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Water–ethanol–sodium chloride system: The main sources of uncertainties in thermodynamic properties determined by potentiometry

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1. Introduction

Material science, petroleum and chemical industries, polymer, pharmaceutical and other industrial sectors today all make use of thermodynamic tools. Analytical forms of characteristic state functions vs. natural set of variables (i.e. thermodynamic models) are necessary for the calculation of chemical and phase equilibria and for the estimation of phase stability in systems with many components. Parameters for such thermodynamic models are calculated through approximation of experimental thermodynamic data measured by a variety of methods. One of the most widespread experimental methods to determine the partial properties of electrolytes in mixed solvents is potentiometry which makes use of traditional or ion-selective electrodes (ISE). In the latter case, it is necessary to fit the primary data (Electromotive Forces (EMF) vs. concentration of solution) to the thermodynamic models for the electrolyte system because a standard electrode potential of the ISE at a fixed temperature is not a constant in contrast to the value, E_0, in traditional electrochemical cells. Every specimen of ISE has unique value of E_0 for the same ion.

The goals of this work are (i) to analyze the influence of various factors on the calculated values of the mean-ion activity coefficient and integral properties of ternary solutions and (ii) to determine the main sources of errors in calculated values. The water–ethanol–sodium chloride system was chosen as a test system because data for the ternary system [1–5] and the binary subsystem [6] were reported by various authors. The properties of the water–alcohol system need to be considered when describing the integral properties of salt solutions in a mixed water–alcohol solvent. In general, many papers present the results only of experimental data approximation without primary data which are required for the tasks formulated above. As a result additional measurements of EMF in cells with ISE were carried out. The conditions for potentiometric measurements were chosen so as to test the reproducibility of the literature data and to widen the temperature and concentration ranges.

A similar task dealing with the mean-ion activity coefficient ($\gamma_{\pm}$) was formulated in earlier works of Esteso et al. [5] and Lopes et al. [4]. As was shown by Esteso et al. [5], the approximation arising from the use of the same set of potentiometric data with the Extended Debye–Hückel Equation (DH), Pitzer model (P) and the so-called chemical model, made it possible to obtain $\gamma_{\pm}$ values that agree with themselves within 0.003. The difference among the values increases with increasing content of alcohol, apparently due to some association process. All measurements were made at 298.15 K over a wide range of alcohol content (20–70 wt.%). Larger deviations between calculated values of mean-ion activities were obtained by Lopes et al. [4]. The ISE measurements in cells with sodium chloride in water–ethanol solvents (5–20 wt.% of C_2H_5OH) at 298.15–323.15 K were approximated using the Pitzer and Pitzer–Simonson (PS) models. They showed that the maximum deviation between $\gamma_{\pm}$ values calculated on the basis of the single set of potentiometric data fitted to the two models is equal to 0.02 (i.e. the order of magnitude higher than in the previous case). At the same time, the absolute deviations of mean-ion activity coefficients in solutions with 20 and 40 wt.% of alcohol and with a molality less

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than 2 *m* at 298.15 K which were calculated using the Pitzer–Simonson model and based on data of Esteso et al. [5] and Lopes et al. [4] are equal to 0.008 and 0.015, respectively. One reason for the significant difference between the $\gamma_\pm$ values calculated above can be the use of different concentration scales (i.e. different reference states of the solution). The values of the mean-ion activity coefficient calculated on a molality scale were compared in the work of Esteso et al. [5] with those in the work of Lopes [4] where additional translation from a mole fraction to a molality scale was carried out.

To the best of our knowledge, there are no examples of systematic analysis of factors influencing on the integral function values of electrolyte solution in mixed solvents calculated on the basis of potentiometric measurements. Therefore, the goal of this work is to determine the main factors that provide uncertainties in the Gibbs energy of solution where potentiometry has been used as the experimental method for the determination of thermodynamic properties. The results of the calculation with

(I) the single model, whose parameters were found by approximation of the potentiometric measurements from different research groups,
(II) different models, whose parameters were found by approximation of potentiometric measurements of one single research group

were analyzed to identify the key factors and their impact on the defined values of thermodynamic functions. We did not set the task to evaluate such factors as an electrochemical cell design, specific features of ISE, the measured system and etc. By comparing our results with similar literature data we confirmed previous conclusions about deviation values of mean-ionic activity coefficients determined by various authors. The main purpose of this work was to estimate factors that can introduce a big error to the integral properties of electrolyte solution in a mixed solvent.

2. Experiment

2.1. Reagents

Sodium chloride (reagent grade, 99.8%) was additionally purified by double crystallization of NaCl during evaporation of the mother liquor; the purified salt was dried in vacuum at 530 K for 48 h. Ethanol (reagent grade, 99.8 wt.%) was kept on zeolites 4A for 7 days and then distilled under atmospheric pressure. The purity of the prepared sample was confirmed by the agreement between the measured boiling point of the pure solvent at atmospheric pressure and the refractive indices with the corresponding published data ($T_b = 351.15$ K and $n^D = 1.3613$ [present work], $T_b = 351.5 \pm 0.2$ K [http://webbook.nist.gov], 351.15 K [7] and $n^D = 1.3600$ [www.sigmaaldrich.com], 1.3615 [8]). Deionized water with a specific conductance of 0.2 μS cm^{-1} was prepared with a Millipore Elix system. The reagents were weighed on a Sartorius analytical balance (Germany) with an accuracy of ±0.0005 g. The purities and sources of chemicals were listed in Table 1.

2.2. Electromotive force (EMF) measurements

Potentiometric measurements were carried out with the use of solutions of sodium chloride in mixed water–ethanol solvents with a constant water-to-alcohol weight ratio. The solutions were magnetically stirred for 30 min immediately before the experiments. The temperature of the samples was maintained constant with an accuracy of ±0.05 K by circulating water heated by an LABT-TZh-TS-01/12 K-20 liquid thermostat.

Electrochemical measurements were carried out in the cell without a liquid junction {I}:

$$Na^+{-}ISE|NaCl(m) + H_2O(100{-}w_{alc}) + C_2H_5OH(w_{alc})|Cl^-{-}ISE, \quad (I)$$

where w_{alc} is the weight percentage of alcohol in a mixed solvent and *m* is the molality of the sodium chloride in the ternary solution. An Elis-131 ion-selective electrode for chloride ions (Cl^-–ISE) (Research and Production Association Izmeritelnaya Tekhnika IT, Russia) was used as the reference electrode and a glass ion-selective electrode for sodium ions (Na^+-ISE) served as the indicator electrode. The ESL-51-07Sr (Gomel ZIP, Belarus) and DX223-Na^+ (Mettler Toledo, Switzerland) ion-selective electrodes were used in experiments simultaneously. The results of experiments performed with the use of two ion-selective electrodes can be considered as independent. The potential of the cell registrated by a Multitest IPL-103 ionometer (Research and Production Association Semiko, Russia). The input impedance of the ionometer was at least 10^{12} Ohm. The EMF values of the cell were assumed to be in equilibrium if the rate of the change in EMF was no higher than 0.01–0.02 mV min^{-1}. The equilibrium was established within 20–30 min. For the more details of the experiments, see paper of Konstantinova et al. [9].

Three series of solutions were investigated: with molality 0.05–3 *m* and alcohol content in mixed solvents 9.99, 19.98 and 39.96 wt.%. In each series of compositions containing a constant fraction w_{alc}, successive measurements were carried out for samples of different molalities starting with the lowest concentration. The lower concentration limit of solutions was specified in accordance with the characteristics of the sodium electrode, for which 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). For the solution with 39.96 wt.% of C_2H_5OH the upper limit of salt concentration was 2 *m* due to the necessity to maintain the homogeneity of the mixtures. The measured EMF values are listed in Table 2.

3. Thermodynamic models

The electromotive force of the electrochemical cell {I} is related to the activity coefficient of the salt by the Nernst equation. This equation can be written in two equivalent form depending on the reference system of solution:

$$E = E_0 - \frac{2RT}{F}\ln(\gamma_{m\pm} m), \quad (1a)$$

Table 1
Purities and sources of chemicals.

Chemical name	CAS number	Source	Initial purity (weight percent)	Purification method	Final purity (weight percent)
NaCl	7647-14-5	Reachim, Russia	99.8	double crystallization and oven drying	99.9
C_2H_5OH	64-17-5	Limited Liability Company Komponent Reaktiv	99.8	drying in a dehydrator with zeolites and distillation	99.98