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Vapor heat capacity of binary and ternary systems

Fang Wen-jun*, Yu Qing-sen, Lin Rui-sen, Zong Han-xing

Department of Chemistry, Zhejiang University, Hangzhou, 310027, People's Republic of China

Abstract

The isobaric vapor heat capacities of five binary systems: ethanol–butanone, ethanol–benzene, ethanol–ethyl acetate, butanone–benzene and butanone–ethyl acetate and two ternary systems: ethanol–butanone–benzene and ethanol–butanone–ethyl acetate, with respect to compositions are determined at ca. 404.6 K and atmospheric pressure by using a constant-flow calorimeter. The accuracy of the calorimeter was checked by measuring the heat capacity of benzene and the benzene–carbon tetrachloride binary system for comparison with the literature data. The experiment error is less than 0.7%. The different changes of the vapor heat capacities with the compositions were discussed under the consideration of the different molecular interactions. Two well-known generalized equations of state were also selected for the estimation of the vapor heat capacities.

Keywords: Binary system; Calorimetry; Flow calorimeter; Heat capacity; Organic vapor; Ternary system

1. Introduction

Heat-capacity data are indispensable in thermodynamic calculation and engineering design. Accurate experimental results are of theoretical importance as they may be used to test and improve known procedures for estimating the heat capacity at constant pressure, C_p, and its deviation from that of ideal gas at the same conditions. The values of this residual heat capacity, ΔC_p, show the influence of pressure on the heat capacity. It can be calculated by substituting the experimental pressure–volume–temperature (PVT) data or the corresponding equation of state in the following rigorous relationship [1,2]:

$$\Delta C_p = \int_{\infty}^{V} T\left(\frac{\partial^2 P}{\partial T^2}\right)_v \mathrm{d}V - \frac{T(\partial P/\partial T)_v^2}{(\partial P/\partial T)_T} - R \tag{1}$$

As shown in Eq. (1), estimation of C_p from the generalized equations of state is not expected to be very accurate since it requires second-order derivatives. Reliable data on this important physical property are not abundant. So the direct measurement of the heat capacity at constant pressure is of academic and technical interest, especially for polar compounds and mixtures. For mixtures, there may exist excess heat capacity, C_p^E, which indicates the influence of the composition on the heat capacity of each mixture.

Flow calorimetry is the most direct and accurate method for the determination of the heat capacity [3,4]. This paper presents the calorimetric results of isobaric vapor capacity for two ternary systems, ethanol–butanone–benzene and ethanol–butanone–ethyl acetate, and their related binary mixture, with respect to compositions at about 404.6 K and atmospheric pressure in a constant-flow calorimeter. This work is a continuation of a program for measuring the heat capacity of multicomponent organic vapor. The purpose of the study was to investigate the effects of different polarity and different molecular interaction on the vapor heat capacities. As an attempt, the ability

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*Corresponding author.

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to calculate multicomponent vapor heat capacities using two equations of state often used in chemical engineering calculations was also investigated.

2. Experimental

2.1. Materials

All liquids, ethanol, benzene, carbon tetrachloride, butanone and ethyl acetate were purified by fractional distillation in a 1.5 m long column from analyzed reagent quality. No peaks of impurities can be observed for these liquids in the gas-chromatography analysis. Their refractive indexes and densities agree well with those reported in the literature [5]. Binary and ternary systems were prepared by weighing and mixing their respective components. The densities of the samples investigated were determined by DMA-45 digital density meter. The values are presented in Tables 1 and Table 2.

Table 1
The liquid densities of the samples for the binary systems at 303.15 K

x	$d/$ (g cm^{-3})	x	$d/$ (g cm^{-3})
$x$ethanol–(1 − x)butanone			
0.0000	0.7949	0.6548	0.7886
0.1914	0.7933	0.7746	0.7868
0.3654	0.7919	1.0000	0.7814
0.4989	0.7903		
$x$ethanol–(1 − x)benzene			
0.0000	0.8687	0.6489	0.8108
0.2003	0.8509	0.7971	0.7982
0.3534	0.8372	1.0000	0.7814
0.5025	0.8239		
$x$ethanol–(1 − x)ethyl acetate			
0.0000	0.8890	0.5154	0.8448
0.1266	0.8789	0.6556	0.8294
0.2714	0.8672	0.8082	0.8103
0.3634	0.8594	1.0000	0.7814
$x$butanone–(1 − x)benzene			
0.0000	0.8687	0.6498	0.8210
0.2018	0.8535	0.7970	0.8099
0.3433	0.8433	1.0000	0.7949
0.4989	0.8323		
$x$butanone–(1 − x)ethyl acetate			
0.0000	0.8890	0.6456	0.8293
0.1997	0.8705	0.7954	0.8149
0.3604	0.8560	1.0000	0.7949
0.4979	0.8433		

Table 2
The liquid densities of the samples for the ternary systems at 303.15 K

x_1	x_2	$d/$ (g cm^{-3})	x_1	x_2	$d/$ (g cm^{-3})
$x_1$ethanol–$x_2$butanone–(1 − x_1 − x_2)benzene					
0.2127	0.3101	0.8314	0.3279	0.5073	0.8061
0.1798	0.4842	0.8203	0.4926	0.1925	0.8181
0.3550	0.1597	0.8323	0.5003	0.3199	0.8065
0.3731	0.3139	0.8183			
$x_1$ethanol–$x_2$butanone–(1 − x_1 − x_2)ethyl acetate					
0.1665	0.3333	0.8435	0.3321	0.5028	0.8098
0.1680	0.4999	0.8272	0.4587	0.2347	0.8248
0.3105	0.2249	0.8413	0.5086	0.3280	0.8087
0.3346	0.3330	0.8277			

2.2. The calorimeter

The heat capacities for organic vapor of pure substances and multicomponent mixtures were measured in a flow calorimeter which was constructed in this laboratory. The apparatus has been described in detail in our previous papers [6,7]. A simplified diagram of the flow system is schematically shown in Fig. 1. In the calorimeter, the vapor flows through a thin-walled stainless steel tube (wall thickness 0.3 mm), which swaged tightly into grooves cut on the surface of two red copper blocks, at a known rate, F, and then the temperature rise, ΔT, due to a known heat input, E, is measured. The apparent heat capacity, $C_{p(\mathrm{app})}$, can be calculated from Eq. (2)

$$C_{p(\mathrm{app})} = E/(F\Delta T) \tag{2}$$

The apparent values of the heat capacity are plotted against the reciprocal of the rate and the true value, C_p, is obtained by extrapolation to infinite rate of flow.

$$C_{p(\mathrm{app})} = C_p + b/F \tag{3}$$

where b is a correlating factor, characteristic of the calorimeter, $C_{p(\mathrm{app})}$ was determined at five or more different flow rates in the (0.1–6.6) ml min^{-1} range. The rate was checked by collecting a timed sample,

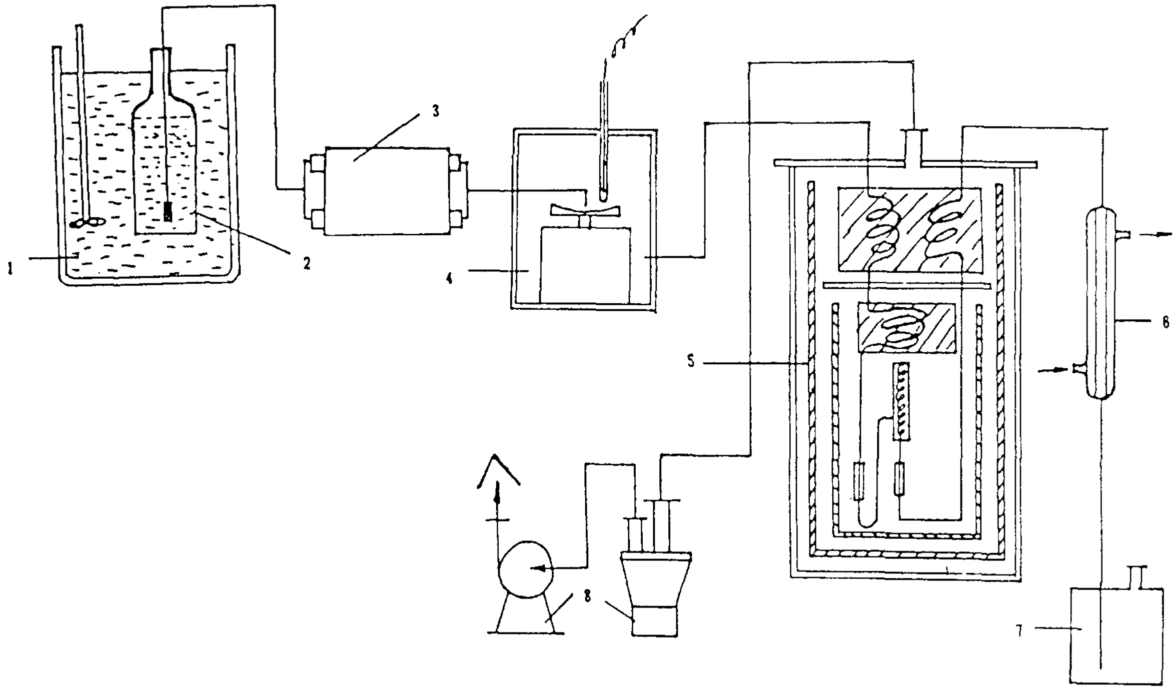

Fig. 1. Schematic diagram of the flow calorimeter system: (1) – water-bath thermostat; (2) – sample tank; (3) – WGP-6 type high-pressure metering pump; (4) – flash boiler; (5) – calorimeter; (6) – water condenser; (7) – container; and (8) – vacuum system.

which showed that the flow rate was stable to within 0.05%. The compositions of the sample before and after vaporization were tested by measuring the density and refractive index. The changes were not in excess of $2 \times 10^{-4}\,\mathrm{g\,cm^{-3}}$ for the density, and 2×10^{-4} for the refractive index.

The accuracy of the calorimeter was checked by measuring the heat capacity of benzene and the benzene–carbon tetrachloride binary system, and comparing these values with the literature data. The experimental error is less than 0.7% [7].

3. Results and discussion

Table 3 presents the calorimetric results of isobaric vapor heat capacities for five binary systems, ethanol–butanone, ethanol–benzene, ethanol–ethyl acetate, butanone–benzene and butanone–ethyl acetate and two ternary systems, ethanol–butanone–benzene and ethanol–butanone–ethyl acetate, with respect to compositions at 404.6 K and atmospheric pressure. The heat-capacity changes, with composition at constant temperature for the binary systems, are given in Fig. 2.

As seen from the results, the plots of butanone–ethyl acetate and butanone–benzene systems are nearly straight lines and their excess vapor heat capacities are nearly zero, whereas that of ethanol–benzene is slightly concave and the excess heat capacities are negative, those of ethanol–butanone, ethanol–ethyl acetate are a little convex and the excess heat capacities are positive. The different phenomena may be mainly ascribed to the different intermolecular forces in the different systems.

Even in the vapor phase of ethanol, there exist many types of hydrogen-bonded complex (cyclic or linear) [8]. Formation of hydrogen-bonded complexes will stabilize the system since this hydrogen-bonding force is stronger than the usual van der Waals forces. Much more heat input must be presented to an associated vapor than in the case where van der Waals forces alone act under the same conditions of composition, temperature and pressure. When such an associated

Table 3
The vapor heat capacities of binary systems at 404.6 K and atmospheric pressure

y	C_p/ (J mol^{-1} K^{-1})	y	C_p/ (J mol^{-1} K^{-1})
$y$ethanol–(1 − y)butanone			
0.0000	131.23	0.6548	107.12
0.1914	123.08	0.7746	99.69
0.3654	115.33	1.0000	85.88
0.4989	111.56		
$y$ethanol–(1 − y)benzene			
0.0000	115.78	0.6489	94.20
0.2003	108.17	0.7971	89.39
0.3534	103.48	1.0000	85.88
0.5025	98.47		
$y$ethanol–(1 − y)ethyl acetate			
0.0000	142.07	0.5154	118.55
0.1266	135.41	0.6556	111.25
0.2714	127.15	0.8082	101.34
0.3634	124.02	1.0000	85.88
$y$butanone–(1 − y)benzene			
0.0000	115.78	0.6498	125.52
0.2018	118.51	0.7970	128.89
0.3433	120.71	1.0000	131.23
0.4989	123.25		
$y$butanone–(1 − y)ethyl acetate			
0.0000	142.07	0.6456	135.03
0.1997	139.39	0.7954	133.57
0.3604	138.80	1.0000	131.23
0.4979	136.83		

vapor is mixed with benzene, a non-polar vapor, the hydrogen bond may be weakened or destroyed. The molecules become more mobile and more sensitive to heat. Thus, the excess heat capacity of ethanol–benzene is negative.

When however ethanol vapor is mixed with butanone or ethyl acetate, the new hydrogen-bonded complexes may be formed between ethanol and butanone molecules or between ethanol and ethyl acetate molecules. In addition, it is difficult for butanone or ethyl acetate to form hydrogen bonds among the same kind of molecules. Thus, in mixtures of ethanol–butanone and ethanol–ethyl acetate, the heat capacities are a little greater than the linear additive values due to the more hydrogen-bonded complexes exist. The positive excess heat capacities can then be found for such binary systems.

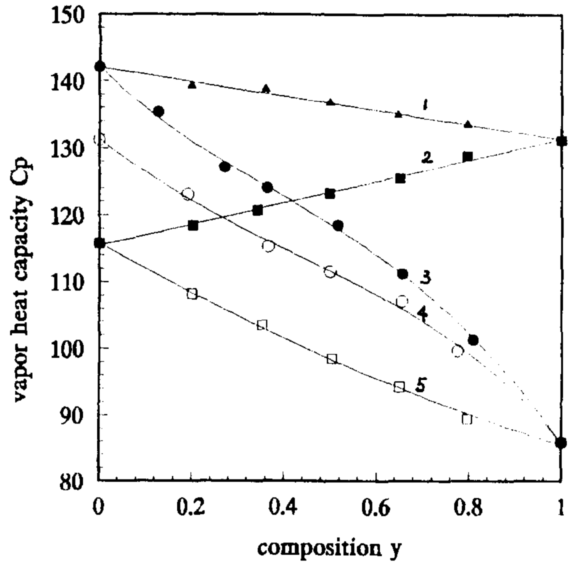

Fig. 2. The heat capacities of binary vapors at 404.6 K and atmospheric pressure:(1) – yC$_2$H$_5$COCH$_3$–(1 − y)CH$_3$COOC$_2$H$_5$; (2) – yC$_2$H$_5$COCH$_3$–(1 − y)C$_6$H$_6$; (3) – yC$_2$H$_5$OH–(1 − y)CH$_3$COOC$_2$H$_5$; (4) – yC$_2$H$_5$OH–(1 − y)C$_2$H$_5$COCH$_3$; and (5) – yC$_2$H$_5$OH–(1 − y)C$_6$H$_6$.

For the binary mixture of butanone-ethyl acetate and butanone–benzene, either the same, or different kinds of molecules can hardly form any associated complexes through chemical forces, such as hydrogen bonding, though butanone and ethyl acetate are polar components. The changes of total molecular interactions are very small because there exist only van der Waals forces in these mixtures. As a result, the vapor heat capacities of the binary systems display linear additivity (see Table 4).

Moreover, two well-known generalized equations of state, the Lee–Kesler EOS [9] and the Martin–Hou EOS [10,11], and their mixing rules were considered to calculate the vapor heat capacities of the investigated binary and ternary systems. The average absolute deviations (AAD) of calculated results for the mixtures are presented in Table 5. As shown in Table 5, relatively better estimations are given by the Martin–Hou EOS. But the calculated deviations of these two equations are a little larger than the inaccuracy of the observed data. This may be ascribed to the drawback of the method of heat-capacity estimation using equations of state.

Table 4
The vapor heat capacities of ternary systems at 404.6 K and atmospheric pressure

y_1	y_2	$C_p/$ (J mol^{-1} K^{-1})	y_1	y_2	$C_p/$ (J mol^{-1} K^{-1})
$y_1$ethanol–$y_2$butanone–$(1-y_1-y_2)$benzene					
0.2127	0.3101	113.33	0.3279	0.5073	117.48
0.1798	0.4842	116.35	0.4926	0.1925	101.44
0.3550	0.1597	106.60	0.5003	0.3199	103.86
0.3731	0.3139	114.17			
$y_1$ethanol–$y_2$butanone–$(1-y_1-y_2)$ethyl acetate					
0.1665	0.3333	127.69	0.3321	0.5028	123.21
0.1680	0.4999	130.35	0.4587	0.2347	118.50
0.3105	0.2249	126.26	0.5086	0.3280	114.26
0.3346	0.3330	126.76			

Table 5
The deviation of calculated results by EOS from the observed vapor heat capacity results

System	Data point	Lee–Kesler		Martin–Hou	
		ADD(%)	Max(%)	ADD(%)	Max(%)
Ethanol–butanone	7	1.87	3.07	1.56	2.60
Ethanol–benzene	7	0.82	2.83	0.94	2.36
Ethanol–ethyl acetate	8	1.85	3.48	1.64	2.93
Butanone–benzene	7	0.70	2.35	0.47	1.75
Butanone–ethyl acetate	7	1.39	2.31	0.50	1.67
ethanol-butanone-benzene	7	1.85	3.82	1.71	3.74
ethanol-butanone-ethyl acetate	7	1.31	3.95	1.10	2.57

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