equal to 0.04*m* and the concentration of NaCl varying from 0.05*m* to 4*m*. The parameters taking into account the interaction of the TRIS · H^+ and Na^+ cations were found.

The parameters of the ion interaction of the TRIS—TRIS · HCl—NaCl—H_2O system are presented in Table 2 along with the standard deviations σ of the measured e.m.f. values from those calculated by Eqs. (3)—(4b). It follows from Table 2 that the σ_A values noticeably exceed the root-mean-square deviation of the single measurement (0.07 mV). It can be assumed that the origin of these deviations is due to the associative properties of the system under study. In the Pitzer method, association is taken into account by the introduction of the additional fitting parameter $\beta^{(2)}{}_{BH,Cl}$. In fact, the introduction of this parameter results in a better agreement between the theoretical estimation and experiment for $\alpha_1 = 2$ and $\alpha_2 = 12$. The $\beta^{(2)}{}_{BH,Cl}$ value was found to depend slightly on the temperature and change from −1.87 (20 °C) to −2.18 (40 °C). It was accepted for the whole temperature region that $\beta^{(2)}{}_{BH,Cl} = -1.93$. Taking into account the $\beta^{(2)}{}_{BH,Cl}$ parameter in the processing of the experimental data, we obtained a new set of parameters presented in Table 3. The standard deviation of the experimental e.m.f. values of cells *A* and *B* from the theoretical estimations with the new set of constants is ~0.15 mV. Good agreement with the isopiestic measurements was also obtained: $\sigma_5 = 0.0010$, $\sigma_{15} = 0.0016$, and $\sigma_{25} = 0.0026$.

The fact that the additional parameter $\beta^{(2)}{}_{BH,Cl}$ is negative and its introduction noticeably enhances the consistence of the e.m.f. measurement of cell *A* with the theoretical estimation indicates association in a solution of TRIS · HCl—H_2O. The Debye—Hückel theory with the fitting parameter of the maximum approach of ions (equal to zero) was used[11] in the processing of the e.m.f. measurements of cell *A*, which also indicates association in the solution. However, further studies by both the isopiestic[10] and e.m.f. method[13] did not confirm this assumption. In our opinion, this is only a seeming contradiction. First, based on the $\beta^{(2)}{}_{BH,Cl}$ value, the associative effect is small. Second, the association is pronounced only at low concentrations and strongly depends on the ionic strength; therefore, it cannot be found by the isopiestic method. When the e.m.f. method was used, the indifferent electrolyte KCl was additionally introduced.[13] If we accept that NaCl and KCl similarly affect the non-ideal behavior of

Table 3. Parameters of ion interaction in the TRIS—TRIS · HCl—NaCl—H_2O system obtained taking into account the association of the TRIS · HCl—H_2O electrolyte ($\beta^{(2)}{}_{BH,Cl} = -1.93$) in the 0—40 °C temperature region

T	$E_A{}^{0'}$	$\beta^{(0)}{}_{BH,Cl}$	$\beta^{(1)}{}_{BH,Cl}$	$C_{BH,Cl}$	$L_{B,BH,Cl}$	$L_{B,Na,Cl}$	$\lambda_{B,B}$	$\mu_{B,B,B}$	$\theta_{Na,BH}$	$\psi_{Na,BH,Cl}$	pK_B	σ_A	σ_{Ba}	σ_{Bb}
/°C	/mV												mV	
0	715.494	0.03244	0.18660	−0.000754	−0.03574	0.01922	0.01492	−0.002011	0.01353	−0.007666	8.8364	0.13	0.08	0.13
5	712.520	0.03310	0.19443	−0.000738	−0.03409	0.01974	0.01758	−0.002405	0.01352	−0.007440	8.6692	0.12	0.09	0.13
10	709.354	0.03376	0.20145	−0.000740	−0.03292	0.01969	0.02051	−0.002809	0.01152	−0.005749	8.5075	0.12	0.11	0.13
15	706.089	0.03442	0.20780	−0.000708	−0.03080	0.02000	0.02343	−0.003221	0.00651	−0.003461	8.3524	0.12	0.12	0.12
20	702.733	0.03508	0.21249	−0.000661	−0.02843	0.02054	0.02543	−0.003506	0.00363	−0.002759	8.2038	0.14	0.13	0.10
25	699.288	0.03574	0.21488	−0.000695	−0.02741	0.02097	0.02591	−0.003734	−0.00086	−0.000405	8.0613	0.15	0.14	0.09
30	695.716	0.03640	0.21608	−0.000721	−0.02632	0.02051	0.02705	−0.003842	−0.00432	0.000100	7.9239	0.13	0.15	0.08
35	692.056	0.03706	0.21679	−0.000788	−0.02545	0.02031	0.02749	−0.003954	−0.00530	0.000954	7.7918	0.15	0.16	0.09
40	688.336	0.03772	0.21920	−0.000863	−0.02441	0.01977	0.02856	−0.004059	−0.00724	0.002145	7.6653	0.14	0.16	0.10

Table 4. Empirical coefficients of Eq. (5) for the calculation of the temperature dependence of pK_{bh} and interaction parameters in the TRIS—TRIS · HCl—NaCl—H_2O system

Parameter	a_0	a_1	a_2	a_3	σ
$\beta^{(0)}_{BH,Cl}$	0.03574	0	0	0.00013	0.00017
$\beta^{(1)}_{BH,Cl}$	0.21452	−5875.10	−36.291	0.05613	0.00063
$C_{BH,Cl}$	−0.000693	251.30	1.775	−0.00313	0.000013
$\lambda_{B,B}$	0.02617	−1692.47	−10.151	0.01524	0.00036
$\mu_{B,B,B}$	−0.003707	−95.29	−0.854	0.00175	0.000031
$\theta_{Na,BH}$	−0.00055	−17353.52	−118.9707	0.20310	0.00057
$\psi_{Na,BH,Cl}$	−0.00095	3920.10	27.114	−0.04657	0.00040
$L_{B,BH,Cl}$	−0.02747	2899.40	20.379	−0.03546	0.00028
$L_{B,Na,Cl}$	0.02067	2475.34	17.384	−0.03045	0.00016
pK_B	8.0610	998.20	−13.308	0.02785	0.00022

Table 5. Thermodynamic constants of dissociation of TRIS · H^+ at 25 °C

Method of determination	ΔG°	ΔH°	ΔS°	ΔC_p°
	J mol^{-1}		J mol^{-1} deg^{-1}	
E.m.f. method[11]	46075	47600	5.1	−64
E.m.f. method[14]	46058	47400	4.5	91
Calorimetry[16]	—	47480	4.7	—
Pitzer method *(this work)*	46011	47675	5.6	−63

the buffer system, for the described experimental conditions[13] the association effect should appear in the product $gm_{BH}\beta^{(2)}_{BH,Cl}$, whose contribution to e.m.f. is insignificant because the g value rapidly tends to zero with an increase in the overall ionic strength of the solution, *i.e.*, the KCl concentration. Thus, our conclusion about the associative character of interaction in the solution of TRIS · HCl—H_2O agrees with the published data[11] and does not contradict the results obtained later.[10,13]

It is seen in Tables 2 and 3 that the interaction parameters of the TRIS—TRIS · HCl—NaCl—H_2O system are monotonic functions of the temperature. Their temperature dependence was approximated by equations in the form

$$y = a_0 + a_1(1/T - 1/T_r) + a_2\ln(T/T_r) + a_3(T - T_r), \quad (5)$$

where T_r = 298.15. The character of Eq. (5) is based on the assumption that the temperature dependence of the heat capacity of the solution is linear. The coefficients of Eq. (5) obtained by the least-squares method are presented in Table 4 as well as the root-mean-square deviations of the experimentally found parameters from the values calculated by Eq. (5). The $E_A^{0'}$ values presented in Tables 2 and 3 make it possible to directly determine the dissociation constant of TRIS · H^+

$$\text{TRIS} \cdot H^+ \rightleftharpoons \text{TRIS} + H^+. \quad (6)$$

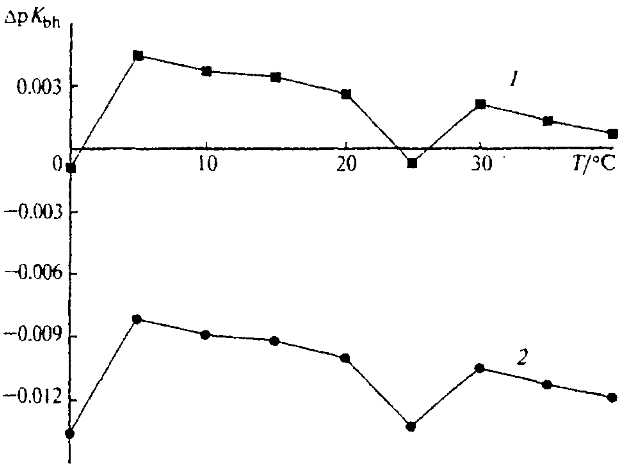

Fig. 1. Divergences between the pK_{bh} values obtained ignoring the association of TRIS · HCl (*1*) and using the additional fitting parameter $\beta^{(2)}_{BH,Cl}$ that takes into account the association of TRIS · HCl (*2*).[11]

Using the empirical equation[14] for the temperature dependence of the standard potential of the silver-chloride electrode and the obtained $E_A^{0'}$ values, we calculated pK_{bh} ($-\log K_{bh}$) (see Tables 2 and 3). The results of our calculations and the published data[11] agree well when association is not taken into account (Fig. 1). The maximum divergence is ~0.004 at 5 °C and almost disappears at 40 °C. However, the introduction of the additional parameter $\beta^{(2)}_{BH,Cl}$ results in a noticeable systematic divergence of ~0.01 pK units.

The temperature dependence of pK_{bh} was also approximated by Eq. (5) (the coefficients are presented in Table 4). The thermodynamic properties (the Gibbs energy, enthalpy, entropy, and heat capacity) for the dissociation of TRIS · H^+ can be calculated by this equation. The results of these calculations for 25 °C and the published data are presented in Table 5. Our results better agree with the data obtained using the Debye—Hückel theory[11] than with the results obtained by the e.m.f. method[13] and calorimetry.[15]

The concentration constant K^* is determined by the expression

$$K^* = K_{bh}\gamma_{BH}/(\gamma_H\gamma_B), \quad (7)$$

where γ_H is the activity coefficient of the hydrogen ion. The concentration constants of equilibrium (6) were measured[16] by potentiometric titration at 25 °C. For the experimental conditions[16] (at the point of equivalence m_{BH} = 0.01), we calculated the pK^* values using the parameters of interaction of the components of the buffer system (see Table 3) and the parameters of the hydrogen ion.[9] The calculated pK^* values are excellently consistent with the results of titration (Fig. 2). It has been mentioned previously[17] that the pK^* value extrapolated to the zero molality of NaCl is higher than the thermodynamic pK value by 0.027 pK units. For moderate and high concentrations, the dependence of pK^* on the NaCl molality is primarily determined by

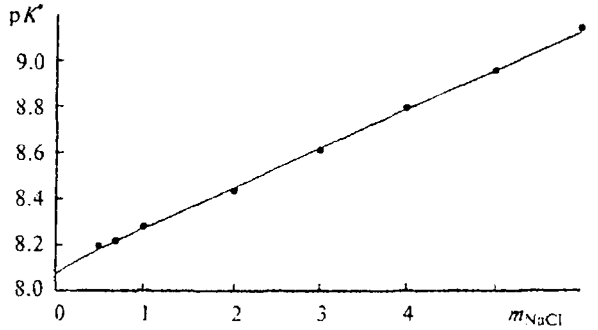

Fig. 2. Comparison of the measured[16] pK^* values of dissociation of TRIS · H^+ in a solution of NaCl (points) with those calculated by the Pitzer method using the parameters in Table 3 (solid line).

the ion interaction parameters $L_{B,Na,Cl}$ and $\theta_{Na,BH}$, which are the coefficients at the linear term. In the low-concentration region, the Debye—Hückel equation plays a noticeable role in the non-ideal behavior of the acid-base forms. As follows from correlation (7), this equation does not contribute to the pK^* value. In other words, retention of the linearity at low concentrations for the dependence of pK^* on m_{NaCl} should be expected, but this does not occur. Moreover, an additional empirical term that takes into account the dependence of pK^* on m_{NaCl} in the region of low concentrations has been introduced in Ref. 16. This indicates the existence of an additional interaction named by us as ion association, which becomes noticeable only in dilute solutions.

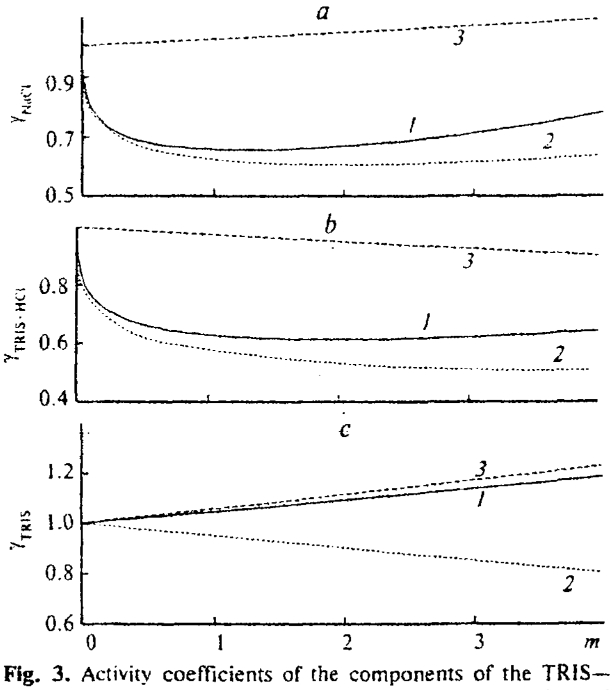

Fig. 3. Activity coefficients of the components of the TRIS—TRIS · HCl—NaCl—H_2O system γ_{NaCl} (*a*), $\gamma_{TRIS \cdot HCl}$ (*b*), and γ_{TRIS} (*c*) in solutions of NaCl (*1*), TRIS · HCl (*2*), and TRIS (*3*).

The influence of the components of the TRIS—TRIS · HCl—NaCl—H_2O buffer system on their activity coefficients is illustrated in Fig. 3. The activity coefficients of NaCl in solutions of TRIS and those of TRIS in solutions of NaCl are higher than unity (see Fig. 3, *a*, *c*), which indicates a "salting out" effect of NaCl on TRIS. The opposite character of the interaction of TRIS · HCl with TRIS molecules appears in mixed solutions, where their activity coefficients become <1. The activity coefficients of the TRIS · HCl electrolyte in neat solutions decrease in the whole concentration range, which confirms the assumption about association in these solutions.

Presently, three types of ion association in solutions are known. Association due to the Coulomb interaction of multicharged ions, for example, in solutions of $MgSO_4$, is most abundant. Polyatomic ions exhibiting donor-acceptor properties with respect to a proton are capable of association due to hydrogen bonds.[6] In a solution of TRIS · HCl—H_2O, this ion is TRIS · H^+. If these cations are associated with each other, the virial coefficient $\lambda^{(2)}_{BH,BH}$ should have a greater negative value. According to the correlations

$$\beta_{BH,Cl} = \lambda_{BH,Cl} + 0.5\lambda_{BH,BH} + 0.5\lambda_{Cl,Cl},$$

$$\theta_{Na,BH} = \lambda_{Na,BH} - 0.5\lambda_{BH,BH} - 0.5\lambda_{Na,Na},$$

this effect appears simultaneously in two experimentally measured parameters $\beta^{(2)}_{BH,Cl}$ and $\theta^{(2)}_{Na,BH}$. In fact, we obtained a negative value ($\beta^{(2)}_{BH,Cl} = -1.93$), but the introduction of $\theta^{(2)}_{Na,BH}$ to the processing of the second series of experiments with cell *B* gave a $\theta^{(2)}_{Na,BH}$ value close to zero and did not improve the agreement between the experimental and theoretical results. It is most likely that the structure of the TRIS · H^+ ion contains intramolecular hydrogen bonds, as assumed previously,[17] and no intermolecular bonds. Therefore, we attribute the observed weak association in solutions of TRIS · HCl—H_2O to "localized hydrolysis." [18,19] In this case, association between the cations and anions occurs through the intermediate H_2O molecule. This association appears only as a change in the $\beta^{(2)}_{BH,Cl}$ parameter due to changing the virial interaction coefficient $\lambda_{BH,Cl}$.

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