ELSEVIER

Thermochimica Acta 352–353 (2000) 19–23

thermochimica acta

www.elsevier.com/locate/tca

Vapor heat capacities of some polar–polar binary systems

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

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

Received 2 June 1999; received in revised form 10 August 1999; accepted 6 September 1999

Abstract

The calorimetric results of isobaric vapor heat capacities are presented by using a constant-flow calorimeter for five polar–polar binary systems, acetone–butanone and chloroform–ethyl acetate at 402.2 K, ethanol–methanol, ethanol–*n*-propanol and ethanol–*n*-butanol at 402.2 and 441.3 K, with respect to compositions at atmospheric pressure. The residual heat capacities and the excess heat capacities of the mixtures are calculated. Relatively significant values of the residual heat capacity are observed even at atmospheric pressure in these polar–polar binary systems. The excess vapor heat capacities of acetone–butanone system are nearly zero, but those of other polar–polar systems have relatively large positive values. These results are discussed under the consideration of the changes of the intermolecular forces. Furthermore, two well-known generalized equations of state are chosen for the estimation of the vapor heat capacities of these binary mixtures. Comparison between the calculated and the experimental results indicates that the two equations of state may be used to the vapor heat capacity estimation near atmospheric pressure even for polar systems. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Binary mixture; Calorimetry; Constant-flow calorimeter; Equation of state; Heat capacity; Organic vapor

1. Introduction

The heat capacity as a function of composition, temperature and pressure is a basic quantity for evaluation of thermodynamic properties of a given chemical system. The heat capacities at constant pressure, C_p, of liquids and solids can be measured in relatively simple experiments, and the heat capacity values of gases at zero pressure (ideal gases), C_p^{id}, are easily obtained from statistical thermodynamics and spectroscopic data, whereas the accurate heat capacity values for real gases have been scarcely reported, especially for organic vapors of polar compounds and their mixtures which exist in liquid state at room temperature and atmospheric pressure. Therefore, the direct calorimetric determination of the vapor heat capacities of mixtures is of interest in our thermochemistry laboratory.

The present work is a continuation of a program [1–3] for measuring the heat capacity of multicomponent organic vapors and investigating the effects of polarity and intermolecular actions on the heat capacities. The vapor heat capacities of five polar–polar binary systems with respect to compositions at atmospheric pressure are presented and the ability to calculate the binary vapor heat capacities using two equations of state, which are often used in chemical engineering calculations, was also investigated.

---

[*] Corresponding author.

PII: S0040-6031(99)00431-1

2. Experimental

2.1. Materials

All pure organic compounds used were obtained from Shanghai Chemical Corporation China. Absolute ethanol with a purity better than 99.9% as claimed by the supplier was used without further purification. The other liquids: acetone, butanone, chloroform, ethyl acetate, methanol, *n*-propanol and *n*-butanol($\geqslant$99.5%, respectively) were all analytical reagent grade and were treated by appropriate procedures introduced by Riddick et al. [4]. They were further purified by fractional distillation in a 1.5-m-long column. No peaks of impurities can be observed for these liquids in the gas chromatography analysis. Binary mixtures were prepared by weighing and mixing their respective components. A Mettlar balance, Switzerland, with a precision of 0.0001 g was used. Precautions were taken in order to minimize evaporation losses during storage and preparation of the solutions. Densities, ρ, of pure liquids were measured to 0.0001 g cm^{-3} with an Anton Paar, DMA-45 digital densimeter. Refractive indices, n_D^{20}, were measured using an Abbe's refractometer. The measured values agree well with those reported in the literature [4].

2.2. Calorimeter

The vapor heat capacities of the binary systems with respect to compositions at atmospheric pressure were measured in a constant-flow calorimeter, which was constructed in this thermochemistry laboratory. The principle, structure and operation of the apparatus has been described in detail in our previous papers [2,5].

For every sample, the values of the apparent heat capacity, $C_{p(\mathrm{app})}$, which were measured at five or more different flow rates in the (0.008–1.667) mmol s^{-1} range, are plotted against the reciprocal of the rate and the true value, C_p, is then obtained by extrapolation to infinite rate of flow:

$$C_{p(\mathrm{app})} = C_p + \frac{b}{F} \tag{1}$$

where b is a correlating factor, characteristic of the calorimeter. Collecting a timed sample, which showed that the flow rate was stable to within 0.05%, checked the flow rate. Measuring the density and refractive index tested the compositions of the sample before and after evaporation. The changes were not in excess of 2×10^{-4} g cm^{-3} for the density, and 2×10^{-4} for the refractive index. Given the relatively small pressure drop through the calorimeter, the energy errors due to the Joule–Thomson effect were negligible. The overall uncertainty in the vapor heat capacity measurements by the calorimeter is less than 0.7% [5].

3. Results and discussion

The calorimetric results of isobaric vapor heat capacities for five polar–polar binary systems, acetone–butanone and chloroform–ethyl acetate at 402.2 K, ethanol–methanol, ethanol–*n*-propanol and ethanol–*n*-butanol at 402.2 and 441.3 K, with respect to compositions at atmospheric pressure are obtained. The heat capacity changes with composition at constant temperature for the binary systems are given in Figs. 1 and 2.

The values of the residual heat capacity, ΔC_p, and the excess heat capacity, C_p^E, which indicate the

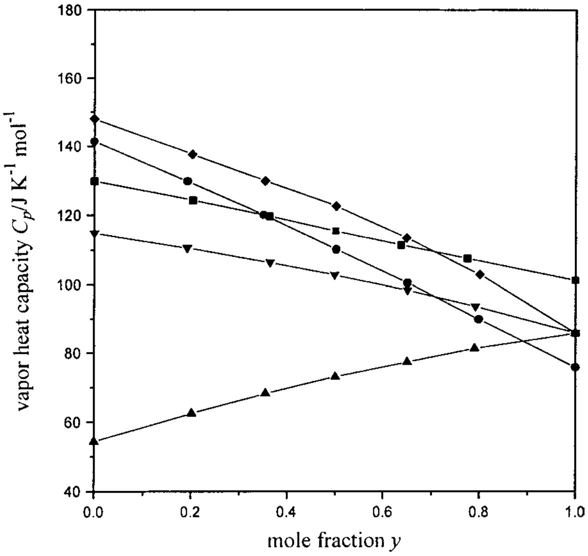

Fig. 1. The vapor heat capacities of polar–polar binary systems at 402.2 K and atmospheric pressure. (■) y acetone–$(1-y)$ butanone; (●) y chloroform–$(1-y)$ ethyl acetate; (▲) y ethanol–$(1-y)$ methanol; (▼) y ethanol–$(1-y)$ *n*-propanol; (◆) y ethanol–$(1-y)$ *n*-butanol.

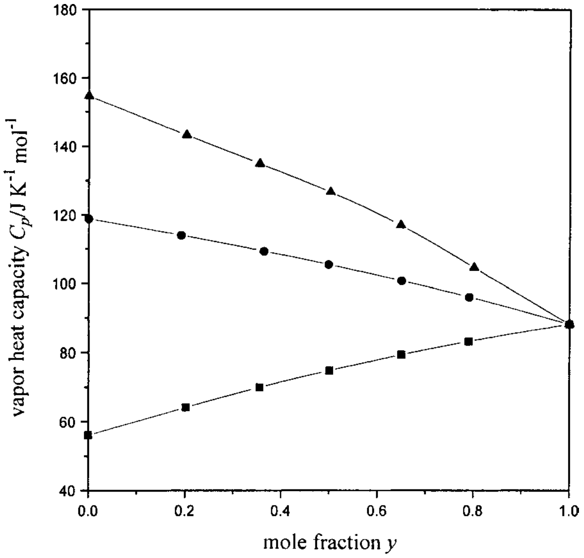

Fig. 2. The vapor heat capacities of polar–polar binary systems at 441.3 K and atmospheric pressure. (■) y ethanol–$(1-y)$ methanol; (●) y ethanol–$(1-y)$ n-propanol; (▲) y ethanol–$(1-y)$ n-butanol.

respective influence of the pressure and the composition on the vapor heat capacity of each mixture, are calculated, respectively, as follows:

$$\Delta C_p = C_p - yC_{p,1}^{\mathrm{id}} - (1-y)C_{p,2}^{\mathrm{id}} \tag{2}$$

$$C_p^{\mathrm{E}} = C_p - yC_{p,1} - (1-y)C_{p,2} \tag{3}$$

where C_p is the experimental vapor heat capacity of the mixture, $C_{p,1}$ and $C_{p,2}$ are the experimental vapor heat capacities of the pure components 1 and 2 at the same temperature and pressure as the mixture, respectively. $C_{p,1}^{\mathrm{id}}$and $C_{p,2}^{\mathrm{id}}$, which are calculated from Reid et al. [6], are the gaseous heat capacities of the pure components 1 and 2 at zero pressure and at the same temperature as the mixture, respectively, and y is the molar fraction of the component 1 in each mixture. From the experimental data and Eqs. (2) and (3), the values of ΔC_p and C_p^{E} are calculated and listed in Table 1.

For the investigated binary systems, the components, acetone, butanone, chloroform, ethyl acetate, methanol, ethanol, n-protanol and n-butanol, are all strong polar substances with the dipole moments of 2.9, 3.3, 1.1, 1.9, 1.7, 1.7, 1.7 and 1.8 debye [6], respectively. Among the assembly of polar molecules, the electrostatic force plays a dominant role in the various intermolecular actions. The strong dipole–dipole interaction makes the dipolar molecules form oriented arrangements and stabilizes the system. As a result, much more heat input must be presented to this polar system, to weaken or to destroy the oriented arrangements, than to the non-polar system which mainly has dispersion force. Furthermore, the vapor heat capacities at constant pressure have obvious deviations from the values of the ideal gaseous system at zero pressure, in which there exist no intermolecular actions. Relatively significant values of ΔC_p even at atmospheric pressure are then observed in these polar–polar binary systems.

As seen from the results, the plots of acetone–butanone system is nearly a straight line. It indicates the excess vapor heat capacities are nearly zero, or the values are not large enough to be detected by this apparatus. But those of other polar–polar systems, chloroform–ethyl acetate at 402.2 K, ethanol–methanol, ethanol–n-propanol and ethanol–n-butanol at 402.2 and 441.3 K are all a little convex with relatively significant positive C_p^{E} values. These results may be also mainly ascribed to the intermolecular forces in the systems. Although both acetone and butanone are strong polar substances, the molecular structures and the properties of them are very similar and the changes of total intermolecular actions are very small before and after mixing.

Thus the vapor heat capacities of the binary system display linear additions. In chloroform–ethyl acetate (acidic proton+Lewis base) system, the two kinds of unlike molecules may associate, and the freedom of mobility of the molecules is then decreased. The overall mixture is therefore less sensitive to heat input compared with the corresponding pure components, which results in positive C_p^{E} values. In the vapor phase of alcohol, there exist cyclic and linear types molecular clusters due to the hydrogen bonding [7]. Furthermore, the strong cross hydrogen bonded complexes may be formed in the mixtures. Formation of these complexes may result in more stable molecular clusters and stabilize the mixture system to a great extent since this hydrogen-bond force is much stronger than the usual van der Waals forces such as dispersion force and electrostatic force. As experimental macro-results, relatively large positive C_p^{E} values of the vapor heat capacity of alcohol–alcohol binary systems are then measured.

Table 1
The residual heat capacity, ΔC_p (J K^{-1} mol^{-1}), and the excess heat capacity, C_p^{E}(J K^{-1} mol^{-1}), of polar–polar binary systems at atmospheric pressure

y	ΔC_p[a]	C_p^{E}[a]	ΔC_p[b]	C_p^{E}[b]	y	ΔC_p[a]	C_p^{E}[a]	ΔC_p[b]	C_p^{E}[b]
y acetone–(1−y)butanone									
0.0000	4.07	0.00			0.6362	7.07	−0.12		
0.2035	5.26	0.19			0.7742	7.73	−0.14		
0.3623	6.01	0.16			1.0000	8.98	0.00		
0.5014	6.40	−0.13							
y chloroform–(1−y) ethyl acetate									
0.0000	2.33	0.00			0.6505	3.25	1.71		
0.1929	3.21	1.11			0.7985	2.22	0.85		
0.3508	3.54	1.63			1.0000	1.12	0.00		
0.5020	3.47	1.75							
y ethanol–(1−y)methanol									
0.0000	2.28	0.00	0.98	0.00	0.6498	6.08	2.66	3.34	2.48
0.2020	4.45	1.82	2.69	1.74	0.7897	5.78	2.11	2.64	1.80
0.3556	5.57	2.66	3.40	2.49	1.0000	4.10	0.00	0.80	0.00
0.5007	6.10	2.94	3.61	2.72					
y ethanol–(1−y) *n*-propanol									
0.0000	5.80	0.00	2.04	0.00	0.6504	7.00	2.30	3.16	1.93
0.1918	6.79	1.31	2.85	1.04	0.7913	6.21	1.76	2.55	1.49
0.3642	7.29	2.11	3.30	1.71	1.0000	4.10	0.00	0.80	0.00
0.4988	7.34	2.39	3.40	1.98					
y ethanol–(1−y) *n*-butanol									
0.0000	9.79	0.00	6.53	0.00	0.6479	11.87	5.76	8.20	5.38
0.2023	10.84	2.20	7.41	2.04	0.8006	9.92	4.68	5.16	3.22
0.3544	11.75	3.98	8.36	3.86	1.0000	4.10	0.00	0.80	0.00
0.5018	12.82	5.88	8.98	5.33					

[a] T=402.2 K.
[b] T=441.3 K.

In chemical engineering process, the heat capacity of fluids at constant pressure is usually estimated from the ideal gaseous heat capacity, C_p^{id}, and the residual heat capacity, ΔC_p, which was calculated by substituting the experimental pressure–volume–temperature (*P*–*V*–*T*) data or the corresponding equation of state (EOS) in the following rigorous relationship [8,9]:

$$\Delta C_p = \int_{\infty}^{V} \left(\frac{\partial^2 P}{\partial T^2}\right)_v \mathrm{d}V - \frac{T(\partial P/\partial T)_v^2}{(\partial P/\partial V)_T} - R \quad (4)$$

In this work, two well known generalized equations of state, Lee–Kesler EOS [10],

$$Z = \frac{P_{\mathrm{r}} V_{\mathrm{r}}}{T_{\mathrm{r}}} = 1 + \frac{B}{V_{\mathrm{r}}} + \frac{C}{V_{\mathrm{r}}^2} + \frac{D}{V_{\mathrm{r}}^5} + \frac{c_4}{T_{\mathrm{r}}^3 V_{\mathrm{r}}^2}\left(\beta + \frac{\gamma}{V_{\mathrm{r}}^2}\right)\exp\left(-\frac{\gamma}{V_{\mathrm{r}}^2}\right) \quad (5)$$

and Martin–Hou EOS [11,12],

$$P = \frac{RT}{V-b} + \frac{A_2 + B_2 T + C_2 \exp(-kT_{\mathrm{r}})}{(V-b)^2} + \frac{A_3 + B_3 T + C_3 \exp(-kT)}{(V-b)^3} + \frac{A_4 + B_4 T}{(V-b)^4} + \frac{B_5 T}{(V-b)^5} \quad (6)$$

are chosen because the former is widely recommended in the application to thermodynamic functions calculation [6,13] and the latter can be used well to strong polar fluids such as alcohol, water and freon [12,14]. Combining Eqs. (4)–(6) and the corresponding mixing rules of the two equations of state, the vapor heat capacities of investigated mixtures are estimated. The average absolute deviations (AAD) and the maximum deviations of calculated results are presented in

Table 2
The deviation of calculated results by two equations of state from the observed vapor heat capacity results

System	*T* (K)	Data point	Lee–Kesler		Martin–Hou	
			AAD (%)	Max (%)	AAD (%)	Max (%)
Acetone–butanone	402.2	7	0.88	3.17	0.55	1.79
Chloroform–ethyl acetate	402.2	7	0.24	0.92	0.19	0.42
Ethanol–methanol	402.2	7	0.94	2.20	0.90	1.81
	441.3	7	0.98	2.32	0.43	0.79
Ethanol–*n*-propanol	402.2	7	0.54	1.75	0.47	1.37
	441.3	7	0.41	1.54	0.41	1.17
Ethanol–*n*-butanol	402.2	7	0.87	1.96	1.07	1.92
	441.3	7	0.50	1.94	0.76	1.82

Table 2. As shown of the maximum deviation of each system in Table 2, relatively better estimations are given by Martin–Hou EOS. But in general, both of the two equations of state give comparable good calculation results with the AAD values less than 1% on the whole. Comparison between the calculated and the experimental results indicates that the two equations of state may be used to estimate vapor heat capacity near atmospheric pressure even for polar systems.

References

[1] Q. Yu, W. Fang, H. Zong, R. Lin, Thermochim. Acta 275 (1996) 173.

[2] W. Fang, Q. Yu, R. Lin, H. Zong, Thermochim. Acta 299 (1997) 43.

[3] W. Fang, Q. Yu, H. Zong, R. Lin, Fuel 77 (1998) 895.

[4] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents. Physical Properties and Methods of Purification Techniques of Chemistry, 4th Edition, Wiley, New York, 1986.

[5] Y. Wu, Q. Yu, H. Zong, R. Lin, Thermochim. Acta 254 (1995) 93.

[6] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, 4th Edition, McGraw-Hill, New York, 1987.

[7] J. Gmehing, D.D. Liu, J.M. Prausnitz, Chem. Eng. Sci. 34 (1979) 951.

[8] R. Solimando, M. Rogalski, Thermochim. Acta 211 (1992) 1.

[9] D. Garipis, M. Stamatoudis, AIChE J. 38 (1992) 302.

[10] B.I. Lee, M.G. Kesler, AIChE J. 21 (1975) 510.

[11] J.J. Martin, Y.C. Hou, AIChE J. 1 (1955) 142.

[12] Y.C. Hou, B. Zhang, H.Q. Tang, J. Chem. Ind. Eng. (China) 32 (1981) 1.

[13] API, Technical Data Book — Petroleum Refining, Vol. 2, API, Washington, 1983 (Chapter 7).

[14] G.S. Chen, Z.L. Wu, Z.X. Chen, Y.C. Hou, Fluid Phase Equlibria 65 (1991) 145.