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Mean ionic activity coefficient ratio of NaBr and DL-valine in the (water + DL-valine + NaBr + K_3PO_4) system at T = (298.2 and 303.2) K

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ABSTRACT

The mean ionic activity coefficient of NaBr in the (water + DL-valine + NaBr + K_3PO_4) system was determined by potentiometry at T = (298.2 and 303.2) K by using two ion-selective electrodes, (Na^+) against (Br^-). The maximum concentrations of sodium bromide, potassium phosphate, and DL-valine were (1.0, 0.01, and 0.4) mol · kg^{-1}, respectively. The activity coefficient of DL-valine was evaluated from mean ionic activity coefficients of NaBr by using a cross-differential thermodynamic relation.

1. Introduction

Growing advances in biotechnology have greatly expanded the production of a wide variety of biochemicals with applications in chemical, pharmaceutical and food industries. The separation and concentration of biomolecules is one of the economically important stages in their production processes and may cost as high as fifty to ninety per cent of the total cost of production [1]. Biomolecules are complex molecules whose behavior in mixtures is governed by many factors such as pH [2–4], temperature [4,5], chemical structure, surface charge distribution, solvent properties [4,6,7] and electrolyte type and concentration [8], and even by the presence of other biomolecules. Among these factors, the interaction of biomolecules with electrolytes has many potential applications in separation and concentration processes for biochemicals. Many separation processes for biomolecules, such as salt-induced precipitation of proteins [9–12], amino acid extraction by emulsion liquid membrane [13] and reverse micellar extraction of proteins and amino acids [14–18] deal directly with the interaction of biomolecules with electrolytes. In some cases, biomolecules are directly produced in aqueous solutions containing electrolytes. Investigating the nature of these interactions is of great importance for the design of suitable separation processes for biomolecules.

Interactions of biomolecules and electrolytes also play a vital role in physiological systems.

The activity coefficient is an equilibrium thermodynamic property that gives insight into the departure of a system from ideal behavior and is a reflection of the interactions between the components in the system [19]. Knowledge of these interactions is important for the selection of the method of separation. Activity coefficients can be determined from experimental measurements and are related to thermodynamic functions such as chemical potential, Gibbs energy [20], Helmholtz energy, *etc.*

Thus, activity coefficients can be modeled through the known expressions for thermodynamic functions. Accurate measurement and correlation of activity coefficient are essential for the design of equilibrium-based separation processes [21].

Amino acids are the simplest biomolecules, and are the building blocks of other biomolecules such as peptides and proteins. Knowledge of their interactions in aqueous and aqueous electrolyte solutions is a first step to a better understanding of the interactions of other more complex biomolecules such as peptides and proteins. In addition, amino acids are valuable bioproducts with a large production rate [1].

The isopiestic method [22–26] and electrochemical method [27–29] are the two major techniques that have been used for the measurement of the activity coefficients of amino acids in aqueous electrolyte solutions. The isopiestic method is reliable at medium and high concentrations. However, at dilute solutions,

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the method may lead to large uncertainties. Another shortcoming of this method is the long time needed for establishment of the equilibrium [23].

The relatively simple and reliable method, especially for dilute solutions is that of electrochemical. Khoshkbarchi and Vera [30] reviewed applications of different electrochemical cells and reported experimental data for the systems of electrolyte and amino acids. Reliable ion-selective electrodes (ISEs) have been utilized for experimental investigation of (salt + amino acid + water) systems [31–36]. The solute activity coefficient was obtained by means of the cross-differential equation. In contrast to the isopiestic method, electrochemical methods deal directly with the thermodynamic properties of the electrolyte.

Following the reported data for the activity coefficients of amino acids at various electrolyte solutions [37–39] and the effect of another electrolyte in the mixture of electrolyte and amino acid [40], it is a natural continuation of the previous works to explore the effect further of the presence of electrolytes. Therefore in the present study, the activity coefficient of DL-valine in aqueous electrolyte solutions of the (DL-valine + NaBr + K_3PO_4 + water) system is determined and compared with those obtained in the previous work for the (DL-valine + NaBr + water) system [38].

2. Materials and experimental

2.1. Materials

Sodium bromide with 0.998 mass fraction purities was obtained from Merck Ltd. and DL-valine with 0.995 mass fraction purity was obtained from Aldrich Ltd (table 1). A Metrohm sodium ion-selective electrode (Model 6.0501.100) and a Metrohm bromide ion-selective electrode (Model 6.0502.100) were used. 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 less than $0.8\ \mu S \cdot cm^{-1}$ was used in all experiments. The conditioning procedure of electrodes conformed exactly to the manufacturer's instructions.

3. Experimental

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 mL of solution. During the experiments, in order to minimize the concentration gradients in the beaker, the solutions were stirred constantly with a magnetic stirrer. The temperature was kept constant at $T = (298.15$ and $308.15)$ K, using a thermostatic bath. Each set of experiments was performed at fixed electrolyte concentration, and the concentration of DL-valine was increased by the addition of solid DL-valine. The concentration of K_3PO_4 was kept constant at $0.01\ mol \cdot kg^{-1}$ throughout the experiment. The readings of the potentiometer were made only when the drift was less than of $0.1\ mV \cdot min^{-1}$.

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

TABLE 1
Provenance and purity of the chemical samples.

Chemical name	Source	Initial mass fraction purity
Sodium bromide	Merck	0.998
DL-valine	Aldrich	0.995
K_3PO_4	Aldrich	0.970

4. Theory

For a system containing an electrolyte at molality m_B, the Nernst equations for the potentials of a cation ion selective electrode against an anion ion-selective electrode $\Delta E^{(I)}$, in the electrochemical cell of type

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

be written as:

$$\Delta E^{(I)} = \Delta E^{\circ} + S \ln\left(m_B \gamma^{I}_{\pm}\right), \tag{1}$$

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

The derivation of the above equations is valid for systems containing only one electrolyte in water. The potential of an electrochemical cell changes in the presence of other solutes as a reflection of the change in the mean ionic activity coefficient of the electrolyte in the presence of other solutes. This is due to the interactions between the molecules of electrolyte, other solutes, and water. By using the same method as above, we can measure the difference between the potentials of a cation and an anion ion-selective electrode, $\Delta E^{(II)}$ in type (II) cell:

$$\text{Cation (Na) ISE}|\text{NaBr } (m_B) + \text{DL} - \text{valine } (m_A)|\text{Anion (Br) ISE (II)}. \tag{II}$$

This potential difference is related to $\gamma^{II}_{\pm}$, which is the mean ionic activity coefficient of the electrolyte at molality m_B in the presence of a solute at molality m_A, by:

$$\Delta E^{(II)} = \Delta E^{\circ} + S \ln\left(m_B \gamma^{II}_{\pm}\right). \tag{2}$$

If we add K_3PO_4 with two specific molalities (m_C), the potential of the electrochemical cell of type (II) changes as a reflection of the change in the mean ionic activity coefficient of the electrolyte. This is due to the change in the ionic conductivity of solution and the interactions between the ions, solutes and water.For the cell (III) containing the mixed aqueous electrolyte (K_3PO_4 and NaBr):

$$\text{Cation (Na) ISE}|\text{NaBr } (m_B) + \text{electrolyte } (m_C) + \text{DL} - \text{valine } (m_A)|\text{Anion (Br) ISE}(III). \tag{III}$$

The Nernst equation is represented as [22]:

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

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:

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

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

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

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 the reference