

Evaluation of the vapour pressure of aqueous NaCl-sorbitol solution and correlation of the water activity on composition and temperature



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ABSTRACT

The vapour pressure over water (1) sodium chloride (2) and sorbitol (3) ternary solutions of different concentrations ($m_i \leq 4$, $i: 2,3$) was measured at 338 K and 348 K. Starting from these data, the values of the experimental water activity (a_1) were calculated. These data and those obtained for other authors at 293 K, 298 K and 308 K were correlated with a previously developed equation for $a_1(m_2, m_3)$. Thus, the equation parameters and their corresponding temperature dependences were obtained. The corresponding root mean square deviation was evaluated, being in all cases less than 0.005.

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1. Introduction

The aqueous solutions containing polyalcohols and electrolytes are widely used in food industry, in order to keep the water activity of foods within a range of suitable values [1]. Moreover, their thermodynamic characterization is challenging because there are interactions of different nature among their components. From one side, the hydrogen bridge interaction between the hydroxyl groups of the alcohol with water and for the other, the interaction of the solvent molecules with the electrolyte ions, which defines the hydration layer surrounding them. In this context, different studies evaluated the water activity of this type of ternary aqueous solutions [2–8]. They were generally carried out at room temperature (298 K), although there are some data at 293 K [4], 308 K [4] and 318 K [5]. The techniques employed were isopiestic measurements, vapour pressure determination, etc. The experimental measurement of the solvent vapour pressure of a solution constituted by non volatile solutes enables the direct calculation of the dependence of the solvent activity on composition. Although the vapour pressure technique has not been used as extensively as the isopiestic method, it has the advantage of giving directly the absolute value of the solvent activity. On the other hand, the correlation of the experimental results of the water activity on composition is

usually carried out on the basis of empirical polynomial expressions, which are employed independently of the chemical nature of the solutes [9–14]. However, these expressions are generally not consistent with the conditions imposed by the thermodynamics of solutions at the infinite dilution limit, which are specific for each type of mixture. In this sense, analytical expressions were recently developed for ternary aqueous systems constituted by two electrolytic solutes [15] and by an electrolyte and a molecular solute [16]. These equations were successfully employed for the correlation of many systems. In this context, the present work describes the results obtained in the determination of the vapour pressure of solutions constituted by water (1), sodium chloride (2) and sorbitol (3) at the temperatures 338 K and 348 K. The experimental dependences of the water activity on composition are correlated with a thermodynamically consistent equation containing binary and ternary parameters. The variation on temperature is also evaluated on the basis of the present results and those of the two studies found in the literature for this system, at 298 K [2], 293 K [4] and 308 K [4].

2. Experimental

The vapour pressure of the ternary system water (1) - sodium chloride (2) - sorbitol (3) was measured at 338 K and 348 K. The values corresponding to the binary system water (1) - sorbitol (3) were also evaluated. All chemicals were provided by Merck with a purity $\geq 99.0\%$ and they were previously treated in vacuum oven at

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60 °C. Solutions were prepared by using ultra pure water (Pure Lab, Helga Lab Water, 18 MΩ cm). The equipment used for the static vapour pressure measurements is illustrated in Fig. 1. It is a modification of that proposed by K. Kim et al. [17]. The equilibration flask was constructed in Pyrex glass with a volume of 125 cm³. It is connected to the vacuum system and to the manometer. The whole system is immersed in a thermostatic water bath controlled by a Lauda Thermostat UB20 (±0.01 K). In order to ensure the temperature uniformity and independently of the thermostat circulator, an external pump (not shown in the Figure) recirculates water from the bottom to the upper part of the device at a flow rate of 4 dm³ min⁻¹.

Solutions were prepared by weight using a Mettler AE200 balance with an accuracy of 1 mg. The water lost by evaporation during the deaeration process was evaluated by weighing the solution after the experiment. Compositions are given in solute molalities (mol kg⁻¹). Moreover, a magnetic stirrer was used in order to decrease the time needed to reach the equilibrium condition and also ensure uniformity in the solution temperature. A digital thermometer Lauda R46, 100 Ω resistance and ±0.01 K accuracy, was used to measure temperature. Pressure was measured by a mercury manometer, using a cathetometer with an accuracy of ±0.1 mm Hg (±0.15 kPa). The maximum reading error was 0.1% corresponding to the smallest pressure value. Absolute pressure values were calculated on the basis of the manometric pressure and taking into account the mercury expansion coefficient [18] and the atmospheric pressure measured with a calibrated precision barometer. The proper functioning of the equipment was verified by the evaluation of the vapour pressure of pure water (P_1^0) at N different temperatures ($310 \leq T/K \leq 350$). The result obtained for the mean value of the relative deviation ($\sum(P_1^{0\text{exp}} - P_1^0)/P_1^0 \cdot 100/N$) was 0.1%.

3. Results and discussion

Vapour pressure was measured for the ternary system water (1) - sodium chloride (2) - sorbitol (3) and for the binary system water (1) - sorbitol (3) at 338 K and 348 K. The results obtained for all the concentrations measured are given on Tables 1 and 2. From these values, the experimental water activity (a_1^{exp}) was calculated by the following equation [19],

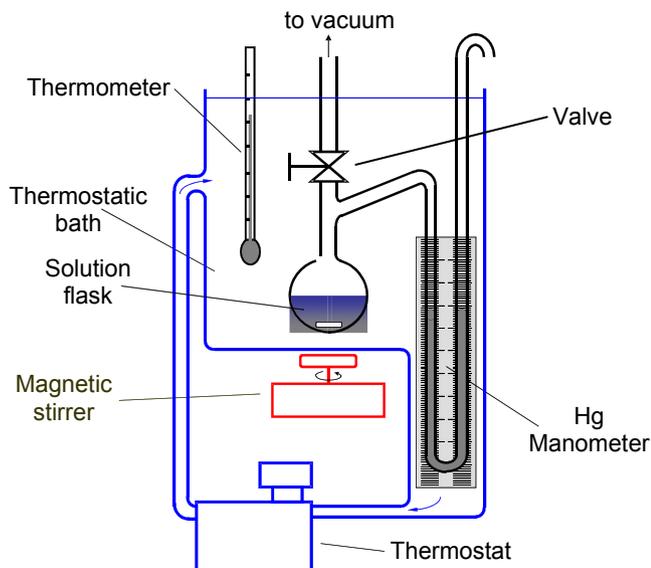


Fig. 1. Scheme of the equipment employed for the determination of the vapour pressure.

Table 1

Vapour pressure and water activity (experimental and correlated) data of the system water (1) – NaCl (2) – sorbitol (3) at 338 K.

Temperature: 338 K					
$m_2/\text{mol kg}^{-1}$	$m_3/\text{mol kg}^{-1}$	P_1/kPa	a_1^{exp}	a_1^{cor}	RD
0.0000	1.0000	24.51	0.9786	0.9817	-0.0031
0.0000	1.9962	24.06	0.9607	0.9629	-0.0023
0.0000	1.9992	24.07	0.9611	0.9628	-0.0018
0.0000	2.9978	23.51	0.9388	0.9437	-0.0052
0.0000	4.9930	22.79	0.9100	0.9050	0.0055
0.0000	5.9498	22.28	0.8899	0.8868	0.0035
0.0000	7.7271	21.49	0.8581	0.8541	0.0046
0.1555	1.3482	24.27	0.9692	0.9709	-0.0018
0.2047	0.8001	24.41	0.9748	0.9796	-0.0050
0.3193	2.2470	23.71	0.9466	0.9490	-0.0025
0.3482	3.1320	23.35	0.9325	0.9294	0.0032
0.4016	1.5951	24.14	0.9641	0.9597	0.0046
0.4040	0.5975	24.60	0.9825	0.9777	0.0049
0.4543	1.0460	24.10	0.9622	0.9685	-0.0065
0.5977	0.4004	24.37	0.9731	0.9754	-0.0024
0.5981	2.3972	23.57	0.9413	0.9377	0.0039
0.7514	0.7503	24.04	0.9600	0.9652	-0.0055
0.7704	0.7500	23.95	0.9564	0.9647	-0.0086
0.8006	1.7350	23.63	0.9438	0.9457	-0.0020
0.8020	0.2066	24.23	0.9677	0.9721	-0.0045
0.8084	1.2064	24.10	0.9625	0.9556	0.0071
0.8169	3.2006	23.00	0.9184	0.9113	0.0077
1.0500	0.4489	24.13	0.9635	0.9608	0.0028
1.0617	2.4501	22.97	0.9171	0.9216	-0.0049
1.1899	0.8007	23.82	0.9512	0.9510	0.0001
1.2142	1.8010	23.01	0.9190	0.9315	-0.0137
1.2574	1.2610	23.60	0.9423	0.9410	0.0013
1.3496	0.1497	23.95	0.9564	0.9547	0.0017
1.5966	0.4000	23.68	0.9456	0.9432	0.0026
1.6032	2.3992	22.69	0.9061	0.9037	0.0027
1.6049	0.3998	23.37	0.9331	0.9429	-0.0105
1.6189	0.3989	23.56	0.9407	0.9425	-0.0018
1.7471	0.7487	23.54	0.9402	0.9333	0.0073
1.8004	1.2047	22.91	0.9148	0.9240	-0.012
1.8384	1.7448	22.71	0.9068	0.9115	-0.0053
2.2479	2.2482	22.17	0.8852	0.8831	0.0024
2.2505	0.2499	22.86	0.9127	0.9208	-0.0089
2.3957	0.5977	22.79	0.9100	0.9117	-0.0018
2.4089	1.5982	22.57	0.9013	0.8938	0.0083
3.1461	0.3499	22.00	0.8785	0.8844	-0.0067

Standard uncertainties: $u(P) = 0.15$ kPa; $u(T) = 0.03$ K; $u(m) = 0.0001$ mol kg⁻¹.

$$a_1^{\text{exp}}(m_2, m_3, T) = \frac{P_1(m_2, m_3, T)}{P_1^0(T)} e^{\frac{(P_1 - P_1^0)}{RT}} [B_1^0(T) - v_1^0(T)] \quad (1)$$

where P_1 and P_1^0 are the vapour pressure of solution and of pure water, respectively. $P_1^0(T)$ values were calculated through the equation proposed by W. Wagner and A. Pruss [20]. The exponential factor is the pressure correction for the deviation from ideal behaviour. $B_1^0(T)$ is the second virial coefficient of pure water vapour [21] and $v_1^0(T)$ is the molar volume of liquid water [22].

The values of $a_1^{\text{exp}}(m_2, m_3, T)$ obtained for all compositions measured at 338 K are illustrated in Table 1, meanwhile those corresponding to 348 K are shown in Table 2. These Tables contain the values of the molalities of sodium chloride (m_2) and sorbitol (m_3), the water vapour pressure (P_1), the experimental water activity (a_1^{exp}) and the correlated water activity (a_1^{cor}). The evaluation of this last value is described in the following item.

3.1. Correlation of water activity

The dependence of water activity on composition for aqueous solutions of an electrolyte (2) and a molecular solute (3) can be described by the following equation [16],

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