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Transfer Properties of Ethanol-Amino Acid-Water System at Different Temperatures

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The densities of sodium chloride, glycine and *dl*-alanine were measured in aqueous ethanol solution at different temperatures. The concentration of sodium chloride, glycine and *dl*-alanine varied from 0.01 to 0.1 molar. In this range transfer functions of electrolyte from water to ethanol solution are found to be identical to complementary transfer functions of ethanol from water to electrolyte solutions. Volume of transfer is found to increase with increase in temperature.

INTRODUCTION

The understanding of the behaviour of a non-electrolyte in aqueous electrolyte solutions is of fundamental importance in life sciences, oceanography and industry. Thermodynamic studies of amino acids as model compound of proteins offer an alternative to understanding the factors governing the stability and thermodynamics of biopolymers. The thermodynamic properties are essential to characterize the non-electrolyte-electrolyte interactions and to predict the temperature and pressure dependence of various equilibrium properties. Salting in and salting out effects which can be estimated from solubility or distribution coefficient measurements, are related to free energies of transfer of non-electrolytes from water to electrolyte solutions[1,2]. Ethanol is soluble in water in all proportions, it is hydrophobic in nature and thermodynamic properties of its aqueous solutions are well known[3–10]. In the present work densities of solutions of sodium chloride, glycine and *dl*-alanine in aqueous ethanol solution at different temperatures were measured. Concentration of sodium chloride, glycine and *dl*-alanine solutions varied from 0.01–0.1 M.

From known apparent molal volume of ethanol in water, the transfer volumes from water to electrolyte solution have been estimated.

EXPERIMENTAL

Glycine and *dl*-alanine of Fluka AG puris grade were dried in vacuum for 3–4 h and used without further purification. Sodium chloride (Merck AnalaR

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grade) was used for preparation of sodium chloride solutions. Densities were measured with double-limbed pycnometer of 50 ml capacity. The height of solution in the limb was measured by travelling microscope of least count 0.001 cm. Accuracy of density measurement was ±0.000005 gm/cc. Temperature was maintained constant to ±0.02°C. All solutions were prepared by weight. Ethanol concentration was maintained around 0.02 molal in all measurements to enable neglecting ethanol-ethanol interactions in comparison to ethanol-electrolyte interactions.

The apparent molal volume, ϕ_v, was calculated from densities of solution using following equation:

$$\phi_v = \frac{M}{d} - \frac{1000(d - d_0)}{mdd_0} \tag{1}$$

where M is molecular weight of solute, m is molality of solute in water or electrolyte solution, d and d_0 densities of solution and solvent respectively.

RESULTS AND DISCUSSION

ϕ_v of sodium chloride and amino acids vary linearly with their concentration in aqueous ethanol and water solutions. Limiting apparent molar volume ϕ°_v was obtained by fitting the apparent molal volume and concentrations by least square method to:

$$\phi_v = \phi^{\circ}_v + S_v m \tag{1}$$

ϕ°_v values at different temperatures are reported in Table 1.

TABLE 1
APPARENT MOLAL VOLUMES AT INFINITE DILUTION AT DIFFERENT TEMPERATURES

Solute in 0.02 molal ethanol	$^{\circ}$v ml mol^{-1}		
	5°C	15°C	25°C
NaCl	14.18	15.60	16.65
Glycine	42.89	43.00	43.10
dl-alanine	57.70	58.97	60.00

Apparent molar volume of transfer at infinite dilution of sodium chloride and amino acids from water to ethanol solutions and its complementary transfer function of ethanol from water to electrolyte solution was obtained by using following equations:

$$\phi^{\circ}_{vtr}\,(\text{water} \rightarrow \text{ethanol aq}) = \phi^{\circ}_v\,(\text{ethanol aq} - \phi^{\circ}_v\ \text{water}) \tag{2}$$

$$\phi^{\circ}_{vtr}\,(\text{water} \rightarrow \text{aq. electrolyte}) = \phi^{\circ}_v\,(\text{aq electrolyte} - \phi_v{}^{\circ}\ \text{water}) \tag{3}$$

Fig. 1 shows that ϕ°_{vtr} from water to aqueous ethanol are all slightly negative. ϕ°_{vtr} of ethanol from water to aqueous electrolyte is as well negative and comparable to its complementary transfer function. As the concentration of electrolyte increases ϕ°_{vtr} becomes more negative (Fig. 1).

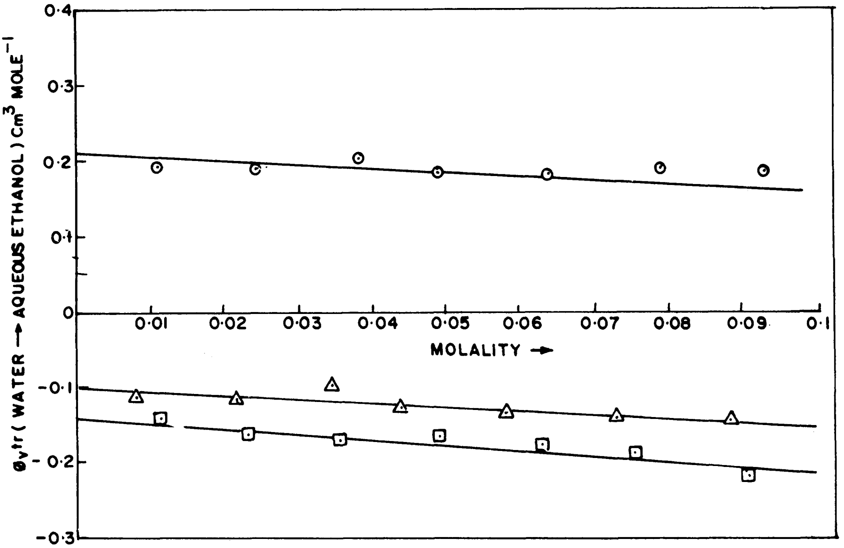

Fig. 1 Plot of ϕ_{vtr} (water → aqueous ethanol) against molality ○—○ NaCl, △—△ glycine and ▣—▣ dl-alanine

These observations can be explained qualitatively considering the ternary system of non-electrolyte (N), water (W) and electrolyte (E). According to Desnoyers[11] for a ternary system the concentration dependence of transfer functions are given by:

$$\frac{d}{dC_E}\{\phi^{\circ}_{vtr}(W \rightarrow W + E)\} = B_{NE} + 2B_{NEE}C_E + \ldots \qquad (4)$$

and

$$\frac{d}{dC_N}\{\phi^{\circ}_{vtr}(W \rightarrow W + N)\} = B_{EN} + 2B_{ENN}C_N + \ldots \qquad (5)$$

where C_E and C_N are the concentrations of electrolyte and non-electrolyte respectively, B_{NE} and B_{EN} are interaction parameters between different solutes in solution including solute- solvent interactions. At low concentration triplet interaction terms B_{NEE} and B_{ENN} became insignificant. Hence, the concentration dependence of two transfer functions can be compared through B_{NE} and B_{EN}. The pair interaction parameter of nonelectrolyte surrounded by ions is thus same as that of an ion surrounded by nonelectrolytes.

Franks *et al*[7] have pointed out that the partial molar volume of a nonelectrolyte is a combination of two factors, *viz.*, the intrinsic volume of solute and volume changes due to its interaction with solvent.

To evaluate the contribution of solute molecules towards its partial molar volume, Shahidi *et al*[13] have shown

$$V^0 = V_{vw} + V_{void} - n\sigma s$$

where V_{vw} is Van der Waals' volume, V_{void} is volume associated with the voids or empty spaces present, σ_s is the shrinkage in volume produced by the interaction of hydrogen bonding groups present in the solute with water molecules and *n* is the potential number of hydrogen bonding atom in the molecule. ϕ°_v of amino acid can be evaluated as

$$\phi^\circ_v = \overline{V}^\circ = V_{vw} + V_{void} - V_{shrinkage}$$

If we assume that V_{vw} and V_{void} remain of the same magnitude in water and aqueous ethanol the negative volumes of transfer for amino acids and sodium chloride can be explained to result from increase in shrinkage volume due to presence of ethanol in aqueous solution. Ethanol-water solution is more structured than pure water due to hydrophobic hydration caused by ethanol. The presence of NH_3^+ and COO^- of amino acid in aqueous ethanol causes electrostriction and rupture of hydrogen bonded network. The negative ϕ°_{vtr} is thus due to electrolyte-nonelectrolyte interactions. Due to these interactions structure enhancing tendency of ethanol will be reduced.

In case of sodium chloride positive volume of transfer results from stronger electrostriction of Na^+ and Cl^- ions.

As the temperature increases from 5° to 25°C the volume of transfer increases becoming less negative at higher temperature (Fig. 2). At lower temperatures water is more structured and hence ethanol electrolyte interaction increases giving more negative ϕ°_{vtr}. At high temperatures hydrogen bonded network of water is broken and ethanol-water interaction is as well preferred reducing nonelectrolyte-electrolyte interaction.

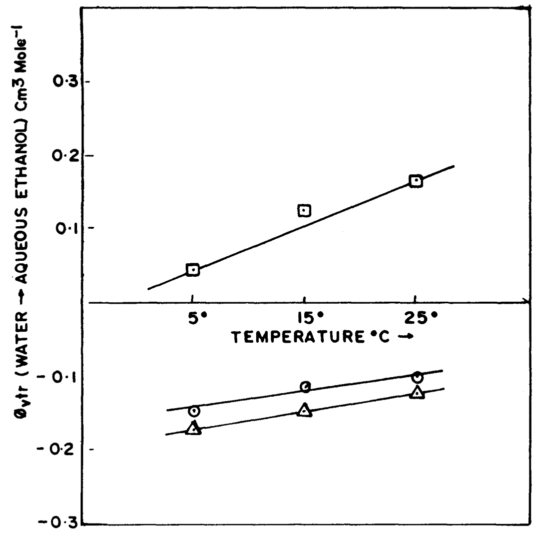

Fig. 2 Plot of ϕvtr (water → aqueous ethanol) against temperature. ⊡-⊡ NaCl, ○—○ Glycine and Δ—Δ dl-alanine

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