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Electromotive Force Measurements and Thermodynamic Modelling of Sodium Chloride in Aqueous-Alcohol Solvents

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1. Introduction

In chemical engineering, the liquid extraction plays an important role as a separation process. In the conventional solvent extraction, the addition of salts generally increases the distribution coefficients of the solute and the selectivity of the solvent for the solute. Processes with mixed solvent electrolyte systems include regeneration of solvents, extractive crystallization, and liquid–liquid extraction for mixtures containing salts. For instance, combining extraction and crystallization allowed effective energy-saving methods to be created for the isolation of salts from mother liquors (Taboada et al., 2004), and combining extraction with salting out and distillation led to a new method for separating water from isopropanol (Zhigang et al., 2001). Every year a great financial support is required for conceptual design, process engineering and construction of chemical plants (Chen, 2002). Chemical engineers perform process modeling for the cost optimization. Success in that procedure is critically dependent upon accurate descriptions of the thermodynamic properties and phase equilibria of the concerned chemical systems.

So there is a great need in systematic experimental studies and reliable models for correlation and prediction of thermodynamic properties of aqueous–organic electrolyte solutions. Several thermodynamic models have been developed to represent the vapor–liquid equilibria in mixed solvent–electrolyte systems. Only a few studies have been carried out concerning solid–liquid, liquid–liquid and solid–liquid-vapor equilibrium calculations. The lists of relevant publications are given in the reviews of Liddell (Liddell, 2005) and Thomsen (Thomsen et al., 2004); some problems with the description of phase equilibria in systems with strong intermolecular interactions are discussed in the same issues. Among the problems are poor results for the simultaneous correlation of solid – liquid – vapor equilibrium data with a single model for the liquid phase. This failure may be due to the lack of reliable experimental data on thermodynamic properties of solutions in wide ranges of temperatures and compositions. Model parameters were determined only from the data on the phase equilibrium conditions in attempt to solve the inverse thermodynamic problem, which, as is known, may be ill-posed and does not have a unique solution (Voronin, 1992). Hence, the introduction of all types of experimental data is required to obtain a credible thermodynamic model for the estimation of both the thermodynamic functions and equilibrium conditions. One of the most reliable methods for the

determination of the activity coefficients of salts in solutions is the Method of Electromotive Force (EMF).
The goal of this work is to review the results of our investigations and literature data about EMF measurements with ion-selective electrodes for the determination of the partial properties of some salts in water-alcohol mixtures. This work is part of the systematic thermodynamic studies of aqueous-organic solutions of alkali and alkaline-earth metal salts at the Laboratory of Chemical Thermodynamics of the Moscow State University (Mamontov et al., 2010; Veryaeva et al., 2010; Konstantinova et al., 2011).

2. Ion-selective electrodes in the thermodynamic investigations

The measurement of the thermodynamic properties of aqueous electrolyte solutions is a part of the development of thermodynamic models and process simulation. There are three main groups of experimental methods to determine thermodynamic properties, i.e., calorimetry, vapour pressure measurements, and EMF measurements. The choice of the method is determined by the specific properties of the studied objects, and purposes which are put for the researcher. EMF method and its application for thermodynamic studies of metallic and ceramic systems has been recently discussed in detail by Ipser et al. (Ipser et al., 2010). The use of this technique in the thermodynamics of electrolyte solutions is described in many books and articles. In this paper we focus on the determination of partial and integral functions of electrolyte solutions using electrochemical cells with ion-selective electrodes (ISE).
Some background information on ISE may be found in Wikipedia. According to the definition given there an ion-selective electrode is a transducer (or sensor) that converts the activity of a specific ion dissolved in a solution into an electrical potential, which can be measured by a voltmeter or pH meter. The voltage is theoretically dependent on the logarithm of the ionic activity, according to the Nernst equation. The main advantages of ISE are good selectivity, a short time of experiment, relatively low cost and variety of electrodes which can be produced.
The principles of ion-selective electrodes operation are quite well investigated and understood. They are detailed in many books; for instance, see the excellent review of Wroblewski (http://csrg.ch.pw.edu.pl/tutorials/ise/). The key component of all potentiometric ion sensors is an ion-selective membrane. In classical ISEs the arrangement is symmetrical which means that the membrane separates two solutions, the test solution and the inner solution with constant concentration of ionic species. The electrical contact to an ISE is provided through a reference electrode (usually Ag/AgCl) implemented in the internal solution that contains chloride ions at constant concentration. If only ions penetrate through a boundary between two phases – a selective membrane, then as soon as the electrochemical equilibrium will be reached, the stable electrical potential jump will be formed. As the equilibrium potential difference is measured between two identical electrodes placed in the two phases we say about electromotive force. Equilibrium means that the current of charge particles from the membrane into solution is equal to the current from the solution to the membrane, i.e. a potential is measured at zero total current. This condition is only realized with the potentiometer of high input impedance (more than 10^{10} Ohm). In the case of the ion selective electrode, EMF is measured between ISE and a reference electrode, placed in the sample solution. If the activity of the ion in the reference phase (a_{ref}) is kept constant, the unknown activity of component in solution under investigation (a_X) is related to EMF by Nernst equation :

$$E = E_0 + \frac{RT}{nF}\ln\frac{a_X}{a_{ref}} = const + S\log a_X\,, \tag{1}$$

where E_0 is a standard potential, S is co-called, Nernst slope, which is equal to $59.16/n$ (mV) at 298.15 K and n - the number of electrons in Red/Ox reaction or charge number of the ion X (z_X). Ions, present in the sample, for which the membrane is impermeable, will have no effect on the measured potential difference. However, a membrane truly selective for a single type of ions and completely non-selective for other ions does not exist. For this reason the potential of such a membrane is governed mainly by the activity of the primary ion and also by the activity of other ions. The effect of interfering species Y in a sample solution on the measured potential difference is taken into consideration in the Nikolski-Eisenman equation:

$$E = const + S\log\left(a_X + K_{XY}a_Y^{\frac{z_X}{z_Y}}\right), \tag{2}$$

where a_Y is the activity of ion Y, z_Y its charge number and K_{xy} the selectivity coefficient (determined empirically). The values of these coefficients for ISE are summarized, for example, in the IUPAC Technical Reports (Umezawa et al., 2000, 2002).

The properties of an ion-selective electrode are characterized by parameters like selectivity, slope of the linear part of the measured calibration curve of the electrode, range of linear response, response time and the temperature range. Selectivity is the ability of an ISE to distinguish between the different ions in the same solution. This parameter is one of the most important characteristics of an electrode; the selectivity coefficient K_{XY} is a quantative measure of it. The smaller the selectivity coefficient, the less is the interference of the corresponding ion. Some ISEs cannot be used in the presence of certain other interfering ions or can only tolerate very low contributions from these ions. An electrode is said to have a Nernstian response over a given concentration range if a plot of the potential difference (when measured against a reference electrode) versus the logarithm of the ionic activity of a given species in the test solution, is linear with a slope factor which is given by the Nernst equation, i.e. $2.303RT/nF$. The slope gets lower as the electrode gets old or contaminated, and the lower the slope the higher the errors on the sample measurements. Linear range of response is that range of concentration (or activity) over which the measured potential difference does not deviate from that predicted by the slope of the electrode by more that ± 2 mV. At high and very low ion activities there are deviations from linearity; the range of linear response is presented in ISE passport (typically, from 10^{-5} M to 10^{-1} M). Response time is the length of time necessary to obtain a stable electrode potential when the electrode is removed from one solution and placed in another of different concentration. For ISE specifications it is defined as the time to complete 90% of the change to the new value and is generally quoted as less than ten seconds. In practice, however, it is often necessary to wait several minutes to complete the last 10% of the stabilization in order to obtain the most precise results. The maximum temperature at which an ISE will work reliably is generally quoted as 50°C for a polymeric (PVC) membrane and 80°C for crystal or 100^0C for glass membranes. The minimum temperature is near 0°C.

The three main problems with ISE measurements are the effect of interference from other ions in solution, the limited range of concentrations, and potential drift during a sequence of measurements. As known, the apparent selectivity coefficient is not constant and depends

on several factors including the concentration of both elements, the total ionic strength of the solution, and the temperature. To obtain the reliable thermodynamic information from the results of EMF measurements it's necessary to choose certain condition of an experiment to avoid the interference of other ions. The existence of potential drift can be observed if a series of standard solutions are repeatedly measured over a period of time. The results show that the difference between the voltages measured in the different solutions remains essentially the same but the actual value generally drifts in the same direction by several millivolts. One way to improve the reliability of the EMF measurements is to use multiple independent electrodes for the investigation the same solution.

Due to the limited size of this manuscript we cannot describe in detail the history of ISE and their applications in physical chemistry. For those interested, we recommend to read the reviews (Pungor, 1998; Buck & Lindner, 2001; Pretsch, 2002; Bratov et al., 2010). The application of ion-selective electrodes in nonaqueous and mixed solvents to thermodynamic studies was reviewed by Pungor et al (Pungor et al., 1983), Ganjali and co-workers (Ganjali et al., 2007) and Nakamura (Nakamura, 2009). In the end of the XX-th century the results of systematic thermodynamic investigations with ISEs were intensively published by Russian (St. Petersburg State University and Institute of Solution Chemistry, Russian Academy of Sciences) and Polish scientists from the Lodz University. At the present time the systematic and abundant publications in this branch of science belong to the Iranian investigators (Deyhimi et al., 2009; 2010). The latter group are specialized in the development of many sensors, and particularly, carrier-based solvent polymeric membrane electrodes for the determination of activity coefficients in mixed solvent electrolyte solutions. Studies of the thermodynamic properties of salts in mixed electrolytes by EMF are also being conducted by Portuguese, Chinese and Chilean scientists.

3. Thermodynamic models for mixed solvent–electrolyte systems

It is well known that nonideality in a mixed solvent–electrolyte system can be handled using expression for the excess Gibbs energy (G^{ex}, J). According to Lu and Maurer (Lu & Maurer, 1993), thermodynamic models for aqueous electrolytes and electrolytes in mixed solvents are classified as either physical or chemical models. The former are typically based on extensions of the Debye–Hückel equation, the local composition concept, or statistical thermodynamics. As some examples of first group of models should be mentioned the Pitzer model (Pitzer & Mayorga, 1973) and its modifications - Pitzer-Simonson (Pitzer & Simonson, 1986) and Pitzer-Simonson-Clegg (Clegg & Pitzer, 1992); eNRTL (Chen et al., 1982; Mock et al., 1986) and its variants developed by scientists at Delft University of Technology (van Bochove et al., 2000) or Wu with co-workers (Wu et al., 1996) and Chen et al (Chen et al., 2001; Chen & Song, 2004); eUNIQUAC (Sander et al., 1986; Macedo et al., 1990; Kikic et al. 1991; Achard et al. , 1994). The alternative chemically based models assume that ions undergo solvation reactions. The most important examples of that group of thermodynamic models are model of Chen (Chen et al, 1999) and chemical models have been proposed by Lu and Maurer (1993), Zerres and Prausnitz (1994), Wang (Wang et al., 2002; 2006) and recently developed COSMO-SAC quantum mechanical model, a variation of COSMO-RS (Klamt, 2000; Lin & Sandler, 2002). The detailed description of those models is given in original papers, the brief reviews are presented by Liddell (Liddell, 2005) and Smirnova (Smirnova, 2003). According to Chen (Chen, 2006), the perspective models of electrolytes in mixed solvents would require no ternary parameters, be formulated in the

concentration scale of mole fractions, represent a higher level of molecular insights, and preferably be compatible with existing well-established activity coefficient models.
The excess Gibbs free energy per mole of real solution comprises three (sometimes, four) terms

$$G^{ex} = G^{ex,\,lr} + G^{ex,\,sr} + G^{ex,\,Born}. \tag{3}$$

The first term represents long range (lr) electrostatic forces between charged species. Usually the unsymmetric Pitzer-Debye-Hückel (PDH) model is used to describe these forces. The second contribution represents the short-range (sr) Van der Waals forces between all species involved. The polynomial or local composition models, based on reference states of pure solvents and hypothetical, homogeneously mixed, completely dissociated liquid electrolytes are applied to represent a short-range interactions. The model is then normalized by infinite dilution activity coefficients in order to obtain an unsymmetric model. And the third term is a so-called the Born or modified Brönsted–Guggenheim contribution. The Born term is used to account for the Gibbs energy of transfer of ionic species from an infinite dilution state in a mixed solvent to an infinite dilution state in the aqueous phase; for the electrolyte MX of 1,1-type:

$$\frac{G^{ex,Born}}{RT} = \frac{x_{MX}e^2}{8\pi\varepsilon_0 k_B T}\left(\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_w}\right)\left(\frac{1}{r_M} + \frac{1}{r_X}\right) \tag{4}$$

where ε_s and ε_w are the relative dielectric constants of the mixed solvent and water, respectively, ε_0 is the electric constant, k_B is the Boltzmann constant and r_M, r_X are the Born radii of the ions (Rashin&Honig, 1985), e is the electron charge. With the addition of the Born term, the reference for each ionic species will always be the state of infinite dilution in water, disregarding the composition of the mixed solvent.
The most frequently and successful model used to describe the thermodynamic properties of aqueous electrolyte solutions is the ion interaction or virial coefficient approach developed by Pitzer and co-workers (Pitzer & Mayorga, 1973). In terms of Pitzer formalizm, the mean ionic activity coefficient of the 1,1-electrolyte in the molality scale ($\gamma_\pm$) is determined according to the following equation:

$$\ln(\gamma_\pm) = -A_\phi\left[\frac{m^{1/2}}{1+1.2m^{1/2}} + \frac{2}{1.2}\ln\left(1+1.2m^{1/2}\right)\right] + B^{\gamma}_{MX}m + C^{\gamma}_{MX}m^2, \tag{5}$$

$$A\phi = \frac{\left(2\pi\rho_s N_A\right)^{1/2}}{3}\left(\frac{e^2}{4\pi\varepsilon_0\varepsilon k_B T}\right)^{3/2}, \tag{5a}$$

$$B^{\gamma}_{MX} = 2\beta^{(0)}_{MX} + \frac{\beta^{(1)}_{MX}}{2m}\left[1-\exp\left(-2m^{1/2}\right)\left(1+2m^{1/2}-2m\right)\right],\ C^{\gamma}_{MX} = const, \tag{5b}$$

The osmotic coefficient (ϕ) of the solvent, the excess Gibbs energy (G^{ex}), and the relative (excess) enthalpy of the solution (L), can be calculated as:

$$1-\phi = A_\phi\left[\frac{m^{1/2}}{1+1.2m^{1/2}}\right] - m\left[\beta_{\mathrm{MX}}^{(0)} + \beta_{\mathrm{MX}}^{(1)}\exp\left(-2m^{1/2}\right)\right] - \frac{2}{3}C_{\mathrm{MX}}^{\gamma}m^2, \tag{6}$$

$$G^{ex} = 2n_s mRT\left(1-\phi+\ln\left(\gamma_\pm\right)\right), \tag{7}$$

$$\begin{aligned} L &= -T^2\left(\partial\left(G^{ex}/T\right)/\partial T\right)_{p,m} = 2mRT^2\left(\left(\partial\phi/\partial T\right)_{p,m} - \left(\partial\ln\left(\gamma_\pm\right)/\partial T\right)_{p,m}\right) = \\ &= 2mRT^2\left[\begin{array}{l}\left(\frac{\partial A_\phi}{\partial T}\right)_{p,m}\left(\frac{2}{1.2}\ln\left(1+1.2m^{1/2}\right)\right) - m\left(\frac{\partial\beta_{\mathrm{MX}}^{(0)}}{\partial T}\right)_{p,m} + \\ +\frac{1}{2}\left(\frac{\partial\beta_{\mathrm{MX}}^{(1)}}{\partial T}\right)_{p,m}\left(\exp\left(-2m^{1/2}\right)\left(1+2m^{1/2}\right)-1\right) + \frac{m^2}{2}\left(\frac{\partial C_{\mathrm{MX}}^{\gamma}}{\partial T}\right)_{p,m}\end{array}\right]. \end{aligned} \tag{8}$$

In the above equations, A_ϕ is the Debye–Hückel coefficient for the osmotic function, ρ_s is the density of solvent, N_A is the Avogadro's number, n_s is the weight of the solvent (kg), M_s is the molar mass of the solvent (g·mol^{-1}), $\beta_{\mathrm{MX}}^{(0)}$, $\beta_{\mathrm{MX}}^{(1)}$, and C_{MX}^{γ} are model parameters characterizing the binary and ternary interactions between ions in the solution. The densities and dielectric constants of the mixed solvent can be obtained experimentally or calculated in the first approximation as (Smirnova, 2003)

$$\rho_s = \rho_n\frac{M_s}{\left(\sum_n x_n' M_n\right)},\ \varepsilon_s = \sum_n \varphi_n\varepsilon_n \tag{9}$$

where x_n' is the salt-free mole fraction of solvent n in the solution, V_n is the molar volume of the pure solvent n, φ_n is the volume fraction of solvent n. Molar mass and the volume fraction of the mixed solvent are represented as

$$M_s = \sum_n x_n' M_n,\ \varphi_n = \frac{x_n' V_n}{\sum_m x_m' V_m} \tag{10}$$

The Pitzer model is widely used but it has some drawbacks: (a) it requires both binary and ternary parameters for two-body and three-body ion–ion interactions; (b) the Pitzer model has the empirical nature, as a result there are some problems with the description of temperature dependences of binary and ternary parameters; (c) it is formulated in the basis of the concentration scale of molality. In practice, the Pitzer model and other similar molality-scale models can only be used for dilute and middle concentration range of aqueous electrolyte systems. Pitzer, Simonson and Clegg (Pitzer & Simonson, 1986; Clegg & Pitzer, 1992) proposed a new version of the Pitzer model, developed at the mole fraction base that can be applied to concentrations up to the pure fused salt for which the molality is infinite. The short-range force term is written as the Margules expansion:

$$\frac{G^{\mathrm{ex,\,sr}}}{RT} = \sum_j\sum_i x_i x_j\left[w_{ij} + u_{ij}(x_i - x_j)\right] + \sum_k\sum_j\sum_i x_i x_j x_k C_{ijk} - \frac{G_S^0}{RT}, \tag{11}$$

where w_{ij}, u_{ij}, and C_{ijk} are binary and ternary interaction coefficients, respectively, x_i is the mole fraction of the species i in the mixture. The last term in Eq.(11) is introduced to account various possible types of reference states for electrolyte in solution - pure fused salt and state of infinite dilution. The contribution from the long-range forces, i.e. Debye–Hückel interactions, is given by

$$\frac{G_{DH}^{ex}}{RT} = -\frac{4A_x I_x}{\rho}\ln\left(\frac{1+\rho I_x^{1/2}}{1+\rho\left(I_x^0\right)^{1/2}}\right) + \sum_M\sum_X x_M x_X B_{MX} g(\alpha I_x^{1/2}), \tag{12}$$

$$\text{with } g(y) = 2\left[1-(1+y)e^{-y}\right]/y^2 \tag{12a}$$

In the above equations x_M, x_X are molar fractions of ionic species in solution; A_x is the Debye–Hückel coefficient for the osmotic function at the molar fraction basis ($A_x = A_\phi / M_s^{1/2}$); I_x is the ionic strength on the mole fraction basis which, for single-charged ions, I_x = 0.5(x_M + x_X); I_x^0 is the ionic strength of solution in a standard state of the pure fused salt, it approaches 0 at infinite dilution for the asymmetric reference state. The parameter ρ is equivalent to the distance of closest approach in the Debye–Hückel theory, both parameters, ρ and α, in Eq.(12) are equal to 13 for 1,1-electrolyties. B_{MX} is a specific parameter for each electrolyte. For a mixture of two neutral species, 1 and 2, and a strong 1:1 electrolyte MX with the reference state of infinite dilution, the contributions of the short and long-range force terms to the mean ionic activity coefficient of the electrolyte MX, at the mole fraction basis can be written as follows:

$$\ln\gamma_x = \ln\gamma_x^{sr} + \ln\gamma_x^{DH}, \tag{13}$$

$$\ln\gamma_x^{DH} = -A_x\left[\frac{2}{\rho}\ln(1+\rho\sqrt{I_x}) + \frac{(1-2I_x)\sqrt{I_x}}{1+\rho\sqrt{I_x}}\right] + x_X B_{MX} g(\alpha\sqrt{I_x}) - \\ - x_M x_X B_{MX}\left[\frac{g(\alpha\sqrt{I_x})}{2I_x} + \left(1-\frac{1}{2I_x}\right)e^{-\alpha\sqrt{I_x}}\right], \tag{13a}$$

$$\ln\gamma_x^{sr} = \frac{x_1 x_2}{f^2}\left\{\left(1-f^2\right)w_{12} + 2\left(x_1-x_2\right)\frac{1-f^3}{f}u_{12} + \left[\left(1-2x_I\right)f^2-1\right]Z_{12MX}\right\} + \\ + \frac{f^2-1}{f}\left(x_1 W_{1MX} + + x_2 W_{2MX}\right) + \frac{x_1}{3f^2}\left[f^3\left(2-2x_1+x_I\right) + x_I f^2\left(3x_1+x_2\right) - 2x_2\right]U_{1MX} + \\ + \frac{x_2}{3f^2}\left[f^3\left(2-2x_2+x_I\right) + + x_I f^2\left(3x_2+x_1\right) - 2x_1\right]U_{2MX} \tag{13b}$$

In the above equations x_I = 2x_M = 2x_X = 1- x_1 - x_2, f = 1 - x_I; w_{12} and u_{12} are model parameters for the binary system (solvent 1 and solvent 2), W_{iMX} and U_{iMX} are model parameters for the binary system - solvent i with MX (i = 1 or 2), Z_{12MX} is a model parameter which accounts for the triple interaction. Formula details can be found in (Lopes et al, 2001).

The approximation of the experimental data in the present study was carried out with the Pitzer and Pitzer-Simonson models. The result of this investigation can be used in future for the development of a new thermodynamic models and verification of existing ideas.

4. EMF measurements of galvanic cells with ternary solutions NaCl – H_2O – $C_nH_{2n+1}OH$ (n = 2-5). Experimental procedure

Sodium chloride (reagent grade, 99.8%) was used in experiments. The salt was additionally purified by the double crystallization of NaCl during evaporation of the mother liquor. The purified salt was dried *in vacuo* at 530 K for 48 h. The isomers of alcohol were used as organic solvents: C_2H_5OH (reagent grade, 99.7%), *1*-C_3H_7OH (special purity grade, 99.94 %), *iso*-C_3H_7OH (reagent grade, 99.2%), *1*-C_4H_9OH (special purity grade, 99.99%) and *iso*-C_4H_9OH (reagent grade, 99.5%), *1*-$C_5H_{11}OH$ (reagent grade, 99.6%) and *iso*-$C_5H_{11}OH$ (reagent grade, 99.5%). To remove moisture, the alcohols were kept on zeolites 4A for 7 days and then distilled under the atmospheric pressure. The purity of alcohols was confirmed by the agreement of the measured boiling points of the pure solvents at atmospheric pressure and the refractive indices with the corresponding published data. Deionized water with a specific conductance of 0.2 μS cm^{-1} used in experiments was prepared with a Millipore Elix filter system.

Electrochemical measurements were carried out with the use of solutions of sodium chloride in mixed water-organic solvents at a constant water-to-alcohol weight ratio. The reagents were weighed on a Sartorius analytical balance with an accuracy of ±0.0005 g. A sample of the NaCl was transferred to a glass cell containing ~30 g of a water-alcohol solution. The cell was tightly closed with a porous plastic cap to prevent evaporation of the solution. The cell was temperature-controlled in a double-walled glass jacket, in which the temperature was maintained by circulating water. The temperature of the samples was maintained constant with an accuracy of ±0.05 K. The solutions were magnetically stirred for 30 min immediately before the experiments. All electrochemical measurements were carried out in the cell without a liquid junction; the scheme is given below (I):

$$Na^+\text{-ISE} \mid NaCl(m)+H_2O(100-w_{alc})+(1\text{- or } iso\text{-})C_nH_{2n+1}OH(w_{alc}) \mid Cl^-\text{-ISE}, \quad (I)$$

where w_{alc} is the weight fraction of alcohol in a mixed solvent expressed in percentage and m is the molality of the salt in the ternary solution. Concentration cell (I) EMF measurements are related to the mean ionic activity coefficient by the equation

$$E = E_0 - \frac{2RT}{F}\ln(\gamma_{\pm} m). \quad (14)$$

An Elis-131 ion-selective electrode for chloride ions (Cl^--ISE) was used as the reference electrode. The working concentration range of the Cl^--ISE electrode at 293 K is from $3 \cdot 10^{-5}$ to 0.1 mol·L^{-1}; the pH of solutions should be in the range from 2 to 11. A glass ion-selective electrode for sodium ions (Na^+-ISE) served as the indicator electrode, which reversibly responds to changes in the composition of the samples under study. The ESL-51-07SR (Belarus) and DX223-Na^+ (Mettler Toledo) ion-selective electrodes were used in experiments. Different concentration ranges of solutions were detected by two glass electrodes. The concentration range for the ESL-51-07SR electrode at 293.15 K is from 10^{-4} to 3.2 mol·L^{-1}; the same for the Mettler electrode is lower (from 10^{-6} to 1 mol·L^{-1}). The results of

experiments performed with the use of two different ion-selective electrodes for Na^+ can be considered as independent. This increases the statistical significance of the EMF values and provides information on their correctness. The potential of the cell was measured with the use of the Multitest IPL-103 ionomer. The input impedance of the ionomer was at least 10^{12} Ohm.

The concentration range of the working solution was determined by two factors. According to the manufacturer, the sodium electrode was more sensitive to protons than to sodium ions and the interfering effect of hydrogen ions can be ignored if $[Na^+]/[H^+] > 3000$ in the solution under consideration (*i.e.*, at (pH – pNa) > 3.5). Therefore, the lower limit of molality in each series of solutions had to be no less than 0.03 mol·kg^{-1}. To meet the condition of solution homogeneity, the highest concentration of NaCl had to be no higher than the solubility of the salt in the mixed solvent. The widest ranges of concentration were investigated in the systems with ethanol and 1-(*iso*-)propanol. All studied systems belong to the class of systems with the top critical point; the area of existence of solutions narrows with temperature increasing. To maintain the homogeneity of mixtures, the concentration of the salt in solutions was kept no higher than the upper solubility limit of sodium chloride in a mixed solvent of a given composition. In each series of experiments successive measurements were carried out for samples with constant ratios of water/alcohol components and different molalities starting with the lowest concentration. The choice of composition range is illustrated at Fig.1 where the fragment of Gibbs-Roseboom triangle of H_2O-C_2H_5OH-NaCl system at 298.15 K is drawn.

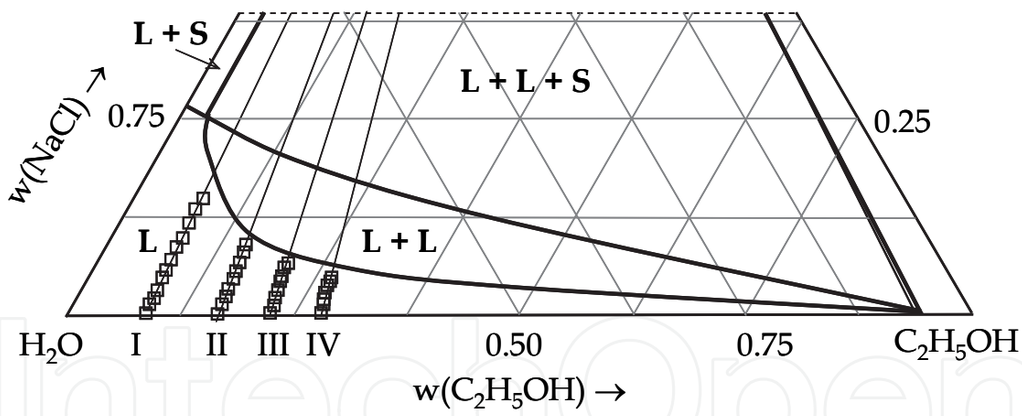


Fig. 1. Fragment of the isothermal (298.15 K) section of sodium chloride – water – ethanol system. Symbols correspond to composition of solutions under investigation. Numbers I, II, III and IV are denoted to solutions with fixed water-alcohol ratio.

Symbols are met the case of real experiment with various sodium chloride molality and constant water-to-alcohol ratios. The symbols L and S denote the Liquid and Solid phases of the ternary system. Each series of solutions was studied at two or three temperatures. The EMF values of the cell were assumed to be equilibrium if the rate of the drift in EMF was no higher than 0.01-0.02 mV·min^{-1}. The equilibrium was established less than 30 min. The constancy of the composition of the solution was confirmed by the fact that the refractive indices measured before and after electrochemical experiments remained practically

coincided. It appeared that a change in the weight fraction of the organic solvent during experiments was at most 0.06 wt.%.

In the first step, the operation of the electrochemical cell (I) containing an aqueous sodium chloride solution (w_{alc} = 0) was tested at 288.15, 298.15, and 318.15 K. The mean ionic activity coefficients of NaCl are consistent with the published data (Silvester & Pitzer, 1977; Truesdell, 1968; Pitzer & Mayorga, 1973; Lide, 2007-2008) within an experimental error. In the second step, electrochemical measurements with the use of sodium chloride solutions in water-alcohol solvents were carried out at various temperatures. Each composition was measured at least two times using the ISE-Na^+ and ISE-Cl^- ion-selective electrodes.

5. Thermodynamic properties of solutions in the NaCl – H_2O – $C_nH_{2n+1}OH$ (n = 2-5) system

5.1 The mean ionic activity coefficient of the sodium chloride in the ternary solutions

The temperature-concentration dependence of the mean ionic activity coefficient of NaCl was approximated using the Pitzer and Pitzer-Simonson model for 1:1 electrolytes. As mentioned above, the electromotive force of the electrochemical cell (I) is related to the activity coefficient of the salt by Eq.(14). In the present work the mean ionic activity coefficient of the salt was calculated with the asymmetric normalization, in which a mixed solvent with a fixed water-to-alcohol ratio and the extremely dilute sodium chloride solution in this mixed solvent served as the standard state of the components of the solutions. The Debye–Hückel coefficient for the osmotic function (A_ϕ) was calculated by Eq. (5a) taking into account the experimental data on the densities and dielectric constants of water and the alcohols in the temperature range under consideration, which were published in (Bald et al., 1993; Frenkel et al., 1998; Balaban et al., 2002; Lide, 2007-2008; Pol & Gaba, 2008; Omrani et al., 2010). The A_ϕ values used for each composition of the solvent at different temperatures are given in Table 1.

The numerical values of the parameters E_0, $\beta^{(0)}_{NaCl}$, $\beta^{(1)}_{NaCl}$, and C^{γ}_{NaCl} were determined by the approximation of the experimental EMF values for each series of measurements. For all the solutions under consideration, the parameter C^{γ}_{NaCl} was insignificant and the error in its determination was higher than the absolute value. Hence, we assumed C^{γ}_{NaCl} = 0. It's known that the term C^{γ}_{NaCl} in Eq. (5) makes a considerable contribution only at high concentrations of the electrolyte, so this approach is valid for systems characterized by a narrow range of the existence of ternary solutions.

The calculated Pitzer model parameters and the errors in their determination (rms deviations) for the aqueous solution of sodium chloride are given in Table 2. The rms dispersions for each series of experimental data are listed in the last column. The parameters of Eq. (5) and (14) are given with an excess number of significant digits to avoid the error due to the rounding in further calculations. As can be seen from the Table 2, the model descriptions of water-salt solutions in both cases are similar, parameters consist within errors. So all experimental data for ternary mixtures were described taking into account the parameters E_0, $\beta^{(0)}_{NaCl}$, and $\beta^{(1)}_{NaCl}$ (see Table 3). Some of those results were published earlier (Mamontov et al., 2010; Veryaeva et al., 2010), thermodynamic assessment of NaCl-H_2O-*1*(or *iso*-)C_4H_9OH system is published in the Fluid Phase Equilibria journal (Konstantinova et al., 2011)

System	w_{Alc}, wt. %	A_ϕ		
		288.15 K	298.15 K	318.15 K
NaCl – H_2O	0	0.3856	0.3917	0.4059
NaCl – H_2O - C_2H_5OH	9.99	0.4232	0.4300	0.4465
	19.98	0.4690	0.4770	0.4953
	39.96	0.5942	0.6047	0.6290
NaCl – H_2O – *1*-C_3H_7OH	9.82	-	0.4437	0.4631
	19.70	-	0.5121	0.5366
	29.62	-	0.6021	0.6339
	39.56	-	0.7231	0.7664
NaCl – H_2O – *iso*-C_3H_7OH	10.00	-	0.4466	-
	20.00	-	0.5207	-
	30.00	-	0.6191	-
	40.00	-	0.7528	-
	49.90	-	0.9373	-
	58.50	-	1.1581	-
NaCl – H_2O – *1*-C_4H_9OH	3.00	0.3958	0.4035	0.4204
	4.49	0.4024	0.4104	0.4279
	5.66	0.4079	0.4161	0.4359
NaCl – H_2O – *iso*-C_4H_9OH	3.00	0.3999	0.4119	0.4394
	4.50	0.4103	0.4231	0.4510
	5.66	0.4187	0.4315	0.4597
NaCl – H_2O – *1*-$C_5H_{11}OH$	2.00	0.3866	0.3929	-
NaCl – H_2O – *iso*-$C_5H_{11}OH$	2.00	0.3860	0.3926	-

Table 1. Debye–Hückel coefficients for the osmotic function in NaCl-H_2O-(*1-, iso-*) $C_nH_{2n+1}OH$ solutions.

T, K	$-E_0 \times 10^3$, V	$\beta^{(0)}_{NaCl}$, kg·mol^{-1}	$\beta^{(1)}_{NaCl}$, kg·mol^{-1}	C^{γ}_{NaCl}, kg^2·mol^{-2}	$s_0(E) \times 10^4$
288.15	113.7 ± 0.2	0.0766 ± 0.002	0.2177 ± 0.02	0	1.2
	113.4 ± 0.2	0.0653 ± 0.007	0.2672 ± 0.03	0.0037 ± 0.002	0.8
298.15	116.1 ± 0.3	0.0838 ± 0.002	0.2285 ± 0.03	0	1.6
	115.9 ± 0.3	0.0720 ± 0.010	0.2802 ± 0.05	0.0039 ± 0.003	1.2
318.15	123.3 ± 0.5	0.0891 ± 0.004	0.2621 ± 0.04	0	2.8
	123.1 ± 0.7	0.0780 ± 0.021	0.3109 ± 0.10	0.0036 ±0.007	2.6

Table 2. Pitzer parameters for solutions of sodium chloride in water.

w_{Alc}, wt. %	m, mol·kg^{-1}	T, K	$-E_0 \times 10^3$, V	$\beta^{(0)}_{NaCl}$, kg·mol^{-1}	$\beta^{(1)}_{NaCl}$, kg·mol^{-1}	$s_0(E) \times 10^4$
1	2	3	4	5	6	7
9.99 % C_2H_5OH	0.050 - 2.999	288.15	136.1 ± 0.4	0.0830 ± 0.003	0.1919 ± 0.04	2.0
		298.15	138.6 ± 0.6	0.0884 ± 0.004	0.2468 ± 0.05	2.8
		318.15	145.5 ± 0.8	0.0927 ± 0.006	0.2976 ± 0.07	4.3
19.98 % C_2H_5OH	0.050 - 2.998	288.15	158.3 ± 0.	0.0861 ± 0.004	0.1567 ± 0.04	2.5
		298.15	160.7 ± 0.6	0.0912 ± 0.004	0.2566 ± 0.05	2.7
		318.15	166.9 ± 0.7	0.0969 ± 0.005	0.3303 ± 0.06	3.9
39.96 % C_2H_5OH	0.050 - 2.000	288.15	203.2 ± 1	0.1109 ± 0.010	0.1165 ± 0.12	4.6
		298.15	205.1 ± 1	0.1204 ± 0.010	0.1714 ± 0.13	4.9
		318.15	212.6 ± 1	0.1189 ± 0.010	0.3497 ± 0.12	4.9
9.82 % *1*-C_3H_7OH	0.0485 - 3.002	298.15	151.9 ± 0.4	0.0877 ± 0.003	0.2352 ± 0.03	2.0
		318.15	159.6 ± 0.3	0.0955 ± 0.002	0.2432 ± 0.03	2.0
19.7 % *1*-C_3H_7OH	0.051 - 1.500	298.15	171.6 ± 0.2	0.0818 ± 0.003	0.2818 ± 0.02	1.0
		318.15	178.3 ± 0.4	0.0906 ± 0.006	0.3442 ± 0.04	2.0
29.62 % *1*-C_3H_7OH	0.049 - 1.199	298.15	190.5 ± 0.2	0.0955 ± 0.007	0.2703 ± 0.04	1.0
		318.15	197.4 ± 0.4	0.1073 ± 0.01	0.3955 ± 0.06	2.0
39.56 % *1*-C_3H_7OH	0.051 - 0.850	298.15	205.9 ± 0.3	0.0911 ± 0.01	0.5852 ± 0.04	1.0
		318.15	216.4 ± 0.5	0.1120 ± 0.02	0.6472 ± 0.09	2.0
10.0% *iso*-C_3H_7OH	0.050 - 3.000	298.15	151.4 ± 0.5	0.0810±0.02	0.3417 ± 0.09	3.2
20.0% *iso*-C_3H_7OH	0.050 - 2.500	298.15	179.9 ± 0.5	0.0859 ± 0.004	0.3290 ± 0.04	2.0
30.0% *iso*-C_3H_7OH	0.050 - 2.000	298.15	198.0 ± 0.3	0.0884 ± 0.004	0.4658 ± 0.03	1.4
40.0 % *iso*-C_3H_7OH	0.100 - 1.400	298.15	222.7 ± 0.5	0.0943 ± 0.007	0.6030 ± 0.06	1.0
49.9 % *iso*-C_3H_7OH	0.050 - 0.952	298.15	243.6 ± 0.6	0.0939 ± 0.02	1.0109 ± 0.09	2.0
58.5% *iso*-C_3H_7OH	0.050 - 0.710	298.15	270.5 ± 0.3	0.1266 ± 0.01	1.2882 ± 0.05	1.0
3.00 % *1*-C_4H_9OH	0.051 - 2.006	288.15	118.4 ± 0.4	0.0774 ± 0.004	0.2090 ± 0.04	1.6
		298.15	120.1 ± 0.4	0.0808 ± 0.004	0.2999 ± 0.03	1.5
		318.15	127.7 ± 0.6	0.0881 ± 0.006	0.3200 ± 0.05	2.5
4.49 % *1*-C_4H_9OH	0.049 – 1.248	288.15	121.4 ± 0.6	0.0763 ± 0.01	0.2032 ± 0.08	2.5
		298.15	123.8 ± 0.6	0.0939 ± 0.01	0.2246 ± 0.08	2.3
		318.15	130.8 ± 0.5	0.0903 ± 0.01	0.3146 ± 0.07	1.8
5.66 % *1*-C_4H_9OH	0.050 – 0.601	288.15	124.0 ± 0.4	0.0952 ± 0.04	0.1501 ± 0.15	2.0
		298.15	127.0 ± 0.4	0.1257 ± 0.03	0.1284 ± 0.11	1.4
		318.15	134.1 ± 0.8	0.0883 ± 0.06	0.3314 ± 0.22	2.3
3.00 % *iso*-C_4H_9OH	0.051 - 2.500	288.15	119.0 ± 0.6	0.0796 ± 0.006	0.1269 ± 0.06	2.8
		298.15	121.3 ± 0.5	0.0839 ± 0.005	0.2565 ± 0.05	2.6
		318.15	128.1 ± 0.8	0.0905 ± 0.007	0.3782 ± 0.08	4.2

w_{Alc}, wt. %	m, mol·kg^{-1}	T, K	$-E_0 \times 10^3$, V	$\beta^{(0)}_{NaCl}$, kg·mol^{-1}	$\beta^{(1)}_{NaCl}$, kg·mol^{-1}	$s_0(E) \times 10^4$
1	2	3	4	5	6	7
4.50 % *iso*-C_4H_9OH	0.049 – 1.799	288.15	1209 ± 0.3	0.0877 ± 0.004	0.1215 ± 0.03	1.2
		298.15	1242 ± 0.3	0.0917 ± 0.004	0.1976 ± 0.03	1.4
		318.15	1301 ± 0.5	0.0873 ± 0.007	0.3961 ± 0.05	2.0
5.66 % *iso*-C_4H_9OH	0.050 – 0.600	288.15	124.8 ± 0.3	0.0765 ± 0.02	0.2322 ± 0.07	0.9
		298.15	127.0 ± 0.3	0.0685 ± 0.02	0.3696 ± 0.07	0.9
		318.15	134.2 ± 0.5	0.0179 ± 0.03	0.6969 ± 0.12	1.6
2.00 % *1*-$C_5H_{11}OH$	0.050-0.600	288.15	114.7 ± 0.6	0.0376 ± 0.04	0.3142 ± 0.15	1.9
		298.15	117.6 ± 0.6	0.0762 ± 0.03	0.2634 ± 0.13	1.8
2.00 % *iso*-$C_5H_{11}OH$	0.050-0.650	288.15	114.8 ± 0.4	0.0598 ± 0.02	0.2772 ± 0.08	1.1
		298.15	117.3 ± 0.5	0.0768 ± 0.03	0.3012 ± 0.10	1.6

Table 3. Pitzer parameters for solutions of sodium chloride in water-alcohol solvent.

As an example, the variation of mean ionic activity coefficient versus the electrolyte molality and various mass fraction percents of ethanol-water mixed solvents at 298.15 K, are shown in Fig. 2 *a*. The calculated values of $\gamma_{\pm}$(NaCl) in mixed *1*-propanol-water solvent are represented by solid lines in Figs. 2 *b*. The transparent symbols correspond to the dependence of mean activity coefficient of the alcohol-free solution obtained in the present study. All the curves show a typical profile of the variation of $\gamma_{\pm}$ with concentrations that, as is well known, are governed by two types of interactions: ion–ion and ion–solvent. For a given temperature, the minimum value of mean ionic activity decreases with the increase of wt.% of alcohol. The trend is identical at other temperatures.

If the parameters of the thermodynamic model are defined the calculation of any thermodynamic function is a routine mathematical operation. For example, Eq. (6) may be used for the estimation of the osmotic coefficient. The concentration dependences of this function in the ternary solutions containing 19.98 wt.% of C_2H_5OH and 3 wt.% of *iso*-C_4H_9OH are shown in Fig. 3.

The NaCl-H_2O-C_2H_5OH solutions belong to the most investigated system in comparison with other analogical objects, so it's possible to estimate the quality of our experimental data not only for aqueous solvent but for mixed solvent as well. Fig.2 *a* demonstrates a good agreement between literature data and the results of the present investigation. Hereinafter the system with ethanol as organic component was accounted as an object to test the various approaches to data approximation. The aim was to reveal the main factors that affected the accuracy of partial and integral properties determination based on the EMF measurements with ion-selective electrodes. The next factors were investigated: (a) a number of experimental points included in approximation; (b) type of thermodynamic model.

Correlation between the quantity of experimental data and the results of calculation of mean ionic activity coefficients in the NaCl-H_2O-C_2H_5OH system at 298.15 K and w_{Alc} = 9.99 % is illustrated by Table 4. The Pitzer's model parameters at various numbers of input data (EMF, m_{NaCl}) are listed. An analysis of the data presented in Table 4 shows that an increase in the number of experimental data (i.e. expansion of concentration range) does give noticeable advantages for the description of Pitzer's model. The standard deviation of approximation for more than seven *E*,*m*-pairs varies slightly (from 2.4 to 2.8) unlike the

significance of parameters; the approximation with only seven experimental points gave insignificant values. To improve a quality of description it is necessary to use more than 10 primary (*E, m*) measurements. In many cases it is impossible to extend the concentration range due to the restrictions for lower and upper limit of molality. So, a number of 12-14 points were considered as optimum set of data in each series of experiments. Other thermodynamic models (Pitzer-Simonson model or eNRTL) are less sensitive to the amount of input data. The advantage of those models is ability to use entire set of experimental data unlike Pitzer model where only the results for solution with a constant water/alcohol ratio are accounted.

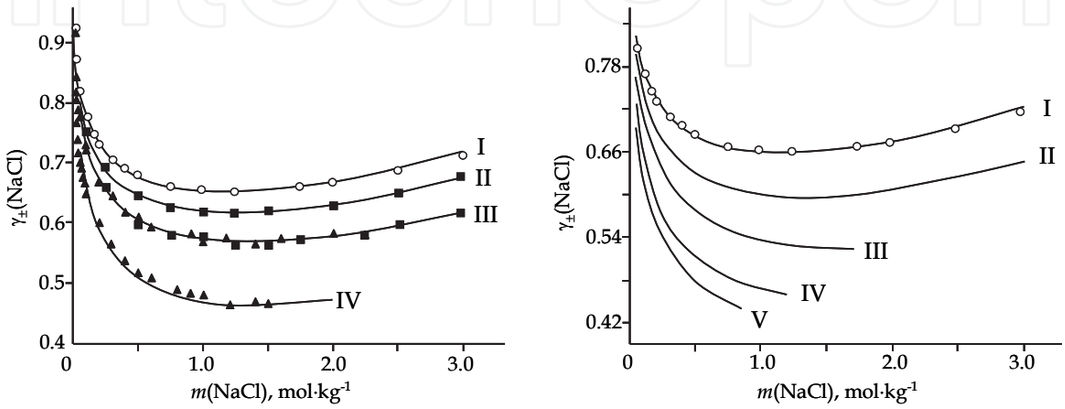


Fig. 2. Mean ionic activity coefficients of NaCl in a NaCl-H_2O-C_2H_5OH (*a*) and NaCl-H_2O-*1*-C_3H_7OH (*b*) solution at 298.15 K. Transparent symbols (○) correspond to the NaCl-H_2O solution without alcohol (Lide, 2007-2008; Silvester & Pitzer, 1977), fill symbols are the literature data (▲ - Esteso et al., 1989; ■ - Lopes et al., 2001), lines are the result of present investigation. Number I, II, III, IV and V correspond to the experimental data for solutions containing (*a*) 0, 9.99, 19.98 and 39.96 wt. % of the ethanol; (*b*) 0, 9.82, 19.70, 29.62, 39.96 wt. % 1-propanol, respectively.

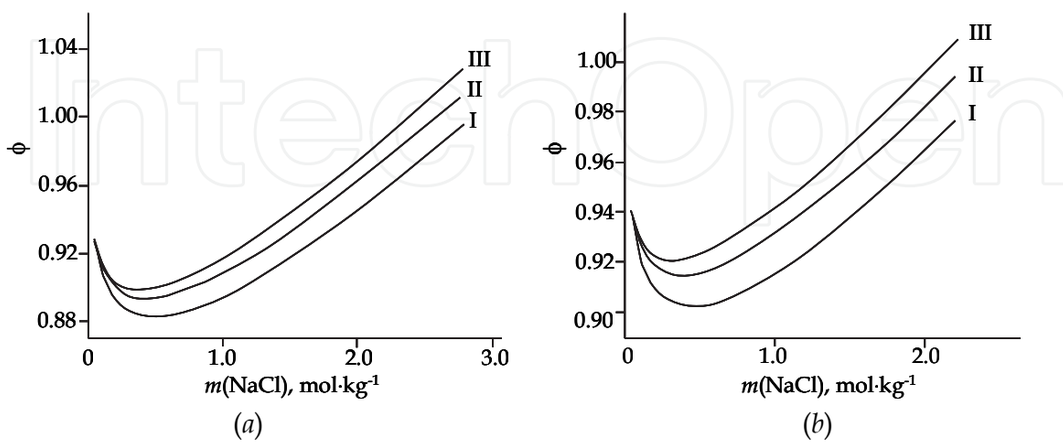


Fig. 3. Osmotic coefficients in NaCl-H_2O-C_2H_5OH (w_{Alc}= 19.98%) (*a*) and NaCl-H_2O-*iso*-C_4H_9OH (w_{Alc}= 3.00%) (*b*) solutions, where the numbers I, II, and III indicate the experimental data at 288.15, 298.15, and 318.15 K, respectively.

Number of experimental points	$-E_0 \times 10^3$, V	$\beta^{(0)}_{NaCl}$, kg·mol^{-1}	$\beta^{(1)}_{NaCl}$, kg·mol^{-1}	$s_0(E) \times 10^4$
7	138.6 ± 1.7	0.1074 ± 0.132	0.2132 ± 0.46	2.8
8	138.3 ± 1.1	0.0810 ± 0.053	0.2994 ± 0.23	2.6
9	138.3 ± 0.9	0.0809 ± 0.027	0.2998 ± 0.14	2.5
10	138.2 ± 0.7	0.0770 ± 0.017	0.3162 ± 0.10	2.4
11	138.4 ± 0.6	0.0823 ± 0.009	0.2889 ± 0.07	2.4
12	138.4 ± 0.5	0.0842 ± 0.007	0.2785 ± 0.06	2.4
13	138.5 ± 0.5	0.0850 ± 0.004	0.2728 ± 0.05	2.3
14	138.6 ± 0.6	0.0884 ± 0.004	0.2468 ± 0.05	2.8

Table 4. A comparison of Pitzer's model parameters with various set of input EMF data. The NaCl-H_2O-C_2H_5OH system (9.99 wt.%) at 298.15 K.

For the estimation of model's type influence on the results of calculation the Pitzer theory was compared with the more complex Pitzer-Simonson model. According to the Pitzer formalism, the mean ionic activity coefficient of a strong electrolyte is defined within the molality mode related to the "ideal dilute standard". But the definitions which use mole fractions are more suitable or even necessary for the calculations of phase equilibria. The Pitzer-Simonson model is based on mole fractions. So initial values of $\gamma_{\pm}$(NaCl) were at first converted to the mole fraction basis by the equation

$$\gamma_x = \gamma_m(1 + 0.001mM_s) = \left(\gamma_{\pm}\right)^2 m(1 + 0.001mM_s), \tag{15}$$

where M_s – is the mean molar mass of solvent. Calculated activity coefficients γ_x were compared with those obtained by Eq. (13). This equation includes two groups of parameters for the description of the Gibbs excess energy of mixing in the frame of Pitzer-Simonson formalism: three pairs of binary parameters "salt-water", "alcohol-water", "salt-alcohol" and one ternary parameter. The long-range parameter for sodium chloride in diluted range (B_{MX}) and short-range interaction parameters (W_{1NaCl} and U_{1NaCl}) related to salt (NaCl) and water (1) were estimated on the base of literature data (Pitzer & Mayorga, 1973) and own experiments. Results of calculation are presented in the Table 5. The binary interaction parameters for a system containing water (1) and ethanol (2) were determined by the minimization of the objective function, which was the sum of the squares of the relative deviations between the calculated and experimental values for different data sets in the H_2O-C_2H_5OH system (see, for instance, Shishin et al. 2010; Konstantinova et al., 2011) or by using literature data (Lopes et al., 2001). The values of short-range interactions parameters W_{nMX}, V_{nMX}, U_{nMX} (n = 1,2) related to sodium chloride and component of mixed solvent, given in Table 5, were obtained from the results of EMF measurements of electrochemical cell (I).

The differences between the activity coefficients of NaCl obtained from the two models are shown in Fig.4 for various temperatures and solvent compositions. The results demonstrate that both methods are adequate for treating the EMF measurements. A comparison of calculations with two models gives the largest difference of 5 % for the alcohol rich solution. At the same time the mean ionic activity coefficients of NaCl are consistent with the published data (Lopes et al., 2001) if the uniform Pitzer-Simonson model is used for data approximation; maximum error is equal to 1.5 % for the solution with w_{Alc} = 19.98% at 318.15

K. An analysis of the data presented in Table 3 and Table 5 confirms the conclusion of Lopes that the variation of the activity coefficients of salt with the temperature or with the alcohol content is always smoother when the Pitzer–Simonson equations are used.

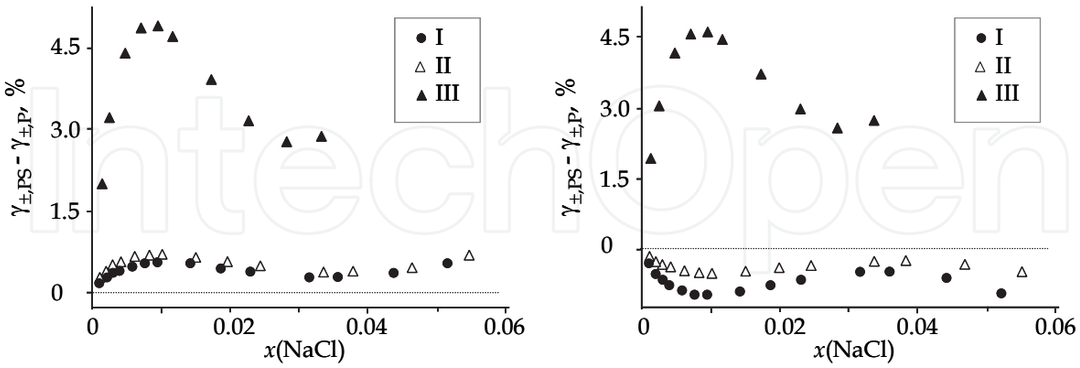


Fig. 4. The difference between Pitzer-Simonson and Pitzer model calculations at 288.15 K (*a*) and 298.15 K (*b*). A number I, II and III corresponds to various composition of solvent: 9.99, 19.98 and 39.96 w.%, respectively.

T, K	288.15	298.15	318.15
w_{12}	1.1934	1.2051	1.2285
u_{12}	0.2123	0.2583	0.3505
$-W_{1NaCl}$	6.1366	5.9187	5.6356
$-U_{1NaCl}$	4.5747	4.1214	3.5427
B_{NaCl}	12.6266	12.8566	14.2752
Z_{12NaCl}	7.2780	2.0676	3.0343
$-W_{2NaCl}$	35.1662	24.7911	16.9476
$-U_{2NaCl}$	31.0909	27.0080	15.8373
$-E^0(w_{Alc}$-9.99%$)\times10^3$,V	373.67	373.76	377.08
$-E^0(w_{Alc}$-19.98%$)\times10^3$, V	439.95	428.07	411.08
$-E^0(w_{Alc}$-39.96%$\cdot)\times10^3$, V	600.63	552.08	488.78
$_{s0}$(E)$\times10^3$	4.2	4.4	4.4

Table 5. Interaction parameters of the Pitzer-Simonson model for the binary NaCl-H_2O and ternary NaCl-H_2O-C_2H_5OH solutions.

Unlike in the Pitzer formalism, some of the binary interaction parameters in the Pitzer-Simonson model are defined independently by the approximation experimental data in Water-Alcohol and Water-Salt systems. In principle, the difference in those parameters can cause discrepancies in the results of calculation from various scientific groups. For the estimation of possible error we calculate the mean ionic activity coefficients with a various sets of water-ethanol interaction parameters. Model parameters were calculated using the primary experimental data about vapour-liquid equilibria that were obtained by various authors in the H_2O-C_2H_5OH system. It was revealed that this factor does not affect to the result of γ_x calculation; the difference in values is less than a hundredth of a percent.

5.2 Integral properties of ternary solutions

The integral properties of solutions were calculated with the Pitzer, Pitzer-Simonson model and by the Darken method. In the former case, the molality concentration scale was used, and the mixed solvent and the extremely dilute solution of the salt in this solvent were taken as the base. The formulas used for the calculation of the integral functions are listed in Section 3.

One of the features of the EMF-experiment with ion-selective electrodes is a step-by-step increase of the molality at a fixed ratio of the solvent components in every experiment. As a result, the composition of the system under investigation is changing through the quasibinary section of ternary system. This allows to use the Darken method for the calculation of the integral properties of such solutions. The essence of this procedure is an integration of the Gibbs-Duhem equation in the ternary solution at a constant ratio for any two components. This method is widely used for the results of the electrochemical measurements for ternary metal alloys but has not been applied yet for the aqueous electrolyte systems.

Since solutions from one series of the EMF-measurements belong to particular NaCl-$[H_2O+Alc]_{H_2O/Alc}$ section of the ternary system with fixed relation of alcohol and water, the following equation can be used for the excess Gibbs energy of such solutions:

$$G_x^{ex} = (1 - x_{\mathrm{NaCl}})\left[G^{ex}_{x_{\mathrm{NaCL}}=0} + \int_0^{x_{\mathrm{NaCl}}} \frac{\mu^{\mathrm{ex}}_{\mathrm{NaCl}}}{(1\text{-}x_{\mathrm{NaCl}})^2} dx_{\mathrm{NaCl}} \right]_{\frac{x_{\mathrm{Alc}}}{x_{\mathrm{H_2O}}}}. \qquad (16)$$

where G_x^{ex} and $G^{ex}_{x_{\mathrm{NaCL}}=0}$ are the excess integral Gibbs energy of solution at mole fractions of sodium chloride equal to x_{NaCl} or 0, respectively. The excess chemical potential of NaCl is connected with the activity coefficient in various concentration scales by the relation

$$\mu^{\mathrm{ex}}_{\mathrm{NaCl}} = RT \ln \gamma_x = RT\left(2\ln \gamma_{\pm} + \ln\left(m\left(1 + 0.001m\left\{ \left(1 - x^{\infty}_{\mathrm{Alc}} \right) M_{\mathrm{w}} + x^{\infty}_{\mathrm{Alc}} M_{\mathrm{Alc}} \right\} \right) \right) \right), \qquad (17)$$

where M_{w}, M_{Alc} are the molar masses of water and alcohol, and $x^{\infty}_{\mathrm{Alc}}$ is the mole fraction of alcohol in salt-free solvent. The temperature-concentrations dependences of the mean ionic activity coefficient of NaCl and the excess Gibbs energies of water-alcohol binary solutions ($G^{ex}_{x_{\mathrm{NaCl}=0}}$) are necessary for the calculation of integral properties of ternary solutions according to Eq. (16). The former may be obtained from the approximation of the results of the EMF measurements. In the case of ISE two unknown values – E_0 and γ - are presented in Eq.(14) unlike common galvanic cells with one unknown γ. The Darken method has obvious advantages for the processing of electrochemical experiments with common electrodes due to the possibility to provide a numerical integration of the Gibbs-Duhem equation. The result of this calculation does not depend upon the type of the model; thus the error in integral properties determination may be reduced. The approximation of EMF-ISE measurements includes a choice of a thermodynamic model. In such situation Darken method can be considered as an alternative way to calculate Gibbs energy of solution in molar mode. For instance, if the Pitzer formalism is used then

the excess Gibbs energy of the ternary solution is calculated by the equation (for more detail see Mamontov et al., 2010):

$$G_x^{ex} = \frac{G^{ex}_{x_{\mathrm{NaCL}}=0}}{(1+0.001\cdot mM)} + \frac{2RT\cdot M}{(1000+mM)}\left(\begin{array}{l} -\frac{2}{1.2}A_\phi m\ln(1+1.2m^{1/2}) + \beta^{(0)}_{\mathrm{NaCl}}\cdot m^2 + \frac{\beta^{(1)}_{\mathrm{NaCl}}m}{2}(1-(1+2m^{1/2})\exp(-2m^{1/2})) + \\ +\frac{C^{\gamma}_{NaCl}}{2}m^3 + \frac{1}{2}\left(m\cdot\ln(m) - 2m + \frac{1000}{M}(1+0.001mM)\ln(1+0.001mM)\right) \end{array}\right) \quad (18)$$

To calculate the excess Gibbs energies of water-alcohol binary solutions it is necessary to construct a thermodynamic model of those solutions. The model parameters of aqueous solutions of alcohols were proposed in numerous studies (see, for example, Gmehling & Onken, 1977 or subsequent Editions). In the present study we used a results of own assessment of Water-Alcohol systems with NRTL model (Shishin et al., 2010; Konstantinova et al., 2011). The main merit of our approach is a use of unified equation of the Gibbs energy of a water-alcohol solution for the description of various types of equilibria: vapor-liquid and liquid-liquid.

Pure alcohol and water, along with a hypothetical infinitely dilute solution of NaCl in the mixed solvent, were chosen as the standard state of the solution components during integration by the Darken's method. To go to the unified reference system (pure solvents and the extremely dilute solution of the salt in water), the so-called Born contribution accounting for the change in the Gibbs energy ($G^{\mathrm{ex}}_{\mathrm{Born}}$) was used (see Eq.(4)). The Gibbs energy of formation of the solution in this reference system can be written as follows:

$$\Delta_{mix}G = RT\cdot\left(x_{\mathrm{H_2O}}\ln x_{\mathrm{H_2O}} + x_{\mathrm{Alc}}\ln x_{\mathrm{Alc}} + x_{\mathrm{NaCl}}\ln x_{\mathrm{NaCl}}\right) + G_x^{\mathrm{ex}} + G^{\mathrm{ex}}_{\mathrm{Born}}\,. \quad (19)$$

Other thermodynamic functions were obtained from Eq.(19) by means of common thermodynamic relations, for example, Gibbs-Helmholtz equation. Next figures illustrate some results of the calculation. Fig. 5 *a,b* shows the isothermal (298.15 K) sections of Gibbs energy surface for the solution formed by sodium chloride, water, and *iso*-propanol with a constant ratio of water and alcohol in solvent, and with a constant mole fraction of sodium chloride. Since all electrochemical measurements were carried out with the use of homogeneous mixtures, no anomalies are observed in the curves in Fig. 5 in the region of the measured compositions (solid lines), and they are shifted with respect to each other in the expected way. Fig. 6 shows the sections of the surface of the enthalpy of mixing of the solution with *iso*-butanol at a constant composition of the solvent and a constant fraction of NaCl at 298.15 K. The relative enthalpy of the ternary solution changes only slightly in the temperature range under consideration.

The Darken method is theoretically justified, so there is no reason to doubt the correctness of the results. Additionally we compared the values of thermodynamic function been calculated with this approach and Pitzer-Simonson model. As can be seen from the Fig.7 the results are in excellent agreement.

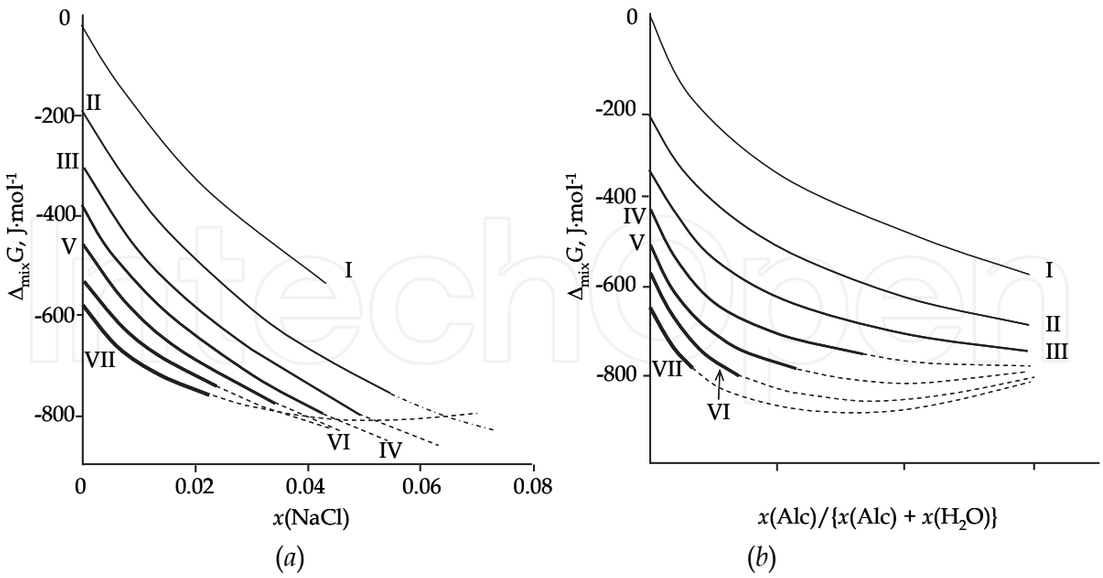


Fig. 5. The isothermal (298.15 K) sections of Gibbs energy surface of solutions of H_2O–*iso*-C_3H_7OH–NaCl with constant (*a*) the ratio of water and alcohol; (*b*) the weight fraction of alcohol in solvent. The numbers correspond to solutions with the weight fraction of alcohol in solvent is: (I) 0, (II) 10.0, (III) 20.0, (IV) 30.0, (V) 40.0, (VI) 49.9, (VII) 58.5 wt. % (*a*); and with mole fraction of sodium chloride equal to: (I) 0, (II) 0.01, (III) 0.02, (IV) 0.03, (V) 0.04, (VI) 0.05, (VI) 0.06 (*b*). Dashed lines indicate the extrapolated values of the $\Delta_{mix}G$ function outside the range of experimental research. The line width increases with the increasing of (*a*) the weight fraction of alcohol in solvent; (*b*) the mole fraction of NaCl.

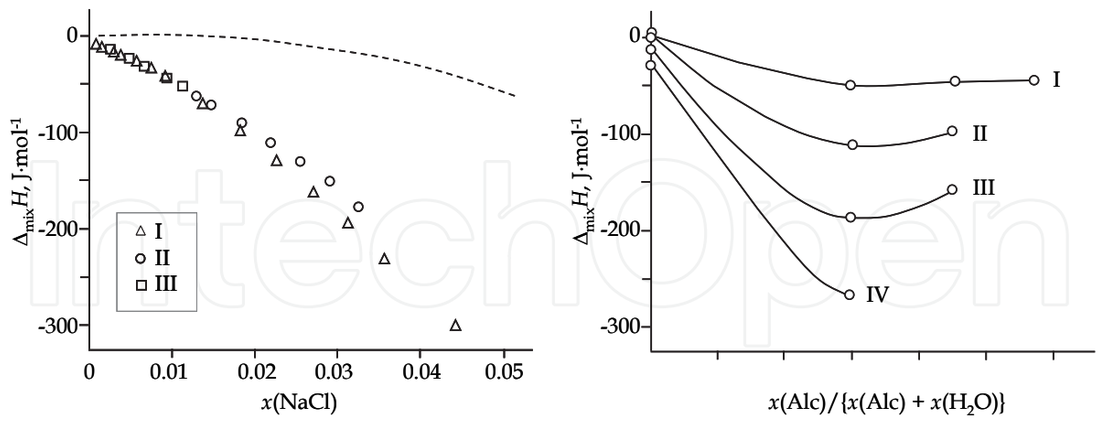


Fig. 6. Isothermal sections of the surface of the enthalpy of mixing of the NaCl–H_2O–*iso*-C_4H_9OH solution at 298.15 K along the sections with constant water-to-alcohol ratios (*a*); the weight fraction of the alcohol in the solvent (w_{Alc}) is (I) - 3.0; (II) - 4.5; (III) - 5.66 wt. %, dashed line – without alcohol; (*b*) along the sections with constant mole fractions of sodium chloride; x_{NaCl} is (I) - 0.01; (II) - 0.02; (III) - 0.03; (IV) - 0.04. The points in each section at (*b*) are connected by a solid line.

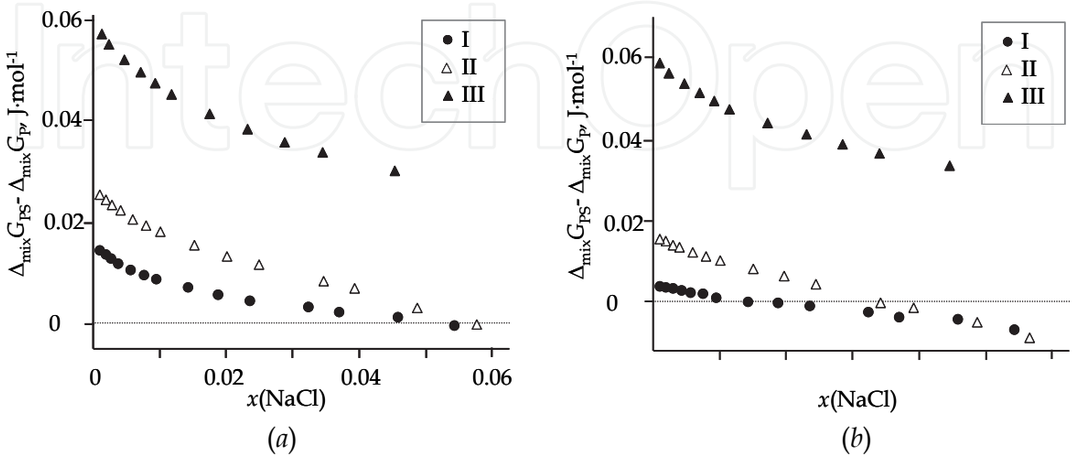


Fig. 7. The difference between results of Gibbs energy calculation of the NaCl-H_2O-C_2H_5OH solution at 298.15 K (*a*) ad 318.15 K (*b*) with Darken method and Pitzer-Simonson model. A number I, II, III corresponds to various composition of solvent: 9.99, 19.98 and 39.96 w.%, respectively.

5.3 Standard thermodynamic functions of transfer of salt from water to the mixed solvent

The electrochemical measurements allowed us not only to calculate the mean ionic activity coefficients, the Gibbs energies, and the enthalpies of mixing of ternary solutions but also to estimate the standard thermodynamic functions of transfer of salt from water to a mixed solvent. The standard Gibbs energy of transfer is defined as the difference between the standard Gibbs energy per mole of electrolyte in a pure solvent, usually water, and that in another pure or mixed solvent. It is a measure of the change in the total energy of the solute when it is transferred from one solvent to another at infinite dilution and can be easily calculated according to the expression:

$$\Delta_{\mathrm{tr}} G_T^{\mathrm{o}} = -F(E_{0,\mathrm{s}} - E_{0,\mathrm{w}}) \tag{20}$$

where $E_{0,\mathrm{s}}$ and $E_{0,\mathrm{w}}$ are the standard electrode potentials of the electrochemical cell (I) for the mixed solvent and water, respectively. The values $\Delta_{\mathrm{tr}} G_T^{\mathrm{o}}$ were calculated for each temperature and the composition of the solution based on the data presented in Table 6. Fig. 8 *a* shows $\Delta_{\mathrm{tr}}G$ *vs*. *n* (number of carbon atoms in *n*- and *iso*-alcohol) for ternary solutions with w_{Alc} = 5 % at 298 K. It is surprising the decrease of Gibbs energy of transfer for aqueous-alcohol mixtures with n > 3. Apparently, this phenomenon requires further investigation.

$w_{alc,}$ %	$-(E_{0,s} - E_{0,w})$, mV			$\Delta_{tr}G^{\circ}_{T}$, J·mol^{-1}		
	288.15 K	298.15 K	318.15 K	288.15 K	298.15 K	318.15 K
Water-ethanol solvent						
9.99	22.4 ± 0.4	22.4 ± 0.4	22.5 ± 0.6	2.16 ± 0.04	2170 ± 60 1910 ± 100 (Mazzarese & Popovych, 1983 5600 ± 100 (Kalida et al., 2000)	2140 ± 80
19.98	44.6 ± 0.5	44.6 ± 0.6	43.6 ± 0.7	4.30 ± 0.05	4300 ± 60 3880 ± 100 (Mazzarese & Popovych, 1983) 6400 ± 100 (Kalida et al., 2000)	4210 ± 70
39.96	89.5 ± 1.0	89.0 ± 1.0	89.3 ± 1.0	8.64 ± 0.10	8590 ± 100 (*) 8330 ± 100 (Mazzarese & Popovych, 1983) 8000 ± 100 (Kalida et al., 2000)	8620 ± 100
Water-*n*-propanol solvent						
9.82	-	22.4 ± 0.7	23.2 ± 0.8	-	2161 ± 70 2036 ± 80 (Gregorowicz et al., 1996)	2238 ± 80
19.70	-	42.1 ± 0.6	41.9 ± 0.7	-	4062 ± 60 3908 ± 80 (Gregorowicz et al., 1996)	4042 ± 70
29.62	-	61.0 ± 0.6	61.0 ± 0.7	-	5885 ± 60 5649 ± 80 (Gregorowicz et al., 1996)	5885 ± 70
39.56	-	76.4 ± 0.7	80.0 ± 0.8	-	7371 ± 70 7451 ± 80 (Gregorowicz et al., 1996)	7718 ± 80
Water-*n*-butanol solvent						
3.00	-4.7 ± 0.4	-4.0 ± 0.4	-4.4 ± 0.6	450 ± 40	390 ± 40 640 ± 70 (Chu et al., 1987)	430 ± 60
4.49	-7.7 ± 0.6	-7.7 ± 0.6	-7.5 ± 0.5	740 ± 60	740 ± 58 960 ± 100 (Chu et al., 1987)	720 ± 50
5.66	-10.3 ± 0.4	-10.9 ± 0.4	-10.8 ± 0.8	990 ± 40	1050 ± 40 1200 ± 120 (Chu et al., 1987)	1040 ± 80
Water-*n*-pentanol solvent						
2.00	-1 ± 0.6	-1.5 ± 0.5	-	99 ± 58	147 ± 48	-

Table 6. Standard Gibbs energy of transfer of NaCl from H_2O to the H_2O (100-w_{alc}%) + $C_nH_{2n+1}OH$ (w_{alc}%) mixed solvent at various temperatures.

It can be seen that the values of the standard functions of transfer determined in the present study do not contradict to those recommended in the literature. Data for the propanols are in satisfactory agreement with results (Gregorowicz et al., 1996). In the case of butanols the values of the standard functions of transfer at 298.15 K are shifted to smaller values

compared to those recommended in the study (Chu et al., 1987). In all cases an increase in the standard Gibbs energy of transfer is observed with the increase of alcohol in the mixture, which would indicate a decrease in hydration of electrolyte in the mixture. Using the Feakins and French equation (Feakins & French, 1957), it is possible to estimate the primary hydration number of the electrolyte based on the dependency between the standard electromotive force of the cell and the logarithm of the mass fraction of water in the mixture:

$$\Delta E_0 = E_{0,s} - E_{0,w} = N_h k_B \log w \tag{21}$$

where k_B is a is the Boltzmann constant. This value varies from 8 for methanol to 0.5 for butanol and coincides for different homologs of alcohols within error. Fig. 8 *b* shows the plot of N_{hyd} *vs*. n. The solid lines in both graphics have no physical meaning, they represent a trend.

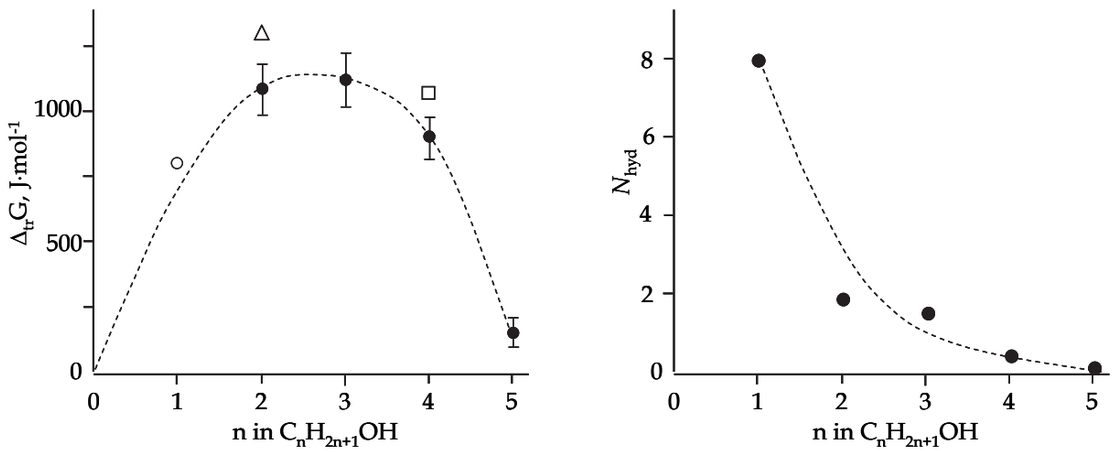


Fig. 8. Plot of $\Delta_{tr}G$ *vs*. n (in $C_nH_{2n+1}OH$) (*a*) and N_{hyd} *vs*. n (*b*) ; the filled symbol - present work, the transparent symbol (Mazzarese & Popovych, 1983; Chu et al., 1987). T = 298.15 K

6. Conclusion

Systematic studies of electrochemical cells with Na+ and Cl- ion-selective electrodes in aqueous-alcohol solvents were performed. Analysis of the results have shown that the major sources of uncertainty of the partial properties in the EMF measurements with the ISE are the choice of model solution and the amount of input data that take into account at the approximation. Therefore, when comparing the activity coefficients of electrolyte obtained in various researches groups should pay particular attention to the method of data processing.

The Darken method was first used to calculate the integral properties of electrolyte solutions. It was shown that the Gibbs energy of mixing calculated by the Pitzer-Simonson model and the Darken method are in excellent agreement.

The results of present investigation can be used to the verification of proposed thermodynamic models and for the development of alternative theories of electrolyte solutions.

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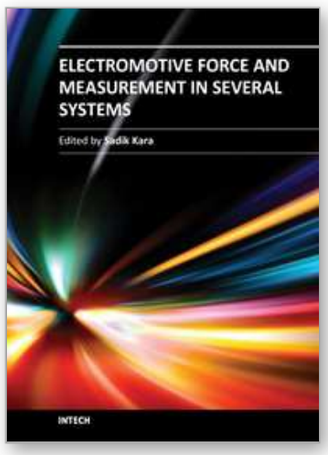
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