Measurements of the Heat Capacity at Constant Volume of $H_2O+Na_2SO_4$ in the Near- Critical and Supercritical Water[1]

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ABSTRACT

Heat capacity at constant volume C_{VX} of Na_2SO_4 aqueous solutions have been measured from 460 K to 669 K at 11 isochores from 250 kg· m^{-3} to 926 kg· m^{-3} for three compositions, namely: 0.0031049; 0.0159697 and 0.0331262 mole fraction of Na_2SO_4. Measurements of isochoric heat capacity C_V for pure water were also made at critical isochore (ρ_C=317.9 kg ·m^{-3}) and at six near-critical isochores, namely: 309.598, 335.570, 354.480, 368.310, 370.370 and 373.340 kg· m^{-3} and the coexistence curve. 368 C_{VX} data for H_2O+Na_2SO_4 and 273 C_V data for pure water were measured along 17 isochores in the one- and two-phase regions. The measurements were made in a high-temperature and high- pressure adiabatic nearly constant-volume calorimeter. The accuracy of the isochoric heat capacity measurements is estimated to be within ±2 %. One- (C'_V) and two-phase (C''_V) heat capacities , temperatures (T_S), and densities (ρ_S) at saturation were obtained by the method of quasi-static thermograms. The experimental C_{VX} results has been compared with a Pitzer's classical equation of state. The relative average deviations for H_2O+Na_2SO_4 solution within about ±2 %, except critical region where differences reached 15-20%.

KEY WORDS: aqueous ionic solutions; coexistence curve; critical point; equation of state; heat capacity; sodium sulfate; water.

1. INTRODUCTION

There has been growing interest in aqueous solutions at near-critical and supercritical conditions due to their importance in supercritical water oxidation (SCWO) technology and other industrial applications [1,2]. Little is known about the thermodynamic behavior of ionic solutions at the conditions encountered in SCWO. SCWO has recently been proposed as an efficient method for chemical waste disposal [3]. Sodium sulfate is one of the most commonly encountered mixed salt systems in prospective applications of SCWO [4]. Na^+ and SO_4^{2-} are important components of natural fluids, and a knowledge of their aqueous solution thermodynamic properties is important in understanding various geochemical processes, such as those related to evaporate formation, subsurface brines, seafloor vents, geothermal energy production, and mineral scaling problems [5].The system $H_2O+Na_2SO_4$ is of interest also intrinsically as a 1-2-type electrolyte. There are many interesting differences between critical behavior of C_{VX} for ionic and nonionic solutions. Adding an electrolyte to water results in a strong shift of the vapor-liquid critical point. P_C-x and T_C-x critical lines for H_2O+salt systems show rapid changes in slope near the critical point pure water that a quantitative change critical behavior of thermodynamic properties, in particular C_{VX} and K_{TX} [6-8]. Universal features of the critical behavior of nonionic fluids and fluid mixtures a well described by the Ising model, as theoretically expected in systems with short-range forces. However, questionable if this stays true when long-range Coulombic forces come into play and, when they are driving forces of the phase transition. The long-range nature of the Coulombic interaction provides the possibility of mean-field critically. However, electrostatic shielding, predicted e.g. by the Debye-Huckel theory, leads to a potential of the mean force which is short-ranged, so that Ising-type criticality may prevail [9].

In this paper, we measured the heat capacity at constant volume of pure water and $H_2O+Na_2SO_4$ solutions under near-critical and supercritical conditions. The

measurements cover the range in temperature from 460 to 669 K at three compositions: 0.0031049; 0.0159697, and 0.0331262 mole fraction of Na_2SO_4. Only one extensive study of the $H_2O+Na_2SO_4$ solution has been reported [5,10].

2. EXPERIMENTS

Isochoric heat capacity was measured with a high-temperature and high-pressure nearly constant-volume adiabatic calorimeter. The apparatus and experimental procedures have been described in detail in our previous publications [11-15], and only a brief description is given here. Essentially, it consist of a inner thin-walled (0.8 mm wall thickness) spherical bomb (diameter 60 mm), the outer spherical shell (7mm wall thickness), thermostating screen, high-precision temperature regulator for thermostat and for adiabatic layer shell, calorimetric heater, stirring branch, digital measuring units for power measurement of the calorimetric heater, platinum resistance thermometer (PRT), and filling capillary. In the gap between the inner thin-walled sphere and the outer shell the highly sensitive semiconducting material (cooper oxide Cu_2O) was situated. A layer of Cu_2O ensured adiabatic protection and acted as a thermal screen. By using a sensitive potentiometer, it was possibly to control the temperature differences between the inner sphere and the first thermal screen with an accuracy of $\pm 10^{-5}$ K. Temperature was measured with a PRT mounted in a tube in the inside of the sphere. The uncertainty in the temperature measurements was less than ± 10 mK. The volume V_{PT} of the calorimeter was corrected for its variation with temperature T and pressure P.

The isochoric heat capacity C_V of the sample was calculated from the measured quantities (ΔQ, ΔT, C_0,m) as follows:

$$C_V = \frac{1}{m}\left\{\frac{\Delta Q}{\Delta T} - C_0\right\}, \qquad (1)$$

where C_0 is the empty-calorimeter heat capacity, ΔQ is the amount of energy released by the inner heater, ΔT is the temperature change resulting from addition of a measured amount of energy ΔQ. The empty-calorimeter heat-capacity C_0 was previously determined using a standard liquid with a well known heat capacity (n-heptane and pure

water) [16]. The scatter of the experimental results was not worse than ±0.3 %. All measurements were made with the samples vigorously stirred using a stirrer made of a thin perforated steel foil. The experimental values of saturation temperatures on each isochores was determined by the method of quasi-static thermograms [13-15,17]. The uncertainty in saturation temperature measured was no worse than ±0.02÷0.05 K. The total uncertainty in reported values for C_{VX} stems from uncertainty in measurement of the quantities C_0, ΔT, m, and ΔQ in Eq. (1). The uncertainties are ±0.2% in C_0, ±0.01% in m, ±3 mK in ΔT, and ±0.1% in ΔQ. The value of correction to C_V connected with working-volume variation was not worse than ± 2 % of the total heat capacity. For the liquid isochores (large m), the uncertainty in C_{VX} is ±0.8%. At vapor isochores (small m), the uncertainty in C_{VX} is ±1-2%. In the region of the immediate vicinity of the critical point the uncertainty in C_{VX} is ±2%.

3. RESULTS

In Tables I and II, some of the measured results for pure water and $H_2O+Na_2SO_4$ solutions are presented. The results given in Table II cover the density range of 250-926 $kg{\cdot}m^{-3}$ at temperatures between 460 and 669 K for three compositions: 0.0031049, 0.0159697, and 0.0331262 m. f. of Na_2SO_4. Measurements was performed along 11 isochores: 250.1, 309.9, 361.9, 521.3, and 664.0 $kg{\cdot}m^{-3}$ for composition of 0.0031049 m. f. of Na_2SO_4; 490.0, 674.7, and 925.9 $kg{\cdot}m^{-3}$ for composition of 0.0159697 m. f. of Na_2SO_4 and 537.6, 697.8, and 774.2 $kg{\cdot}m^{-3}$ for composition of 0.0331262 m. f. of Na_2SO_4. Heat-capacity measurements for pure water and $H_2O+Na_2SO_4$ solutions at near-critical isochores are plotted as a functions of the temperature in Figs.1,2. Fig.3 shows the density dependence of the C_V for pure water and $H_2O+Na_2SO_4$ solution at supercritical isotherm. The experimental results of C_{VX} and T_S-ρ_S data on the coexistence curve which were determined by the method of quasi-static thermograms for this solution are presented in Table III and Figs. 4,5.

4. DISCUSSION

Hovey et al. [18] have correlated the measurements of isothermal vapor-liquid compositions for H_2O+KCl and H_2O+NaCl using the equation of state, which was originally proposed in [19-22] and was improved and used by Tanger and Pitzer [22]. From this equation the isochoric heat capacities may be calculated via the relation:

$$\frac{C_{VX}}{n_{H_2O}} = C_{VH_2O}(T,d) + yV_C \frac{T}{d}\left[\frac{d^2 b_{10}}{dT^2} + y\frac{d^2 b_{20}}{dT^2} - (d\ln d + 1)\frac{d^2 b_{11}}{dT^2}\right] + yC^*_{Na_2SO_4}, \quad (2)$$

where d is the reduced density $\rho(H_2O)/\rho_C(H_2O)$ of pure water in the system with $\rho_C(H_2O)$ the critical density of pure water, y is the mole ratio, $x = y/(1+y)$ mole fraction of salt, V_C is the critical volume of pure water. A Pitzer's Eq. (2) has been used for representation of our new experimental C_{VX} data for H_2O+ Na_2SO_4 solutions. The temperature dependence of the three derivatives d^2b_{10}/dT^2, d^2b_{20}/dT^2, d^2b_{11}/dT^2 and parameter $C^*_{Na_2SO_4}$ for H_2O+ Na_2SO_4 solutions were described by following equations:

$$d^2b_{10}/dT^2 = 93.00625 - 30.64174\,\tau^{-3} - 110.40691\,\tau^{-n_1}, \quad d^2b_{20}/dT^2 = -482.64812\,\tau^{-n_2},$$

$$d^2b_{11}/dT^2 = -0.2103817\,\tau^{-n_3}, \quad C^*_{Na_2SO_4}(T) = 0.1792890\,\tau^{-n_4}, \text{ where } \tau = T/T_C(H_2O). \quad (3)$$

To fit experimental C_{VX} data, one needs, in addition to the equation (2), expression for the $C_{VH_2O}(T,d)$ of pure water. The simple polynomial equation was used for $C_{VH_2O}(T,d)$ [23]. Fig. 6 show the relative percentage deviations of the present experimental C_{VX} data for H_2O+ Na_2SO_4 solutions. It is seen from Fig. 6 that the present and previous results are in satisfactorily agreement with Eq. (2). The average and maximum of the relative deviations are ±2 % and 7 %, respectively. In the immediate vicinity of critical point and phase transition temperatures, differences increase to about 15-20 %. For correctly described of the behavior of C_{VX} for water+salt

solutions near the critical point, the nonclassical equation for isochoric heat capacity of pure water $C_{VH_2O}(T,d)$ [24] one must to use instead the classical expression or to use the crossover theory of ionic solutions [6] which were avoided in these treatments.

5. Conclusion

New measurements of the isochoric heat capacities of pure water and $H_2O+Na_2SO_4$ solutions are reported. The measurements were performed in a high-temperature and high-pressure adiabatic nearly constant-volume calorimeter in the temperature range of 460-669 K at densities from 250 to 926 kg·m^{-3} for three compositions (0.0031049, 0.0159697, and 0.031262), with an uncertainty of ±2%. These measurements include the critical region. In this paper we present also the new C_{VX} and T_S-ρ_S measurements of aqueous Na_2SO_4 solutions and pure water along the coexistence curves in the temperature range from 354 to 648 K. The results for the measurements on Na_2SO_4 are compared with the Pitzer's classical equation of state. We confirm that Pitzer's model and experiment for the C_{VX} of fluids and fluid mixtures outside the critical region are consistent.

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Table I. Experimental Values of Isochoric Heat Capacities C_V for Pure Water at the Critical and Near-Critical Isochores (ρ_C=317.90 kg ·m^{-3}, T_C=647.065 K).

T, (K)	C_v, (kJ· kg^{-1}·K^{-1})	T, (K)	C_v, (kJ· kg^{-1}·K^{-1})	T, (K)	C_v, (kJ· kg^{-1}·K^{-1})
ρ=317.900 kg ·m^{-3}		**ρ=370.370 kg ·m^{-3}**		**ρ=309.598 kg ·m^{-3}**	
645.17	13.682	644.29	9.331	643.30	10.854
645.32	13.684	644.93	9.542	643.64	10.766
645.62	14.122	645.25	9.736	643.98	10.544
646.07	14.616	645.58	9.875	644.33	10.708
646.52	16.040	645.90	10.113	644.67	11.131
646.67	16.948	646.22	10.397	645.02	11.390
646.90	17.986	646.62	10.970	645.36	11.574
647.06	19.146	646.79	11.595	645.53	11.574
647.12	13.674	646.87	12.105	645.70	12.077
647.20	9.868	646.94	13.189	645.87	11.985
647.27	7.800	647.02	7.191	646.04	11.876
647.35	7.021	647.19	5.680	646.21	12.503
647.42	6.615	647.35	5.341	646.38	13.175
647.50	6.678	647.51	5.211	646.55	13.303
647.57	6.319	647.99	4.847	646.72	13.776
647.72	6.071	648.15	4.779	646.89	14.794
647.80	5.945	648.79	4.520	647.07	17.108
648.26	5.254	649.43	4.356	647.24	10.251
648.47	5.151	650.07	4.235	647.41	6.237
649.75	4.740	661.88	3.691	649.46	4.621
656.86	4.063	674.23	3.511	651.93	4.451

Table II. Experimental Values of the Isochric Heat Capacities C_{vx} of $H_2O+Na_2SO_4$ in the One- and Two-Phase Region

x=0.0031049 mole fraction Na_2SO_4

T, (K)	C_{vx}, (kJ· kg^{-1}·K^{-1})	T, (K)	C_{vx}, (kJ· kg^{-1}·K^{-1})	T, (K)	C_{vx}, (kJ· kg^{-1}·K^{-1})
ρ=250.1 kg ·m^{-3}		**ρ=309.9 kg ·m^{-3}**		**ρ=361.9 kg ·m^{-3}**	
585.33	6.231	588.48	5.528	583.75	5.502
586.02	6.443	589.18	5.775	584.45	5.332
629.06	8.971	630.60	8.023	624.79	7.396
629.72	13.405	631.45	8.016	625.47	7.321
629.91	10.349	631.63	8.011	631.11	7.890
630.09	10.296	631.80	8.088	631.18	7.886
630.26	10.293	631.97	8.508	631.45	7.798
631.28	10.339	632.14	12.224	631.63	7.884
631.45	10.340	632.31	9.269	631.80	7.880
631.63	10.236	632.48	9.227	631.97	7.847
646.45	13.321	632.65	9.279	632.14	7.901
646.62	13.575	632.82	9.274	632.31	7.880
646.79	13.703	647.06	13.435	632.48	7.829
646.96	13.618	647.30	14.041	632.65	7.824
647.12	13.518	647.47	14.636	632.82	7.906
647.30	10.299	647.64	15.233	632.99	11.472
647.47	9.032	647.82	16.083	633.16	9.463
647.64	7.134	647.99	16.071	647.47	13.981
647.82	6.078	648.16	6.254	647.82	16.176
647.99	5.971	648.33	5.576	649.52	4.742
649.35	4.053	649.35	5.172	668.37	3.326

Table II . (Continued)

x=0.0159697 mole fraction Na_2SO_4

T, (K)	C_{vx}, (kJ· kg^{-1}·K^{-1})	T, (K)	C_{vx}, (kJ· kg^{-1}·K^{-1})	T, (K)	C_{vx}, (kJ· kg^{-1}·K^{-1})
ρ=490.0 kg ·m^{-3}		**ρ=674.7 kg ·m^{-3}**		**ρ=925.9 kg ·m^{-3}**	
608.97	5.143	607.60	4.682	460.39	3.383
609.15	5.168	607.77	4.828	460.59	3.352
609.67	5.091	608.98	4.850	460.78	3.409
610.01	12.518	609.84	4.851	460.98	3.268
610.18	6.613	610.01	4.854	461.18	2.793
610.36	6.565	610.36	4.798	461.38	2.853
610.53	6.517	610.53	4.790	461.57	3.049
637.41	7.960	610.70	11.604	461.77	2.802
637.58	7.809	611.05	6.468	462.16	2.821
637.75	7.979	611.22	6.419	462.36	2.727
638.27	7.961	611.56	6.397	462.56	2.610
643.05	8.566	611.91	6.352	462.76	2.798
643.90	8.995	612.08	6.400	480.61	2.711
644.07	8.718	612.25	6.342	48081	2.760
644.24	7.506	615.35	6.565	481.00	2.645
644.41	6.606	616.04	2.836	481.20	2.718
644.58	3.201	616.21	2.873	481.40	2.743
644.75	3.476	617.58	2.754		
644.92	3.199	617.76	2.749		
645.09	3.145	631.97	3.049		
647.64	3.248	632.14	3.050		
647.81	3.173	632.65	3.015		

Table II . (Continued)

x=0.0331262 mole fraction Na_2SO_4

T, (K)	C_{vx}, (kJ· kg^{-1}·K^{-1})	T, (K)	C_{vx}, (kJ· kg^{-1}·K^{-1})	T, (K)	C_{vx}, (kJ· kg^{-1}·K^{-1})
ρ=537.6 kg ·m^{-3}		**ρ=697.8 kg ·m^{-3}**		**ρ=774.2 kg ·m^{-3}**	
590.58	4.371	591.97	4.411	589.70	4.398
591.10	4.337	592.50	4.406	590.23	4.397
591.62	4.441	593.54	5.804	592.15	4.396
591.97	4.484	594.24	5.841	592.85	4.327
592.15	4.428	594.41	5.912	593.02	4.403
592.85	5.735	618.62	6.517	593.54	4.400
593.37	5.968	618.96	6.503	593.89	13.419
593.54	6.050	619.13	6.428	594.24	5.892
593.72	5.930	619.30	6.385	602.58	6.053
593.89	6.123	619.47	6.119	602.75	6.032
594.07	6.178	619.64	3.422	602.93	6.027
640.59	7.630	619.82	2.692	603.10	6.025
640.66	7.881	619.99	2.690	603.27	5.979
640.83	7.884	620.16	2.642	603.45	5.984
641.00	7.854	631.63	2.717	603.62	3.565
641.34	7.864	631.80	2.763	603.79	2.497
641.52	8.011	631.97	2.716	603.97	2.440
641.69	8.165	632.14	2.835	604.14	2.557
641.86	8.476	632.31	2.726	604.31	2.439
642.03	8.317	632.82	2.751	604.50	2.678
643.22	2.978	640.49	2.721	604.66	2.678
643.39	2.978	640.83	2.670	605.18	2.678

Table III. Experimental Values of Temperatures T_S, Saturated Densities ρ_S, One-Phase $\tilde{N}'_{vx}$ and Two-Phase $\tilde{N}''_{vx}$ Specific Heats

T_S (K)	ρ_S ($kg \cdot m^{-3}$)	$\tilde{N}'_{vx}$ ($kJ \cdot kg^{-1} \cdot K^{-1}$)	$\tilde{N}''_{vx}$ ($kJ \cdot kg^{-1} \cdot K^{-1}$)
x=0.0031049 mole fraction Na_2SO_4			
647.55	250.1	14.20	9.614
648.08	309.9	16.70	7.200
647.91	361.9	16.546	7.282
638.28	521.3	8.076	3.170
600.42	664.0	5.225	3.038
493.07	860.5	4.500	3.680
x=0.0159697 mole fraction Na_2SO_4			
644.49	490.0	9.104	4.904
615.87	674.7	6.809	3.000
461.08	925.9	3.409	3.093
x=0.0331262 mole fraction Na_2SO_4			
643.05	537.6	7.481	2.978
619.56	697.8	6.119	2.692
603.54	774.2	6.035	2.597
598.59	796.2	6.024	2.634
587.86	830.7	4.265	2.682
579.75	844.8	4.330	2.640
516.63	936.3	3.974	2.891
469.72	989.2	3.954	3.001
384.51	1059.0	3.715	3.527
354.30	1072.5	3.884	3.592

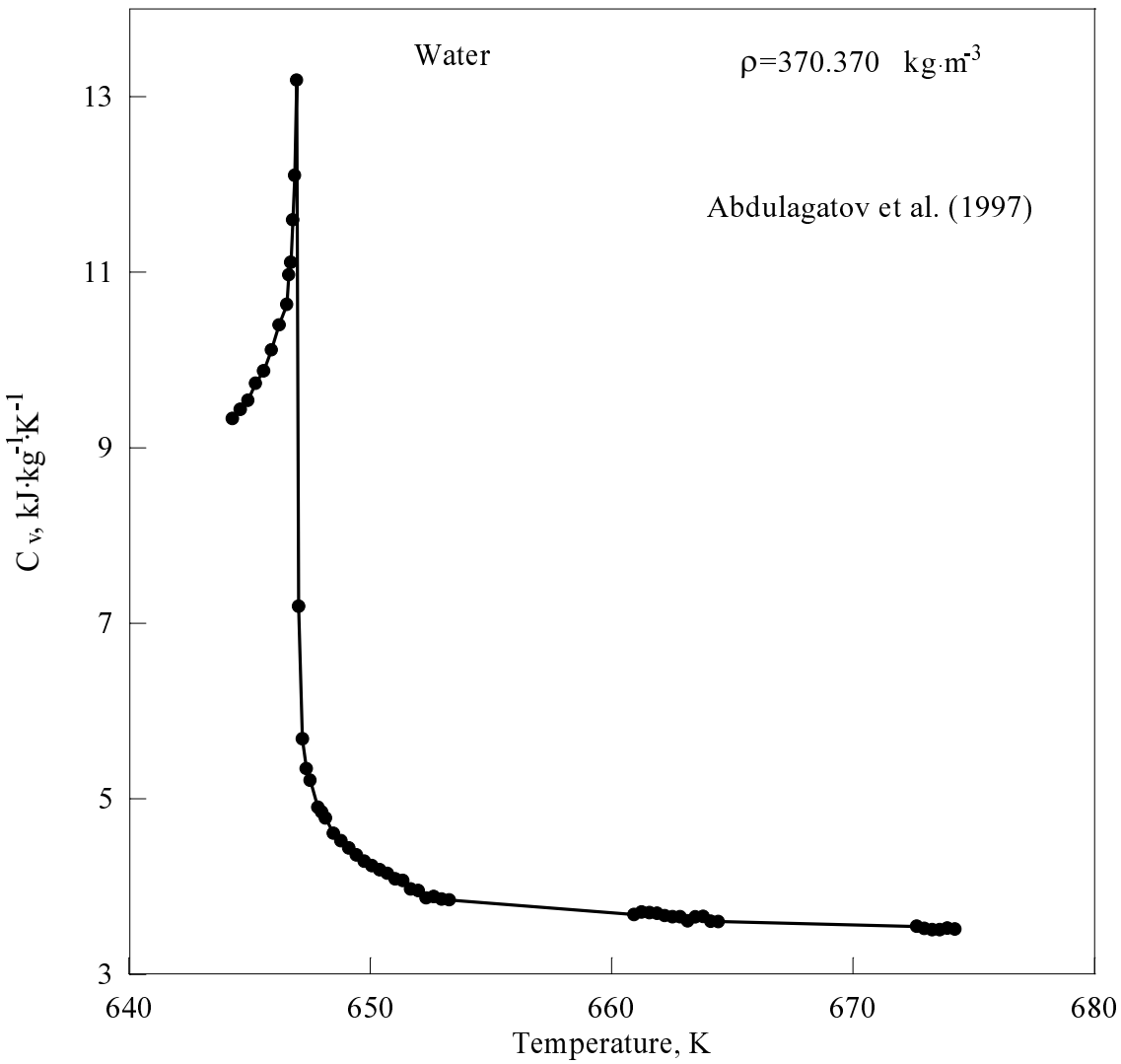

Fig.1 The isochoric heat capacity C_V of the pure water at near-critical isochore as a function of the temperature.

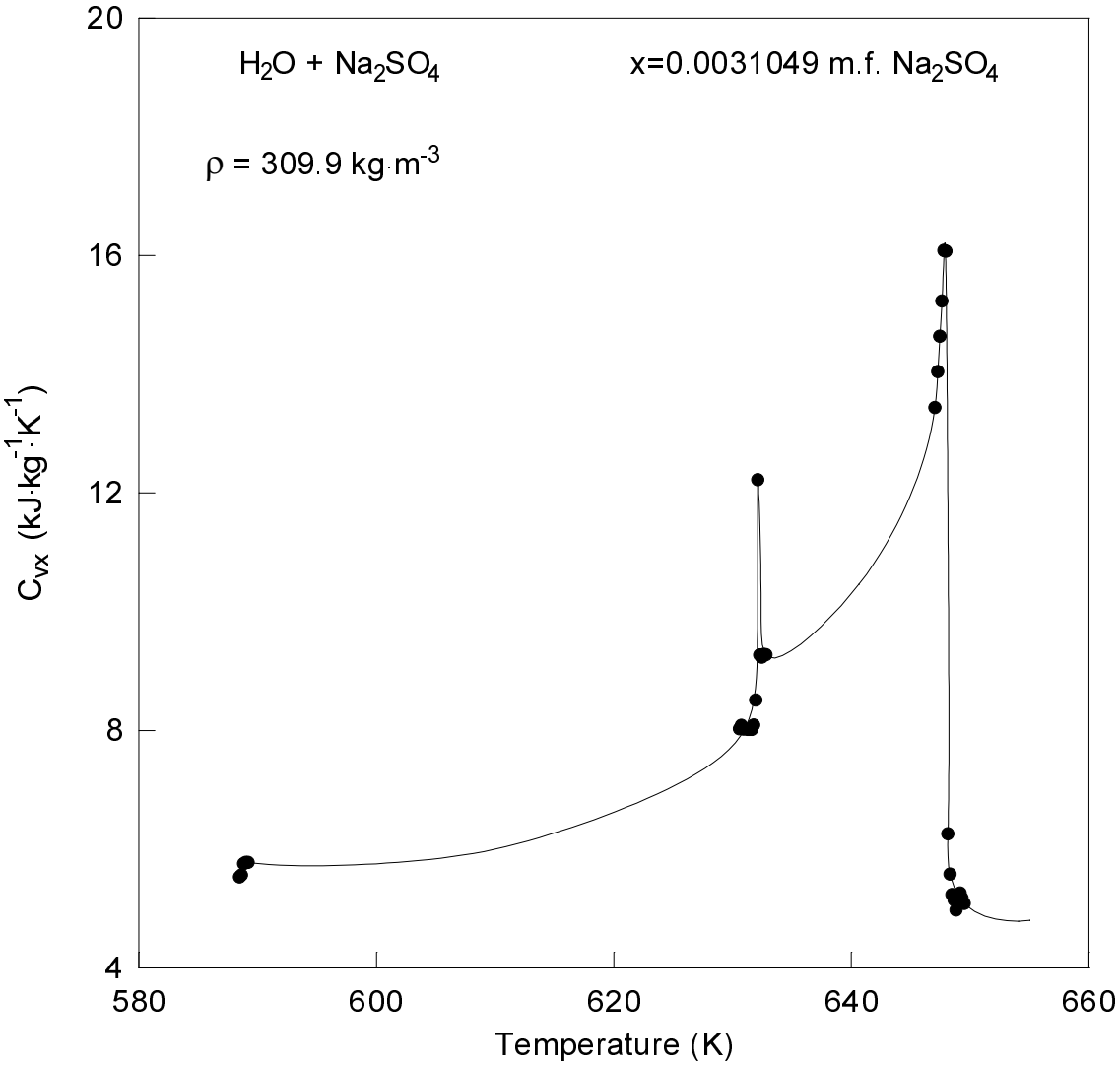

Fig. 2 The isochoric heat capacity C_{VX} of H_2O+ Na_2SO_4 solutions at various near-critical isochore as a function of the temperature near the critical temperature of pure water.

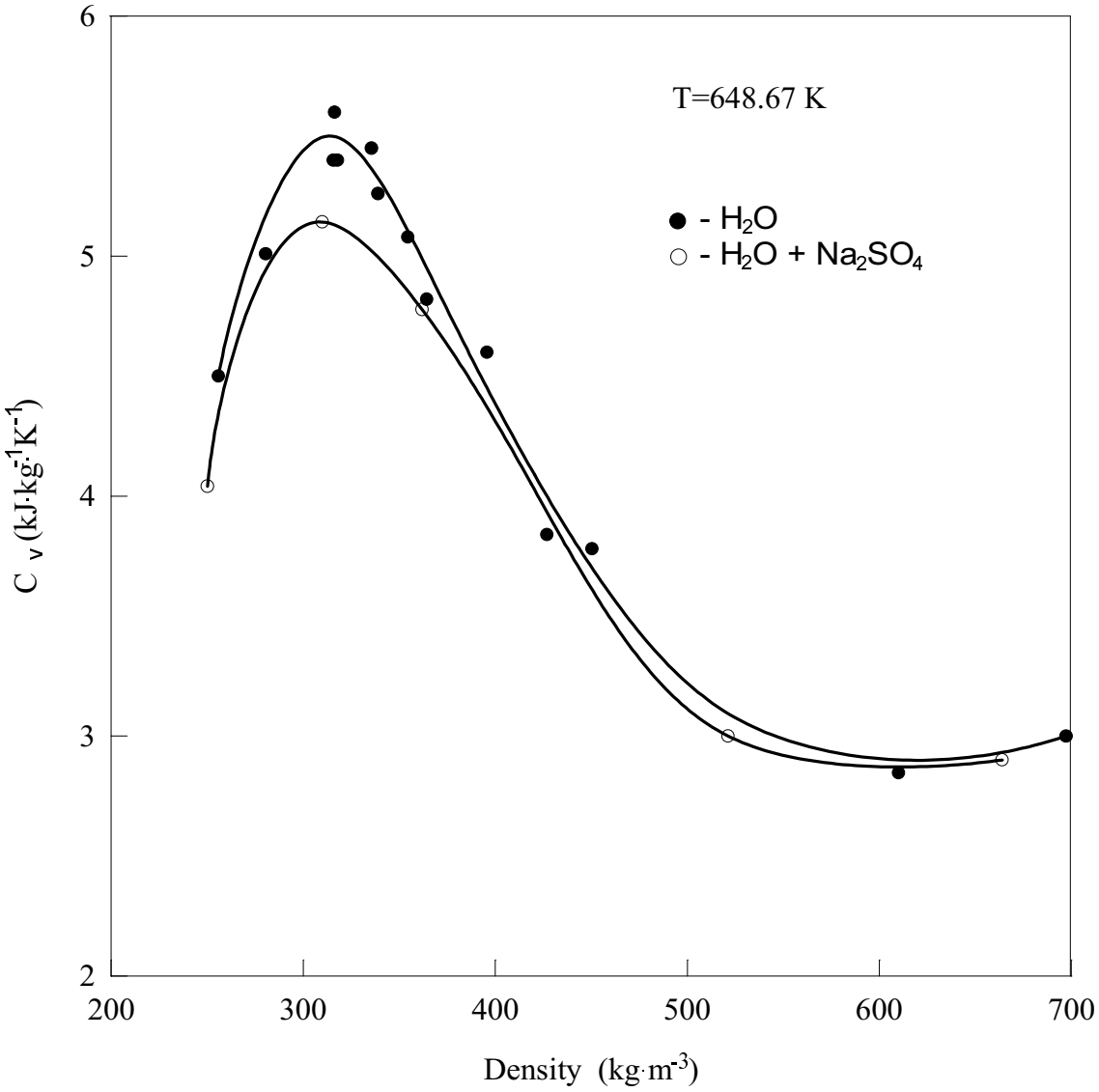

Fig. 3. The isochoric heat capacity of pure water and H_2O+ Na_2SO_4 solutions at supercritical isotherm as a function of the density.

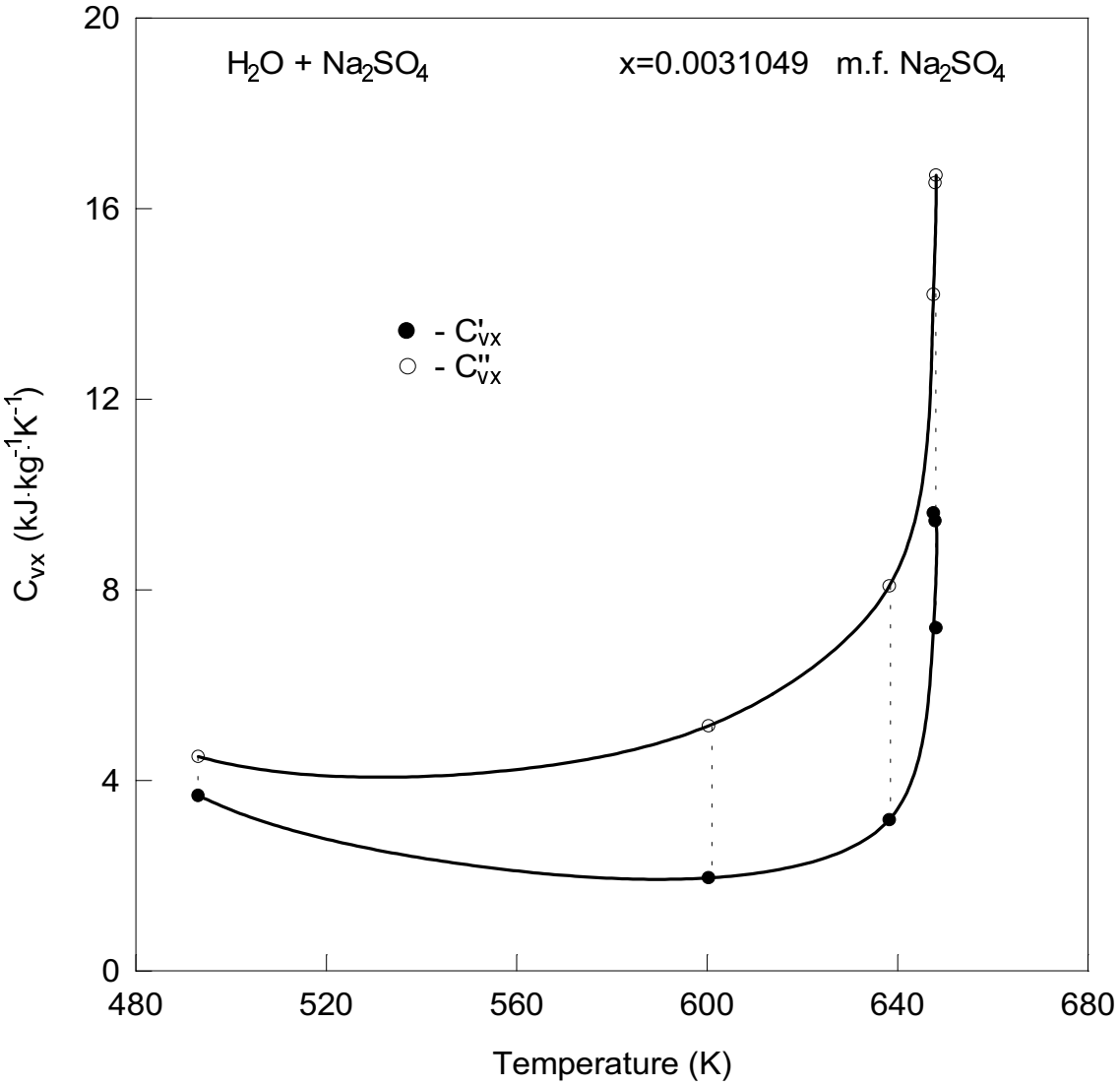

Fig. 4. The isochoric heat capacities $\tilde{N}'_{vx}$ and $\tilde{N}''_{vx}$ of H_2O+ Na_2SO_4 solutions as a function of the temperature on the coexistance curves.

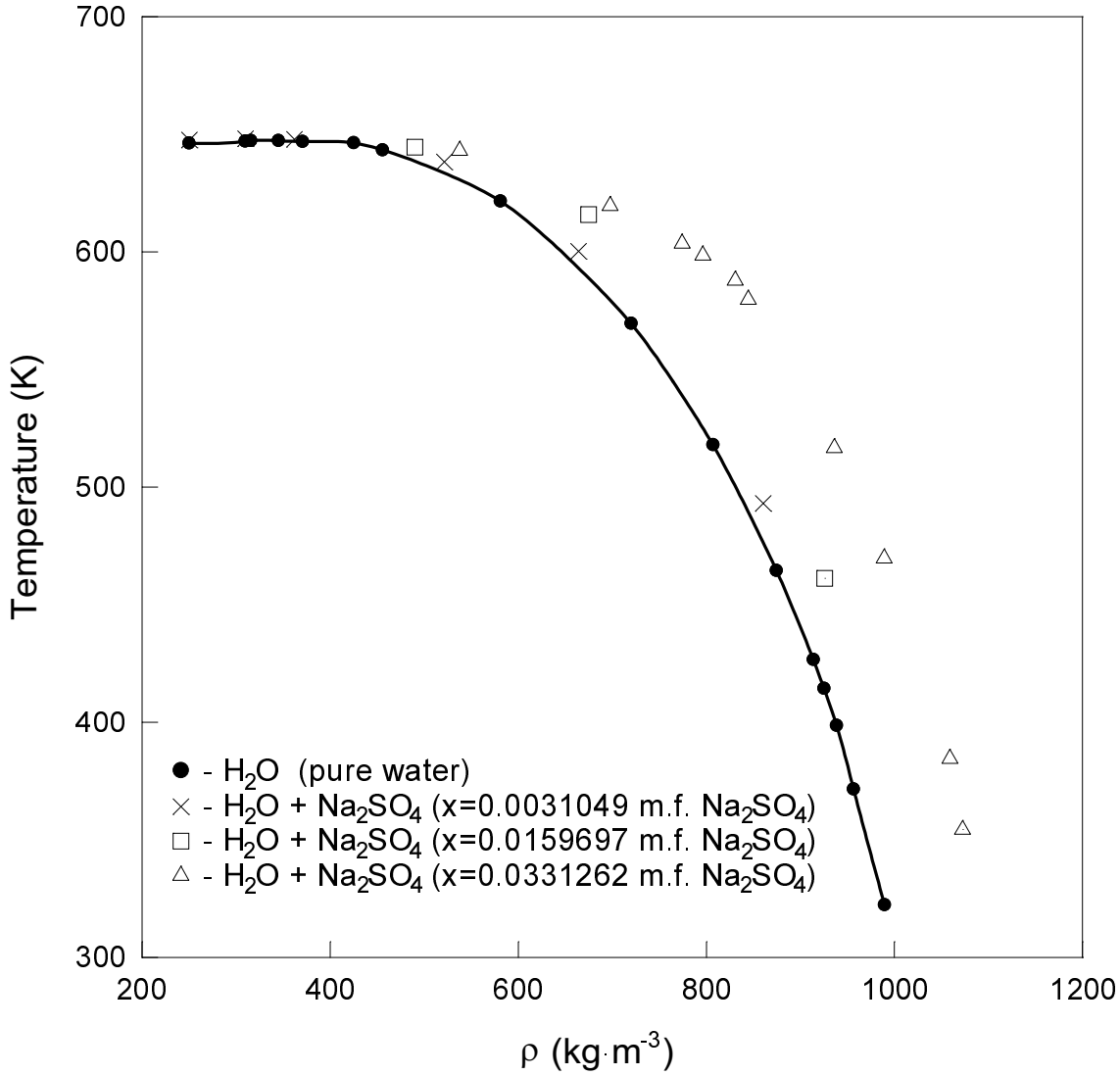

Fig. 5. The curve of coexisting liquid densities for pure water and H_2O+ Na_2SO_4 solutions for various compositions.

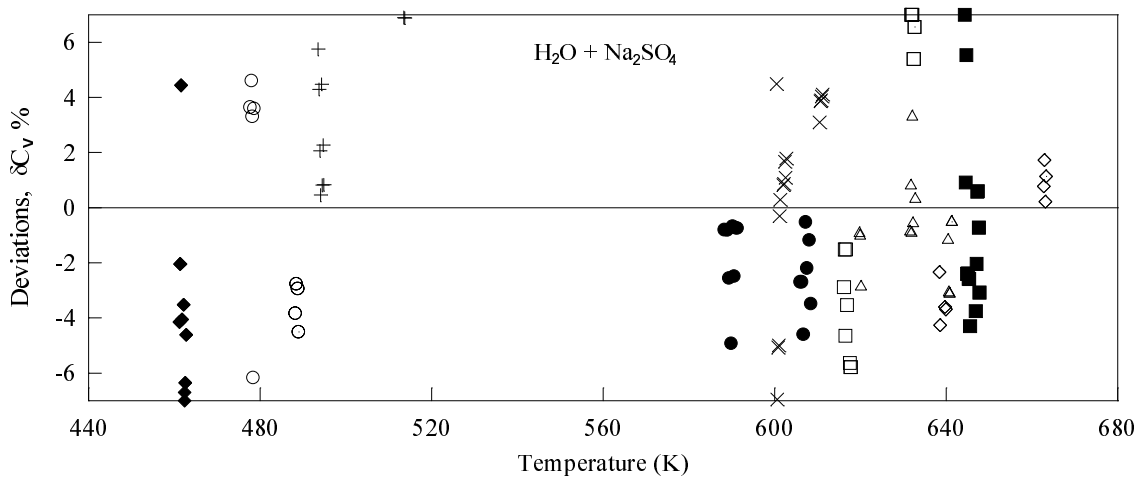

Fig. 6. Percentage deviations of the experimental isochoric heat capacities C_{VX} of H_2O+ Na_2SO_4 obtained in this work from the values calculated with the Eq. (2). x=0.0031 mole fraction of Na_2SO_4: (+)- ρ=860.5 kg·m^{-3}; (×)- ρ=664.00 kg·m^{-3}; (◊)- ρ=521.30 kg·m^{-3}, x=0.0160 mole fraction of Na_2SO_4: (♦)- ρ=925.90 kg·m^{-3}; (□)- ρ=674.70 kg·m^{-3}; (□)- ρ=490.00 kg·m^{-3}, x=0.0331 mole fraction of Na_2SO_4: (o)- ρ=989.20 kg·m^{-3}; (•)- ρ=830.7 kg·m^{-3}; (Δ)- ρ=697.8 kg·m^{-3}.