	1 and 2; T_{c1} and T_{c2}, critical temperatures for gases 1 and 2, respectively
i	denotes component i
m	denotes mixture
n	denotes a nominal outlet condition, in conjonction with H_n^E, P_n, or T_n
P, T	denotes constant temperature and pressure
1	denotes inlet conditions (P_1, T_1) for gas 1
2	denotes inlet conditions (P_2, T_2) for gas 2
0	denotes outlet conditions (P_0, T_0) for mixture

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Excess Isobaric Heat Capacities of Water–*n*-Alcohol Mixtures†

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Excess isobaric heat capacities of binary mixtures of water with methanol, ethanol, and 1-propanol, obtained from flow microcalorimetric measurements at 288.15 and 308.15 K, are reported.

In several recent papers (*1*–*3*) we described investigations of the thermodynamic properties of aqueous alcohol mixtures. One of these (*2*) dealt with measurements of the heat capacities of binary mixtures of water with methanol, ethanol, and 1-propanol over the entire mole fraction range at 298.15 K. The present paper reports similar measurements for the same systems at 288.15 and 308.15 K.

Experimental Section

The samples of the alcohols were the same as used in our previous work (*2*). Densities were determined with an Anton Paar densimeter and corrected for water content (usually less than 0.1% by mass) on the basis of analysis by the Karl Fischer method. The results at 288.15 and 308.15 K are listed in Table I along with values from the literature (*4*) for comparison.

Mixtures with deionized distilled water were prepared by mass. The water content of the alcohol was taken into account in calculating the mole fraction. The error of the mole fraction is estimated to be less than 5 × 10^{-5}.

Differences of volumetric heat capacity were measured between pairs of liquids flowing in the test and reference cells of a Picker microcalorimeter. This apparatus and its operation have been described previously (*5*, *6*). A temperature interval of about 1.6 K centered on the nominal operating temperatures of 288.15 and 308.15 K was adopted. Mixtures were studied in order of their compositions, following a stepwise procedure. Starting with water as the initial reference liquid, each mixture after measurement was used as the reference for the subsequent mixture. Corrections were applied for power losses, and measurements were repeated with the test and reference liquids interchanged to cancel mixing effects (*6*). The latter are relatively large for the present systems since the excess volumes of equimolar mixtures are approximately −1 $cm^3\ mol^{-1}$. The values adopted for the properties of water are summarized in Table I; these were calculated from equations recommended by Kell for the density (*7*) and heat capacity (*8*).

Table I. Physical Properties of Component Liquids

		density/(kg m^{-3})		$C_p{}^*{}_m$/(J K^{-1} mol^{-1})	
component	T/K	measd	lit.	measd	lit.
methanol	288.15	795.84	795.99 (*4*)	78.90	78.72 (*9*)
	308.15	777.02	777.29 (*4*)	83.74	82.59 (*9*)
ethanol	288.15	793.52	793.62 (*4*)	108.07	108.63 (*9*)
	308.15	776.41	776.45 (*4*)	117.75	116.61 (*9*)
1-propanol	288.15	807.55	807.71 (*4*)	138.40	138.49 (*9*) 138.28 (*10*)
	308.15	791.56	791.62 (*4*)	151.93	149.78 (*9*) 148.97 (*10*)
water	288.15		999.10 (*7*)		75.403 (*8*)
	308.15		994.04 (*7*)		75.266 (*8*)

Molar isobaric heat capacities, $C_{p,m}$, were obtained from the experimental results for the volumetric heat capacities, $C_{p,m}/V_m$, using molar volumes, V_m, calculated from the molar excess volumes of the mixtures (*1*) and the densities of the pure components given in Table I. Molar excess isobaric heat capacities were calculated from the relation

$$C_p{}^E{}_m = C_{p,m} - xC_p{}^*{}_1 - (1 - x)C_p{}^*{}_2 \qquad (1)$$

where x is the mole fraction of water in the mixture, and $C_p{}^*{}_1$ and $C_p{}^*{}_2$ are the molar isobaric heat capacities of pure water and n-alcohol, respectively. The error of $C_p{}^E{}_m$ is estimated to be less than 0.05 J K^{-1} mol^{-1}.

Results and Discussion

The molar isobaric heat capacities measured for the pure alcohols are listed in Table I, where the values recommended in the survey of literature data by Sriskandarajah (*9*) and the recent results for 1-propanol by Kalinowska et al. (*10*) are also shown. The agreement at 288.15 K is good (within ~0.5%)

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Table II. Experimental Results for the Molar Excess Isobaric Heat Capacity, $C_p{}^E{}_m$, of Water (1)-*n*-Alcohol (2) Mixtures at Mole Fraction, *x*, of Water

x	$C_p{}^E{}_m$/(J K^{-1} mol^{-1})	x	$C_p{}^E{}_m$/(J K^{-1} mol^{-1})	x	$C_p{}^E{}_m$/(J K^{-1} mol^{-1})	x	$C_p{}^E{}_m$/(J K^{-1} mol^{-1})
Water (1)–Methanol (2) at 288.15 K							
0.063 36	0.15	0.426 91	2.41	0.728 38	4.93	0.919 08	4.60
0.115 68	0.39	0.454 53	2.54	0.749 67	5.06	0.927 50	4.31
0.146 87	0.54	0.476 54	2.81	0.774 52	5.34	0.931 36	4.17
0.162 51	0.66	0.513 81	3.03	0.795 44	5.50	0.938 55	3.87
0.199 91	0.90	0.537 06	3.26	0.810 85	5.60	0.948 71	3.37
0.234 23	1.12	0.568 96	3.50	0.827 48	5.65	0.951 08	3.27
0.274 68	1.43	0.593 11	3.61	0.851 05	5.65	0.959 00	2.84
0.299 27	1.53	0.628 07	4.01	0.875 73	5.48	0.969 69	2.20
0.330 16	1.77	0.658 89	4.23	0.879 90	5.47	0.975 03	1.85
0.352 61	1.87	0.676 12	4.41	0.898 97	5.14	0.980 81	1.45
0.369 56	2.02	0.680 56	4.47	0.909 17	4.90	0.987 02	1.00
0.415 35	2.37	0.709 13	4.72				
Water (1)–Methanol (2) at 308.15 K							
0.052 94	0.77	0.490 53	5.94	0.728 48	7.79	0.899 45	5.68
0.147 26	1.93	0.539 56	6.36	0.735 47	7.81	0.918 96	4.88
0.149 67	1.96	0.541 25	6.51	0.754 86	7.81	0.925 99	4.57
0.193 58	2.51	0.578 42	6.83	0.776 49	7.78	0.946 25	3.47
0.238 82	3.10	0.586 21	6.80	0.783 02	7.73	0.946 62	3.42
0.293 65	3.79	0.622 70	7.18	0.791 65	7.66	0.951 89	3.19
0.294 34	3.83	0.626 34	7.25	0.824 18	7.46	0.954 81	3.02
0.299 80	3.92	0.634 02	7.19	0.829 64	7.30	0.966 61	2.29
0.311 30	4.04	0.643 34	7.37	0.839 90	7.17	0.967 74	2.23
0.343 72	4.36	0.654 92	7.34	0.850 77	7.04	0.973 83	1.83
0.387 46	4.89	0.655 06	7.39	0.875 06	6.47	0.978 05	1.53
0.445 94	5.44	0.673 80	7.54	0.893 68	5.86	0.984 53	1.10
0.480 56	5.82	0.689 45	7.53				
Water (1)–Ethanol (2) at 288.15 K							
0.050 22	1.23	0.659 37	11.09	0.824 31	13.81	0.935 40	8.94
0.094 62	2.33	0.700 73	11.75	0.830 53	13.68	0.945 69	7.73
0.157 33	3.69	0.722 48	11.96	0.841 86	13.91	0.947 30	7.56
0.187 92	4.30	0.724 12	12.06	0.849 80	13.59	0.948 08	7.44
0.274 47	5.74	0.729 63	12.14	0.859 42	13.70	0.951 44	7.01
0.285 83	5.93	0.750 65	12.49	0.872 45	13.40	0.958 82	6.09
0.342 11	6.73	0.753 48	12.38	0.879 95	13.14	0.970 17	4.53
0.404 52	7.56	0.754 62	12.47	0.889 96	12.65	0.974 79	3.87
0.473 36	8.47	0.756 59	12.45	0.900 40	11.95	0.979 07	3.24
0.491 77	8.66	0.768 91	12.80	0.906 98	11.56	0.980 22	3.07
0.564 17	9.62	0.771 98	12.87	0.907 76	11.45	0.984 83	2.38
0.578 31	9.79	0.797 68	13.31	0.931 20	9.35	0.989 76	1.62
0.615 46	10.42	0.797 90	13.13				
Water (1)–Ethanol (2) at 308.15 K							
0.055 64	2.03	0.395 05	10.09	0.691 97	13.81	0.851 54	13.96
0.077 79	2.78	0.429 28	10.45	0.694 44	13.61	0.875 79	13.43
0.105 37	3.60	0.453 46	10.82	0.720 85	14.00	0.890 18	12.80
0.105 37	3.63	0.453 46	10.89	0.747 51	14.14	0.900 56	11.80
0.124 90	4.20	0.493 50	11.46	0.749 73	14.13	0.909 97	11.27
0.166 35	5.44	0.543 33	12.12	0.749 73	14.32	0.914 87	10.91
0.190 87	6.15	0.573 61	12.49	0.771 92	14.36	0.926 15	9.72
0.243 91	7.25	0.595 20	12.79	0.797 62	14.34	0.936 76	8.59
0.265 88	7.65	0.622 15	13.00	0.797 97	14.48	0.958 78	5.80
0.304 82	8.53	0.649 32	13.25	0.824 32	14.39	0.966 64	4.83
0.354 19	9.33	0.649 32	13.37	0.849 83	13.95	0.978 20	3.19
0.356 78	9.45	0.664 51	13.46	0.851 54	13.90	0.985 14	2.15
Water (1)–1-Propanol (2) at 288.15 K							
0.011 68	0.52	0.264 17	8.10	0.630 50	11.87	0.876 33	14.58
0.026 55	1.14	0.291 84	8.22	0.680 90	12.45	0.909 08	14.93
0.045 60	1.85	0.346 82	9.28	0.694 46	12.57	0.924 82	14.61
0.060 20	2.55	0.365 06	9.37	0.720 21	12.62	0.929 64	14.32
0.076 48	3.18	0.400 88	9.83	0.746 21	13.02	0.947 21	11.74
0.098 16	3.70	0.410 22	10.24	0.772 51	13.21	0.959 14	9.08
0.123 47	4.68	0.428 48	10.04	0.794 97	13.62	0.959 92	8.90
0.127 78	4.77	0.476 82	10.75	0.798 60	13.70	0.964 80	7.77
0.128 90	4.75	0.506 69	10.94	0.825 75	13.79	0.971 93	6.22
0.152 49	5.42	0.525 12	11.26	0.853 24	14.27	0.977 32	5.00
0.197 70	6.49	0.554 03	11.51	0.854 20	14.35	0.986 68	2.95
0.215 65	7.00	0.567 45	11.41	0.874 00	14.49	0.993 79	1.39
0.245 04	7.45	0.606 66	11.77				
Water (1)–1-Propanol (2) at 308.15 K							
0.038 63	1.81	0.279 52	9.46	0.646 64	13.47	0.909 93	11.96
0.055 67	2.67	0.319 04	10.23	0.676 27	13.47	0.921 17	11.68
0.078 73	3.64	0.345 16	10.75	0.702 99	13.54	0.931 37	11.30
0.088 44	4.08	0.368 56	11.20	0.750 29	13.48	0.941 25	10.53

Table II (*Continued*)

x	$C_p{}^E{}_m$/(J K^{-1} mol^{-1})	x	$C_p{}^E{}_m$/(J K^{-1} mol^{-1})	x	$C_p{}^E{}_m$/(J K^{-1} mol^{-1})	x	$C_p{}^E{}_m$/(J K^{-1} mol^{-1})
0.120 12	5.20	0.388 36	11.39	0.771 19	13.19	0.950 04	9.45
0.124 23	5.42	0.430 76	12.05	0.797 11	13.11	0.960 70	7.70
0.150 36	6.19	0.489 06	12.60	0.817 87	13.07	0.971 36	5.66
0.184 20	7.19	0.513 51	12.87	0.848 59	12.78	0.978 33	4.29
0.201 58	7.57	0.552 82	13.26	0.869 76	12.68	0.990 61	1.83
0.237 99	8.54	0.580 21	13.34	0.886 76	12.34	0.995 17	0.94
0.263 45	9.18	0.623 22	13.52	0.900 34	12.10		

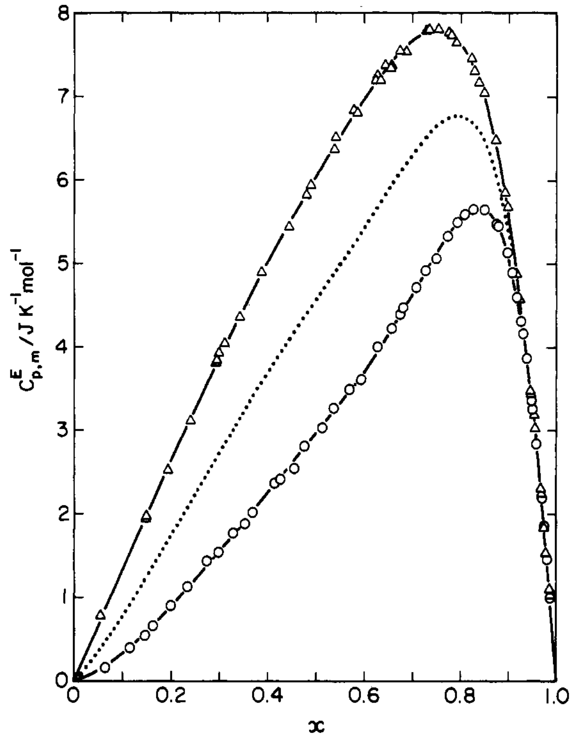

Figure 1. Molar excess isobaric heat capacity, $C_p{}^E{}_m$, of aqueous methanol mixtures vs. mole fraction, x, of water. Present work: (○) 288.15 K; (△) 308.15 K. Curves: (—) least-squares representations by eq 2; (···) smoothed results for 298.15 K (*2*).

but at 308.15 K our values are 1-2% higher than the results of earlier investigations.

Experimental results for the molar excess isobaric heat capacites of the mixtures $x H_2O + (1 - x)C_nH_{2n+1}OH$ (n = 1, 2, 3) are listed for 288.15 and 308.15 K in Table II. Each set of results was fitted with the polynomial function

$$C_p{}^E{}_m = \phi(1 - \phi)\sum_{j=1}^{\nu} a_j(1 - 2\phi)^{j-1} \quad (2)$$

in the volume fraction of water

$$\phi = xV^*{}_1/[xV^*{}_1 + (1 - x)V^*{}_2] \quad (3)$$

stated in terms of the unmixed components. Values of the coefficients, a_j, determined by the method of least-squares with each point assigned unit weight, are given in Table III along with the standard deviation, σ, of the representation.

Table III. Coefficients and Standard Deviation for Least-Squares Representations of $C_p{}^E{}_m$ for Water (1)–n-Alcohol (2) Mixtures at 288.15 and 308.15 K by Eq 2

	methanol		ethanol		1-propanol	
	288.15 K	308.15 K	288.15 K	308.15 K	288.15 K	308.15 K
a_1	18.157	30.535	50.841	57.210	54.457	51.876
a_2	−16.857	−8.415	−27.108	−8.430	−12.644	9.624
a_3	15.889	5.688	32.798	28.225	56.922	66.558
a_4	1.081	8.457	56.041	39.824	−81.164	−23.218
a_5	−13.998	−5.426	−76.195	−47.525	87.174	−55.256
a_6			−11.832	9.551	329.514	98.550
a_7			67.466	50.365	−394.415	56.480
a_8					−185.895	
a_9					336.536	
σ	0.03	0.04	0.09	0.08	0.13	0.13

Graphical presentations of the results are given in Figures 1–3 where the experimental points are plotted along with curves calculated from eq 2. Smooth representations of our previous measurements at 298.15 K (*2*) are shown as dotted curves in these figures. All of the $C_p{}^E{}_m$ curves are asymmetric, being skewed toward x = 1. For methanol and ethanol, $C_p{}^E{}_m$ increases with temperature at all mole fractions and the maximum broadens and shifts to lower values of x. Presumably this behavior reflects an increasing net disruption of hydrogen bonds with increasing temperature. Over most of the mole fraction range, $C_p{}^E{}_m$ for 1-propanol mixtures also increases with temperature; however, the isotherms cross near x = 0.8, and for high mole fractions of water $C_p{}^E{}_m$ decreases with increasing temperature. Although an explanation of this different behavior is currently lacking, it is interesting to note that an unexpected maximum and minimum of $C_p{}^E{}_m$ have been reported for low mole fractions of 1-propanol (0.05–0.15) in binary mixtures with n-hexane and n-heptane (*11*).

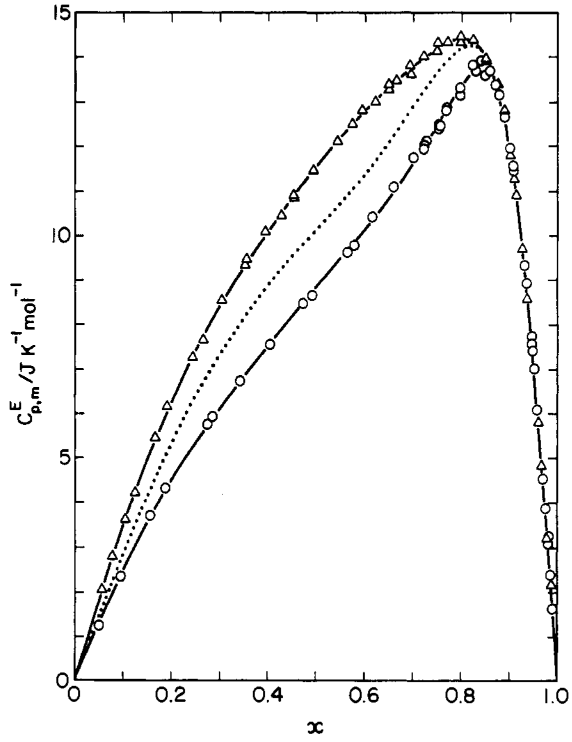

Figure 2. Molar excess isobaric heat capacity, $C_p{}^E{}_m$, of aqueous ethanol mixtures vs. mole fraction, x, of water. Present work: (○) 288.15 K; (△) 308.15 K. Curves: (—) least-squares representations by eq 2; (···) smoothed results for 298.15 K (*2*).

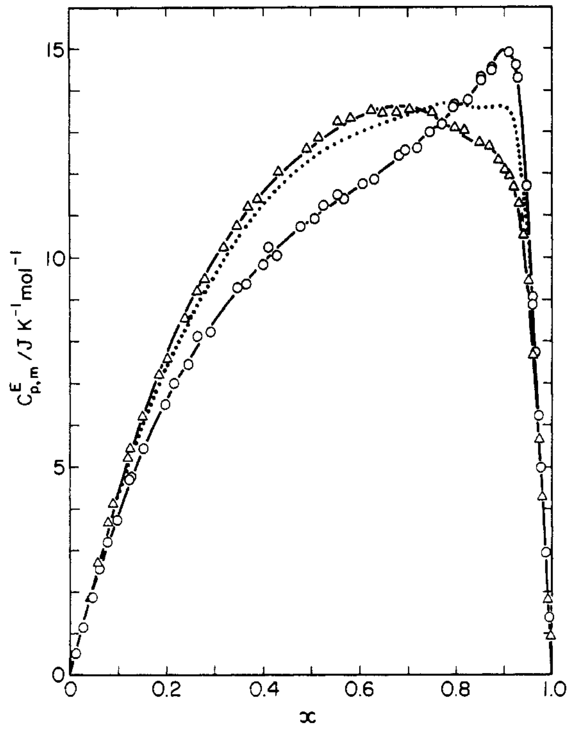

Figure 3. Molar excess isobaric heat capacity, $C_p{}^E{}_m$, of aqueous 1-propanol mixtures vs. mole fraction, x, of water. Present work: (○) 288.15 K; (△) 308.15 K. Curves: (—) least-squares representations by eq 2; (···) smoothed results for 298.15 K (*2*).

Acknowledgment

We are indebted to Dr. O. Kiyohara for discussions of this work and to Mr. C. J. Halpin for technical assistance.

Glossary

a_1, a_2, ..., a_i	coefficients in representation of $C_p{}^E{}_m$ by eq 2
$C_{p,m}$	molar isobaric heat capacity, J K^{-1} mol^{-1}
V_m	molar volume, cm^3 mol^{-1}
x	mole fraction of water

Greek Letters

ϕ	volume fraction of water
ν	number of coefficients in eq 2
σ	standard deviation

Subscripts

1	water component
2	*n*-alcohol component

Superscripts

E	excess quantity
*	pure-component value

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Solubility of Oxalic Acid Dihydrate in Nitric and Sulfuric Acid Solutions at 0, 25, and 50 °C

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The solubility of oxalic acid dihydrate (ethanedioic acid) has been determined at 0, 25, and 50 °C in nitric–sulfuric acid solutions. This study covers four levels of nitric acid concentration in two concentrations of sulfuric acid. A mathematical model equation (log $S = A/T + B$, where S is oxalic acid solubility (wt %), T is the absolute temperature, and A and B are functions of the acid concentrations) was developed to predict the solubility of oxalic acid within the experimental ranges of the acid concentrations.

Introduction

One method for the production of oxalic acid is the use of nitric acid to oxidize cellulose in the presence of sulfuric acid (*1*, *2*). Values for the solubility of oxalic acid dihydrate in nitric–sulfuric acid solutions typical of those employed are required for the development of the process. Various authors (*3*–*6*) report the solubility of oxalic acid in single-mineral acids, but none give data for mixtures of these acids. The results reported here were obtained at three temperatures and four nitric acid concentrations in two levels of sulfuric acid concentration.

Experimental Section

Reagent-grade nitric acid, sulfuric acid, and oxalic acid dihydrate were used without further purification. Eight solutions of 100 g each were prepared of the initial compositions shown in Table I. $H_2C_2O_4{\cdot}2H_2O$ (21 g) was added to each of these solutions. The solutions were placed in a water bath at 25 ±