

A thermodynamic study of the ternary system water + glucose + electrolyte at 298.15 K

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Abstract

The standard free energies of transfer of KCl, NaCl, HCl, MgCl₂ and CaCl₂ from water to aqueous solutions of 5, 10, 15, 20, 25 and 30 Wt.% glucose have been determined at 298.15 K from e.m.f. measurements of cells without liquid junctions. It has been shown that the standard free energy of transfer for each of the electrolytes investigated increases linearly with increasing mole fraction of glucose in the mixed media. Free energies of pair interaction have also been calculated: these were found to be positive for NaCl–glucose, HCl–glucose and CaCl₂–glucose pairs, and nearly zero for KCl–glucose and MgCl₂–glucose pairs in water. The experimental results are discussed in terms of solute–solvent and solute–solute interactions in water + glucose + electrolyte systems.

INTRODUCTION

During the last decade, aqueous solutions of hydrophilic non-electrolytes have received considerable attention. They are generally characterized by weak non-bonding intermolecular interactions that, because of their low specificity, are of interest for biological systems [1]. Glucose has been regarded as one of the typical hydrophilic non-electrolytes resembling urea. The excess free energies [2], excess enthalpies [3], excess volumes [4, 5], excess heat capacities [4, 6], excess expansivities and excess isoentropic compressibilities [4] of aqueous solutions of glucose have been extensively studied. Excellent reviews on the thermodynamic properties of aqueous glucose solutions have been recently published by Goldberg and Tewari [7] and Barone [8].

Despite the interest in glucose + water mixtures, relatively few studies [9, 10] have been reported on the thermodynamics of water + glucose + electrolyte systems. As part of the continuing study of the thermodynamic

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properties of water + hydrophilic non-electrolyte + electrolyte systems [11–13], we present here the results for the standard free energies of transfer of potassium chloride, sodium chloride, hydrochloric acid, magnesium chloride and calcium chloride from water to water + glucose mixtures containing 5, 10, 15, 20, 25 and 30 wt.% glucose, and those for the free energies of pair interaction between the electrolyte and glucose in water at 298.15 K. It is expected that our studies will provide additional information on solute–solute and solute–solvent interactions in these systems.

Measurements were made of the e.m.f.'s of the cells (A) and (B) at $m_s = m_w$

(A) Electrode reversible to M^+ or $M^{2+} \mid MCl$ or $MCl_2(m_s), N(Y) \mid AgCl, Ag$

(B) Electrode reversible to M^+ or $M^{2+} \mid MCl$ or $MCl_2(m_w), H_2O \mid AgCl, Ag$

where m is the molality of the electrolyte. The subscripts w and s refer to water and aqueous glucose solvent mixtures, respectively. Y in parentheses is the wt.% of glucose in the mixed solvents.

EXPERIMENTAL

Anhydrous glucose (A.R. Shanghai Chem. Co.) was dried under vacuum at 70°C to constant weight and used without further purification. NaCl and KCl (A.R. Shanghai Chem. Co.) were purified as before [13]. Stock aqueous solutions of electrolytes were prepared by weight except for those of $CaCl_2$ and $MgCl_2$ (A.R. Beijing Chem. Co.), whose composition in stock solutions were determined gravimetrically because these salts are not easy to weigh accurately in air. Conductivity water, with a specific conductivity of $1.1 \mu\Omega^{-1} \text{cm}^{-1}$, was prepared by distilling the deionized water from alkaline permanganate in an all-Pyrex still. All test solutions were made by weighing water, glucose and the stock aqueous solution of the respective electrolyte.

An Na^+ glass electrode (Jiangsu 312), a K^+ PVC membrane electrode (Orion 93-19), a Ca^{2+} PVC membrane electrode (Suzhou) and a divalent cationic PVC membrane electrode (Jiangsu 404) were used in this work. These ion selective electrodes (ISE) were activated before use according to the manufacturer's instruction. The silver–silver chloride electrodes were produced by the thermal electrolytic method [14]. Only those silver–silver chloride electrodes whose bias potential was less than 0.04 mV were used. Over the time interval of the measurement program, the experimental slopes of the electrodes were 59.5 ± 0.1 mV for the Na^+ electrode, 60.0 ± 0.2 mV for the K^+ electrode, 29.50 ± 0.05 mV for the Ca^{2+} electrode and 29.10 ± 0.07 mV for the divalent cationic electrode, as obtained by the procedure described earlier [11, 12]. The e.m.f. measurements on the cells (A) and (B) were carried out using an Orion PH/ISE meter (Model 720 A) with a resolution of 0.1 mV.

It has been shown by a number of investigations [15, 16] that the e.m.f. of a cell usually changes slowly with time because of the asymmetry potential of the ISE. This problem restricts extensive use of ISE for accurate thermodynamic measurement. To provide high accuracy of the experimental results, the principles for eliminating the asymmetry potential proposed by Feakins et al. [17] were applied in this work. For a measurement, two Ag–AgCl electrodes were soaked overnight in an aqueous solution of a given salt molality and a glucose + water solution of the same salt molality. Two cells containing these solutions and the electrodes, such as cells (A) and (B), were then set up in a water bath at 298.15 ± 0.02 K. After 40 min, the e.m.f. of the cell normally changed very slowly with time. When the e.m.f. of the cell was constant within 0.1 mV for at least 10 min, each ISE was then transferred to the other cell. While its drift rate of potential was the same as in the first cell, the e.m.f. of the cells was recorded. The ISEs were then interchanged between the cells until the potential difference between the two cells was constant to within 0.1 mV for three consecutive transfers.

To simplify the treatment of the experimental data, the volalities, m_s and m_w , were made equal to each other in the ternary and binary systems. The molality of electrolyte in the cell solutions was in the range of 0.007–0.10 mol kg⁻¹ and accurate to approx. 0.01%. Y is known to within ± 0.005 .

RESULTS AND DISCUSSION

Electrolyte–solvent interaction in the ternary system

As an example, the observed differences in e.m.f. ΔE , between cells (A) and (B) for different molalities of NaCl in different glucose + water mixtures are listed in Table 1.

TABLE 1

ΔE /mV between cells (A) and (B) at different molalities of NaCl in different glucose + water mixtures

$m/(\text{mol kg}^{-1})$	Y					
	5	10	15	20	25	30
0.006999	-3.1	-6.45	-10.0	-13.8	-17.7	-21.8
0.01500	-3.0	-6.3	-9.65	-13.4	-17.2	-21.3
0.02500	-3.0	-6.15	-9.55	-13.2	-16.8	-20.95
0.04000	-2.85	-5.95	-9.3	-12.9	-16.55	-20.4
0.07000	-2.8	-5.8	-9.0	-12.65	-16.1	-19.95
0.09998	-2.6	-5.7	-8.95	-12.2	-15.8	-19.6

The standard ΔE^\ominus values were obtained by extrapolating the function $\Delta E'$, defined by eqn. (1), against I to $I = 0$

$$\begin{aligned}\Delta E' &= \Delta E + (vk/n)[f(m_s) - f(m_w)] \\ &= \Delta E^\ominus - (vk/n) \Delta bI\end{aligned}\quad (1)$$

where

$$f(m) = -A |Z_+ Z_-| I^{1/2} / (1 + B\hat{a}I^{1/2}) - \log(1 + 0.001vmM_s)$$

where v is the number of ions into which the electrolyte dissociates, $k = 2.3026 RT/F$, I is the ionic strength (molality scale) in solutions, Δb is the difference between the coefficients of the first power of I in the extended Debye–Hückel equation in the two solvents and a constant depending upon the solute and solvent properties, \hat{a} is the ion size parameter, and M_s is the mean or the simple molar mass of the mixed solvents or water, respectively. A and B are the conventional Debye–Hückel constants given by the equations

$$A/(\text{mol}^{-1/2} \text{kg}^{1/2} \text{K}^{3/2}) = 1.8246 \times 10^5 d^{1/2} (DT)^{-3/2} \quad (2)$$

$$B/(\text{cm}^{-1} \text{mol}^{-1/2} \text{kg}^{1/2} \text{K}^{1/2}) = 50.29 d^{1/2} (DT)^{-1/2} \quad (3)$$

Other terms have their usual meanings. Because alteration of the value of \hat{a} caused no significant change in ΔE^\ominus , the usual values [13] of 4.4 Å for KCl and NaCl, 4.7 Å for CaCl₂ and 5.0 Å for MgCl₂ were used in all cases. Values for the dielectric constant D were taken from the data of Malmberg and Maryott [18] and the density values d were calculated from the equation given by Daldrup and Schönert [5]. In fact, a least-squares analysis was used to obtain values of ΔE^\ominus . The standard deviation in ΔE^\ominus was less than 0.1 mV for most of the systems and not greater than 0.1 mV for the worst case. The ΔE^\ominus values of the HCl + H₂O + glucose system were computed from the E^\ominus values of cell (C) [19] and cell (D) [20].

(C) Pt, H₂ | HCl, glucose + H₂O | AgCl, Ag

(D) Pt, H₂ | HCl, H₂O | AgCl, Ag

The standard free energies of transfer, ΔG_t^\ominus , of electrolyte from water to glucose + water mixtures on a molality scale were calculated from the equation

$$\Delta G_t^\ominus = -nF\Delta E^\ominus \quad (4)$$

where F is the Faraday constant. The values of ΔG_t^\ominus are summarized in Table 2.

The standard free energy of transfer is an important index of the difference in interactions of ion or electrolyte with solvent molecules in the two different solvents. Figure 1 shows the variation of the ΔG_t^\ominus values of the electrolytes with mole fraction of glucose (x_N) in the mixed solvents.

TABLE 2

Values of ΔG_i^\ominus /(kJ mol⁻¹) (molality scale) in glucose + water mixtures at 298.15 K

Electrolyte	Y						
	0	5	10	15	20	25	30
KCl	0	0.26	0.53	0.80	1.08	1.40	1.74
NaCl	0	0.31	0.65	1.00	1.39	1.77	2.20
HCl ^a	0	0.36	0.79	—	1.73	—	2.78
MgCl ₂	0	0.35	0.69	1.08	1.49	1.92	2.37
CaCl ₂	0	0.62	1.31	2.05	2.86	3.75	4.70

^a ΔG_i^\ominus values for this system were calculated from E^\ominus values in the literature [19, 20].

These profiles of ΔG_i^\ominus against composition illustrate some interesting features. As the proportion of glucose increases, the ΔG_i^\ominus values for the electrolytes examined become increasingly positive, indicating increased destabilization and decreased solvation in the mixed solvents. Similar trends of ΔG_i^\ominus were observed for the transfer of some electrolytes from water to aqueous mixtures of methanol [21], ethanol [22], ethylene glycol [23], propylene glycol [24], glycerol [25], mannitol [26], sorbitol [26] and sucrose [13]. This possibly results partly from Born-type electrostatic

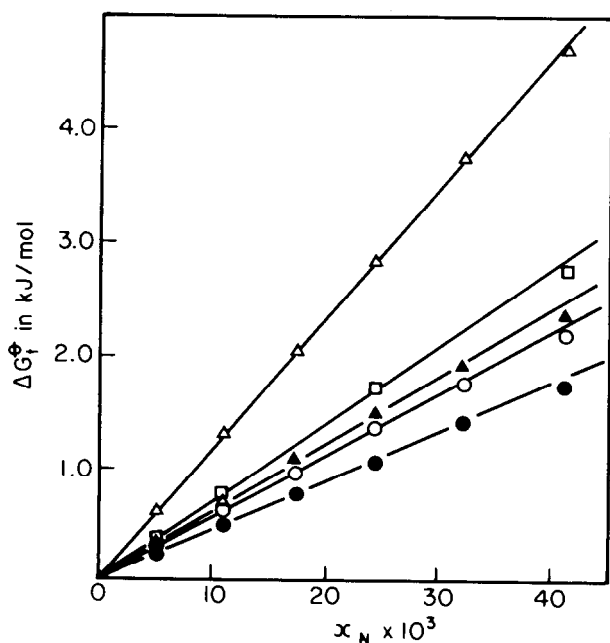


Fig. 1. Variation of ΔG_i^\ominus for the electrolytes with mole fraction of glucose (x_N) in mixed solvents: ●, KCl; ○, NaCl; □, HCl; ▲, MgCl₂; △, CaCl₂.

effects [27] arising from decreasing dielectric constant of the mixed solvents [18], and partly from chemical effects [28] arising from solvent acidity–basicity [29], preferential solvation [30] and structural aspects of the mixed solvent.

However, it was not expected that the values of $\Delta G_1^\ominus(\text{MgCl}_2)$ would be close to those of $\Delta G_1^\ominus(\text{HCl})$, $\Delta G_1^\ominus(\text{NaCl})$ and $\Delta G_1^\ominus(\text{KCl})$ or much smaller than $\Delta G_1^\ominus(\text{CaCl}_2)$ values. The molecular reason for this phenomenon is not at all understood, but it seems likely that the lower values of $\Delta G_1^\ominus(\text{MgCl}_2)$ (relative to CaCl_2) reflects the lower hydration number of MgCl_2 . In effect Mg^{2+} is less sensitive to changes in solvent composition than would be expected because it interacts directly with fewer solvent molecules than does Ca^{2+} . Neutron diffraction studies may give unambiguous information about the arrangement of solvent molecules around ions in aqueous solution. These studies [31, 32] indicate a hydration number of around 6 for Mg^{2+} , and a little less for K^+ , while the value for Ca^{2+} is around 10. In addition, a value of 6 was indicated for Na^+ from molecular dynamics simulations [33]. This supports the explanation above for the ΔG_1^\ominus values of the different electrolytes.

Electrolyte–glucose interaction in water

The free energy parameters of pair interaction g_{NE} (where N and E stand, respectively, for non-electrolyte and electrolyte) between the electrolyte and glucose in water were derived as described previously [13, 34]. They are presented in Table 3. These parameters characterize the mean behavior of all the pair interactions between glucose and each of the ions of a given electrolyte. Here, for instance, for electrolyte– CaCl_2 , it follows that

$$g_{\text{NE}} = (g_{\text{glucose}-\text{Ca}^{2+}} + 2g_{\text{glucose}-\text{Cl}^-})/3 \quad (5)$$

and $2vg_{\text{NE}}$ reflects the interaction of the electrolyte–glucose pair. It is apparent from Table 3 that: (a) the $2vg_{\text{NE}}$ values for the pairs glucose– NaCl , glucose– HCl and glucose– CaCl_2 are positive, indicating a repulsive interaction between these electrolytes and glucose, and (b) in the case of glucose– KCl and glucose– MgCl_2 , no significant interaction is observed. This means that glucose is salted-out by the addition of NaCl , HCl and CaCl_2 , whereas the effects of KCl and MgCl_2 are negligible. The ob-

TABLE 3

Free energy interaction parameter g_{NE} for electrolyte–glucose pairs in water, and salting constants k_s for glucose in aqueous electrolyte solutions at 298.15 K

Parameter	KCl	NaCl	HCl	MgCl ₂	CaCl ₂
$2vg_{\text{NE}}/(\text{J kg mol}^{-2})$	9	207	395	≈0	877
$k_s/(\text{kg mol}^{-1})$	0.004	0.084	0.159	≈0	0.354

ervation here for NaCl and KCl is qualitatively consistent with results reported by Morel et al. [9]. Kelly [35] has investigated the effect of electrolytes on the solubility of glucose in water. From his experimental data, it can be concluded that CaCl_2 reduces the solubility of glucose, while KCl and NaCl increase the solubility of glucose in water. Compared to our results, this underlines that fact that the interactions between electrolyte and glucose in dilute aqueous solutions are sometimes very different from those in concentrated solutions. A similar conclusion was drawn from activity coefficient studies on the NaCl + water + sucrose system [36].

However, if the $2v_{g_{NE}}$ values of the electrolyte (KCl, NaCl, MgCl_2 and CaCl_2)–sucrose pairs [13] are plotted against those of the corresponding electrolyte–glucose pairs reported in this work, a straight line through the origin is obtained (Fig. 2). The slope of this straight line is found to be about 1.39, suggesting that the interaction of a given electrolyte with sucrose is, on average, 1.39 times that of the same electrolyte with glucose. This proportion should reflect differences in the molecular structure and hydration properties of sucrose and glucose. The molar mass ratio, OH group number ratio and mean e-OH group number ratio of sucrose to glucose is 1.90, 1.60 and 1.38 [37], respectively. This appears to suggest that the difference in the mean e-OH group number of the sugar molecules is one of the important factors leading to differences in the interactions of a given electrolyte with sucrose and glucose. Moreover, the linear relation

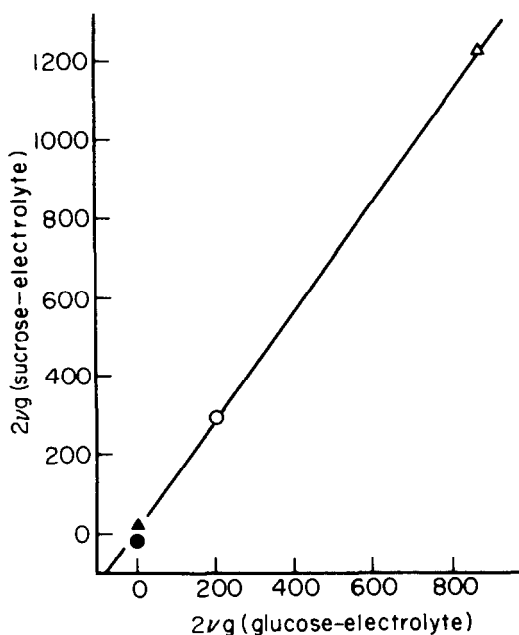


Fig. 2. Relations between the free energy interaction parameters for electrolyte–sucrose pairs and for electrolyte–glucose pairs in water: ●, KCl; ○, NaCl; ▲, MgCl_2 ; △, CaCl_2 .

shown in Fig. 2 can be used to estimate the value of the free energy of interaction of an electrolyte with sucrose (or glucose) from that of this electrolyte with glucose (or sucrose). For example, although the $g_{\text{sucrose-HCl}}$ value is not easy to obtain experimentally, by the using $2vg_{\text{glucose-HCl}}$ value given in Table 3, $2vg_{\text{sucrose-HCl}}$ can be found to be about $550 \text{ J kg mol}^{-2}$ from an interpolation of the straight line mentioned above.

In fact, salting-in and salting-out are usually expressed in terms of the salting constant. According to the approach of Desnoyers and his coworkers [34], the salting constant can be related to the pair free energy interaction parameter by

$$k_s = 2vg_{\text{NE}}/RT \quad (6)$$

The salting constants of the electrolyte–glucose systems calculated from relation (6) are also given in Table 3. This constant is usually around $\pm 0.7 \text{ mol}^{-1} \text{ kg}$ [38]. The electrolyte–glucose systems have k_s , values well within these limits. Lilley and coworkers have determined the activity coefficients of NaCl [39] and CaCl_2 [40] in aqueous solutions of various amino acids and some peptides at 298.15 K using cells with transference and a Ca^{2+} ion-exchange electrode, respectively. They tabulate values of a parameter A , where our salting constant $k_s = 2A$ for NaCl, and $k_s = 3A \ln 10$ for CaCl_2 . Thus salting constants obtained are negative enough for all amino acid (or peptide)–electrolyte system. These correspond to extensive salting-in of the amino acid (or peptide) by the electrolytes, in contrast to the salting-out of glucose by NaCl, HCl and CaCl_2 . However, the k_s values for the amino acid– CaCl_2 systems are considerably greater than $\pm 0.7 \text{ kg mol}^{-1}$.

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