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Measurement and modelling of mean activity coefficients of aqueous mixed electrolyte solution containing glycine

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Abstract

Electrochemical measurements were made on (H_2O + NaBr + K_3PO_4 + glycine) mixtures at $T = 298.15$ K by using ion selective electrodes. The mean ionic activity coefficients of NaBr at molality 0.1 were determined at five K_3PO_4 molalities (0.01, 0.03, 0.05, 0.07, and 0.1) $\text{mol} \cdot \text{kg}^{-1}$. The activity coefficients of glycine were evaluated from mean ionic activity coefficients of NaBr. The modified Pitzer equation was used to model the experimental data.

Keywords: Activity coefficient; Amino acid; Mixed electrolyte solution; Ion selective electrodes; Modified Pitzer

1. Introduction

The rapid progress in biotechnology has resulted in much attention to the development of efficient methods for separation, concentration and purification of valuable bio products [2]. Amino acids are important due to their application in various fields such as pharmaceutical, chemical and food industries. The physical and thermodynamic properties of amino acids such as activity coefficients in the presence of electrolytes provide key knowledge in separation processes [2,3], so access to experimental data are essential in development, design and modelling of these systems. On the other hand, thermodynamics properties of amino acids in mixed electrolyte solution are important in their biological role in marine systems, because salinity seems to be an important factor in regulating the assimilation of amino acids [4].

Our group recently reported data for activity coefficients of glycine in mixed electrolyte solution containing NaBr and K_3PO_4 at constant molality of K_3PO_4 and different molalities of NaBr and glycine [1]. As the molality of K_3PO_4 was kept constant, the effect of variation of K_3PO_4 molality on activity coefficients of NaBr and glycine was not investigated. However, it was shown that in the presence of K_3PO_4, low molalites of NaBr caused a decrease in mean ionic activity coefficient ratio of NaBr, whereas at high molalities it caused an increase.

In this work as a continuation of our previous study, the mean ionic activity coefficient ratio of NaBr, is measured over a different range of molalities. The molality of NaBr was kept constant at 0.1 molal and the molalities of glycine and K_3PO_4 were changed to allow the activity coefficient ratio of glycine to be calculated by means of a cross differential equation from the activity coefficient of NaBr. Also the effect of K_3PO_4 interference in the mean ionic activity coefficient ratio of NaBr is investigated.

To correlate the activity coefficient ratio of NaBr in a mixed electrolyte solution containing glycine, the Modified Pitzer equation as presented by Merida *et al.* [5] was changed and then simplified. Ordinarily in systems where a non-electrolyte component is included, it is difficult to choose an equation to fit activity coefficient values adequately. However, the Pitzer equation is probably the best, not only because it facilitates good fitting with the help of just a few

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mixing parameters but also these parameters are representative of the solute–solute interactions that take place in the system [6].

2. Experimental and materials

2.1. Materials

The sodium bromide of 0.995 mass fraction purity was obtained from Merck Ltd. and the glycine with 0.999 mass fraction purity was obtained from Vel Ltd. A Metrohm sodium ion-selective electrode (Model 6.0501.100) and a Metrohm bromide ion-selective electrode (Model 6.0502.100) were used in the experiments. A Jenway ion analyzer (Model 3045), with a resolution of ±0.1 mV was used to monitor electromotive force (e.m.f.) measurements. All of the solutions were prepared by mass based on molality concentration scale. Deionised water with a conductivity of 0.5 to $1\,\mathrm{S \cdot \mu S \cdot cm^{-1}}$ was used in all experiments.

2.2. Experimental

The experimental set-up comprised a sodium ISE and a bromide ISE that measured the electrode potential of NaBr in a $(\mathrm{NaBr + K_3PO_4 + glycine + water})$ solution. The experimental set-up resembled that described in [10]. When the bromide ISE is used as reference electrode for the sodium ISE, the liquid-junction potential can be eliminated [9]. Salt solutions were prepared gravimetrically by the use of a balance with a resolution of 0.1 mg. The calibration procedure of electrodes was followed exactly according to the instructions of the manufacturers. The experiments were done by measuring the e.m.f. of the cation ion-selective electrode against the anion ion-selective electrode in a jacketed glass beaker containing $250\,\mathrm{cm^3}$ of solution. During the experiments in order to minimize the concentration gradients, the solutions were stirred constantly with a magnetic stirrer. The temperature was kept constant at $T = 298.15$ K using a thermostatic bath. The concentration of NaBr was constant at 0.1 mol in all experiments and the concentration of K_3PO_4 was varied from 0.01 mol to 0.1 mol. The concentration of glycine was increased by the addition of solid glycine. The readings of the potentiometer were made only when the drift was less than $0.1\,\mathrm{mV \cdot min^{-1}}$.

All experiments were replicated at least three times, and the data reported are the average of the replicas. Sample variances were obtained from the replicas for each point and a pooled standard deviation was calculated using these values.

3. Theory

According to the Nernst equation the potential difference between the ion selective electrodes (ISE), of the cell (I) with following setup:

$$\text{Cation(Na) ISE}\,|\text{electrolyte}(m_B)|\,\text{Anion(Br) ISE} \qquad \text{(I)}$$

is expressed as

$$\Delta E^{(\mathrm{I})} = \Delta E^{\circ} + 2S \ln\left(m_B \gamma_{\pm}^{\mathrm{I}}\right), \qquad (1)$$

where ΔE° is the difference between the standard electrode potentials of the cell (I), and S is the Nernstian slope. The S can be calculated from linear regression of values of $\Delta E^{(\mathrm{I})}$ *versus* $(\ln m_B \gamma_{\pm}^{\mathrm{I}})$.

The presence of other solutes such as amino acid (glycine) changes the mean ionic activity coefficients of electrolyte NaBr that results in a change in cell (II) with the following setup:

$$\text{Cation(Na) ISE}|\text{NaBr}(m_B) + \text{glycine}(m_A)|\text{Anion(Br) ISE} \qquad \text{(II)}$$

Therefore, the Nernst equation for cell (II) is expressed as

$$\Delta E^{(\mathrm{II})} = \Delta E^{\circ} + 2S \ln\left(m_B \gamma_{\pm}^{\mathrm{II}}\right), \qquad (2)$$

where $\gamma_{\pm}^{\mathrm{II}}$ indicates the mean ionic activity coefficient of NaBr with molality m_B in the presence of the second solute glycine.

For the cell (III) containing the mixed aqueous electrolyte (K_3PO_4 and NaBr):

$$\text{Cation(Na) ISE}|\text{electrolyte}(m_B) + \text{electrolyte}(m_C) + \text{solute } m_A|\text{Anion (Br) ISE} \qquad \text{(III)}$$

The Nernst equation is represented as [18]

$$\Delta E^{(\mathrm{III})} = \Delta E^{\circ} + S \ln(a_B + K \cdot a_C), \qquad (3)$$

where K is the selectivity coefficient of ISE for the electrolyte (K_3PO_4), a_B and a_C are the activities of NaBr and K_3PO_4, respectively. The selectivity coefficient is introduced in the Nernst equation to include the ability of the ISE to distinguish between different ions in the same solution. For many applications, this interference is insignificant and can often be ignored. However, in our measurements, it should be examined if the ISE is far more sensitive to the interfering ions (K^+ and PO_4^{3-}) than to the primary ions (Na^+ and Br^-). In this case the selectivity coefficient K is important and should be to taken into account. In order to measure the selectivity coefficient of Na-ISE and Br-ISE with respect to Na^+ and PO_4^{3-}, a cell (IV) with following arrangement is used:

$$\text{Cation(Na) ISE}|K_3PO_4(m_C)|\text{Anion(Br) ISE} \qquad \text{(IV)}$$

By using equation (3) for the cell (IV), the value of K can be calculated as

$$K = \exp[(\Delta E^{\mathrm{IV}} - \Delta E^{\circ})/S]/\left(m_C \gamma_{C,\pm}\right)^4, \qquad (4)$$

where $\gamma_{C,\pm}$ refers to the mean ionic activity coefficient of pure K_3PO_4 in water at $T = 298.15$ K and can be extracted from reference [7]. The standard e.m.f. of the cell (ΔE°) and the slope (S) in equation (4) must be known in prior to the determination of K. Since the same ISEs were used in the cells (I), (II), and (III), and the measured slope S deviates only slightly from the Nernstian slope, the values of ΔE°