



Water activities of sodium molybdate solutions at different temperatures

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ABSTRACT

The water activities of sodium molybdate in aqueous solutions at $T = (303.15, 313.15, 323.15$ and $333.15)$ K were determined, using vapor pressure osmometry. The range of salt concentration was from 0.06 to 2.2 mol kg^{-1} . The results show that sodium molybdate has a significant effect on the water activity. Values of the vapor pressure, osmotic and activity coefficient of the solutions were determined from the activity data. Finally, the studied system was modeled with the Pitzer model which allowed correlating the properties of these aqueous solutions obtaining a good agreement between the experimental data and the correlated values.

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1. Introduction

Chile is one of the largest world producers of copper and molybdenum concentrates. In the production of these concentrates, the molybdenum is one of the most important products. Molybdenum is one of the rare metals with high-melting point, which is used extensively in many industries, such as agrochemical, steel, general electronic and nuclear. The common use of this metal is due to its essential characteristics, such as its ability to resist extreme temperatures without significantly softening or expanding, its high degree of weld ability, its ability to significantly resist corrosion and its low density [1]. The recovery or extraction of molybdenum requires fundamental information, such as the thermodynamic properties to design extraction process.

Thermodynamic property data of aqueous electrolyte systems are useful in varied fields such as hydrometallurgy, geochemistry, oceanography, chemical engineering, etc.

The thermodynamic properties such as water activities, osmotic and activity coefficients of sodium molybdate were scarcely reported. Robinson and Sinclair [2] reported one vapor pressure data of sodium molybdate at 298.15 K for the concentration of $0.1604 \text{ mol kg}^{-1}$. Zhidikova et al. [3] determined activity coefficients

of sodium molybdate in aqueous solutions at 25 and 300°C for three molalities from 1.29 to 3.16 mol kg^{-1} . Wu et al. [4] reported the activity and osmotic coefficients of sodium tungstate and sodium molybdate at $T = 298.15 \text{ K}$ in the range 0.3 – 2.5 mol kg^{-1} by the isopiestic method. Moreover, Rard [5] analyzed and recalculated the reported data by Wu et al. [4] based on the theory and mathematics and concluded that hydrolysis of molybdate ion and the formation of different ionic species would be predominant if the sodium molybdate concentrations were within the range of 0.2 – 0.9 mol kg^{-1} .

Ning et al. [6] measured and correlated the solubility of sodium molybdate in the $(\text{Na}^+ + \text{MoO}_4^{2-} + \text{SO}_4^{2-})$ system at $T = (293.15$ – $343.15) \text{ K}$. Pitzer model was used to correlate the ternary and binary systems. For the $\text{Na}_2\text{MoO}_4 + \text{H}_2\text{O}$ system, the authors correlated the data reported by Wu et al. [4].

In the present work, water activities of sodium molybdate in aqueous solutions at $T = (303.15, 313.15, 323.15$ and $333.15) \text{ K}$ are reported. Also, these experimental data are correlated by Pitzer model.

2. Experimental

2.1. Chemicals

Sodium molybdate dihydrate and sodium chloride with purities of >0.995 were purchased from Merck and used without further

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Table 1
General description of the chemicals used.

Chemical	Source	Mass fraction purity	Conductivity/ $\mu\text{S}\cdot\text{cm}^{-1}$	Purification method
$\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$	Merck	>0.995		None
NaCl	Merck	>0.995		None
H_2O			0.054	Deionization

purification. Deionized water was used in all experiments (Milli-Q, Millipore, $\kappa = 0.054 \mu\text{S cm}^{-1}$). Table 1 shows the general descriptions of the salt used.

2.2. Apparatus and procedure

The water activities for the binary system were determined using a KNAUER K-7000 vapor pressure osmometer with temperature control of $\pm 0.001 \text{ K}$ at $T = (303.15, 313.15, 323.15 \text{ and } 333.15)$.

With the help of a microsyringe, droplets of pure solvent were applied to the thermistors. After the baseline was stable, the reading was adjusted to zero. The measurements were made by replacement of one drop of pure solvent with one drop of the solution. Consequently, it leads to a difference in vapor pressure between the two drops. With the increase of vapor pressure of the solution droplet, the temperature increases and the temperature difference (ΔT) between the thermistors is achieved. This increase is measured as a difference in their resistance (ΔR), because the thermistors are part of a Wheatstone bridge. The same size and shape of the drop attached to both thermistors should be maintained. A minimum of five readings were carried out for each solution and the mean value was calculated.

The equipment was calibrated using aqueous NaCl solutions of known osmolality with water as reference, for which the osmotic coefficient data were taken from literature [7]. The combined uncertainty of the water activity for the aqueous NaCl solutions was $\pm 3 \cdot 10^{-4}$. The details of the calibration of the osmometer for aqueous solutions were described previously [8]. During the measurements, the salt concentration range was between 0.06 and 2.2 mol kg^{-1} . The combined uncertainty in activity water measurements was $\pm 4 \cdot 10^{-4}$. All the solutions were prepared by mass in a Mettler Toledo analytical balance (model AX204) with a precision of $\pm 0.1 \text{ mg}$. The water content in the studied compound was accounted for upon solution preparation.

3. Results and discussion

3.1. Experimental results

The experimental water activities of the $\text{Na}_2\text{MoO}_4 + \text{H}_2\text{O}$ system at $T = (303.15, 313.15, 323.15 \text{ and } 333.15) \text{ K}$ were obtained through the osmolality and from these data, vapor pressures, osmotic and activity coefficients, and excess Gibbs free energy of solution were determined.

The water activity is related to the total osmolality of the aqueous multicomponent solution by Refs. [9,10]:

$$\ln a_w = \frac{\text{osmolality}}{55.51} = \frac{\sum v_i m_i \phi}{55.51} \quad (1)$$

where v_i is the number of ions produced on dissociation of i th component, 55.51 is the number of moles of water in 1 kg of water, m_i is the molality and ϕ is the osmotic coefficient. In the present work, a complete dissociation of sodium molybdate was considered.

The vapor pressure can be calculated based on the experimental data of activity:

$$\ln a_w = \ln \left(\frac{p}{p^0} \right) + \frac{(B_w - V_w)(p - p^0)}{RT} \quad (2)$$

where B_w is the second virial coefficient of water vapor, V_w is the molar volume of liquid water, p^0 is the vapor pressure of pure water, R is the universal gas constant and T is the temperature.

The vapor pressures values of pure water 4.241, 7.375, 12.34 and 19.92 kPa at $T = (303.15, 313.15, 323.15 \text{ and } 333.15) \text{ K}$ were used, respectively [11]. For the second virial coefficients of water vapor the values $-1.073 \cdot 10^{-3}$, $-0.930 \cdot 10^{-3}$, $-0.812 \cdot 10^{-3}$ and $-0.715 \cdot 10^{-3}$ at $T = (303.15, 313.15, 323.15 \text{ and } 333.15) \text{ K}$ were used, respectively [12]. Molar volumes of liquid water were calculated using water density data at different temperatures [13].

Table 2
Water activity (a_w)^a and vapor pressures (p)^b as function of molality, m , for the $\text{Na}_2\text{MoO}_4 + \text{H}_2\text{O}$ system at $T = (303.15, 313.15, 323.15 \text{ and } 333.15) \text{ K}$ and pressure $P = 101.3 \text{ kPa}$ ^c.

$m/\text{mol}\cdot\text{kg}^{-1}$	$T = 303.15 \text{ K}$		$T = 313.15 \text{ K}$		$T = 323.15 \text{ K}$		$T = 333.15 \text{ K}$	
	a_w	p/kPa	a_w	p/kPa	a_w	p/kPa	a_w	p/kPa
0.060	0.9967	4.227	0.9976	7.357	0.9977	12.311	0.9972	19.862
0.080	0.9959	4.223	0.9969	7.351	0.9970	12.302	0.9963	19.845
0.100	0.9950	4.220	0.9961	7.345	0.9963	12.293	0.9954	19.828
0.200	0.9907	4.201	0.9922	7.317	0.9925	12.246	0.9912	19.743
0.400	0.9822	4.165	0.9843	7.258	0.9844	12.147	0.9827	19.574
0.600	0.9739	4.130	0.9760	7.197	0.9759	12.041	0.9742	19.403
0.800	0.9657	4.095	0.9674	7.133	0.9669	11.929	0.9656	19.231
1.000	0.9575	4.060	0.9585	7.068	0.9575	11.813	0.9568	19.055
1.200	0.9491	4.025	0.9493	7.000	0.9479	11.694	0.9478	18.875
1.400	0.9405	3.988	0.9398	6.929	0.9380	11.572	0.9385	18.689
1.600	0.9316	3.950	0.9299	6.857	0.9281	11.449	0.9289	18.497
1.800	0.9222	3.910	0.9198	6.782	0.9182	11.326	0.9189	18.297
2.000	0.9122	3.868	0.9093	6.704	0.9083	11.204	0.9085	18.088
2.200	0.9016	3.823	0.8985	6.625	0.8986	11.084	0.8976	17.870

^a Experimental values.

^b Derived values.

^c The standard uncertainties u are $u(T) = 0.01 \text{ K}$ and $u(P) = 1 \text{ kPa}$. The combined standard uncertainties u_c are $u_c(m_i) = 0.005 \text{ mol kg}^{-1}$, $u_c(a_w) = 4 \cdot 10^{-4}$, $u_c(p_i) = 0.004 \text{ kPa}$.

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