Available online at www.sciencedirect.com

ScienceDirect

J. Chem. Thermodynamics 39 (2007) 1176–1181

JCT

www.elsevier.com/locate/jct

The vapour pressures over saturated aqueous solutions of sodium and potassium acetates, chlorates, and perchlorates

Alexander Apelblat *, Emanuel Manzurola

Department of Chemical Engineering, Ben Gurion University of the Negev, Beer Sheva 84105, Israel

Received 7 November 2006; received in revised form 29 November 2006; accepted 7 December 2006
Available online 16 December 2006

Abstract

Vapour pressures of water over saturated solutions of sodium acetate, potassium acetate, sodium perchlorate, and potassium perchlorate were determined over the (278 to 318) K temperature range and compared with available in the literature data. The cases of saturated solutions of sodium chlorate and potassium chlorate are also considered. The determined vapour pressures were used to obtain the water activities, the osmotic coefficients, and the molar enthalpies of vaporization in considered systems.

Keywords: Sodium acetate; Potassium acetate; Sodium chlorate; Potassium chlorate; Sodium perchlorate; Potassium perchlorate; Aqueous saturated solutions; Vapour pressures; Water activities

1. Introduction

In the continuation of studies on vapour pressure of water over saturated solutions of electrolytes having industrial or biological importance [1–15], the acetates, chlorates, and perchlorates of sodium and potassium are considered. The knowledge of vapour pressures when expressed in hygroscopic terms (relative humidity) is important in handling, storage, shipping, and purity of compounds as well as in providing constant humidity in enclosed spaces. In the literature, the vapour pressure determinations were performed many times in the (CH_3COOK + water) system [16–25], less in the (CH_3COONa + water) system [17–20]. Unfortunately, the available data in the ($NaClO_3$ + water), ($KClO_3$ + water), ($NaClO_4$ + water), and ($KClO_4$ + water) systems are very scarce [16–27,30].

The determined vapour pressures, in the $T = (278$ to $318)$ K temperature range, served to obtain the water activities, $a_1(m_{\text{sat.}}, T)$, the osmotic coefficients, $\phi(m_{\text{sat.}}, T)$ and the molar enthalpies of vaporization, molar enthalpies of vaporization, $\Delta H_{\text{m}}(m_{\text{sat.}}, T)$ in investigated systems.

2. Experimental

Sodium acetate, CH_3COONa (0.995 mass fraction purity); potassium acetate, CH_3COOK, (>0.99 mass fraction purity); sodium perchlorate, $NaClO_4$, (>0.990 mass fraction purity), and potassium perchlorate, $KClO_4$ (0.990 mass fraction purity) were from Fluka. All reagents were used in experiments without further purification.

The vapour pressures over saturated solutions were determined using the Rotronic HYGROMER AwV C instrument, which was equipped with an electrolyte sensor C 94 and a sample cup WP-40. The thermal stability of the measuring system is estimated to be ±0.05 K and the sensitivity of the used electronic hygrometer is about ±0.003 kPa at $T = 298.15$ K. The prepared saturated solutions (with an excess of solid phase) were introduced into

* Corresponding author. Tel.: +972 8 6461487; fax: +972 8 6472916.
E-mail address: apelblat@bgu.ac.il (A. Apelblat).

0021-9614/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jct.2006.12.006

the sample cups. They remain there unstirred during experiments. The employed procedure was described in detail elsewhere [6–8].

3. Results and discussion

The vapour pressures of water over saturated aqueous solutions of sodium acetate, potassium acetate, sodium perchlorate, and potassium perchlorate were determined in this work and they are presented in table 1 together with the literature values. In the case of potassium perchlorate, the measured by us vapour pressures p were practically indistinguishable from those of pure water p^* at the same temperature (for p^* values see reference [33]). This results from the fact that contrary to sodium perchlorate, the solubility of potassium perchlorate in water is very low [32]. The vapour pressures over saturated solutions of sodium and potassium chlorates were not determined in this work, nevertheless they are also considered here. Some quantitative information is available for these solutions basing on the data from the literature (tables 1 and 2).

The vapour pressures over saturated aqueous solutions of sodium and potassium acetates were reported a number of times in the literature [16–25]. As can be observed in figure 1 there is a very good agreement between these investigations and this work in the case of sodium acetate, but not for potassium acetate where our results are systematically lower and the effect is more pronounced at higher temperatures (figure 2). Considering that vapour pressures of both acetates were measured under similar conditions, the reason for observed discrepancies is not clear. It is worthwhile to note that significant differences in the solubility and vapour pressures of the acetates in saturated solutions ($m_{sat.}(CH_3COONa, T = 298.15\ K) = 6.14\ mol \cdot kg^{-1}$; $p(CH_3COONa, 298.15\ K) = 2.398\ kPa$ and $m_{sat.}(CH_3COOK, T = 298.15\ K) = 27.4\ mol \cdot kg^{-1}$; $p(CH_3COOK, T = 298.15\ K) = 0.581\ kPa$). The osmotic coefficients defined by, $\phi = -55.508 \cdot \ln a_1/(2 \cdot m_{sat.})$, can be compared with those of Voznesenskaya [24], $\phi(CH_3COONa, m_{sat.} = 6 \cdot 10\ mol \cdot kg^{-1}) = 1.402$ and $\phi(CH_3COOK, m_{sat.} = 23.8\ mol \cdot kg^{-1}) = 1.745$ (see table 2).

Determined vapour pressures p, permit to calculate the activities of water $a_1 = p/p^*$, where p^* are vapour pressures of pure water at given T and they are available from the Saul and Wagner equation [33]. The temperature dependence of the vapour pressure of saturated solutions can be expressed by the Clausius–Clapeyron equation [31]

$$d \ln p/d(1/T) = -\Delta_{vap.}H_m(T)/R, \tag{1}$$

where $\Delta_{vap.}H_m(T)$ is the molar enthalpy change associated with evaporating of water and simultaneous crystallization of the salt. If over the considered temperature range $\Delta_{vap.}H_m(T)$ depends linearly on T, then the integral form of equation (1) is

$$\ln[p(T, m_{sat.})/kPa] = A + B(T/K)^{-1} + C \ln(T/K), \tag{2}$$

and

TABLE 1

Vapour pressures p of saturated aqueous solutions of sodium acetate, potassium acetate, sodium perchlorate, potassium perchlorate, sodium chlorate, and potassium chlorate at temperatures, T

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
		CH_3COONa			
278.65	0.714	296.25	2.157	305.95	3.603
280.65	0.819	296.35	2.162	306.35	3.67
282.65	0.938	298.15	2.313 [20]	307.65	3.902
284.55	1.065	298.15	2.440 [17]	307.95	3.973
286.35	1.199	298.15	2.300 [19]	308.35	4.05
288.45	1.368	298.15	2.399	309.95	4.366
290.35	1.535	298.25	2.403	310.45	4.461
292.25	1.72	298.65	2.452	310.93	4.431 [18]
292.45	1.74	300.15	2.671	310.45	4.461
293.15	1.754 [20]	300.85	2.765	311.75	4.739
293.15	1.777	301.95	2.943	312.65	4.937
293.35	1.83	302.45	3.005	313.15	4.945 [18]
294.25	1.932	303.15	3.035 [20]	314.25	5.298
294.45	1.948	303.15	3.029 [18]	315.45	5.593
295.35	2.05	304.05	3.276		
295.93	2.075 [18]	304.05	3.276		
		CH_3COOK			
278.15	0.166 [18]	283.15	0.473 [16]	302.35	0.714
278.15	0.218 [21]	293.15	0.468 [20]	303.15	0.934 [20]
278.65	0.180	293.15	0.540 [25]	303.15	0.917 [25]
280.65	0.205	293.15	0.514 [25]	303.15	0.976 [21]
282.65	0.234	293.15	0.538 [21]	303.15	0.934 [18]
283.15	0.258 [20]	293.15	0.468 [25]	303.45	0.956 [16]
283.15	0.287 [25]	294.45	0.476	304.21	0.969 [22]
283.15	0.295 [21]	294.82	0.593 [22]	304.15	0.854 [17]
284.37	0.313 [22]	294.95	0.520 [16]	304.35	0.787
284.55	0.264	295.93	0.635 [18]	306.35	0.860
285.04	0.326 [22]	296.15	0.560 [16]	306.6	1.104 [16]
285.15	0.295 [17]	296.45	0.532	308.15	1.294 [21]
285.65	0.344 [17]	298.15	0.713 [20]	308.25	0.933
286.65	0.303	298.15	0.729 [21]	310.25	1.016
288.15	0.409 [21]	298.15	0.711 [23]	310.93	1.336 [18]
288.15	0.399 [25]	298.15	0.748 [24]	312.25	1.097
288.45	0.339	298.45	0.590	313.15	1.476 [20]
289.21	0.423 [22]	298.65	0.653 [16]	313.15	1.698 [21]
290.45	0.383	299.76	0.760 [22]	314.15	1.183
292.09	0.515 [22]	300.45	0.653	316.15	1.297
292.45	0.430	300.85	0.749 [16]		
		$NaClO_4$			
277.59	0.427 [30]	292.45	1.040	306.30	2.111
278.65	0.453	292.45	1.041	307.35	2.212
278.65	0.450	292.75	1.058	307.35	2.210
279.15	0.470	294.45	1.163	308.25	2.308
280.75	0.517	294.45	1.160	308.25	2.310
280.75	0.520	296.35	1.288	308.35	2.327
282.65	0.587	296.35	1.290	310.15	2.524
282.65	0.590	296.45	1.296	310.15	2.520
283.15	0.602	296.45	1.300	310.25	2.530
283.15	0.600	298.15	1.375 [24]	310.30	2.539
284.55	0.656	298.35	1.430	310.93	2.873 [30]
284.55	0.660	298.65	1.460	311.90	2.720
285.05	0.674	299.82	1.547 [30]	311.95	2.734
285.05	0.670	300.35	1.588	311.95	2.730
287.05	0.762	300.35	1.590	312.05	2.749
286.55	0.741	302.35	1.747	313.90	2.965
287.05	0.762	302.35	1.750	313.95	2.981
287.05	0.760	303.15	1.813	313.95	2.970
288.55	0.836	303.15	1.810	314.05	2.973

(*continued on next page*)