

## EXCESS ISOBARIC HEAT CAPACITIES FOR WATER + ALKANOL MIXTURES AT 298.15 K \*

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### ABSTRACT

Excess isobaric heat capacities for water + methanol, + ethanol, + 1-propanol and + 1-butanol mixtures were measured at 298.15 K. The apparatus used in this study was a flow microcalorimeter designed and constructed in our laboratory recently, which can determine excess heat capacities directly by a method different from that of a Picker type calorimeter.

The results obtained are roughly in agreement with the literature values, except for the water + 1-propanol mixture. This discrepancy from the literature values may arise from the thermodynamic instability of the water + alkanol mixture with the long-chain alkyl group and the difference in the procedure for obtaining the excess heat capacity.

### INTRODUCTION

Benson and co-workers have reported the various kinds of thermodynamic properties for water + alkanol mixtures in a series of papers [1–4], and have often compared their work with reliable data of other investigators. However, the comparison of excess isobaric heat capacities,  $C_p^E$ , for these mixtures did not agree well, because it is rather difficult to measure  $C_p^E$  accurately compared to other thermodynamic excess functions such as excess enthalpy,  $H^E$ , and excess volume,  $V^E$ . It seems that the large discrepancy between reported values for aqueous alcohol mixtures is attributed to the large dependence of  $C_p^E$  on temperature, difference in preparation of samples and in the measuring method, and so on [4–7].

This paper reports  $C_p^E$  measurement for water + alkanol ( $C_1$  to  $C_4$ ) mixtures at 298.15 K using a flow microcalorimeter, in order to define the source of the discrepancy described above.

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\* Dedicated to Professor Syûzô Seki in honor of his contribution to Calorimetry and Thermal Analysis.

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## EXPERIMENTAL

*Materials*

Water was deionized and twice distilled with  $\text{KMnO}_4 + \text{NaOH}$  aq. solution. All the alkanols, Special-Grade Reagent methanol (MeOH), 1-propanol (PrOH), 1-butanol (BuOH) and Super-Special-Grade Reagent ethanol (EtOH), were purchased from Wako Pure Chemical Ind. Ltd. (Japan) and stored over 3A molecular sieves before purification. The materials, except for BuOH, were fractionally distilled under a stream of  $\text{N}_2$  gas with a 1-m packed column, and BuOH was transferred over 3A molecular sieves under vacuum. The water content in the purified alkanols was estimated to be less than 0.083 mol% from the calibration curve using a GLC (Shimadzu GC-3BT, Japan). The TSG-1 column (acrylic resin coated on polytetrafluoroethylene, Shimalite F) sharply separated the peak of water from those of alkanols, except for PrOH.

Before use, all the samples were degassed sufficiently by boiling in a flask under reduced pressure, in order to avoid air bubbles being produced in the apparatus on mixing.

Densities and heat capacities of the alkanol samples used are presented in Table 1 with the literature values.

*Apparatus and procedure*

We found several problems with our flow microcalorimeter, reported previously [8], which affected the results for the water + EtOH mixture. Then, the apparatus was improved in the following three ways:

(1) The stainless-steel tube of the mixing zone, in which two component liquids were mixed and heat change due to the mixing was exchanged thermally with the thermostated water, was lengthened to more than 1 m long, resulting in a homogeneous solution in the direct mixing mode.

TABLE 1

Densities,  $\rho$ , and molar heat capacities,  $C_p$ , for the component liquids at 298.15 K

Liquid	$\rho$ ( $\text{g cm}^{-3}$ )		$C_p$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	
	exp.	lit.	exp.	lit.
Water	0.997047 <sup>a,b</sup>		75.296 <sup>a,e</sup>	
Methanol	0.786573	0.786350 <sup>c</sup>	80.28	81.21 <sup>g</sup>
Ethanol	0.785095	0.784962 <sup>c</sup>	112.36	112.64 <sup>g</sup>
1-Propanol	0.799572	0.799353 <sup>c</sup>	143.65 <sup>a,f</sup>	144.10 <sup>g</sup>
1-Butanol	0.805737	0.80570 <sup>d</sup>	177.18	177.08 <sup>h</sup>

<sup>a</sup> Standard liquid described in text.

<sup>b</sup> Ref. 20. <sup>c</sup> Ref. 1. <sup>d</sup> Ref. 21. <sup>e</sup> Ref. 12. <sup>f</sup> Ref. 11. <sup>g</sup> Ref. 2. <sup>h</sup> Ref. 22.

(2) An oil diffusion pump was connected to a vacuum system, resulting in the reduction of heat losses and a greater reproducibility of data.

(3) The correction of the effective heating power to heat losses from cells was carried out more rigorously, and the accuracy of  $C_p^E$  was thus improved. The detailed procedure of the correction will be given elsewhere [9].

The two piston pumps were filled with the two component liquids, water and alkanol, respectively, and by the direct mixing method the mixture was prepared in the apparatus, and then the mixture was free from moisture in the air. The concentration of the mixture was calculated from the ratio of the flow rate of the component liquids. The total flow rate of both pumps was kept at  $5.5 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$  in this study, in order to keep the samples in the cells at thermodynamic equilibrium.

The value of  $C_p^E$  was determined directly from the ratio of the molar heat capacity,  $C_p$ , of the mixture to those of the two component liquids before mixing.  $C_p$  of pure alkanols were determined by using the delay-loop method which was the same as that reported by Fortier et al. [10]. In this method, PrOH was adopted as a standard liquid, and Kalinowska et al.'s  $C_p$  value for PrOH [11] was used in estimating those of the other alkanols. For water, Stimson's  $C_p$  value [12] was used. So far, water has often been adopted as a standard liquid. However, there is the so-called "boundary effect" in the delay loop and also, since the volumetric heat capacity,  $C_p/V$ , of water is very different from those of alkanols, the values of  $C_p/V$  for alkanols can not be accurately determined, as described elsewhere in detail [9].

The values of  $C_p$  used for  $C_p^E$  calculation are listed in Table 1 along with literature values. Reproducibilities of  $C_p$  and  $C_p^E$  were estimated to be less than 0.02 and 0.01  $\text{J K}^{-1} \text{ mol}^{-1}$ , respectively, except for the concentration range of  $0.65 < x < 0.94$  of the water + PrOH mixture.

## RESULTS

$C_p^E$  is defined as follows:

$$C_p^E = C_p - xC_{p,1}^* - (1 - x)C_{p,2}^* \quad (1)$$

where  $C_{p,1}^*$  and  $C_{p,2}^*$  are the molar isobaric heat capacities of water and alkanol, respectively, and  $C_p$  is the molar isobaric heat capacity of a mixture at the mole fraction of water,  $x$ . In fact,  $C_p^E$  was estimated by the relation given in a previous work [8], which was derived to satisfy eqn. (1).

$C_p^E$  for the water + MeOH, +EtOH, +PrOH and +BuOH mixtures were determined at 298.15 K and the results obtained are summarized in Table 2. It was difficult to fit the data to the simple least-squares representation over the whole range of  $x$ , since the  $C_p^E$  results had maximum values at extremely high  $x$  values. The concentration dependence of  $C_p^E$  for the water + PrOH mixture did not show a monotonous parabolic curve.  $C_p^E$  for

TABLE 2

Excess isobaric heat capacities,  $C_p^E$ , for  $x$  water +  $(1-x)$  alkanol mixtures at 298.15 K

$x^a$	$C_p^E$ (J K <sup>-1</sup> mol <sup>-1</sup> )	$x^a$	$C_p^E$ (J K <sup>-1</sup> mol <sup>-1</sup> )
<i>x</i> water + (1 - <i>x</i> ) methanol			
0.09996	1.114	0.69990	6.388
0.19992	2.049	0.74991	6.690
0.29990	3.026	0.79993	6.808
0.34989	3.496	0.84994	6.497
0.39989	3.937	0.87495	6.093
0.44988	4.365	0.89996	5.479
0.49988	4.823	0.92497	4.550
0.54988	5.204	0.94998	3.305
0.59989	5.624	0.97499	1.775
0.64989	6.016		
<i>x</i> water + (1 - <i>x</i> ) ethanol			
0.04998	1.848	0.59988	11.990
0.09996	3.448	0.64989	12.587
0.14994	4.780	0.69989	13.146
0.19992	5.876	0.74991	13.658
0.24991	6.832	0.79992	14.008
0.29990	7.705	0.84994	13.852
0.34989	8.489	0.84994	13.842
0.39988	9.264	0.89996	12.008
0.44988	9.993	0.92497	9.904
0.49988	10.660	0.94998	6.966
0.54988	11.314	0.97499	3.594
<i>x</i> water + (1 - <i>x</i> ) 1-propanol			
0.09997	4.861	0.72493	14.145
0.14996	6.501	0.74993	13.906
0.19994	7.868	0.79994	13.650
0.24994	9.118	0.84995	13.250
0.29993	10.350	0.87496	12.886
0.34992	11.306	0.89997	12.187
0.39992	11.912	0.89997	12.213
0.44991	12.548	0.92498	11.929
0.49991	13.015	0.92498	11.937
0.54991	13.477	0.94329	10.644
0.59992	13.862	0.94998	9.651
0.64992	14.185	0.97499	5.200
0.69993	14.457	0.98750	2.575
0.69993	14.457		
<i>x</i> water + (1 - <i>x</i> ) 1-butanol			
0.09997	5.293	0.98500	3.839
0.19995	8.434	0.99000	2.618
0.29993	10.665	0.99250	1.971
0.39992	12.036	0.99500	1.318

<sup>a</sup> Mole fraction of water.

the water + BuOH mixture could not be obtained in the range  $0.45 < x < 0.98$  because of phase separation.

The results for the water + MeOH and + EtOH mixtures were fitted to a Redlich-Kister type polynomial by the least-squares method:

$$C_p^E = f(1-f) \sum_{i=1}^n A_i (1-2f)^{i-1} \quad (2)$$

where  $f$  is a concentration factor transformed from  $x$  by the following relation:

$$f = \frac{x}{x + k(1-x)} \quad (3)$$

where  $k$  is a constant pre-selected before computation. If  $k$  is pre-selected for  $f=0.5$  against  $x$  at the maximum  $C_p^E$  value, the best fit is obtained by eqn. (2) with fewer terms. In fact,  $k$  was chosen as the ratio of the molar volume of alkanols to that of water,  $V_2/V_1$ , and then  $f$  should be regarded with respect to the volume fraction of water,  $\phi$ .

For the water + PrOH and + BuOH mixtures, all the data were divided into three parts: that is, the lower  $x$ , higher  $x$  and the middle, and  $C_p^E$  data in the first two parts were fitted to the following polynomials, respectively: at lower  $x$ ,

$$C_p^E = \sum_{i=1}^n A_i x^i \quad (4)$$

at higher  $x$ ,

$$C_p^E = \sum_{i=1}^n A_i (1-x)^i \quad (5)$$

TABLE 3

$A_i$  coefficients and standard deviations,  $s$ , of the fits for least-squares representation by eqns. (2), (4) or (5) of  $C_p^E$  for water + alkanol mixtures at 298.15 K

Water +	Methanol	Ethanol	1-Propanol		1-Butanol	
	eqn. (2) $k = 2.25453$	eqn. (2) $k = 3.24758$	eqn. (4) $x < 0.66$	eqn. (5) $x > 0.93$	eqn. (4) $x < 0.42$	eqn. (5) $x > 0.98$
$A_1$	25.397	55.085	61.061	221.08	63.99	269.91
$A_2$	-12.020	-12.628	-164.43	-577.7	-128.3	-917
$A_3$	11.02	32.50	387.6		109.2	
$A_4$	4.70	34.03	-553.2			
$A_5$	-8.31	-73.12	312.9			
$A_6$	4.11	18.86				
$A_7$		75.52				
$s$	0.020	0.022	0.085	0.087	0.144	0.010

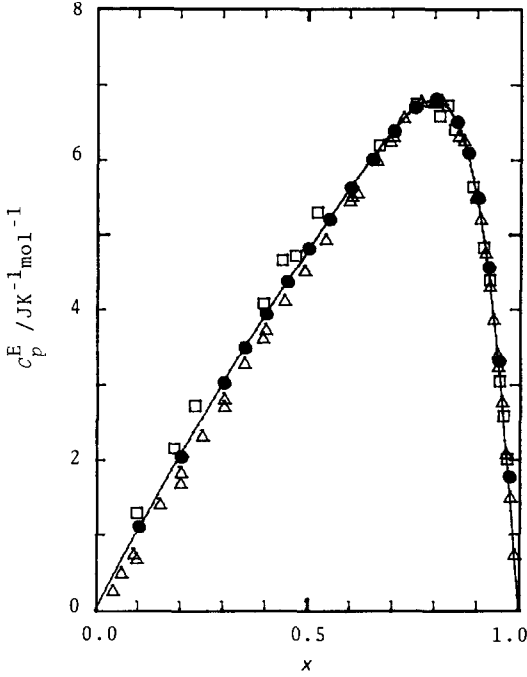


Fig. 1. Excess heat capacity for  $x$  water +  $(1-x)$  methanol mixtures at 298.15 K. (●) Present results, (△) Benson et al. [2], (□) Grolier et al. [13]. Curve calculated from eqn. (2) with coefficients given in Table 3.

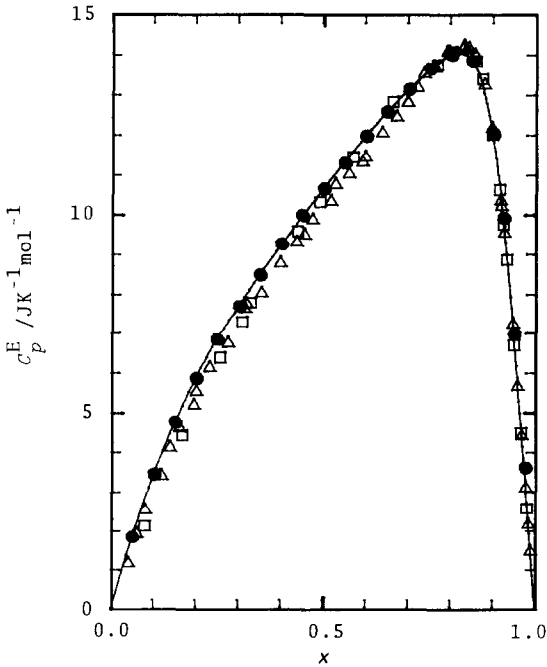


Fig. 2. Excess heat capacity for  $x$  water +  $(1-x)$  ethanol mixtures at 298.15 K. (●) Present results, (△) Benson et al. [2], (□) Grolier et al. [14]. Curve calculated from eqn. (2) with coefficients given in Table 3.

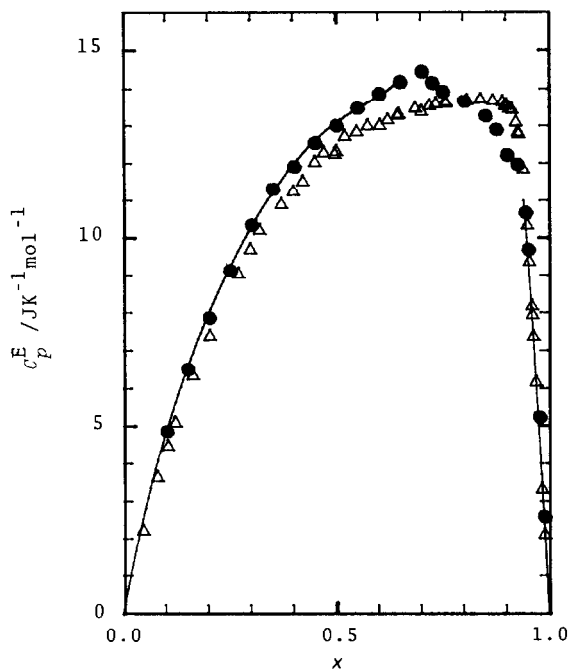


Fig. 3. Excess heat capacity for  $x$  water +  $(1-x)$  1-propanol mixtures at 298.15 K. (●) Present results, (Δ) Benson et al. [2]. Curves calculated from eqns. (4) and (5) with coefficients given in Table 3.

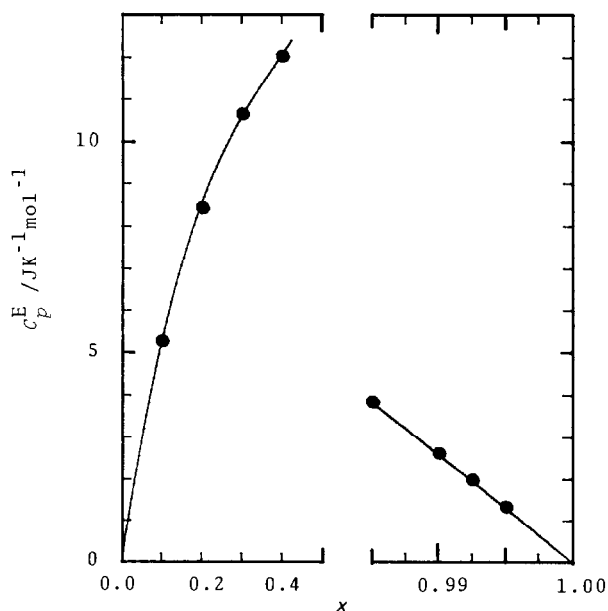


Fig. 4. Excess heat capacity for  $x$  water +  $(1-x)$  1-butanol mixtures at 298.15 K. (●) Present results. Curves calculated from eqns. (4) and (5) with coefficients given in Table 3.

The  $A_i$  coefficients and the equation used are given in Table 3, along with the standard deviation,  $s$ , of the fits for each mixture.

The results of  $C_p^E$  for these mixtures were plotted in Figs. 1–4 with the recent values obtained from direct calorimetry by other investigators. The smoothed curve shown in these figures was calculated from the eqns. (2), (4) or (5) by using the values of  $A_i$  given in Table 3.

## DISCUSSION

As shown in Figs. 1 and 2, our present results for the water + MeOH and + EtOH mixtures were roughly in agreement with those of Benson et al. [2] and those of Grolier et al. [13,14] within  $\pm 0.6 \text{ J K}^{-1} \text{ mol}^{-1}$ . However, our results are slightly higher than those of the former in the region of  $x < 0.7$ , and the concentration dependence of  $C_p^E$  is slightly simpler than that of Benson et al., in which several points of inflection exist. Plotting the results for these mixtures against  $\phi$  in replacement for  $x$ , the  $\phi$  dependence of  $C_p^E$  of Benson et al. is more complicated than ours in the region  $0.2 < \phi < 0.6$ . Such discrepancy of  $C_p^E$  cannot be explained at this stage. However, this suggests a closer examination of the accuracy of the determination.

As shown in Fig. 3, our result for the water + PrOH mixture is higher than that of Benson et al., similar to the mixtures described above, and the large discrepancy between our result and Benson's was observed in the range  $0.65 < x < 0.94$ . The result in the above range deviates remarkably from the smoothed curve interpolated from the concentration dependence at both sides of  $x$ . This tendency was also recognized from the results of Benson et al. Such a complicated curve has frequently been observed, e.g. when  $H^E$  was measured for a mixture undergoing phase separation. In that case,  $H^E$  varies linearly with  $x$  in the concentration range occurring during phase separation. However, phase separation was not observed for the present mixture and there has been no paper reporting it.

The excess Gibbs energy,  $G^E$ , for this mixture was reported to be positive and large [15]. This suggests that PrOH is not very miscible with water. In addition, it is predicted from the Kirkwood–Buff integrals,  $G_{ij}$ , reported by Matteoli et al. [16], that the local concentration fluctuates remarkably in the range  $0.7 < x < 0.9$ . Of the thermodynamic excess functions,  $C_p^E$  is related the most closely to the behavior of component molecules in the solution state and, thus, it will be connected with the local concentration fluctuation in solution. It is supposed speculatively from the above information that it takes a long time to reach equilibrium thermodynamically after mixing. If this is true, the  $C_p^E$  difference from Benson's data may be explained to be due to the different preparation procedure of the mixture. In our procedure, the samples for measurement are prepared directly in the mixing zone of the apparatus. On the other hand, in Benson's procedure, they were prepared in



a bottle beforehand. Normally, in the flow method, there is only a short flowing path from the heating part to the temperature-detecting part, in which case it may be doubtful whether or not the sample liquid attains thermodynamic equilibrium during such a short period. Therefore, for a mixture having a long thermal hysteresis, it is difficult to determine  $C_p^E$  in a flow method precisely.

$C_p^E$  for the water + BuOH mixture shows almost the same value as that for the water + PrOH mixture, as shown in Fig. 4. It was very difficult to measure  $C_p^E$  because of the very narrow miscible region. In such a case, the concentration of the mixture is not determined accurately enough, because of the large difference of the flow rate in the pumps. There do not appear to be any data in the literature suitable for comparison with the present result, except for the partial molar heat capacity at infinite dilution,  $C_{p,i}^\infty$  for this mixture [17].

$C_p^E$  values for binary mixtures may also be determined by the indirect method, such as the dependence of  $H^E$  on temperature,  $dH^E/dT = C_p^E$ . For example, supposing a mixture of  $H^E = 1000 \text{ J mol}^{-1}$  and  $C_p^E = 10 \text{ J K}^{-1} \text{ mol}^{-1}$  at the given concentration,  $H^E$  measurement must be carried out with an accuracy of 0.05% in a temperature interval of 5 K, for the estimation of  $C_p^E$  with 1% accuracy. However, it is quite difficult to determine  $H^E$  with such accuracy, as concluded from our experience in the use of any flow microcalorimeter for  $H^E$  [18]. In addition,  $H^E$  must be determined in a smaller temperature interval, because the temperature dependence of  $C_p^E$  for aqueous alcohol mixtures is relatively large and complicated, as reported by Benson et al. [4]. Therefore, comparison of precise  $C_p^E$  values from direct calorimetry with those obtained from indirect methods is not considered to be suitable, as described generally in the experimental thermodynamic field.

Recently, we have determined  $C_p^E$  for methanol + alkanol mixtures at 298.15 K in succession of this work [19]. Since the behavior of alcohol was found to be quite different in water, methanol and heptane, respectively, we shall discuss it quantitatively in a forthcoming communication of this series, since there has been no discussion of it so far.

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