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Determination of water activity, osmotic coefficient, activity coefficient, solubility, excess Gibbs energy and transfer Gibbs energy of KCl-D-sucrose-water mixture at 298.15 K



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1. Introduction

ABSTRACT

In this paper, we present the results of investigations of the KCl-D-sucrose-H₂O ternary system using hygrometric method based on measurement of the relative humidity at the wide range of concentration to about saturation for both KCl and D-sucrose in different molalities of D-sucrose of (0.20, 0.50, 1.00, 2.00, 3.00, 4.00, 5.00 and 6.00) mol.kg⁻¹ with the molality of KCl ranged from (0.20 to 4.50) mol.kg⁻¹ at 298.15 K. The measured data are used to determine the water activities and osmotic coefficients. These studies are complemented using Pitzer-Simonson-Clegg model to understand different interactions involved between carbohydrates and KCl. Therefore, the water was considered as reference state in this study. Thus four mixture parameters are determined and used to predict the mean activity coefficients of KCl and D-sucrose. The solubility, excess Gibbs energy and transfer Gibbs energy are also calculated for this system.

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D-sucrose has long been a very interesting subject and continues to attract the intention of researchers in terms of structural and theoretical investigations. The characterization of the thermodynamic properties of electrolytes and non-electrolyte solutions is useful to understand the nature of the structure of aqueous electrolytes, and for practical application in different industrial fields and domain of science and technology such as food processing, chemical and pharmaceutical industries, biochemical systems [1– 3]. Other objectives to study the ionic interactions involved in an aqueous solution of D-sucrose with an electrolyte is due to the presence of ions in systems in the biology domain. Among the ions that have a very important interest in biological systems are Ca²⁺, Na⁺, K⁺, and Cl⁻ which play a vital role in metabolic activities. Ionic groups can participate in determining the form and the function of biomolecules. In particular, ion Potassium is the main intracellular cation in mammals. It is implicated in many physiological functions, as the control of cell volume, enzymatic activities, the nerve impulse conduction, and the regulation of blood pH. The knowledge about potassium metabolism in presence with the sugar, and the different interactions that occur in the mixtures is a great interest in patho-physiological conditions, with their consequences on the health.

Several methods are used to measure some thermodynamic parameters of the aqueous solution composed by D–sucrose and electrolyte such as the e.m.f. techniques [4–6], isopiestic vapour pressure [7,8], and calorimetric method [9,10].

The thermodynamic properties of this system have been well characterized by many studies. Kelley [11] determined the phase diagrams at 30 °C for systems water-D-sucrose and KCl, NaCl, MgSO₄, CaCl₂, CdI₂, or CuSO₄, Kim and Reinfelds [12] have determined the diffusion coefficients for two compositions of the system H₂O-D-sucrose-KCl at 25 °C. Herrington and Meunie [13] using the freezing points of the ternary system KCl-D-sucrose-H₂O to measure the osmotic coefficients of this ternary system in the concentration range (0.2–2.8) mol.kg⁻¹ at 0 °C Wang et al. [14] have determined the Standard Gibbs energies of transfer, of

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KCl, NaCl, MgCl₂, and CaCl₂, from water to aqueous solutions of (5, 10, 15, 20, 25 and 30) wt% of D-sucrose at 298.15 K from e.m.f measurements. Liu et al. [15] have reported the viscosities and densities at 298.15 K and 308.15 K for NaCl and KCl in aqueous D-sucrose solutions. The other thermodynamic properties and behaviour of such chemical systems are poorly known. The osmotic and activity coefficients of the KCl-D-sucrose-H₂O system at relative molalities up to saturation are not reported in the literature, hence the need to pursue experimental and theoretical studies with adequate models to understand the behaviour and obtain sufficient data on the mixture of aqueous D-sucrose with KCl. Therefore, this paper is the continuation of the research in ternary aqueous of electrolytes and non-electrolyte solutions mixtures [16]. In this work, we measure and compute some thermodynamic parameters to develop our knowledge on this system and we study the influence of the two ions K⁺. Cl⁻ on D-sucrose and on ionic interactions.

We have performed the measurements of the relative humidity of mixture of KCl-D-sucrose-H₂O over the wide range of concentration studied for both KCl and D-sucrose for different molality of the D-sucrose of (0.20, 0.50, 1.00, 2.00, 3.00, 4.00, 5.00 and 6.00) mol.kg⁻¹ with the molality range of KCl from (0.20 to 4.50) mol.kg⁻¹ at constant temperature of 298.15 K. From these measurements, the osmotic coefficients were deduced. The solute activity coefficients, excess Gibbs energy, transfer Gibbs energies of KCl from water to mixture (water + D-sucrose) and KCl solubility in water-D-sucrose system are calculated by using the Pitzer-Simonson-Clegg model [17–19]. The reference state considered in the present work is water as solvent.

2. Experimental

Measurements of water activity of aqueous ternary system for the mixture of electrolyte with non-electrolyte KCl-D–sucrose- H_2O are performed using our apparatus described in our previous studies [20,21]. This method was validated by determination of the thermodynamic properties of binary aqueous chlorides [22], sulphates [23], and ternary mixed electrolytes [24–26].

This apparatus is based on hygrometric measurements of the relative humidity of the solution by determination of the diameter of the droplet formed from previously calibrated reference solutions. The diameter is measured by a microscope equipped with a micrometric screw. The drops of reference solutions NaCl(aq) or LiCl(aq) are pulverised on the spider thin thread which is kept tense and fixed over the solution. The vessel containing the studied solution is placed in a thermostatted box. A microscope

The drop diameter $D(a_{w(ref)})$ is measured for the reference solution above the same reference solution and the same diameter $D(a_w)$ above the studied solution. Thus, we calculate the growth ratio K ($K = D(a_{w(ref)})/D(a_w)$) of the drop. From the ratio K, we determine the water activity of studied solution using the variation of K versus the water activity of reference solution of sodium chloride or lithium chloride. The reference relative humidity is taking as 0.84 or 0.98 for dilute solution.

The preparation of the solutions were made from the anhydrous materials from Panreac, Merck and Fluka (Table 1) without other

purification and with deionized distilled water (conductivity $\langle 5 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1} \rangle$). The molality uncertainty is about $u(m) = 0.01 \text{ mol.kg}^{-1}$ and is checked by refractive index with uncertainty of $u(n) = 2 \times 10^{-4}$. The relative humidity uncertainties are mainly due to the drop diameters measurements and are estimated to $u(rh) = 5 \ 10^{-4}$ for $a_w > 0.95$ and $u(rh) = 2 \times 10^{-3}$ for $a_w < 0.95$. The temperature is fixed at T = 298.15 K with uncertainty of u(T) = 0.05 K.

3. Theoretical model

Several models are used to correlate the thermodynamic properties of aqueous solutions of electrolytes and non-electrolytes. The Pitzer-Simonson-Clegg equations [17–19] is one of the widely employed by researchers in the domain of thermodynamic of the solutions, because it can represents the osmotic activity and activity coefficients with acceptable agreement [27]. We have used this model to determine thermodynamic properties of the studied system and correlate some parameter obtained by measurement of water activity of the ternary system KCl-D–sucrose-water.

3.1. The Pitzer-Simonson-Clegg model

The excess Gibbs energy per mole is the contribution of a longrange electrostatic g_{PDH}^{ex} and a short-range interaction g_{PSC}^{ex} :

$$\frac{g^{Ex}}{RT} = \frac{g^{ex}_{PDH}}{RT} + \frac{g^{ex}_{PSC}}{RT},$$
(5)

where R is the universal constant of ideal gas and T is the Temperature. For water (1)-D–sucrose (2)-potassium chloride (MX) system, the long-range term is given by:

$$\begin{aligned} \frac{g_{ISC}^{FSC}}{RT} &= x_1(x_1 \cdot W_{1,MX} + x_2 W_{2,MX}) + x_I^2(x_1 \cdot U_{1,MX} + x_2 U_{2,MX}) \\ &+ x_I^2(x_1^2 \cdot V_{1,MX} + x_2^2 V_{2,MX}) \\ &+ x_1 x_2 \bigg[W_{12} + U_{12}(x_1 - x_2) + x_I \bigg(Y_{1,2,MX}^0 + Y_{1,2,MX}^1 \frac{x_I^2}{4} \bigg) \bigg], \end{aligned}$$
(6)

where x_1 , x_2 , and x_l are the mole fraction of water, of D-sucrose and the total mole fraction of ion ($x_l = 1 - x_1 - x_2$), respectively. $W_{1,MX}$, $U_{1,MX}$ and $V_{1,MX}$ are the equation parameters adjusted from experimental data of single electrolyte KCl-water system. W_{12} and U_{12} are the model parameters for the description of D-sucrose-water system. $W_{2,MX}$, $U_{2,MX}$, $V_{2,MX}$, $Y_{1,2,MX}^0$ and $Y_{1,2,MX}^1$ are the model parameters used to represent the interactions arising in mixtures including both non-ionic and ionic solutes.

The long-range Pitzer-Debye-Hückel term is expressed by:

$$\frac{g_{PDH}^{ex}}{RT} = -\left(\frac{4A_xI_x}{\rho}\right)\ln\left(1+\rho\cdot I_x^{1/2}\right) + \left(\frac{x_I^2}{4}\right)\left[B_{MX}g\left(\alpha\cdot I_x^{1/2}\right)\right],\tag{7}$$

 A_x is the Debye–Hückel parameter and equal to 2.917 [27], ρ represents the closest approach parameter and takes the value of 14.0292. B_{MX} is the Pitzer's parameter of MX. α the standard value equal to 13.0 [27]. I_x is the ionic strength $(I_x = \frac{1}{2}\sum_{i=1}^{2} z_i^2 x_i)$.

Hu and Guo [27] have postulated in their work that the determination of thermodynamic properties using Debye-Hückel

Table 1					
Descriptions	of	the	used	Chemicals	

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	Component	Cas Reg. No.	Suppliers	Initial mass fraction purity given by suppliers	Density g·cm ^{-3} (20 °C) given by suppliers
	Potassium Chloride	7447-40-7	Honeywell Fluka™	≥0.99	1.98
	Sodium Chloride	7647-14-	Merck KGaA	≥ 0.9999	2.17
	Lithium Chloride	5	Merck KGaA	≥ 0.99	2.07
	D-sucrose	7447-41-8	Panreac Quimica S.L.U.	≥ 0.990	n.a.
		57-50-1			

parameter A^{ϕ} and the closest approach distance for the ions ρ gives a large deviation from experimental data for D–sucrose solutions. In this study, taking account of this remark, we have used the density ρ_A and the dielectric constant *D* of water for estimating the Debye-Hückel parameter A_x . The function $g(y = \alpha \sqrt{I_x})$ is done as:

$$g(y) = \frac{2}{y^2} [1 - (1 + y)\exp(-y)]$$
(8)

The differentiation of Eqs. (6) and (7) allows obtaining the equations of activity coefficients of different components in mixed aqueous solution.

The water activity coefficient is expressed as:

$$\begin{aligned} \ln(\gamma_{1}) &= \frac{2 \cdot A_{X} \cdot I_{X}^{3/2}}{1 + \rho \cdot I_{X}^{1/2}} - I_{X}^{2} B_{MX} \exp\left(-\alpha \cdot I_{X}^{1/2}\right) \\ &+ x_{I}[(1 - x_{1}) \cdot W_{1,MX} - x_{2} \cdot W_{2,MX}] \\ &+ x_{I}^{2}[(1 - 2 \cdot x_{1}) \cdot U_{1,MX} - 2 \cdot x_{2} \cdot U_{2,MX}] \\ &+ x_{I}^{2}\left[x_{1}(2 - 3 \cdot x_{1}) \cdot V_{1,MX} - 3 \cdot x_{2}^{2} \cdot V_{2,MX}\right] \\ &+ \left[2x_{2} \cdot I_{x} \cdot (1 - 2 \cdot x_{1}) \cdot Y_{1,2,MX}^{0} + \left(\frac{x_{I}^{3}}{4}\right) \cdot x_{2} \cdot (1 - 4 \cdot x_{1}) \cdot Y_{1,2,MX}^{1}\right] \\ &+ x_{2} \cdot \left[(1 - x_{1}) \cdot W_{12} + (2 \cdot (x_{1} - x_{2}) \cdot (1 - x_{1}) + x_{2}) \cdot U_{12}\right], \end{aligned}$$
(9)

The D-sucrose activity coefficient is given as:

$$\begin{aligned} \ln(\gamma_{2}) &= \frac{2 \cdot A_{X} \cdot I_{X}^{3/2}}{1 + \rho \cdot I_{X}^{1/2}} - I_{X}^{2} B_{MX} \exp\left(-\alpha \cdot I_{x}^{1/2}\right) \\ &+ x_{I}[(1 - x_{2}) \cdot W_{2,MX} - x_{1} \cdot W_{1,MX}] \\ &+ x_{I}^{2}[(1 - 2 \cdot x_{2}) \cdot U_{2,MX} - 2 \cdot x_{1} \cdot U_{1,MX}] \\ &+ x_{I}^{2}\left[x_{2}(2 - 3 \cdot x_{2}) \cdot V_{2,MX} - 3 \cdot x_{1}^{2} \cdot V_{1,MX}\right] \\ &+ \left[2x_{1} \cdot I_{x} \cdot (1 - 2 \cdot x_{2}) \cdot Y_{1,2,MX}^{0} + \left(\frac{x_{I}^{3}}{4}\right) \cdot x_{1} \cdot (1 - 4 \cdot x_{2}) \cdot Y_{1,2,MX}^{1}\right] \\ &+ x_{1} \cdot \left[(1 - x_{2}) \cdot W_{12} + (2 \cdot (x_{1} - x_{2}) \cdot (1 - x_{2}) - x_{1}) \cdot U_{12}\right] \\ &- [W_{12} + U_{12}], \end{aligned}$$
(10)

The ionic mean activity coefficient of KCl in D-sucrose-water system is:

$$\begin{split} \ln(\gamma_{\pm}) &= -A_{X} \left[\left(\frac{2}{\rho} \right) \ln \left(1 + \rho \cdot I_{x}^{1/2} \right) + \frac{I_{x}^{1/2} (1 - 2 \cdot I_{x})}{1 + \rho \cdot I_{x}^{1/2}} \right] \\ &+ \left(\frac{I_{x}}{2} \right) B_{MX} \left[g \left(\alpha \cdot I_{x}^{1/2} \right) + \exp \left(-\alpha \cdot I_{x}^{1/2} \right) (1 - x_{I}) \right] \\ &+ (1 - x_{I}) [x_{1} \cdot W_{1,MX} + x_{2} \cdot W_{2,MX}] + 2 \\ &\cdot x_{I} (1 - x_{I}) [x_{1} \cdot U_{1,MX} + x_{2} \cdot U_{2,MX}] \\ &+ x_{I} (2 - 3 \cdot x_{I}) [x_{1}^{2} \cdot V_{1,MX} + x_{2}^{2} \cdot V_{2,MX}] + x_{1} \\ &\cdot x_{2} \left[(1 - 4 \cdot I_{x}) \cdot Y_{1,2,MX}^{0} + \left(3 \cdot I_{x}^{2} - \cdot x_{I}^{3} \right) \cdot Y_{1,2,MX}^{1} \right] - x_{1} \\ &\cdot x_{2} \cdot [W_{12} + 2 \cdot (x_{1} - x_{2}) \cdot U_{12}] - W_{1,MX} \end{split}$$
(11)

4. Results and discussion

4.1. Water activity and osmotic coefficient

The water activities have been measured for the range of D–sucrose molalities of (0.20, 0.50, 1.00, 2.00, 3.00, 4.00, 5.00 and 6.00) mol.kg⁻¹ at different molality of KCl from (0.20 to 4.50) mol.kg⁻¹. The values obtained are listed in Table 2 and presented in Fig. 1. The trend of a_w presents a decreases as the molality increases for different quantities of D–sucrose. This general trend is also observed for the most aqueous non-volatile electrolytes.

The osmotic coefficients are determined from our experimental results of water activity $a_{w(exp)}$. The calculated values are listed in Table 2 and shown in Fig. 2. The uncertainty on the osmotic coefficients is estimated to be $u(\phi) = 0.006$.

4.2. Activity coefficient

The unknown model parameters of Eq.6, for water-D-sucrosepotassium chloride, are calculated by the general least-squares method. The osmotic coefficients and ionic mean activity coefficients of single electrolyte system of KCl-water, obtained in our previous work [22] and combined with those of Hamer and Wu [28] were used for adjustment of model parameters B_{MX} , $W_{1,MX}$, $U_{1,MX}$ and $V_{1,MX}$. Table 3 gives these estimated parameters with the root mean square deviation σ_{ϕ} and σ_{γ} for each type of data. The obtained parameters in this study are compared to those adjusted by Hu and Guo [27], and to those of Clegg et al. [18] estimated from experimental data of Tang et al. [29] with a good agreement between our calculated values and experimental data of literature [22,28].

The parameters W_{12} and U_{12} of Eq. 9 are evaluated in the previous work[16] from experimental data of Robinson et al. [30] relative to the ϕ and γ of water-D-sucrose at 298.15 K. Table 3 shows the calculated parameters with the root mean square deviation (RMSD) of ϕ and γ for each type of data. These parameters are compared to those adjusted by Hu and Guo [27] with a good correlation of ϕ and γ .

The parameters $W_{2,MX}$, $U_{2,MX}$, $V_{2,MX}$, $Y_{1,2,MX}^0$ and $Y_{1,2,MX}^1$ are required to predict the mean activity coefficients of KCl and the activity coefficient of D-sucrose in the mixture. These parameters are adjusted from the osmotic coefficients obtained in this work for the studied mixture for (0.20, 0.50, 1.00, 2.0, 3.00, 4.00, 5.00 and 6.00) mol.kg⁻¹ of the D-sucrose in the molality range of KCl from (0.20 to 4.50) mol.kg⁻¹. These parameters are listed in Table 3 with the corresponding standard errors σ_s and standard deviations of the fit. The mean activity coefficients γ_{\pm} of KCl and the activity coefficient γ of D-sucrose in the ternary mixture are listed in Table 4. The plots of mean activity coefficients of KCl and the activity coefficients of D-sucrose as a function of molality of KCl are shown in Figs. 3 and 4, respectively.

Analysis of the optimized values of mixing model parameters for the system water-D-sucrose-KCl presents interesting characteristics concerning the aspect of the different interactions that can occur between species in the studied ternary system. The addition of D-sucrose to the KCl-water mixture has a significant effect on the thermodynamic properties of this salt. Indeed, the properties of mixed system depend on the interactions between KCl-Dsucrose, D-sucrose-water and KCl-water. We give in this section an interpretation of these different interactions for this mixture. These interactions are influenced by the degree of hydration of the electrolyte in presence of water, and consequently, the variation of the water activity, the practical osmotic coefficient of the mixture and activity coefficients of components. Fig. 1 presents the water activity of KCl versus $m_{\rm KCl}$ at different D-sucrose molalities. It can be seen from this Figure that the addition of a large amount of D-sucrose while keeping the same amount of KCl causes a significant reduction of the water activity, and therefore the reduction of the water vapor pressure above the solution. This trend can be explained that the water molecules are closely related to solutes. The water activity are arranged in the following order a_w $(m = 0.00) > a_w$ $(m = 0.20) > a_w$ $(m = 0.50) > a_w$ $(m = 1.00) > a_w$ $(m = 2.00) > a_w$ $(m = 3.00) > a_w$ $(m = 4.00) > a_w$ $(m = 5.00) > a_w$ (m = 6.00). For all mixture of two or more electrolytes in water,

Table 2

Water activities a_w and osmotic coefficients ϕ of KCl-D-sucrose-H₂O for (0.20, 0.50, 1.00, 2.00, 3.00, 4.00, 5.00 and 6.00) mol.kg⁻¹ (per 1 kg of pure water) of the D-sucrose $m_{D-sucrose}$ in the molality range m_{KCl} of KCl from 0.2 to 4.5 mol·kg⁻¹ (per 1 kg of pure water) at the temperature 298.15 K and p = 0.1 MPa.

$m_{\rm D-sucrose}/{\rm mol.kg^{-1}}$	$m \ { m KCl/mol.kg^{-1}}$	a _w	φ	$m_{\rm D-sucrose}/{\rm mol.kg}^{-1}$	$m _{\rm KCl}/{ m mol.kg^{-1}}$	a _w	φ
0.20	0.20	(0.9898)	0.9485	0.50	0.20	(0.9842)	0.9823
0.20	0.50	(0.9804)	0.9156	0.50	0.50	0.9749	0.9407
0.20	1.00	0.9649	0.9015	0.50	1.00	0.9596	0.9156
0.20	1.50	0.949	0.903	0.50	1.50	0.944	0.907
0.20	2.00	0.934	0.908	0.50	2.00	0.929	0.908
0.20	2.50	0.918	0.918	0.50	2.50	0.914	0.912
0.20	3.00	0.902	0.928	0.50	3.00	0.898	0.920
0.20	3.50	0.885	0.941	0.50	3.50	0.882	0.928
0.20	4.00	0.869	0.954	0.50	4.00	0.866	0.939
0.20	4.50	0.852	0.969	0.50	4.50	0.850	0.950
1.00	0.20	0.9742	1.0364	2.00	0.20	0.9523	1.1304
1.00	0.50	0.9652	0.9831	2.00	0.50	0.9437	1.0722
1.00	1.00	0.9503	0.9432	2.00	1.00	0.9297	1.0115
1.00	1.50	0.936	0.924	2.00	1.50	0.9161	0.9728
1.00	2.00	0.921	0.915	2.00	2.00	0.9026	0.9480
1.00	2.50	0.906	0.912	2.00	2.50	0.8892	0.9312
1.00	3.00	0.891	0.913	2.00	3.00	0.8759	0.9194
1.00	3.50	0.876	0.915	2.00	3.50	0.8626	0.9116
1.00	4.00	0.861	0.921	2.00	4.00	0.8493	0.9067
1.00	4.50	0.846	0.928	2.00	4.50	0.836	0.9039
3.00	0.20	0.928	1.222	4.00	0.20	0.902	1.308
3.00	0.50	0.920	1.160	4.00	0.50	0.894	1.245
3.00	1.00	0.907	1.087	4.00	1.00	0.882	1.165
3.00	1.50	0.894	1.036	4.00	1.50	0.870	1.103
3.00	2.00	0.882	0.997	4.00	2.00	0.859	1.055
3.00	2.50	0.870	0.969	4.00	2.50	0.848	1.017
3.00	3.00	0.858	0.946	4.00	3.00	0.838	0.984
3.00	3.50	0.846	0.928	4.00	3.50	0.827	0.957
3.00	4.00	0.835	0.913	4.00	4.00	0.817	0.934
3.00	4.50	0.823	0.902	4.00	4.50	0.807	0.915
5.00	0.20	0.874	1.390	6.00	0.20	0.844	1.470
5.00	0.50	0.866	1.327	6.00	0.50	0.838	1.406
5.00	1.00	0.855	1.241	6.00	1.00	0.827	1.317
5.00	1.50	0.844	1.174	6.00	1.50	0.817	1.244
5.00	2.00	0.834	1.118	6.00	2.00	0.808	1.182
5.00	2.50	0.825	1.071	6.00	2.50	0.800	1.129
5.00	3.00	0.815	1.031	6.00	3.00	0.791	1.082
5.00	3.50	0.806	0.996	6.00	3.50	0.784	1.041
5.00	4.00	0.798	0.966	6.00	4.00	0.776	1.004
5.00	4.50	0.789	0.939	6.00	4.50	0.769	0.972

Standard uncertainty of molality (per 1 kg of pure water) is $u(m) = 0.01 \text{ mol.kg}^{-1}$, temperature is u(T) = 0.05 K, and pressure is u(p) = 5 hPa. The standard uncertainty of water activity is $u(a_w) = 0.005$ for $a_w > 0.95$ and $u(a_w) = 0.002$ for $a_w < 0.95$, osmotic coefficient ϕ where $u(\phi) = 0.006$. The reference water activity is 0.84; numbers in parentheses are for reference water activity of 0.98.

1.000 0.950 0.900 0.850 0.800 0.750 0.700 0.00 0.50 1.00 1.50 2.00 2.50 3.00 3.50 4.00 4,50 5.00 mka/(mol.kg⁻¹)

Fig. 1. Water activity a_w of KCl - D-sucrose(aq) against molality of KCl m_{KCl} at different molalities of D-sucrose of: •; 0.20, \Box ; 0.50, \blacktriangle ; 1.00, \times ; 2.00, \divideontimes ; 3.00, •; 4.00, +; 5.00 and •; 6.00 mol.kg⁻¹.

we note that the water activities of the mixture are between the water activities of the binaries, but for the mixture of the non-electrolyte with an electrolyte, this trend is not observed, and these water activities are located below those of binaries for concentrated solutions having molality greater than 2 mol.kg⁻¹. This can be explained that there is a strong interaction between D-sucrose-water or solute-water.



Fig. 2. Osmotic coefficient ϕ of KCl-D–sucrose(aq) against molality of KCl m_{KCl} at different molalities of D–sucrose of: •; 0.20, \Box ; 0.50, \blacktriangle ; 1.00, \times ; 2.00, \divideontimes ; 3.00, •; 4.00, +; 5.00 and •; 6.00 mol.kg⁻¹.

In Fig. 2 are presented the osmotic coefficients of the studied ternary aqueous solution. It appears from this Figure that as the concentration of KCl is fixed, the osmotic coefficient increases with increasing content of D-sucrose in mixed solution when KCl molalities are less than 3 mol.kg⁻¹ and decreases with D-sucrose molality at high concentration of KCl.

Table 3						
Model Parameters for	r system KCl-H ₂ O, D-sucrose-H ₂ O a	and Mixing mo	odel parameters for syste	m KCl-D-sucrose-	H_2O at 298 K and $p =$	0.1 MPa.
KCI-H-O	$m_{\rm max}/({\rm mol} {\rm kg}^{-1})$	Bury	II. ww	V	Wing	SE

KCl-H ₂ O	$m_{\rm max}/({\rm mol.kg}^{-1})$	B_{MX}	$U_{1,MX}$	$V_{1,MX}$	$W_{1,\mathrm{MX}}$	$SD_{\phi}^*10^3$	$SD_\gamma \times 10^3$
This work	6.00	5.5419	-2.4581	0	-3.3603	1.6537	3.5332
Clegg et al. [17,18]	6.00	9.0912	-2.2831	0	-3.2686	6.6931	14.4810
D-sucrose-H ₂ O	$m_{\rm max}/({\rm mol.kg^{-1}})$	W ₁₂	U ₁₂			$\mathrm{SD}_\phi imes 10^2$	$SD_{\gamma} imes 10^2$
Previous work [16]	6.00	-11.0138	1.7533			1.2124	2.0183
Hu and Guo [22]	6.00	-5.8444	-0.2250			0.9130	7.7966
KCl-D-sucrose-H ₂ O	N ^a	$U_{2,MX}$	$V_{2,MX}$	$W_{2,MX}$	$Y_{1,2,MX}^{0}$	$Y_{1,2,MX}^{1}$	${ m SD}_{\phi} imes 10^4$
This work	80	-7.02378	0	-11.1251	0	93.2628	0.27

 ρ = 14.0292 and α = 13.0 [27].

SD values are standard deviation of the fit from experimental data used in the optimization parameters.

^a The number of data points

Table 4

Mean activity coefficients γ_{\pm} of KCl (aq), activity coefficients	of D–sucrose and excess Gibbs energy (J•mol ⁻¹) of KCl-D-sucrose(aq) at the temperature	298.15 K and <i>p</i> = 0.1 MPa.
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$m_{\mathrm{D-sucrose}}/\mathrm{mol.kg^{-1}}$	$m_{ m KCl}/ m mol.kg^{-1}$	γ_{\pm} kci	γD–sucrose	$G^{\rm ex}/{ m RT}$	$m_{\rm D-sucrose}/{ m mol.kg^{-1}}$	$m_{ m KCl}/ m mol.kg^{-1}$	γксі	γD−sucrose	$G^{\rm ex}/{ m RT}$
0.20	0.20	0.716	1.030	-0.0919	0.50	0.20	0.711	1.089	-0.0707
0.20	0.50	0.647	1.016	-0.3147	0.50	0.50	0.643	1.075	-0.2944
0.20	1.00	0.601	0.994	-0.7509	0.50	1.00	0.597	1.052	-0.7321
0.20	1.50	0.580	0.972	-1.2133	0.50	1.50	0.576	1.028	-1.1965
0.20	2.00	0.570	0.950	-1.6767	0.50	2.00	0.566	1.005	-1.6618
0.20	2.50	0.566	0.929	-2.1281	0.50	2.50	0.563	0.982	-2.1153
0.20	3.00	0.567	0.908	-2.5598	0.50	3.00	0.563	0.960	-2.5489
0.20	3.50	0.570	0.889	-2.9667	0.50	3.50	0.566	0.940	-2.9578
0.20	4.00	0.576	0.871	-3.3455	0.50	4.00	0.572	0.920	-3.3384
0.20	4.50	0.583	0.853	-3.6939	0.50	4.50	0.580	0.901	-3.6884
1.00	0.20	0.704	1.196	0.0054	2.00	0.20	0.689	1.436	0.3086
1.00	0.50	0.636	1.180	-0.2199	2.00	0.50	0.622	1.417	0.0791
1.00	1.00	0.591	1.154	-0.6608	2.00	1.00	0.577	1.386	-0.3696
1.00	1.50	0.570	1.128	-1.1287	2.00	1.50	0.557	1.354	-0.8462
1.00	2.00	0.560	1.102	-1.5978	2.00	2.00	0.547	1.322	-1.3245
1.00	2.50	0.556	1.077	-2.0551	2.00	2.50	0.543	1.292	-1.7912
1.00	3.00	0.557	1.053	-2.4926	2.00	3.00	0.544	1.262	-2.2381
1.00	3.50	0.560	1.030	-2.9051	2.00	3.50	0.548	1.232	-2.6599
1.00	4.00	0.566	1.008	-3.2892	2.00	4.00	0.554	1.205	-3.0529
1.00	4.50	0.574	0.986	-3.6424	2.00	4.50	0.562	1.178	-3.4147
3.00	0.20	0.674	1.716	0.8092	4.00	0.20	0.659	2.043	1.5025
3.00	0.50	0.609	1.694	0.5743	4.00	0.50	0.595	2.016	1.2610
3.00	1.00	0.564	1.656	0.1157	4.00	1.00	0.551	1.970	0.7905
3.00	1.50	0.544	1.617	-0.3716	4.00	1.50	0.531	1.923	0.2903
3.00	2.00	0.534	1.579	-0.8613	4.00	2.00	0.521	1.876	-0.2128
3.00	2.50	0.530	1.541	-1.3396	4.00	2.50	0.518	1.830	-0.7049
3.00	3.00	0.531	1.504	-1.7983	4.00	3.00	0.518	1.785	-1.1774
3.00	3.50	0.535	1.468	-2.2316	4.00	3.50	0.522	1.740	-1.6247
3.00	4.00	0.541	1.433	-2.6361	4.00	4.00	0.528	1.697	-2.0430
3.00	4.50	0.549	1.400	-3.0091	4.00	4.50	0.536	1.656	-2.4296
5.00	0.20	0.645	2.421	2.3840	6.00	0.20	0.630	2.856	3.4489
5.00	0.50	0.582	2.388	2.1346	6.00	0.50	0.568	2.816	3.1904
5.00	1.00	0.538	2.332	1.6501	6.00	1.00	0.525	2.749	2.6900
5.00	1.50	0.518	2.276	1.1352	6.00	1.50	0.505	2.681	2.1583
5.00	2.00	0.508	2.219	0.6167	6.00	2.00	0.495	2.613	1.6224
5.00	2.50	0.505	2.163	0.1087	6.00	2.50	0.492	2.545	1.0967
5.00	3.00	0.505	2.108	-0.3799	6.00	3.00	0.492	2.478	0.5901
5.00	3.50	0.509	2.054	-0.8433	6.00	3.50	0.495	2.413	0.1085
5.00	4.00	0.515	2.001	-1.2776	6.00	4.00	0.501	2.348	-0.3440
5.00	4.50	0.522	1.950	-1.6801	6.00	4.50	0.509	2.286	-0.7646

Fig. 3 shows the stoichiometric ionic mean activity coefficients of KCl versus m_{KCl} at different D–sucrose molalities. It can be seen from this figure that at constant content of D–sucrose in aqueous solution, the activity coefficients of KCl, first decreases, passes through a minimum for molalities around 3.00 mol.kg⁻¹ and then increases very slightly with increasing molality of KCl. The comparison of the order of the curves of $\ln\gamma_{\pm}$ of KCl versus m_{KCl} at different D–sucrose molalities shows that the curves are arranged in similarly way in the following order $\gamma_{\pm}(m = 0.00) > \gamma_{\pm}(m = 0.20) > \gamma_{\pm}(m = 0.50) > \gamma_{\pm}(m = 1.00) > \gamma_{\pm}(m = 2.00) > \gamma_{\pm}(m = 3.00) > \gamma_{\pm}(m = 4.00) > \gamma_{\pm}(m = 5.00) > \gamma_{\pm}(m = (6.00)$. This trend of decreasing of activity coefficient of KCl may be due to interaction phenomenon occurred between D–sucrose and KCl molecules.

The competition in terms of hydration between carbohydrates and ions of KCl becomes important and causes an increase in the hydration of salt ions in the presence of D-sucrose molecules. The effect of D-sucrose on potassium chloride is to decrease the activity coefficient of the latter by 50% (Fig. 3), and similarly the addition of potassium chloride decreases the activity coefficient of D-sucrose by 20% (Fig. 5) in the studied molality range. In Fig. 5, the activity coefficients of D-sucrose in the aqueous solution increase with increasing of its molality at different constant molalities *m* of potassium chloride in the order: $\gamma_{\pm}(m = (6.00) > \gamma_{\pm}(m = 5.00) > \gamma_{\pm}(m = 4.00) > \gamma_{\pm}(m = 3.00) > \gamma_{\pm}(m = 2.00) > \gamma_{\pm}(m = 1.00) > \gamma_{\pm}(m = 0.50) > \gamma_{\pm}(m = (0.20)$. We note also, that the variation of activity coefficients of D-sucrose by addition of potassium



Fig. 3. Natural logarithm of mean activity coefficient for KCl versus square root of molality of KCl at different molalities of D-sucrose of: $\langle \rangle$; 0.00 [23], \bigcirc ; 0.20, \square ; 0.50, \blacktriangle ; 1.00, \times ; 2.00, \bigstar ; 3.00, \bigcirc ; 4.00, +; 5.00 and \diamondsuit ; 6.00 mol.kg⁻¹.



Fig. 4. Natural logarithm of activity coefficient for D-sucrose versus molality of KCl at different molalities of D-sucrose of: •; 0.20, \Box ; 0.50, \blacktriangle ; 1.00, \times ; 2.00, \mathbb{X} ; 3.00, **•**; 4.00, +; 5.00, **•**; 6.00 mol.kg⁻¹.



Fig. 5. Activity coefficient for D-sucrose versus molality of D-sucrose at different molalities of KCl of: (0.00,); 0.20,); 0.50, ; 1.00, ; 1.50, ; 2.00, ; 2.00, ; 2.50, ; 3.00, ; 3.50, ; 4.00, ; 4.50 mol.kg⁻¹.

chloride doesn't present a great variation at different amount of KCl. The curves of the activity coefficient for KCl and D-sucrose in the mixture are similar to those in their binary solutions versus the amount of added component. The surprising result is that the interaction between D-sucrose-potassium chloride is of comparable magnitude with that of D-sucrose-water, if we consider D-sucrose as the support. This trend is due to the either D-sucr ose-D-sucrose interactions or else D-sucrose-water is dominant, presumably indicating a greater degree of hydrogen bonding in D-sucrose. The KCl at different amount doesn't influence significantly this interaction.

The results for D-sucrose-KCl interactions in the ternary system exhibits salting-in of the non-electrolyte by the electrolyte,

indicating considerable attraction (presumably via hydrogen bonding) between D-sucrose molecules in solution, whereas for Dsucrose-NaCl are salted-out by the addition of electrolyte.

The increase in the degree of hydration of ions shows that the addition of D-sucrose increases the number of water molecules related to the potassium and chloride ions. This trend is the inverse that observed for ternary system NaCl-D-sucrose-water in term of activity coefficient, reported by other studies on the physicochemical properties of electrolytes in the presence of sugars [31-34], and also reported in our previous work [16], showing that the addition of D-sucrose decreases the number of water molecules around the ions. This process leads to decrease of the activity coefficient of KCl. We conclude that the KCl is affected strongly by D-sucrose molecules, but the D-sucrose is affected weakly by the presence of the ions K⁺ and Cl⁻. These results show that these aqueous systems are largely dominated by the D-sucrose-D-sucr ose and D-sucrose-water interactions in term of the hydrogen bond of the OH groups, whereas the potassium and chloride ions act too weakly on the molecular groups of D-sucrose and do not disturb the structure of the carbohydrate.

4.3. Excess Gibbs energy and Gibbs energy of transfer

From obtained activity coefficients data, we have determined the excess Gibbs energy of ternary system water-D-sucrosepotassium chloride using the following expression:

$$\frac{g^{ex}}{RT} = \sum_{i=1} x_i \ln(\gamma_i) = x_1 \cdot \ln(\gamma_1) + x_2 \cdot \ln(\gamma_2) + 2x_I \cdot \ln(\gamma_{\pm})$$
(12)

 g^{ex} is excess Gibbs energy per mole of particles. γ_1 , γ_2 are the activity coefficients of water, and D-sucrose, respectively. γ_{\pm} is the mean activity of KCl. The excess Gibbs energy G^{ex} for any amount of material is $G^{ex} = \sum_i n_i g^{ex}$. The results obtained for G^{ex} are listed in Table 4.

The standard free energy of transfer presents an important parameter because it takes into account of the interactions of ion present in the mixed aqueous solution with solvent molecules.

The Gibbs energy of transfer of potassium chloride G_{tr}^{KCl} from water (W) to D-sucrose-water (W + S) mixtures is calculated using the expression [35]:

$$G_{tr}^{KCl}(W \to W + S) = \upsilon RT \ln\left(\frac{f_{KCl}}{f_{KCl}^0}\right),\tag{13}$$

where υ is the number of ions into which the electrolyte dissociates, f_{KCl} and f_{KCl}^{0} are the mole fraction activity coefficients of KCl in ternary system KCl-D-sucrose-H₂O and binary system KCl-H₂O, respectively. Using the model, the calculated result of the transfer Gibbs energies of potassium chloride from water to water-D-sucrose mixtures are plotted in Fig. 6 as a function of salt molality and at different molality of KCl. The transfer Gibbs energies for KCl decrease by increasing the D-sucrose molality. At molality between 1 and 4 mol.kg⁻¹, the transfer Gibbs energies are in this order: $G_{tr}^{KCl}(4)$ $> G_{tr}^{KCl}(3) > G_{tr}^{KCl}(2)$, but this trend is inversed for molalities between 0.5 and 1 mol·kg⁻¹ in this order $G_{tr}^{KCl}(1) < G_{tr}^{KCl}(0.5) < G_{tr}^{KCl}(0.2)$. Thus the interaction between the D-sucrose and potassium chloride becomes favourable by increasing the D-sucrose concentration and decrease of salt concentration to about 2 mol. kg^{-1} . This trend shows the increased stabilization by increased hydration in the mixture but this behaviour becomes unfavourable above 1 mol. kg⁻¹ by decreasing salt composition. This phenomenon can also be explained by the weak interaction between D-sucrose and water in dilute solution. This behaviour is also observed in water activities results of the mixture mentioned above for molality about 2 mol.kg^{-1} .



Fig. 6. Transfer Gibbs energy of KCl from water to water + D-sucrose mixtures as function of molality of D-sucrose at different molality of KCl of: •; 0.20, \Box ; 0.50, **A**; 1.00, ×; 2.00, **X**; 3.00, •; 4.00 mol.kg⁻¹.

We can also illustrate the different electrolyte-D-sucrose interactions in water to study the free energy parameters of pair interaction g_{NE} (E and N are assigned, respectively, to electrolyte and non-electrolyte) between the electrolyte and D-sucrose in water [36,37]. These quantities characterize the mean comportment of all the pair interactions between D-sucrose and different ions of given salt.

By applying McMillan–Mayer's theory of solutions, the transfer Gibbs energies of transfer for KCl from water to water + D–sucrose mixtures at constant temperature and pressure can be expressed as:

$$G_{tr}^{KCl}(W \to W + S) = 2\upsilon m_N g_{EN} + 6\upsilon m_E m_N g_{EEN} + 3\upsilon^2 m_N^2 g_{ENN}$$
(14)

where m_N and m_E are the molality of Nonelectrolyte (D–sucrose) and Electrolyte (KCl), respectively. g_{EN} , g_{EEN} and g_{ENN} are the pair interaction and the triplet interaction parameters. The data of transfer Gibbs energy of KCl from water to mixture (water + D–sucrose) were used for optimization of g_{EN} , g_{EEN} and g_{ENN} . Table 5 shows the values of pair interaction parameters and triplet interaction parameters. It can be seen from this Table that the value of triplet interaction parameters g_{EEN} and g_{ENN} are low compared to that of parameter g_{EN} . Thus, at low concentrations of electrolyte and nonelectrolyte species, the contribution of all triplet interaction terms can be neglected and the salting coefficient η_s can be determined from the pair interaction parameter g_{EN} by using the following equation [34]:

$$RT\eta_s = 2 \upsilon g_{EN},\tag{15}$$

The salting constant is used to express the effects of salting-in and salting-out. The obtained value of salting constant is given in Table 5. For comparison, the interaction parameters and the salting constant values available or calculated from data in literature, constant η_s is in close agreement with that reported by Herrington and Meunie [13], and Wang et al. [31].

The obtained values for pair interaction parameters and for salting constant for potassium chloride in the aqueous solution in presence of D-sucrose are positive (Table 5). The pair D-sucrose-KCl interaction parameter g_{EN} is negative, and this result indicates

attractive interaction between ions and D–sucrose. This can be explained by the fact that the D–sucrose is salted-in by adding KCl. These behaviours are the inverse of those reported for NaCl–D–sucrose in literature [19,38]. It may be explained this difference in behaviours to the preferential solvation of ions Na + and K + in different mixtures of D–sucrose-water. Therefore, the interactions of salt with D–sucrose appear to be induced by the average number of D–sucrose molecules in OH group, which remain one of the most important factors in this mixture. At high molality of both components (KCl and D–sucrose), the phenomenon of salting-in occurs for the studied system. The salting constant η_s of the mixture KCl-D–sucrose-water calculated from Eq. (15) is -0.0121 kg.mol⁻¹ (Table 5). Thus, this negative value corresponds to extensive to the salting-in of D–sucrose by KCl.

4.4. Solubility prediction

The solubility of D-sucrose m_s in an aqueous solution containing an electrolyte can be calculated by the following equilibrium equation as:

$$m_s \gamma_s = m_s^0 \gamma_s^0, \tag{16}$$

 m_s and m_s^0 are the molality of D-sucrose in ternary system potassium chloride-D-sucrose-water and in binary system D-sucrosewater, respectively. γ_s and γ_s^0 are the activity coefficients of D-sucrose in ternary system potassium chloride-D-sucrose-water and in binary system D-sucrose –water, respectively. The molality and activity coefficient at saturation point for system D-sucrose-water at 25 °C are taking from literature [33]. The calculated and experimental solubility values of D-sucrose in ternary system potassium chloride-D-sucrose-water at 298.15 K are shown in Table 6. The predicted solubilities in this work are compared to those measured data obtained from Kelly [11]. The average mean relative deviation for all predicted D-sucrose solubility data in the ternary system at 25 °C was 0.155%. The developed model in this work was used for prediction of potassium chloride solubility in system KCl-D-sucro

Table 6

Comparison of experimental and predicted solubility of D-sucrose in the ternary system KCI-D-sucrose-H₂O at 298.15 K and p = 0.1 MPa.

$m_{KCl}/mol.kg^{-1}$	D-sucrose S	olubility/mol.kg ⁻¹	%RE
	Exp.	Cal.	
0.0000	6.0006	6.0085	-0.1317
0.1341	6.0211	6.0276	-0.108
0.2683	6.0415	6.0466	-0.0844
0.4024	6.0649	6.0658	-0.0148
0.5365	6.0854	6.0852	0.0033
0.6707	6.1058	6.1049	0.0147
0.8048	6.1263	6.1249	0.0229
0.9390	6.1438	6.1452	-0.0228
1.0731	6.1642	6.1657	-0.0243
1.3414	6.2022	6.2074	-0.0838
2.0120	6.2986	6.3156	-0.2699
2.6827	6.3921	6.4241	-0.5006
		%MRE = 0.1068	

The experimental values were taken from Ref. [11].

Table 5

Interaction parameters of Gibbs energies of transfer of KCl from water to mixture (water + D-sucrose) and salting constants η_c at 298.15 K.

	$g_{\rm EN}/{\rm J\cdot kg\cdot mol^{-2}}$	g _{EEN} /J·kg·mol ⁻³	$g_{\rm ENN}/J\cdot kg\cdot mol^{-3}$	$\eta_{\rm s}/{ m kg}\cdot{ m mol}^{-1}$
This work Wang <i>et al.</i> [14]	-7.51 -5.00	0.3941	-0.2214	-0.0121 -0.0070
Herrington Meunier [13]*	-25.00	-	-	-0.0440

The data of Herrington and Meunier were obtained at 0 °C.

8

 Table 7

 Predicted solubility of KCl in the ternary system KCl-D-sucrose- H_2O at 298.15 K and p = 0.1 MPa.

$m_{\rm D-sucrose}/{\rm mol.kg^{-1}}$	KCl Solubility/mol.kg ⁻¹
0.00	4.7949
0.50	4.8353
1.00	4.8773
1.50	4.9210
2.00	4.9663
2.50	5.0133
3.00	5.0619
3.50	5.1123
4.00	5.1642
4.50	5.2179
5.00	5.2732
5.50	5.3301
6.00	5.3888

se-water at 298.15 K. The KCl dissolution in aqueous solutions KCl-D-sucrose-water system is given as:

$$k_{sp} = m_{K^+} \gamma_{K^+} m_{Cl^-} \gamma_{Cl^-} = m^2 \gamma_{\pm}^2 (KCl), \qquad (17)$$

 $\gamma_{\pm}(KCl)$ is the ionic mean activity coefficient of KCl, m_{KCl} is its molality and k_{sp} its solubility product. The result of calculation is given in Table 7. It can be seen from this Table that the solubility of potassium chloride increases with increasing the molality of D–sucrose.

5. Conclusion

Using the hygrometric method, we have determined the water activities of KCl-D-sucrose-H₂O mixtures at 298.15 K. Furthermore, the osmotic coefficients of KCl-D-sucrose-H₂O were fitted by PSC equation for mixtures to obtain the four parameters. Comparing the recalculated osmotic coefficients and the experimental ones, we note that the relative deviation is acceptable in the studied molality range. The activity coefficients of KCl and D-sucrose in the KCl-D-sucrose-water are also calculated using the model of PSC using our obtained interaction parameters. The results indicate that the presence of these carbohydrates affects the properties of KCl in the mixture and its thermodynamic behaviour, but KCl affects weakly the properties of D-sucrose.

The Gibbs excess energy and the Gibbs energy of transfer are also determined for this studied system from the obtained results for the osmotic and activity coefficients. It has been shown that the Gibbs energy of transfer for each of the electrolytes investigated decreases with increasing mole fraction of D-sucrose in the mixed solutions. Free energies of pair interaction have also been calculated and are negative for KCl-D-sucrose in water. The experimental results are discussed in terms of solute-solvent and solute-solute interactions in water –D-sucrose-KCl system. The solubilities of KCl and of D-sucrose in mixture are also predicted.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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