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The vapor heat capacities of acetone-chloroform, benzene-carbon tetrachloride and benzene-ethanol binary mixtures

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Abstract

The vapor heat capacities of acetone-chloroform, benzene-carbon tetrachloride and benzene-ethanol binary mixtures as a function of temperature and composition have been measured under atmospheric pressure in a multicomponent vapor flow calorimeter. It was found that the heat capacities of benzene-carbon tetrachloride vapors display ideal behavior, while those of acetone-chloroform vapors demonstrate positive deviation and those of benzene-ethanol vapors, negative deviation from the ideal linear additive values. These phenomena are explained and discussed.

Keywords: Binary system; Flow calorimeter; Heat capacity; Vapor

1. Introduction

Accurate heat capacity values of pure substances and mixtures are necessary for the calculation of thermodynamic processes. The heat capacities of gases at zero pressure (ideal gases), $C_p^\ominus$, are either available or are easy to calculate from literature data [1–4]. Because of the scarcity of experimental data, particularly for polar compounds and mixtures, the heat capacity at constant pressure, C_p, is usually estimated as the sum of the ideal gas value, $C_p^\ominus$, and the residual heat capacity, ΔC_p, from generalized equations of state (EOS) [5–7]. This is not expected to be very accurate as it involves a double differentiation. Therefore, accurate experimental values of the heat capacity for real

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gases and organic vapors are very important from both research and industrial points of view.

Accurate values of vapor heat capacity can be obtained from precision flow calorimetry. The present paper reports the vapor heat capacities of three binary systems, acetone-chloroform, benzene-carbon tetrachloride and benzene-ethanol, measured directly under atmospheric pressure by a multicomponent vapor flow calorimeter. The experimental results are discussed with respect to the molecular interactions in the vapor phase.

2. Experimental

2.1. Calorimeter

The heat capacity measurements were carried out in a multicomponent vapor flow calorimeter with a flash boiler which was a modification of that developed in this laboratory [8], described in detail previously [9, 10]. The calorimeter was designed to be operated at temperatures up to 700 K and at pressures up to 20 MPa. The calibration of the apparatus was monitored using benzene, as recommended by IUPAC over the temperature range from 350 to 650 K with deviations of less than 0.7%.

2.2 Materials

The analytical reagents, acetone, benzene, carbon tetrachloride, chloroform and ethanol (Shanghai Chemical Corporation), were all purified by fractional distillation in a 1.5-m-long column and dehydrated by standing over 4-A molecular sieves. The absolute deviations of the densities determined using a DMA-45 digital density meter and of their refractive indices were all within ±0.0002 compared with those in the literature [11]. All mixtures were prepared by weight, with an uncertainity of less than ±0.02%.

3. Results

The vapor heat capacities of benzene measured under atmospheric pressure and the corresponding interpolated literature values [12, 13] are listed in Table 1. It can be seen that they are in reasonable agreement which demonstrates the good performance of the calorimeter.

The measured values of vapor heat capacity of the three binary mixtures, acetone-chloroform, benzene-carbon tetrachloride and benzene-ethanol, at various temperatures and at atmospheric pressure are given in Tables 2–4. Figs. 1–3 show the relationships between the heat capacity and the compositions of the mixtures. The experimental data as functions of temperature and composition are fitted to Eq. (1) which was obtained by a least-squares procedure

$$C_p = a + bT^* + cyT^* + dy + ey^2 + f(T^*)^2 \qquad (1)$$

Table 1
Vapor heat capacities of benzene at atmospheric pressure

No.	T/K	C_p/J K^{-1} mol^{-1}		
		This work	Ref. [12]	Ref. [13]
1	363.58	103.97		104.19
2	373.20	107.65	107.75	106.95
3	382.60	109.18	110.33	109.61
4	396.44	113.29	114.08	113.45
5	406.88	116.18	116.87	116.30
6	413.83	118.54	118.71	118.17
7	432.55	122.65	123.60	123.09
8	455.60	129.81	129.44	128.94
9	471.58	133.47	133.36	132.87
10	493.47	138.54	138.54	138.06
11	522.03	144.42	144.92	144.52
12	565.34	154.58		153.65
13	583.77	157.93		157.29
14	605.33	161.96		161.35
15	623.72	165.23		164.67
16	650.60	169.70		169.24

Table 2
Vapor heat capacities (J K^{-1} mol^{-1}) of $y$acetone + $(1-y)$chloroform binary system at atmospheric pressure

T/K	y							
	0.0000	0.1208	0.2526	0.3583	0.5084	0.6465	0.8032	1.0000
372.26	74.81	79.24	83.13	87.01	90.76	93.74	95.93	98.64
402.02	75.78	80.07	83.88	87.78	91.44	94.87	98.12	101.13
436.74	76.97	81.34	85.73	88.97	93.14	96.53	99.86	103.26
473.58	78.71	83.05	87.47	90.78	95.13	98.77	102.47	106.48
514.70	81.17	85.39	89.85	93.26	97.84	101.78	105.94	110.54

Table 3
Vapor heat capacities (J K^{-1} mol^{-1}) of $y$benzene + $(1-y)$carbon tetrachloride binary system at atmospheric pressure

T/K	y					
	0.0000	0.2018	0.4209	0.5940	0.8028	1.0000
373.20	93.30	96.32	99.08	101.63	105.14	107.65
397.90	93.86	98.03	101.45	105.41	110.20	113.92
424.24	94.83	99.79	105.64	109.48	115.65	121.16
476.86	96.74	104.59	112.63	118.20	126.98	134.64
514.31	97.78	106.78	117.24	124.72	134.39	143.18

Table 4
Vapor heat capacities ($J\ K^{-1}\ mol^{-1}$) of ybenzene + (1 − y)ethanol binary system at atmospheric pressure

T/K	y						
	0.0000	0.2029	0.3511	0.4975	0.6466	0.7997	1.0000
404.56	85.88	89.39	94.20	98.47	103.48	108.17	115.78
436.29	87.83	94.22	99.19	104.36	109.89	115.85	124.06
475.34	92.09	99.78	105.65	111.64	117.95	124.99	133.78
514.63	96.57	105.96	112.56	119.68	126.64	133.92	143.49

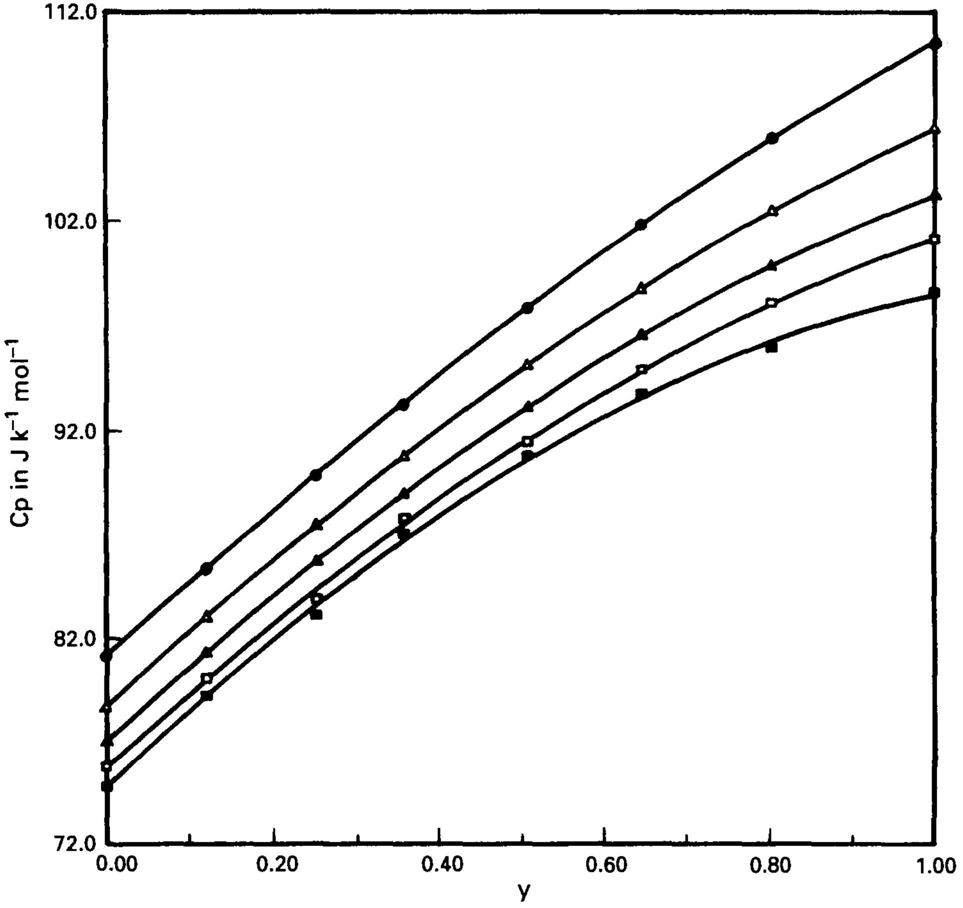

Fig. 1. The vapor heat capacities of y acetone + (1 − y) chloroform binary system at atmospheric pressure. Key: ■, 372.26 K; □, 402.02 K; ▲, 436.74 K; △, 473.58 K; ●, 514.70 K.

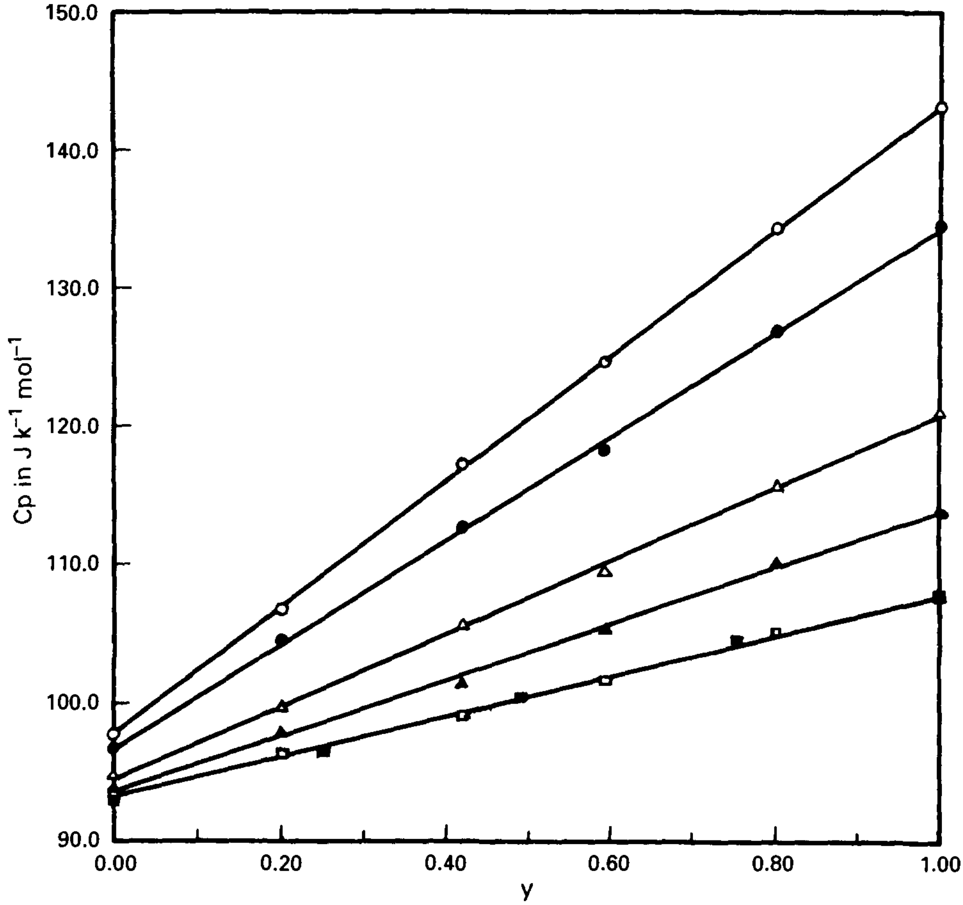

Fig. 2. The vapor heat capacities of y benzene + $(1 - y)$ carbon tetrachloride binary system at atmospheric pressure. Key: ■, 373.2 K, Sinke and Vries [14]; □, 373.2 K, this work; ▲, 397.90 K; △, 424.24 K; ●, 476.86 K; ○, 514.31 K.

where $T^* = T/273.15$ and C_p (J K^{-1} mol^{-1}) is the vapor heat capacity at constant y, T and P. The coefficients a, b, c, d, e and f are listed in Table 5.

4. Discussion

The vapor heat capacity measurements on a series of benzene-carobon tetrachloride mixtures over the temperature range from 373 to 515 K show that the observed values at 373.2 K are in good agreement with the literature data [14] and that the heat capacity changes linearly with composition in mole fraction at various temperatures as given in Table 2 and Fig. 2. The observed ideal behaviour derives from benzene-carbon tetrachloride being a typical non-polar binary system within which the main intermolecular forces are the van der Waals forces. When the molecules of the

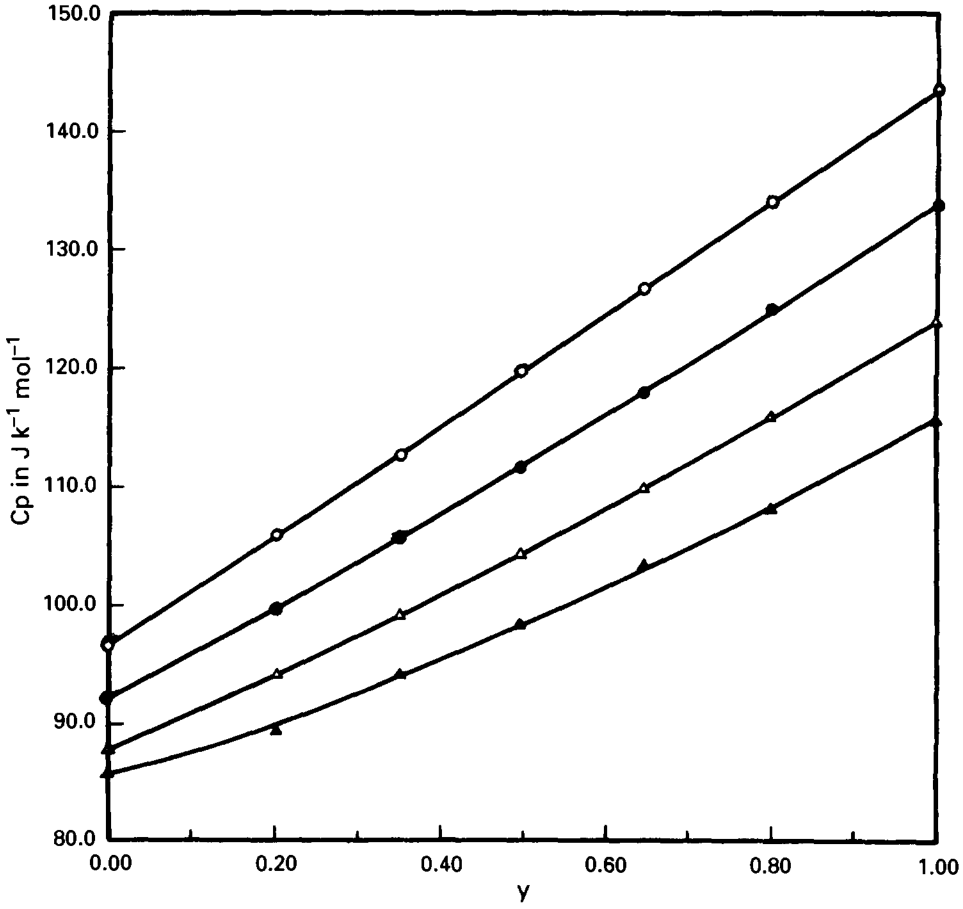

Fig. 3. The vapor heat capacities of y acetone + $(1-y)$ ethanol binary system at atmospheric pressure. Key: ▲, 404.56 K; △, 436.29 K; ●, 475.34 K; ○, 514.63 K.

Table 5
The values of coefficients in Eq. (1)

System	Temperature range/K	*a*	*b*	*c*	*d*	*e*	*f*
Acetone-chloroform	370–520	88.574	−24.202	10.196	20.935	−10.785	10.599
Benzene-carbon tetrachloride	370–520	80.338	9.2778	60.009	−67.282	0	0
Benzene-ethanol	400–520	57.548	8.7569	40.738	−34.690	5.2699	6.4528

two components are mixed together, the mobility of the molecules is virtually unaffected because the intermolecular forces are almost unchanged by mixing. Thus, to a great extent, the vapor heat capacity of the binary system displays ideal behavior.

However, the measurements on the acetone-chloroform and benzene-ethanol vapors suggest far from ideal behavior. The former system displays positive deviations and the latter negative deviations with respect to the ideal linear additive values, as shown in Figs. 2 and 3 respectively. It follows that the effect of molecular interactions on the heat capacity the mixtures cannot be neglected, even in the vapor state.

The chloroform molecule has three chlorine atoms on the same carbon with an active hydrogen atom but has no donor atoms, whereas the acetone molecule contains a donor atom (oxygen) but no active hydrogen atom. Neither chloroform nor acetone can form intermolecular hydrogen bonds. But in the mixtures, acetone can form hydrogen bonds with chloroform, from the oxygen of acetone to the hydrogen of chloroform, i.e. $[(CH_3)_2C=O \cdots H-CCl_3]$ [15]. The chemical force of a hydrogen bond is much greater than van der Waals forces. For a given temperature increase and a constant amount of binary vapor, part of the heat input must first weaken or destroy the hydrogen-bonded complexes. As a result of this, much more heat input is needed for the associated vapors than for the ideal mixtures. Thus, the excess vapor heat capacities of the acetone-chloroform binary system are positive.

The ethanol molecule contains both an active hydrogen atom and a donor atom. Both linear and cyclic hydrogen bonds can be formed among the ethanol molecules, even in the vapor state. The association effect on the heat capacity for the pure alcohol has been investigated by Strömsoe et al. [16]. When such an associated vapor is mixed with non-polar vapors, such as benzene vapor, the hydrogen bond is weakened and, to some extent, destroyed. In other words, the degree of association decreases with respect to the ideal mixtures. In contrast to the hydrogen bond effect in the acetone-chloroform vapors, the heat capacities of ethanol-benzene vapors show negative deviations from ideality.

The lower the experimental temperature, the greater the excess vapor heat capacity for both the non-ideal binary systems. This can be attributed to the change in the degree of association of the molecules with temperature. With increase in temperature, the hydrogen bond becomes more and more weak. At high temperature, the van der Waals forces dominate, the association may be negligible, and the excess heat capacity is approximately zero.

5. Conclusions

Vapor heat capacities of three binary mixtures as a function to temperature have been measured with uncertainties of less than 0.7% in a multicomponent flow calorimeter constructed in this laboratory. The heat capacities of benzene-carbon tetrachloride vapors display ideal behavior, whereas those of the other systems under study are far from ideal. The vapor heat capacities of acetone-chloroform mixtures show positive deviations and those of ethanol-benzene mixtures show negative deviations from ideal linear additive values. The phenomena can be explained by the different intermolecular forces acting in the mixtures.

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