

## Behavior of Heat Capacity at Constant Volume in Aqueous Solutions of Homologous Alcohol

Hiroshi Kitajima<sup>1</sup>, Noboru Kagawa<sup>2\*</sup>, and Harumi Endo<sup>3</sup>

<sup>1</sup> Technical Research and Development Institute, Japan Defense Agency, Ichigaya 162-8830, Japan

<sup>2</sup> Department of Mechanical Systems Engineering, National Defense Academy, Yokosuka 239-8686, Japan

<sup>3</sup> Department of Applied Physics, National Defense Academy, Yokosuka 239-8686, Japan

\*E-mail: kagawa@nda.ac.jp

Isochoric heat capacities ( $c_v$ ) of water, methanol, ethanol, 1-propanol, and their aqueous solutions were measured in the temperature range from 280 to 420 K and at pressures up to 30 MPa. The measurements were carried out on liquid-phase samples with a twin-cell type adiabatic calorimeter. Liquid density information was also obtained on the basis of the mass of the sample and the volume of the calorimetric cell. The experimental expanded uncertainty (with a coverage factor  $k = 2$ ) of isochoric heat capacity is estimated to be 2.2 % for the liquid-phase measurements, and for density it is 0.16 %. The behavior of  $c_v$  is anomalous, indicating that the aqueous solutions of alcohol are strongly associated due to the influence of hydrogen bonds. The plots of  $c_v$  versus temperature ( $T$ ) of each aqueous solution show the small maximum of heat capacity,  $c_{v,max}$ , for each composition. The temperature, which shows the  $c_{v,max}$ , is in so far from the critical temperature. And then, the  $pVT$  and  $c_v$  data of ethanol were correlated with a fifteen-parameter equation of state [1] by using a least-squares optimization. The density values calculated by this equation agree within  $\pm 0.25$  % with the fitted experimental data [2-10]. And calorimetric and acoustic properties are compared with earlier works. Also, it is verified that the behavior of excess isochoric heat capacity for the alcohol aqueous solution is represented with a convexly quadratic expression which will be explained by fluctuations of concentration based on a theoretical approach.

### 1. Introduction

It is well known that water and alcohols are highly polar substances that associate by hydrogen bonding in solution. Due to the presence of strong hydrogen bonds, interactions between water and alcohol molecules can lead to anomalous behavior of thermodynamic properties. Measurements of thermodynamic properties are essential to characterize such interactions and to accurately model this behavior.

The theoretical studies of  $c_v$  in liquid phase have been provided by earlier works [11-14]. The attentions [15] of these studies on the  $c_v$  have focused on the divergence at a critical point. But, the behavior of  $c_v$  provides significant information for theoretical and engineering studies. In the compressed liquid phase, measurements of  $c_v$  have been reported for methanol (CH<sub>3</sub>OH) and ethanol (C<sub>2</sub>H<sub>5</sub>OH)[10], for C<sub>2</sub>H<sub>5</sub>OH + H<sub>2</sub>O mixtures [16], and for CH<sub>3</sub>OH + H<sub>2</sub>O mixtures and 1- C<sub>3</sub>H<sub>7</sub>OH +

H<sub>2</sub>O mixtures [17], over temperature range 280 to 420 K and pressure range 1 to 30 MPa.

The equation of state for ethanol was correlated with a fifteen-parameter equation of state [1] by using a least-squares optimization. The density values calculated by this equation agree within  $\pm 0.25$  % with fitted experimental data [2-10]. And calorimetric and acoustic properties are compared with earlier works [18-28]. We obtain excess isochoric heat capacities,  $c_v^E$ , of C<sub>2</sub>H<sub>5</sub>OH + H<sub>2</sub>O mixtures with this equation of state for ethanol and an equation of state for water formulated by Wagner and Pr $\ddot{u}$ ß [29]. For the aqueous solutions of alcohols, the behaviors of  $c_v$  and  $c_v^E$  show for the appropriate convexly quadratic equation for temperature. We have become of interest in studying such anomalies of the temperature dependence of  $c_v$ . The behavior of  $c_v$  can be represented with a convexly quadratic expression which will be explained by fluctuations of concentration, based on a theoretical approach.

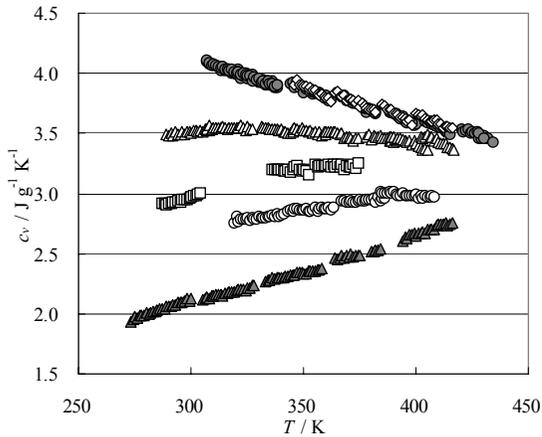


Fig. 1. Isochoric heat capacities for  $\{x\text{CH}_3\text{OH} + (1-x)\text{H}_2\text{O}\}$ .  $\diamond$ ,  $x = 0.059$ ;  $\Delta$ ,  $x = 0.352$ ;  $\square$ ,  $x = 0.502$ ;  $\circ$ ,  $x = 0.708$ ;  $\Delta$ ,  $\text{CH}_3\text{OH}$ ;  $\circ$ ,  $\text{H}_2\text{O}$ .

## 2. Experimental Methods

The isochoric heat capacities were measured with a twin-cell type adiabatic calorimeter. The calorimeter and experimental procedures have been described previously in detail [10,17]. The experimental expanded uncertainty (with a coverage factor  $k = 2$ ) of the absolute temperature measurement is 13 mK, and that of the pressure measurement is 8 kPa. The estimated expanded uncertainty of density is 0.16 %, and that of the sample mole fraction in composition is 0.1 %. And, the expanded uncertainty of  $c_v$  is 2.2 % for the liquid phase measurements of alcohol solutions.

Figures 1-3 show  $c_v$  measurements for the alcohol aqueous solutions. It exhibits an interesting behavior of the thermodynamic surface of the mixtures. We find that the slope of these plots  $(\partial c_v / \partial T)_\rho$  is positive for each of the alcohols but is negative for water, and changes smoothly from one to the other as the mixture composition is changed. The  $c_v$  behaviors are strongly influenced by temperature in this region, and all  $c_v$  for a constant composition could be adequately represented with a single line. Each isochore has a maximum point in the liquid phase. The  $c_v$  of  $\text{CH}_3\text{OH} + \text{H}_2\text{O}$  mixtures with  $x = 0.352$ , 0.502, and 0.708 show  $c_{v\max}$  at (approximately) 323, 363 and 457 K, respectively. Similarly, the  $\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$  mixtures have temperatures at  $c_{v\max}$ ,  $T_{\max} = 322$ , 378, 392, 429 and 490 K with  $x = 0.253$ , 0.396, 0.498, 0.601 and 0.755, respectively. In the  $1\text{-C}_3\text{H}_7\text{OH} + \text{H}_2\text{O}$  system,  $T_{\max}$  are 345, 392 and 435 K with  $x = 0.255$ , 0.510 and 0.738, respectively. Figure 4 shows  $T_{\max}$

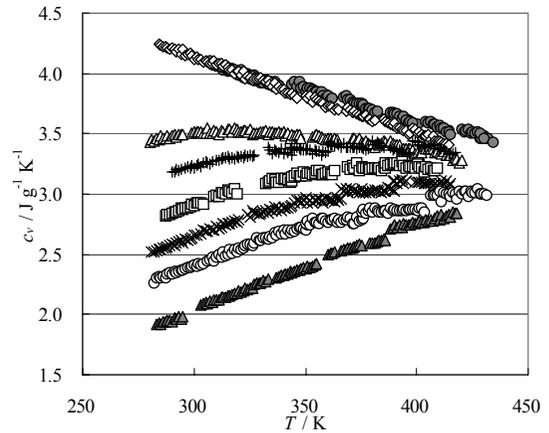


Fig. 2. Isochoric heat capacities for  $\{x\text{C}_2\text{H}_5\text{OH} + (1-x)\text{H}_2\text{O}\}$ .  $\diamond$ ,  $x = 0.104$ ;  $\Delta$ ,  $x = 0.253$ ;  $+$ ,  $x = 0.396$ ;  $\square$ ,  $x = 0.498$ ;  $\times$ ,  $x = 0.601$ ;  $\circ$ ,  $x = 0.755$ ;  $\Delta$ ,  $\text{C}_2\text{H}_5\text{OH}$ ;  $\circ$ ,  $\text{H}_2\text{O}$ .

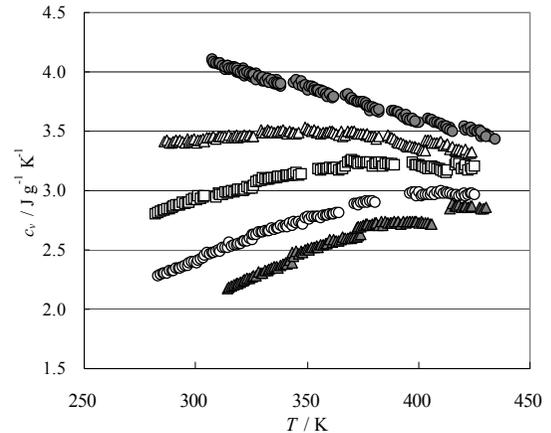


Fig. 3. Isochoric heat capacities for  $\{x1\text{-C}_3\text{H}_7\text{OH} + (1-x)\text{H}_2\text{O}\}$ .  $\Delta$ ,  $x = 0.255$ ;  $\square$ ,  $x = 0.510$ ;  $\circ$ ,  $x = 0.738$ ;  $\Delta$ ,  $1\text{-C}_3\text{H}_7\text{OH}$ ;  $\circ$ ,  $\text{H}_2\text{O}$ .

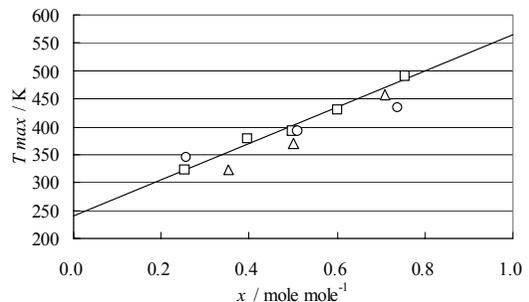


Fig. 4. Behavior of  $T_{\max}$  with alcohol composition.  $\Delta$ ,  $x\text{CH}_3\text{OH} + (1-x)\text{H}_2\text{O}$ ;  $\square$ ,  $x\text{C}_2\text{H}_5\text{OH} + (1-x)\text{H}_2\text{O}$ ;  $\circ$ ,  $x1\text{-C}_3\text{H}_7\text{OH} + (1-x)\text{H}_2\text{O}$ .

with alcohol mole fraction. The straight line represents a correlation for the  $C_2H_5OH + H_2O$  system. All of the data distribute almost linearly. On the other hand, no maximum  $c_v$  for small alcohol compositions of  $x = 0.059$  ( $CH_3OH + H_2O$ ) and  $0.104$  ( $C_2H_5OH + H_2O$ ) are observed.

### 3. Formulation of Equation of State

**3.1. Available Experimental Studies** Eight experimental studies of the  $p\nu T$  properties of ethanol exist. Lo et al. [2] reported 162 data in the range of temperatures from 473.15 to 623.15 K and pressures from 8.27 to 68.95 MPa. Guputa et al. [3] published 24 data in the temperature range from 273.15 to 363.15 K and pressures from 2.76 to 22.06 MPa. Tanaka et al. [4] reported 46 data from 298.15 and 323.15 K, and from 0.1 to 348.6 MPa. Golbev et al. [5] published 54 data from 200 to 570 K and from 1 to 50 MPa. Ortega [6] reported 6 data from 293.15 to 353.15 K at 0.1 MPa. Sauermann et al. [7] reported 96 data in the range of temperatures from 263.15 to 469.95 K and pressures up to 56.7 MPa. Takiguchi et al. [8,9] published 308 data from 310 to 480 K and up to 200 MPa. Kitajima et al. [10] reported 116 data in the range of temperatures from 283.15 to 418.15 K and pressures up to 30 MPa.

**3.2. Formulating Equation of State** The experimental data have been correlated using the equation of state proposed by Sato [1]:

$$v_r = \frac{D}{(p_r + A)^C} + Ep_r \quad (1)$$

$$A(T_r) = \sum_{i=0}^3 a_i T_r^i, \quad C(T_r) = \sum_{i=0}^2 c_i T_r^i$$

$$D(T_r) = \sum_{i=0}^3 d_i T_r^i, \quad E(T_r) = \sum_{i=0}^3 e_i T_r^i$$

where  $v_r$  is the reduced volume,  $v_r = v/v_c$ , and the  $p_r$  is the reduced pressure,  $p_r = p/p_c$ . In the present equation,  $T_c = 513.9$  K,  $p_c = 6.148$  MPa, which were published by Ambrose et al. [30], and  $v_c = 1/0.276$  cm<sup>3</sup>/g by Kobe et al. [31]. The correlation was formulated based on the  $p\nu T$  data by Ortega,

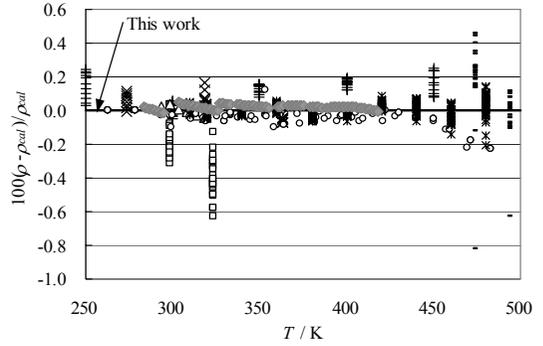


Fig. 5. Density deviations from equation of state for  $C_2H_5OH$ . -, Lo et al. [2];  $\times$ , Gupta et al. [3];  $\square$ , Tanaka et al. [4]; +, Golubev et al. [5];  $\Delta$ , Ortega [6];  $\circ$ , Sauermann et al. [7]; \*, Takiguchi et al. [8,9];  $\diamond$ , Kitajima et al. [10].

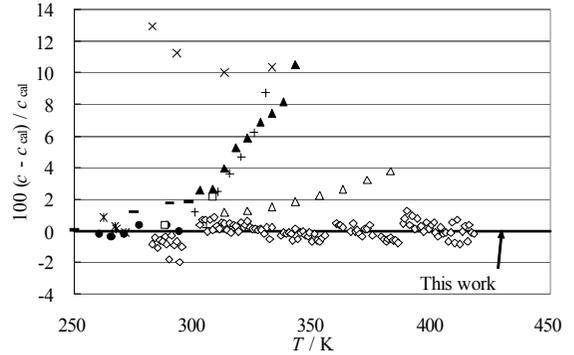


Fig. 6. Heat capacity deviations from equation of state for  $C_2H_5OH$ . \*, Gibson et al. [18]; +, Williams [19]; -, Parks [20];  $\diamond$ , Kelly [21];  $\Delta$ , Fiock et al. [22];  $\blacktriangle$ , Blacet et al. [23];  $\times$ , Katayama [24];  $\square$ , Benson et al. [25];  $\diamond$ , Kitajima et al. [10].

Sauermann et al., Takiguchi et al., and Kitajima et al. The density deviations of the available experimental data from Eq. (1) are shown in Fig. 5. The fitted data are represented within  $\pm 0.25$  % in density. The unused data exhibit the maximum deviation  $+2.94$  % in density near the critical point.

Table 1. The coefficient of equation for ethanol.

$i$	$a_i$	$c_i$	$d_i$	$e_i$
0	$2.89343 \times 10$	$-2.39361 \times 10^{-1}$	$5.00513 \times 10^{-1}$	$2.30016 \times 10^{-3}$
1	6.01996	$4.14618 \times 10^{-1}$	$-8.21688 \times 10^{-2}$	$-7.82473 \times 10^{-3}$
2	$-8.65487 \times 10$	$-2.87156 \times 10^{-1}$	$-1.96497 \times 10^{-1}$	$8.41892 \times 10^{-3}$
3	$5.08454 \times 10$		$3.24012 \times 10^{-1}$	$3.25844 \times 10^{-3}$

The correlation of the virtual ideal isobaric heat capacity,  $c_{p0}$ , at the  $p = 0$  MPa was determined by using our experimental  $c_v$  data.

$$c_{p0} = -6.47136 \times 10^2 + 1.15577 \times 10^3 T_r^{-1} + 1.49909 \times 10^3 T_r - 1.43982 \times 10^3 T_r^2 + 6.07197 \times 10^2 T_r^3. \quad (2)$$

By these equations, the  $c_v$  data are represented within  $\pm 2.0\%$ . Figure 6 shows deviations of experimental  $c_v$  [10] and isobaric heat capacities,  $c_p$  [18-25]. The caloric data measured by Gibson et al. [18], Parks [20] and Kelly [21] are represented well within  $-0.5$  to  $+2\%$ . The other data [19,22-25] deviate by 0 to 13%. And the acoustic data obtained by Wilson et al. [26] slightly deviate by 0 to  $-6\%$ . On the other hand, the data by Aleksandrov et al. [27] and those by Hawley et al. [28] are represented well within  $\pm 2\%$  (see Fig. 7). We calculate the excess isochoric heat capacities,  $c_v^E$ , based on this equation of state. Figure 8 shows  $c_v^E$  of the aqueous solution of ethanol. The behavior of  $c_v^E$  implies a convexly quadratic expression, and the maximum  $c_v^E$  deviates by 14% from its ideal solution.

#### 4. Discussion

The Helmholtz free energy,  $F$ , is expressed in term of the deviation from the mean concentration  $\hat{x}$  by the expression of Ginzburg and Landau [32],

$$F = F_0 + \int [\alpha \Delta x(\mathbf{r})^2 + g |\nabla \Delta x(\mathbf{r})|^2] dV, \quad (3)$$

where the deviation  $\Delta x(\mathbf{r}) = x(\mathbf{r}) - \hat{x}$ ,  $\alpha = \alpha_0(T - T_0)$ , distance  $\mathbf{r}$ , the  $F_0$ ,  $\alpha_0$ ,  $T_0$  and  $g$  are constants, respectively. This expression is proposed for the study of concentration fluctuations of mixtures. Equation (3) is available for investigation of the homogeneous aqueous solutions of alcohol under the conditions of  $T \ll T_0$ .

By using of the Fourier transforms of functions of  $\Delta x(\mathbf{r})$ , the averaged  $q$ -dependent concentration fluctuations are given by,

$$\langle |\Delta x_{\mathbf{q}}|^2 \rangle = \frac{k_B T}{2V(\alpha + g\mathbf{q}^2)}, \quad (4)$$

where  $\mathbf{q}$  is the wave number.

The correlation function,  $G(\mathbf{r})$  [32] and correlation length,  $\zeta$ , are given by

$$G(\mathbf{r}) = \frac{k_B T \exp(-r/\zeta)}{8\pi g \mathbf{r}},$$

$$\text{and } \zeta = \sqrt{\frac{g}{\alpha}} = \sqrt{\frac{g}{\alpha_0 |T - T_0|}}.$$

The entropy associated with fluctuation is available by

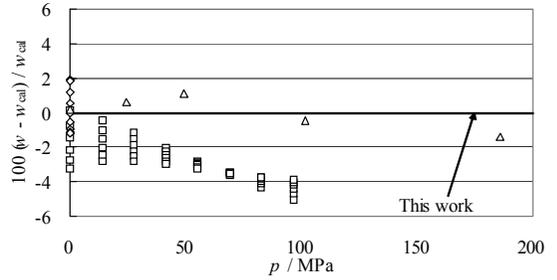


Fig. 7. Speed of sound deviations from equation of state for  $C_2H_5OH$ .  $\square$ , Wilson et al. [18];  $\diamond$ , Aleksandrov et al. [19];  $\triangle$ , Hawley et al. [20].

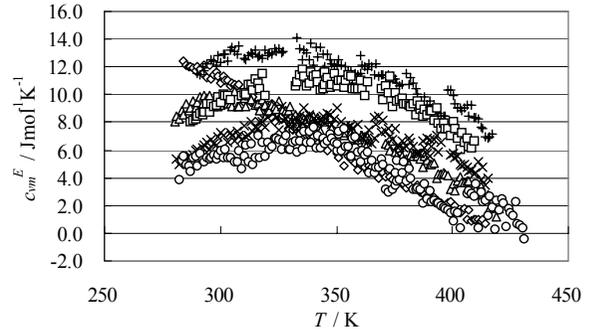


Fig. 8. Excess isochoric heat capacities for  $\{xC_2H_5OH + (1-x)H_2O\}$ .  $\diamond$ ,  $x = 0.104$ ;  $\triangle$ ,  $x = 0.253$ ;  $+$ ,  $x = 0.396$ ;  $\square$ ,  $x = 0.498$ ;  $\times$ ,  $x = 0.601$ ;  $\circ$ ,  $x = 0.755$ .

$$\Delta S = - \left( \frac{\partial \alpha}{\partial T} \right)_v \Delta x(\mathbf{r})^2. \quad (5)$$

The entropy change due to fluctuation is explained by the ensemble average of Eq. (5),

$$\langle \Delta S \rangle = -\alpha_0 \sum_{\mathbf{q}} \langle |\Delta x_{\mathbf{q}}|^2 \rangle,$$

where

$$\sum_{\mathbf{q}} \rightarrow \frac{V}{8\pi^3} \int_0^{q_{\max}} d\mathbf{q},$$

and

$$\langle |\Delta x_{\mathbf{q}}|^2 \rangle \rightarrow gG(\mathbf{q}).$$

The excess isochoric heat capacity due to fluctuation is given by

$$c_v^E = - \left[ \frac{\partial \langle \Delta S \rangle}{\partial T} \right]_v. \quad (6)$$

In the expression of this equation, we assume a case of  $q_{\max} \zeta \gg 1$  where the empirical equation is obtained, because concentration fluctuations are sufficiently large number in our experimental range.

$$c_v^E = - \frac{k_B \alpha_0 q_{\max}}{16\pi^3} T - \frac{k_B \alpha_0}{32\pi^3 g q_{\max}} T^2. \quad (7)$$

Equation (7) under the conditions of  $q_{\max}\zeta \gg 1$  shows a quadratic equation with respect to temperature corresponding to Fig. 8 which shows the anomalous behavior. It is to be emphasized that Eq. (3) is applicable to the aqueous solutions of alcohol [33].

## 5. Conclusions

The isochoric heat capacity data for aqueous solutions of alcohol show anomalous properties, which are likely caused by the presence of the hydrogen bonding. The temperatures at the maximum isochoric heat capacity show straight line similarity with each concentration.

The proposed equation of state for the liquid ethanol is expressed by the reduced volume function as a function of reduced temperature and reduced pressure. The derived  $p\nu T$  and calorific properties were in good agreement with our experimental data and earlier works.

The temperature dependence of  $c_v$  was described by a quadratic expression. And using the concentration fluctuation model of Ginzburg and Landau, the quadratic expression of temperature was obtained. The quadratic equation with respect to temperature is accessible from the conditions of  $q_{\max}\zeta \gg 1$ . In the case of the aqueous solutions of alcohol, our quadratic expression is in qualitative agreement with the experimental data.

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