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MEASUREMENT OF EXCESS MOLAR HEAT CAPACITIES BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Specific heat capacities were measured by differential scanning calorimetry (DSC) from −7 to 45°C on ethanol, toluene, and five mixtures near 0.45 mole fraction of ethanol. Excess molar heat capacities computed from these data agree within experimental error with two previous studies performed by different methods. The present study demonstrates the feasibility of DSC for rapid and accurate measurements of excess molar heat capacities over a large temperature range.

INTRODUCTION

Differential scanning calorimetry (DSC) is a powerful tool for the measurement of specific heat capacities; temperature spans are limited only by the instrument cooling system and sample container–internal pressure relationships, or by chemical decomposition at higher temperatures. To demonstrate the capability of DSC for the measurement of excess molar heat capacities (C_p^E), a study was undertaken to measure the specific heat capacities of ethanol + toluene. This system was chosen because previous measurements were reported by Hwa and Zeigler [1] who used adiabatic calorimetry to obtain data from −95 to 35°C. In addition Van Ness et al. [2] published a thermodynamic correlation of excess Gibbs energy (G^E) and heat-of-mixing (H^E) data for ethanol + toluene, which included excess molar heat capacities at 30°C.

Excess molar heat capacity data are valuable for the extension of phase equilibria, particularly vapor–liquid equilibria, to higher or lower temperatures [2,3]. C_p^E data as a function of temperature can be combined with H^E and G^E data at a single temperature to compute G^E and therefore VLE over a wide temperature range. Hence, phase-equilibria data can be measured at an experimentally convenient temperature and then rigorously extrapolated to the temperature of interest.

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EXPERIMENTAL

The toluene was reagent grade (99.5 + mol%) used as received. The ethanol was anhydrous-spirits grade, 200 proof, undenatured material. Five mixtures near a mole fraction of 0.45 ethanol were prepared: 0.4467, 0.4489, 0.4500, 0.4502 and 0.4510. This concentration was chosen because of the proximity to the literature data cited above; determinations were performed on these nearly replicate mixtures to test precision. Each mixture was measured in duplicate.

Specific heat capacities were measured with a Perkin-Elmer differential scanning calorimeter (DSC-2). Standard DSC specific heat capacity procedures [4] were used: an empty volatile sample pan and cover were scanned over a specific temperature range, likewise for a synthetic sapphire in the same pan and cover; the liquid sample was hermetically sealed in a nitrogen atmosphere in the same container and scanned over the same temperatures as the other two runs. The results of the three DSC curves were processed on a CDC 1700 computer to give a specific heat capacity–temperature table. These points were fitted by a polynomial regression to obtain estimates of standard deviation, percent differences of calculated-to-experimental data and constants of first, second and third order equations as a function of temperature.

RESULTS AND DISCUSSION

Table 1 contains the pure component and mixture specific heat capacity–temperature data from −7 to 45°C. The specific heat capacities

TABLE 1

Specific heat capacity of ethanol (X_1) and toluene (cal g^{-1} °C^{-1})

t(°C)	Ethanol	Toluene	X_1				
			0.4510	0.4502	0.4500	0.4489	0.4467
−7	0.5375	0.3865	0.4644	0.4701	0.4614	0.4637	0.4594
0	0.5501	0.3920	0.4765	0.4814	0.4732	0.4755	0.4713
5	0.5596	0.3960	0.4851	0.4895	0.4816	0.4840	0.4797
10	0.5694	0.3999	0.4937	0.4976	0.4900	0.4924	0.4882
15	0.5796	0.4038	0.5024	0.5057	0.4984	0.5008	0.4967
20	0.5901	0.4077	0.5110	0.5138	0.5068	0.5093	0.5051
25	0.6011	0.4117	0.5196	0.5219	0.5152	0.5177	0.5136
30	0.6123	0.4156	0.5283	0.5300	0.5236	0.5262	0.5220
35	0.6240	0.4195	0.5369	0.5381	0.5320	0.5346	0.5305
40	0.6360	0.4234	0.5455	0.5463	0.5404	0.5430	0.5390
45	0.6484	0.4274	0.5541	0.5544	0.5488	0.5515	0.5474
Standard deviation of the fit	0.0031	0.0027	0.0021	0.0020	0.0025	0.0023	0.0021

TABLE 2

Ethanol (X_1)–toluene, coefficients from polynominal regression analysis for C_p as a function of temperature

X_1	A	B	C
1.0[a]	0.55013	1.8543×10^{-3}	7.2994×10^{-6}
0.0[b]	0.39205	7.8476×10^{-4}	
0.4510	0.47647	1.7262×10^{-3}	
0.4502	0.48142	1.6210×10^{-3}	
0.4500	0.47319	1.6798×10^{-3}	
0.4489	0.47554	1.6870×10^{-3}	
0.4467	0.47127	1.6925×10^{-3}	

[a] $C_p = A + Bt + Ct^2$, where C_p = cal g^{-1} °C^{-1} and t = °C.

[b] Toluene and all mixtures, $C_p = A + Bt$, where C_p = cal g^{-1} °C^{-1} and t = °C.

determined here are for the saturated liquid, C_σ. However, the difference between C_p, the isobaric specific heat capacity, and C_σ is less than 0.01% at these low temperatures; hence, these data will be designated C_p. Standard deviations of the experimental-to-calculated values are given. Coefficients of the equations for C_p as a function of temperature are listed in Table 2.

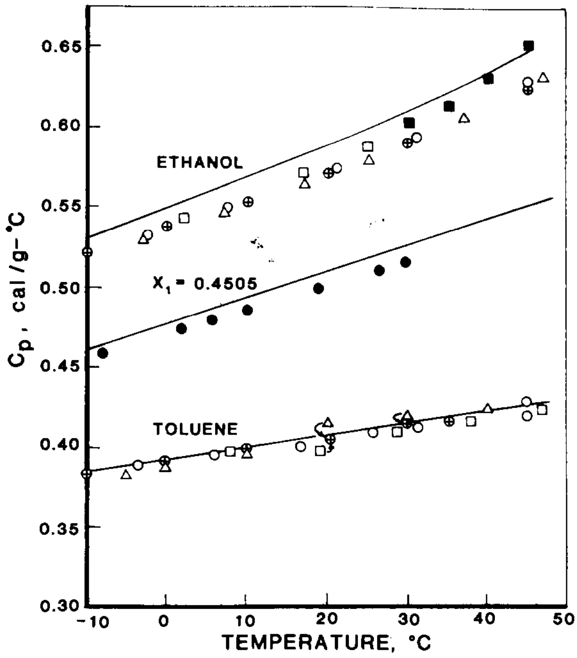

Fig. 1. Specific heat capacity–temperature data for ethanol (X_1), toluene and a mixture $X_1 = 0.4505$. Pure ethanol data: (———) this work; (⊕) Touloukian and Makita [5]; (○) Hwa and Zeigler [1]; (□) Parks [6]; (△) Green [7] and Blacet et al. [8]. Pure toluene data: (———) this work; (⊕) Touloukian and Makita [5]; (○) Hwa and Zeigler [1]; (△) Kurbatov [9] and (□) Burlew [10]. For $X_1 = 0.4505$: (———) this work and (●) Hwa and Zeigler [1].

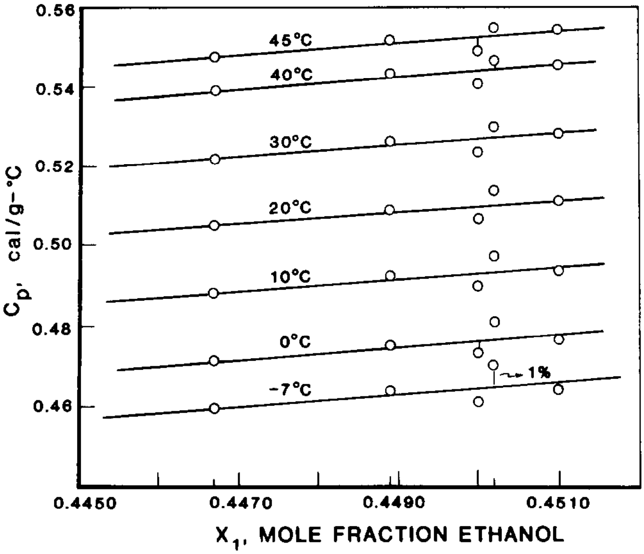

Fig. 2. Ethanol–toluene, specific heat capacity vs. mole fraction ethanol. (○) Data points from Table 1; (———) smoothed data, $C_p = A + BX_1$.

The C_p values for ethanol reported here are about 3% higher than published data as shown in Fig. 1. However, these measured data are sufficiently reliable to provide a baseline for the excess property calculations. As shown in Fig. 1, the toluene data are in excellent agreement with literature values, particularly for ref. 5—at 0°C the difference is 0.08% and at 45°C the difference is 0.30%.

Experimental mixture specific heat capacities summarized in Tables 1 and 2 are shown in Fig. 2 as plots of C_p vs. mole fractions of ethanol, X_1, at different temperatures. Only data for the mixtures of $X_1 = 0.4500$ and 0.4502

TABLE 3

Ethanol (X_1)–toluene, interpolated C_p values for $X_1 = 0.4505$ [a] and C_p^E values as a function of temperature

Temperature (°C)	C_p (cal g^{-1} °C^{-1}) [b]	C_p^E (cal mol^{-1} °C^{-1})
−7.0	0.4655	2.50
0.0	0.4773	2.81
10.0	0.4940	3.20
20.0	0.5108	3.57
30.0	0.5276	3.91
40.0	0.5444	4.22

[a] Mixture molecular weight, 71.381.

[b] $C_p = 0.47726 + 1.6791 \times 10^{-3} t$, where C_p = cal g^{-1} °C^{-1} and t = °C.

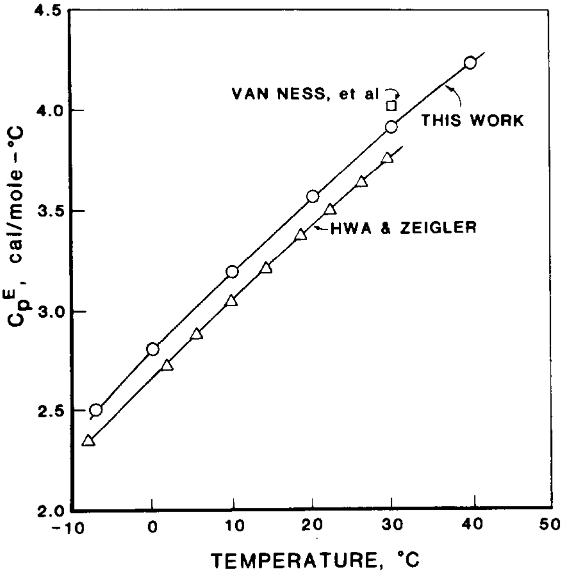

Fig. 3. Ethanol (X_1)–toluene, excess molar heat capacities for $X_1 = 0.4505$ mole fraction ethanol. (□) Van Ness et al. [2]; (△) Hwa and Zeigler [1]; (○) this work.

deviate from the smoothed curve by 1%. Smoothed data were generated from fitted linear equations in X_1 for each temperature parameter (Fig. 2). This plot illustrates the sensitivity and accuracy of the Perkin-Elmer DSC-2 on these closely-spaced mixtures. In addition to the above correlations, the linear equations were used to interpolate C_p data for $X_1 = 0.4505$ mole fraction ethanol at various temperatures. For comparison with Hwa and Zeigler's data [1] see Table 3 and Fig. 1. These interpolated values were used for subsequent calculations and comparison of C_p^E.

Excess molar heat capacity is computed for the equation

$$C_p^E - C_p^M = \left(X_1 C_{p1}^0 + X_2 C_{p2}^0\right) \quad (\text{cal mol}^{-1}\ {}^\circ\text{C}^{-1})$$

where C_p^E = excess molar heat capacity (cal mol^{-1} °C^{-1}); C_p^M = mixture molar heat capacity (cal mol^{-1} °C^{-1}); X_1 = mole fraction ethanol; X_2 = mole fraction toluene; C_{p1}^0 = molar heat capacity of ethanol (cal mol^{-1} °C^{-1}); and C_{p2}^0 = molar heat capacity of toluene (cal mol^{-1} °C^{-1}).

Excess molar heat capacities for $X_1 = 0.4505$ at several temperatures are listed in Table 3 and shown in Fig. 3. The mixture molecular weight is given in the table and is based on molecular weights of 46.068 and 92.134 for ethanol and toluene, respectively. Standard errors in $C_p^E(\sigma_{C_p^E})$ calculated by a propagation-of-error technique for the five mixtures studied here are 0.21, 0.21, 0.23, 0.22 and 0.21 cal mol^{-1} °C^{-1}; hence $\sigma_{C_p^E}$ for $X_1 = 0.4505$ would be 0.22 cal mol^{-1} °C^{-1}.

The excess data for ethanol $X_1 = 0.4505$ from Hwa and Zeigler's [1] work

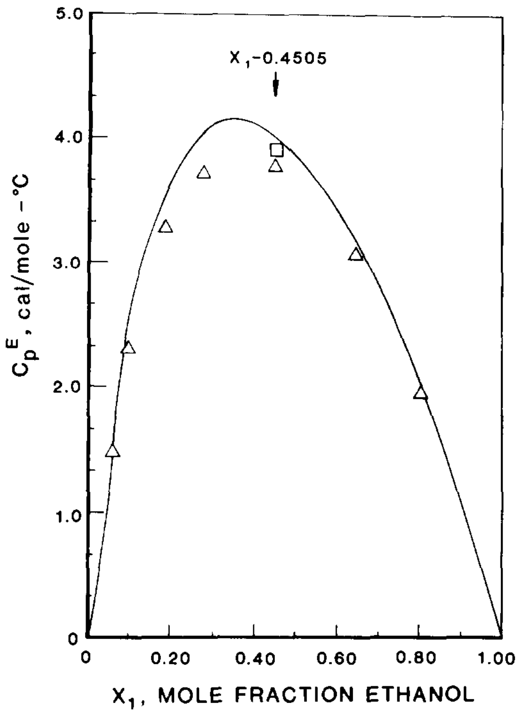

Fig. 4. Excess molar heat capacity for ethanol (X_1)-toluene at 30°C. (———) Van Ness et al. [2] correlated values; (△) Hwa and Zeigler [1] data; and (□) this work $X_1 = 0.4505$.

are shown in Fig. 3. At this mixture concentration only one point (30°C) is available from the correlation of Van Ness et al. [2]. Figure 4 shows C_p^E vs. ethanol mole fraction at 30°C for these previous studies and the point at $X_1 = 0.4505$ from this work. The agreement is within experimental error for these derived quantities (3–6%). Numerical values for the three studies are

	C_p^E(cal mol^{-1} °C^{-1}), $X_1 = 0.4505$, 30°C
Hwa and Zeigler [1]	3.77
Van Ness et al. [2]	4.02
This work	3.91

CONCLUSION

The data presented here show that the Perkin-Elmer DSC-2 is capable of measuring specific heat capacities with sufficient accuracy to obtain the excess function.

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