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## Apparent molar volumes, $V_{\phi}$ , of calcium acetate ( $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$ ) at 273.15 to 353.15 K and pressures up to 100 MPa

DUYGU UYSAL ZIRAMAN<sup>1</sup>, JAVID T. SAFAROV<sup>2,3\*</sup>, ÖZKAN MURAT DOĞAN<sup>1</sup>,  
EGON P. HASSEL<sup>2</sup> and BEKIR ZÜHTÜ UYSAL<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Engineering, Gazi University, Maltepe, Ankara, Turkey, <sup>2</sup>Lehrstuhl für Technische Thermodynamik, Universität Rostock, Albert-Einstein-Str.2, D-18059, Rostock, Germany and <sup>3</sup>Department “Heat Energy”, Azerbaijan Technical University, H. Javid Av. 25, AZ1073 Baku, Azerbaijan

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**Abstract:** Pressure, density and temperature ( $p$ ,  $\rho$ ,  $T$ ) data and apparent molar volumes,  $V_{\phi}^{\circ}$ , of aqueous calcium acetate solutions  $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$  over a wide range of temperatures from 273.15 to 353.15 K, pressures up to  $p = 100$  MPa and molalities  $m$ , of 0.04918, 0.09367, 0.23797, 0.36365, 0.85923, 1.06930, 1.35223 and 1.81668 mol·kg<sup>-1</sup> of  $\text{Ca}(\text{CH}_3\text{COO})_2$  are reported. The combined expanded uncertainty of the density ( $\rho$ ) measurements at the 95 % confidence level with a coverage factor of  $k = 2$  was estimated to be  $U_c(\rho) = \pm 0.3 \text{ kg}\cdot\text{m}^{-3}$ . The measurements were realized with an Anton Paar DMA HPM vibration tube density meter. The system was calibrated using double-distilled water, aqueous NaCl solutions, methanol, toluene and acetone. An equation of state for fitting of the ( $p$ ,  $\rho$ ,  $T$ ) data of aqueous calcium acetate was developed as a function of pressure, temperature and molality. After a thorough analysis of literature values and validity of the constructed equation of state, various thermophysical properties, such as isothermal compressibility, isobaric thermal expansibility, differences in isobaric and isochoric heat capacities, thermal pressure coefficient and internal pressure at the investigated state parameter intervals were calculated.

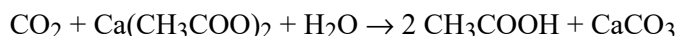
**Keywords:** density; aqueous calcium acetate solution; apparent molar volume; isothermal compressibility; isobaric thermal expansibility.

### INTRODUCTION

It is accepted that the main reason of global warming is the increment of the concentration of greenhouse gases, especially  $\text{CO}_2$ . The most effective way to combat and prevent the increasing concentration of  $\text{CO}_2$  in the atmosphere is to

\* Corresponding author. E-mail: javid.safarov@uni-rostock.de  
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capture and store it, or preferably utilize it. Many technologies have been developed to capture CO<sub>2</sub>, such as, absorption, adsorption, cryogenic separation, membrane separation or microbial/algal systems. Amongst these systems, the mostly used one in post-combustion systems is absorption of CO<sub>2</sub> with appropriate solutions.<sup>1</sup> In conventional systems for the capture of CO<sub>2</sub> mostly acyclic primary amine, acyclic secondary or tertiary amine solutions or cyclic amine-based solutions (piperazine, morpholine, *etc.*) or their mixtures are used.<sup>2</sup> In post-combustion carbon dioxide absorption systems, cooled flue gas is first sent to the absorber in which the carbon dioxide in the flue gas is contacted with an amine solution. Here, the absorber is typically operated at 40–60 °C to ensure high affinity for CO<sub>2</sub> absorption.<sup>3</sup> After the flue gas is water-washed to balance water in the system and to remove any solvent droplets or solvent vapor, it can be emitted to the atmosphere. The rich solvent (CO<sub>2</sub> containing solvent) stream leaves the absorber and is sent to the regeneration unit. The stripper here is operated at high temperature (100–140 °C) and pressure (1.5–2 atm) to ensure lower affinity for CO<sub>2</sub> absorption.<sup>3,4</sup> In the stripper, the desorption process is endothermic, heat must be applied to the absorbent to maintain its temperature. However, the operation of such systems is very energy consuming due to the high pressure and temperature values in the absorption and desorption units, thus decreasing the overall power plant efficiency. Moreover, systems with amine solutions have some more drawbacks, such as low loading capacity (kg CO<sub>2</sub> per kg of solvent), high degradation of solvents with SO<sub>2</sub> and O<sub>2</sub> that may be present in flue gas, high equipment corrosion rate, high degradation of solvents at high temperatures and high volatility.<sup>1,5,6</sup> Thus, alternative solutions are being investigated. Due to its alkaline nature and the ability to react with CO<sub>2</sub> at ambient temperatures, calcium acetate Ca(CH<sub>3</sub>COO)<sub>2</sub> could be a better alternative. The overall reaction between CO<sub>2</sub> and Ca(CH<sub>3</sub>COO)<sub>2</sub> is:<sup>7</sup>



In order to investigate the reaction kinetics and mass transfer effects in this reaction, first it is important to obtain the values of thermophysical parameters: pressure, density and temperature ( $p$ ,  $\rho$ ,  $T$ ) of aqueous Ca(CH<sub>3</sub>COO)<sub>2</sub> solutions.

Analysis of the literature density results<sup>8,9</sup> at high pressures and over a temperature range of 283.15–308.15 K (Table I) showed the necessity of careful experimental ( $p$ ,  $\rho$ ,  $T$ ) measurements of Ca(CH<sub>3</sub>COO)<sub>2</sub>(aq) over a wide range of temperatures and pressures. Saury *et al.*<sup>8</sup> in 1993 investigated the solubility of Ca(CH<sub>3</sub>COO)<sub>2</sub> in the temperature range 273.15–373.15 K, at ambient pressure and molar concentrations from 0.35 to 1.77 mol·L<sup>-1</sup>. The authors demonstrated that the solubilities of calcium acetate monohydrate and hemihydrate in aqueous solution decrease with increasing temperature, the former and later phases being stable below and above  $T = 331.15$  K, respectively. They also analyzed the density of Ca(CH<sub>3</sub>COO)<sub>2</sub> concentrations at  $T$  of 283.15–318.15 K.

TABLE I. A literature revision of experimental works dedicated to the thermodynamic properties of Ca(CH<sub>3</sub>COO)<sub>2</sub>(aq),  $p = 0.101$  MPa

Ref.	Year	Properties	$T / \text{K}$	$c / \text{mol} \cdot \text{L}^{-1}$
8	1993	Density	283.15–308.15	0.35 to 1.77
9	1964	Density	298.15	0.06 to 1.57

Some density points are given in the chemistry handbook edited by Nikolskiy<sup>9</sup> in 1965. These values were determined at  $T = 298.15$  K, at ambient pressure and in the  $0.06$ – $1.57$  mol L<sup>-1</sup> molar concentration range of Ca(CH<sub>3</sub>COO)<sub>2</sub>.

Since, There are no high-pressure values of the thermophysical properties of Ca(CH<sub>3</sub>COO)<sub>2</sub>(aq) in the literature and only two works with ambient pressure values of density over a small range of temperatures were found.

This paper is a continuation of previous publications on the thermophysical properties of aqueous electrolyte solutions.<sup>10–14</sup> In the present paper, the ( $p$ ,  $\rho$ ,  $T$ ) properties, and apparent molar volumes,  $V_\phi$ , of Ca(CH<sub>3</sub>COO)<sub>2</sub>(aq) over a wide range of temperatures from  $273.15$  to  $353.15$  K, pressures up to  $p = 100$  MPa and molalities of  $0.04918$ ,  $0.09367$ ,  $0.23797$ ,  $0.36365$ ,  $0.85923$ ,  $1.06930$ ,  $1.35223$  and  $1.81668$  mol·kg<sup>-1</sup> of calcium acetate are reported for the first time, and the apparent molar volumes at infinite dilution,  $V_\phi^0$ , have been evaluated. An empirical correlation for apparent molar volumes of Ca(CH<sub>3</sub>COO)<sub>2</sub> (aq) with pressure, temperature and molality has been derived.

#### EXPERIMENTAL

Calcium acetate (product No.: C1000; CAS No.: 62-54-4, molecular weight:  $0.1581672$  kg·mol<sup>-1</sup>, chemical formula: Ca(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>) was purchased from Sigma–Aldrich (BASF, quality,  $\geq 99$  %). In order to remove all volatile impurities, the sample was dried under vacuum for 48 h at a temperature of  $423.15$  K. The mass fraction of water determined after drying by means of a Karl–Fisher titration was  $w = 10^{-4}$  mass fraction. Double distilled water was used for the preparation of the solutions.

The ( $p$ ,  $\rho$ ,  $T$ ) measurements were performed using a modernized high pressure – high temperature Anton-Paar DMA HPM vibration tube densimeter, which is based on the dependence of the period of oscillation of a unilaterally fixed U-tube (Hastelloy C-276) on its mass. The sample in the oscillating tube is part of a complex system. Inertia shear forces occur on the wall, influencing the resonant frequency of the oscillator. The mPDS2000V3 control unit measures the vibration period with an accuracy of  $\Delta\tau = \pm 0.001$   $\mu\text{s}$ . The temperature in the measurement cell, where the U-tube is located, is controlled using a thermostat (F32-ME Julabo, Germany) with a  $\Delta T = \pm 10$  mK uncertainty of the measurement and is measured using the (ITS-90) Pt100 thermometer (type 2141) with a  $\Delta T = \pm 15$  mK experimental uncertainty of the measurement. The pressure was measured using different pressure transmitters for precision measurements (WIKA Alexander Wiegand GmbH & Co., Germany) with a  $\pm 0.1$  % standard uncertainty of the measured maximum value: for pressure  $0.101 < p < 0.25$  MPa and for pressure  $0.25 < p < 2.5$  MPa two different model of pressure transmitter P-30 and for pressure  $2.5 < p < 100$  MPa pressure transmitter P-10.

The ( $p$ ,  $\rho$ ,  $T$ ) properties over a wide range of temperatures from  $273.15$  to  $353.15$  K and pressures up to  $p = 100$  MPa were measured up to maximum solubility of the salt in water

( $m = 1.81668 \text{ mol}\cdot\text{kg}^{-1}$ ). This method gives the viscosity effect of vibration tubes. However, the viscosity of the prepared samples was not high enough for this effect to require attention. The system was calibrated using double-distilled water, aqueous NaCl solutions, *etc.* As NaCl(aq) up to maximum molality (also electrolyte water solution) was used during the calibration, in this case, the viscosity influence was considered during the calibration procedures. The deviation between the corrected viscosity and non-corrected viscosity values of  $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$  was smaller than the combined expanded uncertainty of the density  $\rho$  measurements. According to the specifications of Anton Paar and the calibration procedures, the observed repeatability of the density measurements in this work at temperatures from 273.15 to 353.15 K and pressures up to  $p = 100 \text{ MPa}$  was within  $\Delta\rho = \pm 0.3 \text{ kg}\cdot\text{m}^{-3}$  or 0.01 to 0.03 % percent deviation (at the 95 % confidence level with a coverage factor of  $k = 2$ ).<sup>15,16</sup>

The density of  $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$  at ambient pressure and at temperatures from 273.15 to 353.15 K was measured using the Anton Paar DSA 5000M and DMA HPM vibration tube densimeters with an uncertainty of  $\pm 5 \times 10^{-3}$  and  $\pm 0.3 \text{ kg}\cdot\text{m}^{-3}$ , respectively. These values are necessary to check the accuracy of ambient pressure density measurements using the high pressure – high temperature DMA HPM vibration tube densimeter. The standard deviation between ambient pressure density measured using the Anton Paar DSA 5000M and DMA HPM vibration tube densimeters were smaller than  $\Delta\rho = \pm 0.35 \text{ kg}\cdot\text{m}^{-3}$ .

Specific quantities of calcium acetate and water were evacuated, degassed in two separate flasks and connected using an adapter.<sup>17</sup> Water flowed into another flask and the concentration of the solution was defined using the weight of the flask with the solution on an electronic scale (Sartorius ED224S, Germany) with reproducibility of  $\pm 0.0001 \text{ g}$ .

## RESULTS AND DISCUSSION

In the present paper, the ( $p, \rho, T$ ) properties, and apparent molar volumes  $V_\phi$  of  $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$  over a wide range of temperatures from 273.15 to 353.15 K, pressures up to  $p = 100 \text{ MPa}$  and molalities of 0.04918, 0.09367, 0.23797, 0.36365, 0.85923, 1.06930, 1.35223 and  $1.81668 \text{ mol}\cdot\text{kg}^{-1}$  of  $\text{Ca}(\text{CH}_3\text{COO})_2$  are reported for the first time. The experimental values of density,  $\rho$ , isothermal compressibility,  $\kappa_T$ , isobaric thermal expansibility,  $\alpha_p$ , difference in isobaric and isochoric heat capacities,  $c_p - c_v$ , thermal pressure coefficient,  $\gamma$ , internal pressure,  $p_{\text{int}}$ , of  $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$  are listed in Table S-I of the Supplementary material to this paper.

Using a program for standard thermodynamic analysis to describe the ( $p, \rho, T$ ) properties of  $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$ , the equation of state (1) from the literature<sup>18</sup> was used:

$$p(\rho, T) / \text{MPa} = A(T)(\rho / \text{g cm}^{-3})^2 + B(T)(\rho / \text{g cm}^{-3})^8 + C(T)(\rho / \text{g cm}^{-3})^{12} \quad (1)$$

where  $A$ ,  $B$  and  $C$  are the coefficients and all are functions of temperature and molality in the following form:

$$A = \sum_{i=1}^4 T^i \sum_{j=0}^3 a_{ij} m^j, \quad B = \sum_{i=0}^3 T^i \sum_{j=0}^3 b_{ij} m^j, \quad C = \sum_{i=0}^3 T^i \sum_{j=0}^3 c_{ij} m^j \quad (2)$$

The  $a_{ij}$ ,  $b_{ij}$  and  $c_{ij}$  are the coefficients of the polynomials and are tabulated in Table II. The Eqs. (1) and (2) reproduce the experimental values with  $\Delta\rho/\rho = \pm 0.014\%$  average deviation. Figs. 1–3 show the plot of pressure  $p$  of Ca(CH<sub>3</sub>COO)<sub>2</sub>(aq) against density  $\rho$  at  $m = 1.35223 \text{ mol}\cdot\text{kg}^{-1}$ , plot of density  $\rho$  of Ca(CH<sub>3</sub>COO)<sub>2</sub>(aq) against pressure  $p$  at  $T = 298.15 \text{ K}$  and of the deviations of the experimental density ( $\rho_{\text{exp.}}$ ) of the investigated samples from the calculated density ( $\rho_{\text{cal.}}$ ) obtained from Eqs. (1) and (2) vs. pressure  $p$  at  $T$  from 273.15 to 353.15 K, respectively. Fig. 4 show the plot of deviations of ambient pressure density measured using DSA 5000M densimeter  $\rho_{\text{DSA5000M}}$  from the measured using DMA HPM densimeter  $\rho_{\text{DMA HPM}}$  of the investigated samples against temperature  $T / \text{K}$  at various molalities of CaAc.

TABLE II. Values of the coefficients  $a_{ij}$ ,  $b_{ij}$  and  $c_{ij}$  in Eqs. (1) and (2) for the Ca(CH<sub>3</sub>COO)<sub>2</sub> water solutions; average absolute percent deviation:  $\Delta\rho/\rho = 100(\rho_{\text{exp}} - \rho_{\text{cal}})/\rho_{\text{exp}} = \pm 0.014\%$  for Ca(CH<sub>3</sub>COO)<sub>2</sub>(aq)

$a_i$	$b_i$	$c_i$
$a_{10} = 11.5480210732$	$b_{00} = -633.252168596$	$c_{00} = 0$
$a_{11} = -2.2417448526$	$b_{01} = 201.182476867$	$c_{01} = 0$
$a_{12} = 0.717151395727$	$b_{02} = -117.142042425$	$c_{02} = -44.3505701315$
$a_{13} = -0.208651279157$	$b_{03} = 48.1842815654$	$c_{03} = 0$
$a_{20} = -0.114792498299$	$b_{10} = 5.34627013801$	$c_{10} = -0.595099686219$
$a_{21} = 0.781720693673 \times 10^{-2}$	$b_{11} = 0$	$c_{11} = 0.328292076809$
$a_{22} = 0$	$b_{12} = 0$	$c_{12} = 0.285922890841$
$a_{23} = 0$	$b_{13} = 0$	$c_{13} = -0.051644218105$
$a_{30} = 0.321070650674 \times 10^{-3}$	$b_{20} = 0$	$c_{20} = 0$
$a_{31} = 0$	$b_{21} = -0.87953050099 \times 10^{-2}$	$c_{21} = 0$
$a_{32} = 0$	$b_{22} = -0.299281890713 \times 10^{-3}$	$c_{22} = 0$
$a_{33} = 0$	$b_{23} = 0$	$c_{23} = 0$
$a_{40} = -0.281995859116 \times 10^{-6}$	$b_{30} = -0.112082284453 \times 10^{-4}$	$c_{30} = 0$
$a_{41} = -0.161183213861 \times 10^{-7}$	$b_{31} = 0.142014188321 \times 10^{-4}$	$c_{31} = 0$
$a_{42} = -0.481248915786 \times 10^{-8}$	$b_{32} = 0$	$c_{32} = 0$
$a_{43} = 0$	$b_{33} = 0.115748877103 \times 10^{-5}$	$c_{33} = -0.516250841572 \times 10^{-6}$

The apparent molar volumes  $V_\phi$  of the Ca(CH<sub>3</sub>COO)<sub>2</sub> in water are defined by Eq. (3) and are listed in Table S-II of the Supplementary material:

$$V_\phi = 1000(\rho_w - \rho_s)/(m\rho_s\rho_w) + M/\rho_s, \quad (3)$$

where  $\rho_w$  and  $\rho_s$  are densities of the water and solution,  $\text{g}/\text{cm}^3$ , and  $m$  is the molality of solution,  $\text{mol kg}^{-1}$ , and  $M$  is the molar mass of the dissolved Ca(CH<sub>3</sub>COO)<sub>2</sub>,  $\text{g mol}^{-1}$ .

The uncertainty in derived values of  $V_\phi$  depends strongly on  $m$ ,  $\rho_w$  and  $\rho_s$ . The maximum relative uncertainty,  $\Delta V_\phi$ , in the apparent molar volume  $V_\phi$  can be estimated using the following equation:

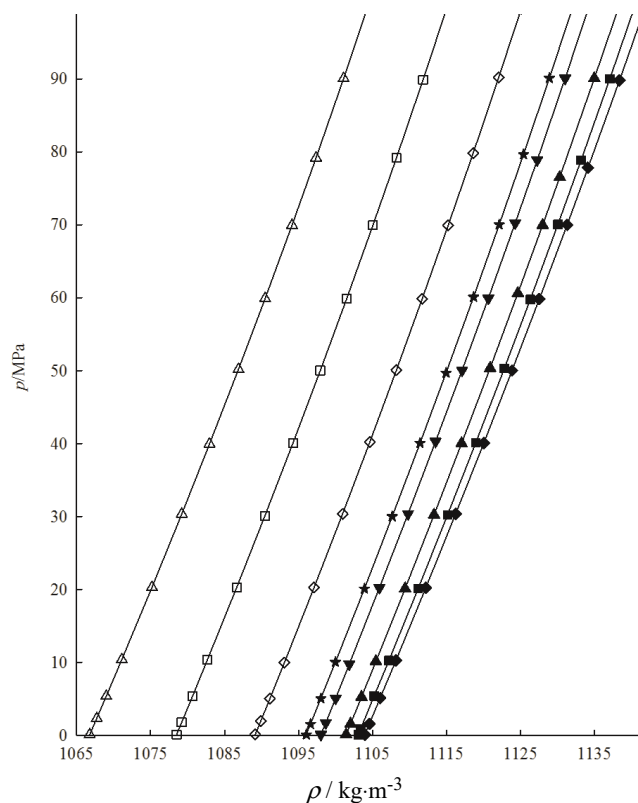


Fig. 1. Plot of pressure of  $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$  against density at  $m = 1.35223 \text{ mol}\cdot\text{kg}^{-1}$  at the temperature of:  $\blacklozenge$ , 273.16  $\blacksquare$ , 277.15;  $\blacktriangle$ , 283.15;  $\blacktriangledown$ , 293.15;  $\blackstar$ , 298.15;  $\diamond$ , 313.15;  $\square$ , 333.15;  $\triangle$ , 353.15 K; —, fitted to Eqs. (1) and (2).

$$\delta V_\phi = \left(1 - \frac{Mm}{1000}\right) \left(\frac{\rho_w}{\rho_w - \rho_s}\right) \delta \rho_s + \left(\frac{\rho_s}{\rho_w - \rho_s}\right) \delta \rho_w + \delta m, \quad (4)$$

where  $\delta V_\phi$  is the uncertainties in the apparent molar volumes,  $\delta \rho_w = \pm 0.001 \%$  is the uncertainty in the IAPWS pure water,  $\delta \rho_s = \pm 0.03 \%$  is the uncertainty in the solution density, and  $\delta m = \pm 0.75\%$  (at low concentrations) and  $\pm 0.065\%$  (at high concentrations) are the uncertainty in the concentration, respectively. The average uncertainties of  $\delta V_\phi$  at the investigated concentrations are  $\delta V_\phi = 6.67, 3.59, 1.41, 0.91, 0.34, 0.27, 0.19, 0.12 \%$ , respectively.

The plots of apparent molar volumes,  $V_\phi / \text{cm}^3\cdot\text{mol}^{-1}$ , of  $\text{Ca}(\text{CH}_3\text{COO})_2$  in water *versus* molality,  $m / \text{mol}\cdot\text{kg}^{-1}$ , at  $T = 283.15 \text{ K}$  are shown in Fig. 5. The plots of apparent molar volumes of  $\text{Ca}(\text{CH}_3\text{COO})_2$  in water against pressure at  $m = 1.81668 \text{ mol}\cdot\text{kg}^{-1}$  are shown in Fig. 6.

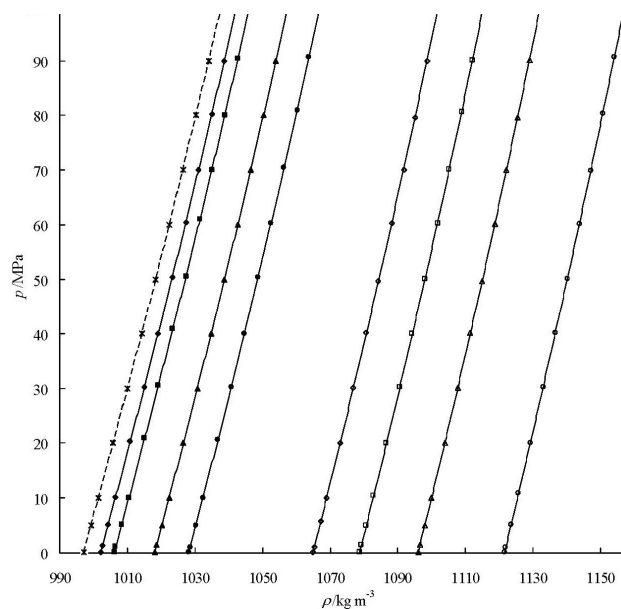


Fig. 2. Plot of density of  $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$  against pressure at  $T = 298.15$  K and molalities of:  $*$ , 0;  $\blacklozenge$ , 0.04918;  $\blacksquare$ , 0.09367;  $\blacktriangle$ , 0.23797;  $\bullet$ , 0.36365;  $\diamond$ , 0.85923;  $\square$ , 1.06930;  $\triangle$ , 1.35223;  $\circ$ , 1.81668  $\text{mol}\cdot\text{kg}^{-1}$ .

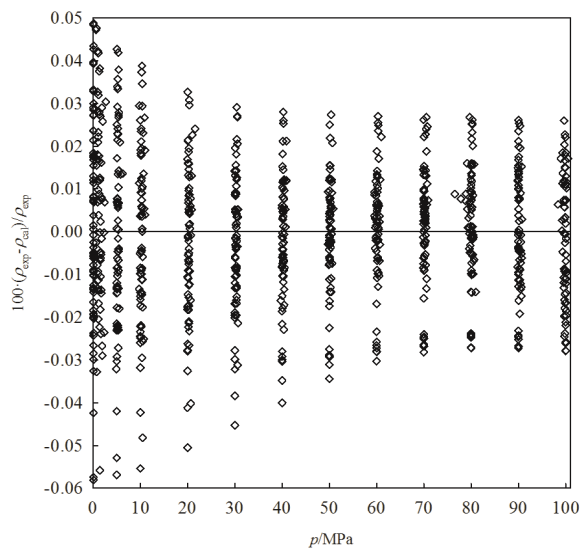


Fig. 3. Plot of deviations of the experimental density of the investigated samples from the calculated density obtained from Eqs. (1) and (2) against pressure at  $T = 273.15$  to  $353.15$  K.

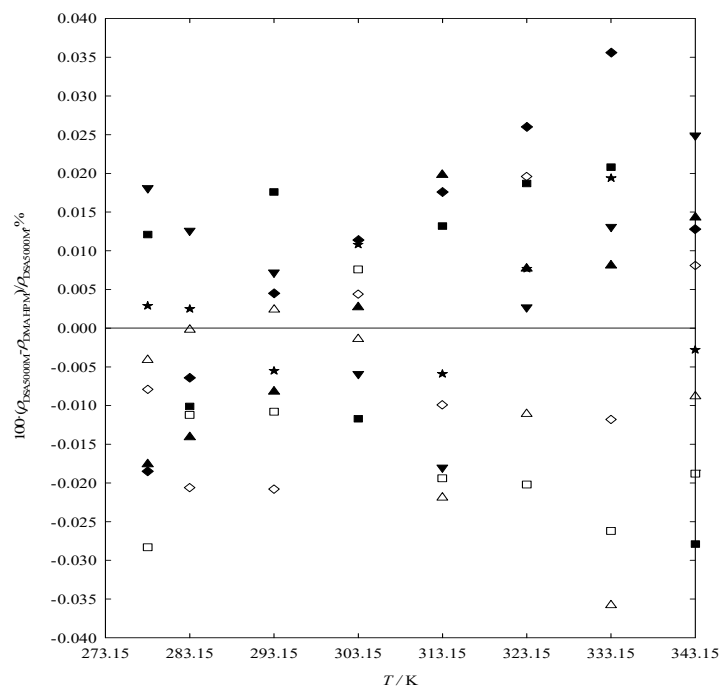


Fig. 4. Plot of deviations of ambient pressure density measured using DSA 5000M densimeter from the measured using DMA HPM densimeter of the investigated samples against temperature at various molalities of CaAc: and molalities of: \* , 0;  $\blacklozenge$  , 0.04918;  $\blacksquare$  , 0.09367;  $\blacktriangle$  , 0.23797;  $\bullet$  , 0.36365;  $\diamond$  , 0.85923;  $\square$  , 1.06930;  $\triangle$  , 1.35223;  $\circ$  , 1.81668 mol $\cdot$ kg $^{-1}$ .

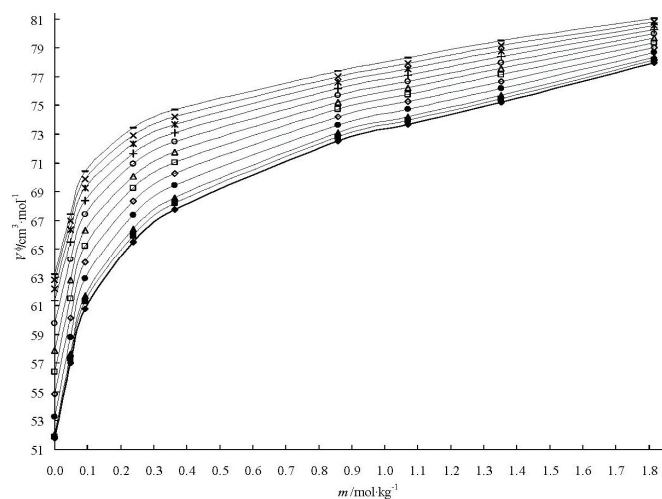


Fig. 5. Plots of apparent molar volumes of  $\text{Ca}(\text{CH}_3\text{COO})_2$  in water against molality at  $T = 283.15$  K and the pressures of:  $\blacklozenge$  , 0.101;  $\blacksquare$  , 5;  $\blacktriangle$  , 10;  $\bullet$  , 20;  $\diamond$  , 30;  $\square$  , 40;  $\triangle$  , 50;  $\circ$  , 60;  $\oplus$  , 70;  $\ast$  , 80;  $\times$  , 90;  $-$  , 100 MPa; —, fitting lines.



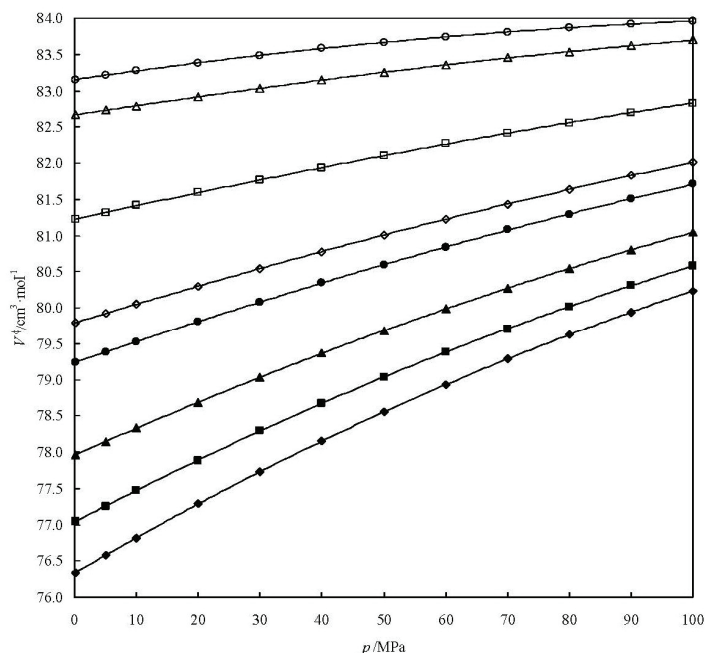


Fig. 6. Plots of apparent molar volumes of  $\text{Ca}(\text{CH}_3\text{COO})_2$  in water against pressure at  $m = 1.81668 \text{ mol}\cdot\text{kg}^{-1}$  the temperature of:  $\blacklozenge$ , 273.16  $\blacksquare$ , 277.15;  $\blacktriangle$ , 283.15;  $\blacktriangledown$ , 293.15;  $\star$ , 298.15;  $\diamond$ , 313.15;  $\square$ , 333.15;  $\triangle$ , 353.15 K; —, fitting lines.

The apparent molar volume of  $\text{Ca}(\text{CH}_3\text{COO})_2$  at infinite dilution,  $V_\phi^0$ , at constant temperature and pressure can be evaluated from the following equation:

$$V_\phi = V_\phi^0 + A_v m^{0.5} + B_v m \quad (5)$$

where  $A_v$  is the Debye–Hückel limiting slope,  $m$  is the molality and  $B_v$  is an adjustable parameter. Redlich *et al.*<sup>19,20</sup> attempted to prove the Masson hypothesis for deriving  $A_v$  by using the Debye–Hückel theory:<sup>21</sup>

$$A_v = kw^{3/2} \quad (6)$$

where:  $k$  and  $w$  were expressed as:

$$k = N_A^2 e^3 \left( \frac{8\pi}{1000D^3 RT} \right)^{0.5} \frac{\partial \ln D}{\partial p} - \frac{\beta}{3} \quad (7)$$

and

$$w = 0.5 \sum_i \nu_i z_i^2 \quad (8)$$

where  $N_A$  is Avogadro's number,  $e$  is the electric charge,  $D$  is the dielectric constant of the solvent,  $R$  is the gas constant,  $T$  is the absolute temperature,  $\beta$  is

the compressibility of the solvent,  $v_i$  is the number of ions of species  $i$  and valency  $z_i$  formed by one molecule of electrolyte. According to Eq. (8) for an electrolyte of a fixed valence type,  $w$  is constant and the limiting slope  $A_v$  depends only on the temperature and the physical properties of the solvent  $D$ ,  $\partial \ln D / \partial p$  and  $\beta$ . As a rule, this relationship is applied at fixed pressure  $p$  and temperature  $T$ . The infinite-dilution values  $V_\phi^0$  of the apparent molar volumes  $V_\phi$  are obtained by polynomial extrapolation of Eq. (5) to zero molality of the solution ( $m = 0$ ). Archer and Wang<sup>22</sup> calculated the values of  $A_v$  for 1:1 electrolytes ( $w = 1$ ). The value  $w = 3$  was used for  $\text{Ca}(\text{CH}_3\text{COO})_2$  during the calculations. The apparent molar volumes of calcium acetate at infinite dilution  $V_\phi^0$  are listed in Table III and the adjustable parameter  $B_v$  in Table IV.

TABLE III. Apparent molar volumes at infinite dilution,  $V_\phi^0 / \text{cm}^3 \cdot \text{mol}^{-1}$ , of  $\text{Ca}(\text{CH}_3\text{COO})_2$  in water

$p / \text{MPa}$	$T / \text{K}$							
	273.16	277.15	283.15	293.15	298.15	313.15	333.15	353.15
0.101	40.229	45.963	51.789	54.858	56.737	58.521	61.380	62.525
5	41.612	46.833	51.874	55.518	56.607	58.503	61.624	62.588
10	43.095	47.771	52.075	55.699	56.476	58.365	61.919	62.577
20	46.086	49.667	53.264	56.056	56.519	58.518	62.062	62.099
30	49.127	52.198	54.838	56.397	56.974	58.967	62.626	62.382
40	52.102	54.619	56.381	57.745	58.018	59.821	63.482	62.652
50	55.129	56.608	57.888	58.763	59.339	60.541	64.627	63.026
60	57.401	58.888	59.774	60.058	60.336	61.958	65.443	63.270
70	59.849	60.618	61.332	61.327	61.018	63.053	66.240	63.929
80	61.565	62.113	62.170	61.989	61.979	63.830	67.436	64.146
90	62.500	62.550	62.816	62.640	62.742	64.479	68.197	64.471
100	62.744	63.144	63.162	63.097	63.202	65.632	68.762	64.484

TABLE IV. Apparent molar volume concentration dependence constant,  $B_v / \text{cm}^3 \cdot \text{kg} \cdot \text{mol}^{-2}$ , of  $\text{Ca}(\text{CH}_3\text{COO})_2$  in water

$p / \text{MPa}$	$T / \text{K}$							
	273.16	277.15	283.15	293.15	298.15	313.15	333.15	353.15
0.101	137.0451	104.1870	68.6835	61.4388	47.5898	42.7518	28.0683	16.1675
5	132.6794	101.8267	73.3467	56.5026	52.2222	45.1311	27.8416	17.0701
10	126.0210	98.9334	75.5932	58.9067	56.8291	49.9098	28.2226	19.9141
20	115.4637	95.9972	76.0178	63.6131	63.7798	54.7222	33.5480	30.2721
30	102.7879	85.3287	72.0192	68.2598	66.1271	57.2992	34.1431	33.4164
40	90.3993	75.2613	68.0577	64.1735	64.2107	55.3759	32.5548	36.4379
50	75.9623	69.5737	64.2262	62.3017	60.2361	55.7892	28.7887	36.9629
60	68.1523	58.7116	56.0964	58.3521	58.4288	49.6848	27.2094	39.8319
70	56.0022	53.0622	50.1657	54.4857	58.7023	45.7195	25.6405	38.0841
80	50.3448	47.4538	50.6604	54.7706	56.9203	43.9168	19.6359	40.8731
90	48.5741	52.0900	50.9087	55.0534	54.9713	44.3615	18.1203	41.2042
100	52.9825	51.1558	53.1684	55.1191	55.0656	38.3125	16.3811	43.6498

## CONCLUSIONS

The thermophysical properties ( $p, \rho, T$ ) of aqueous  $\text{Ca}(\text{CH}_3\text{COO})_2$  solutions of eight different concentrations, at temperatures of 273.15 to 353.15 K and pressures up to 100 MPa were experimentally investigated. The measurements were performed at molalities of 0.04918, 0.09367, 0.23797, 0.36365, 0.85923, 1.06930, 1.35223 and 1.81668  $\text{mol}\cdot\text{kg}^{-1}$  of calcium acetate. A thermodynamic equation of state (1) over a well specified range of state parameters was constructed, which was applied for the calculation of the apparent molar volumes,  $V_\phi$ ,  $\text{cm}^3\cdot\text{mol}^{-1}$ , of  $\text{Ca}(\text{CH}_3\text{COO})_2$  in water. The Debye–Hückel theory for the investigated solutions was examined. These investigations were examined for the first time and the data gathered here could contribute greatly to further work in this field.

The apparent molar volumes of  $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$  at 273.15 to 353.15 K and pressures up to 100 MPa are reported, and the apparent molar volumes of  $\text{Ca}(\text{CH}_3\text{COO})_2$  at infinite dilution  $V_\phi^0$  were evaluated.

## SUPPLEMENTARY MATERIAL

The experimental values of density,  $\rho$ , isothermal compressibility,  $\kappa_T$ , isobaric thermal expansibility,  $\alpha_p$ , difference in isobaric and isochoric heat capacities,  $c_p - c_v$ , thermal pressure coefficient,  $\gamma$ , internal pressure,  $p_{\text{int}}$ , and the apparent molar volumes,  $V_\phi$ , of the  $\text{Ca}(\text{CH}_3\text{COO})_2$  in the water are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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## ИЗВОД

ПРИВИДНЕ МОЛАРНЕ ЗАПРЕМИНЕ,  $V_\phi$ , КАЛЦИЈУМ-АЦЕТАТА ( $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$ ) НА  $T = 273,15$  ДО  $353,15$  К И ПРИТИСЦИМА ДО 100 МПа

DUYGU UYSAL ZIRAMAN<sup>1</sup>, JAVID T. SAFAROV<sup>2,3</sup>, ÖZKAN MURAT DOĞAN<sup>1</sup>, EGON P. HASSEL<sup>2</sup> и BEKIR Z. UYSAL<sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Faculty of Engineering, Gazi University, Maltepe, Ankara, Turkey,

<sup>2</sup>Lehrstuhl für Technische Thermodynamik, Universität Rostock, Albert-Einstein-Str.2, D-18059, Rostock,

Germany и <sup>3</sup>Department „Heat Energy“, Azerbaijan Technical University, H. Javid Avn. 25, AZ1073 Baku, Azerbaijan

Представљени су ( $p, \rho, T$ ) подаци и привидне моларне запремине,  $V_\phi$ , водених раствора калцијум-ацетата,  $\text{Ca}(\text{CH}_3\text{COO})_2(\text{aq})$ , у широком опсегу температура, од 273,15 до 353,15 К, притисцима до  $p = 100$  МПа и молалитетима од 0,04918; 0,09367; 0,23797; 0,36365; 0,85923; 1,06930; 1,35223 и 1,81668  $\text{mol}\cdot\text{kg}^{-1}$ . Проширена комбинована несигурност мерења густине, нивоа поузданости од 95 % и фактора покривености  $k = 2$ , је процењена на  $U_c(\rho) = 0,3 \text{ kg}\cdot\text{m}^{-3}$ . Мерења су извршена коришћењем Anton Paar DMA НРМ густиномера са вибрирајућом цеви. Систем за мерење је калибрисан применом двоструко дестиловане воде, водених раствора  $\text{NaCl}$ , метанола, толуена и ацетона. Развијена је једначина стања за корелисање ( $p, \rho, T$ ) података водених раствора калцијум-ацетата као функција притиска, температуре и молалитета. Након детаљне анализе литературних вредности и валидности изведене једначине стања, прорачуната су разна термо-

динамичка својства као што су изотермска компресибилност, изобарска топлотна експанзивност, разлике изобарског и изохорског топлотног капацитета, топлотни коефицијент притиска и унутрашњи притисак на испитиваним опсезима параметара стања.

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