HEAT CAPACITIES OF SOME ALKYL ACETATES AT 295–323 K

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Molar heat capacities $C_{p,m}$ at constant atmospheric pressure have been determined with a typical uncertainty of about 0.3% for eight liquid alkyl acetates $H(CH_2)_nOCOCH_3$ ($n = 6–12$, 14), over the temperature range 295–323 K. The $C_{p,m}$ values were found to be a linear function of temperature. A comparison of experimental data with those predicted by the group additivity method demonstrated a rather limited capability of the additivity scheme to predict correctly the $C_{p,m}$ values for higher ($n > 10$) homologues in the series.
Key words: Heat capacity; n-Alkyl acetates.

The liquid heat capacity, $C_{p,l}$, is an important physicochemical property of pure liquids used, for instance for calculations of the vapor pressure behavior of liquids at low pressures[1] or for correction and standardization of the gas chromatography-based enthalpies of vaporization[2]. For higher n-alkyl acetates, which are pheromonal components of lepidopteran moths, knowledge of these properties at ambient temperature is essential to model and/or optimize their applications involving synthetic pheromone blends in insect pest control strategies. Unfortunately, only scarce physicochemical data, including heat capacities, are available for this class of compounds. To our knowledge, data concerning the temperature dependence of $C_{p,l}$ are only available for low members of the acetate homologous series, from methyl to hexyl acetate[3]. In addition, the $C_{p,l}$ data for octyl and decyl acetates at the single temperature of 298 K have also been reported[4].

The objective of this study is (i) to provide liquid heat capacity data for n-alkyl acetates $H(CH_2)_nOCOCH_3$ with n varying from 6 to 14 and their temperature dependence over the range of 295 to 323 K, and (ii) to check the prediction potential of the group contribution method[5] currently recommended for predicting the temperature dependence of heat capacities by using the observed experimental $C_{p,l}$ data of acetates as a validation set.

EXPERIMENTAL

Acetate samples were prepared by esterification of the corresponding pure (>99%) alcohols (Fluka) and purified by liquid chromatography (light petroleum–ethyl acetate, gradient) and subsequent fractional distillation on a packed column. The dryness of the samples was checked by the standard Fischer test and their final purity by GC on fused silica capillary column (HP-1, 25 m). Density measurements for each acetate were made at 298.15 K using a PAAR-A 45 vibrational densimeter. Characteristic data of the compounds are summarized in Table I.

All heat capacity measurements were performed in an adiabatic type calorimeter with a small controlled heat flux from the warmer calorimetric vessel to the colder controlling thermostatted wall. The calorimetric vessel had volume 11 cm^3 and, after being filled with the substance at atmospheric pressure, the remaining vapor space was about 0.5 cm^3. The ratio of the heat capacity of the empty vessel to the capacity of the full one was approximately 0.6. The temperature increase during measurement was about 3–10 K and the heat capacity values obtained refer to the average temperature of this interval. Both the device and procedure have been described in detail previously[9]. The accuracy of the measurement was tested using heptane as a reference material and performing measurements over the same temperature range. A comparison between the experimental and literature[3] results showed a mean deviation of about 0.3%. The heat capacity data for acetates can be expected to have similar errors as the heptane results.

RESULTS AND DISCUSSION

The measured values of molar heat capacities for all acetates at five temperatures are given in Table II. Note that the experiments were made far below the normal boiling temperature for each substance, in the low-vapor pressure region. Therefore, the data at atmospheric pressure can be regarded as the isobaric heat capacities.

TABLE I
Specification of n-alkyl acetates $H(CH_2)_n$–$OCOCH_3$

Acetate[a]	Purity (GC) %	d^b, g cm^{-3}
6	99.9	0.86848 (0.8679[c], 0.8688[d], 0.8686[e])
7	99.9	0.86623 (0.8656[c], 0.8664[d])
8	99.9	0.86415 (0.8630[c], 0.8656[d], 0.8644[e])
9	99.9	0.86275 (0.8612[c])
10	99.4	0.86130 (0.8628[d], 0.8623[e])
11	99.8	0.86101
12	99.5	0.85978 (0.8593[c], 0.8597[e])
14	98.6	0.85877 (0.8581[c], 0.8584[e])

[a] The codes of acetates are based on the number of –CH_2– groups, n. [b] Density at 25 °C, literature values in parentheses. [c] Ref.[6]. [d] Ref.[7]. [e] Values calculated from the linear d vs T relationships (ref.[8]).

In the temperature range of 295 K to 325 K, the molar heat capacities, $C_{p,m}$, were found to be linearly dependent on temperature according to the equation

$$C_{p,m}/R = a + bT \ , \tag{1}$$

where R is the universal gas constant.

The parameters a and b of Eq. (*1*) based on a least-squares fit of the data are given in Table III together with the corresponding standard errors. A comparison between the temperature dependences of heat capacities determined here and those reported previously[3,4] shows (Fig. 1) that both data sets are mutually consistent with rather similar differences in $C_{p,m}$ corresponding approximately to 30 J K^{-1} mol^{-1} per CH$_2$ group. Note that the trends observed for acetates **6–14**, while varying temperature, follow those for acetates **1–6** in a consistent fashion. The largest deviation from the general behavior show the previously reported data for pentyl[3] and decyl acetates[4]. However, the old literature data for pentyl acetate suffer from a relatively low precision, while the reported[4] single value for decyl acetate appears to be a print error. Errors associated with the $C_{p,m}$ data given in Table II are difficult to assess directly since only a few literature data of uncertain quality are available. Taking into account the mutually consistent picture shown in Fig. 1 for the complete ($n = 1$ to 14) acetate homologous series and assuming that the literature values for **6** and **8** are correct, the maximum error of 1.8% might be estimated.

TABLE II
Molar heat capacities (J K^{-1} mol^{-1}) of n-alkyl acetates at various temperatures (K)

Acetate[a]	Temperature				
	300.295	305.007	309.739	314.270	318.809
6	288.2	289.5	292.1	292.7	295.0
7	316.2	317.4	319.5	321.8	322.4
8	346.2	350.1	361.1	354.0	355.1
9	375.9	377.2	379.9	381.3	384.3
10	406.4	407.7	411.1	412.5	413.8
11	441.2	442.9	446.1	447.4	449.7
12	471.7	474.1	478.9	480.0	483.9
14	534.0	536.9	539.8	542.7	546.7

[a] For numbering of acetates see Table I.

Our alkyl acetate series is an attractive validation set for testing the predictive power of additivity schemes that correlate heat capactities with molecular structure. Accordingly, we compared our experimental $C_{p,m}$ data with those predicted by a second-order group additivity method by Ruzicka and Domalski[5] which permits the estimation of the heat capacity as a function of temperature. It is based on the standard additivity-scheme equation $C_{p,m}/R = \Sigma n_i \Delta C_i$ with the ΔC_i term expressed as

$$\Delta C_i = a_i + b_i T/100 + d_i(T/100)^2 , \tag{2}$$

where n_i is the number of structural increments ΔC_i, and a_i, b_i and d_i are tabulated[5] adjustable parameters, and T is temperature in K.

The results of this comparison are shown in Fig. 2. It may be observed that the predicted values for acetates up to $n = 10$ fit the observed data very well, the error not exceeding 0.5%. For acetates with $n > 10$ the error of prediction gradually increases, approaching about 3% for tetradecyl acetate. To explain this behavior, let us briefly examine the $C_{p,m}$ data of n-alkyl acetates as a function of the number of methylene groups. Taking the temperature of 298.15 K as a reference point, the average –CH$_2$– increment for acetates **6** to **10** is 29.55 J K^{-1} mol^{-1} while it amounts to 31.72 J K^{-1} mol^{-1} for acetates **10** to **14**. If the data down to $n = 1$ are considered, an average increment of 28.16 J K^{-1} mol^{-1} may be found[3,10] for acetates with n up to 4. This trend demonstrates that
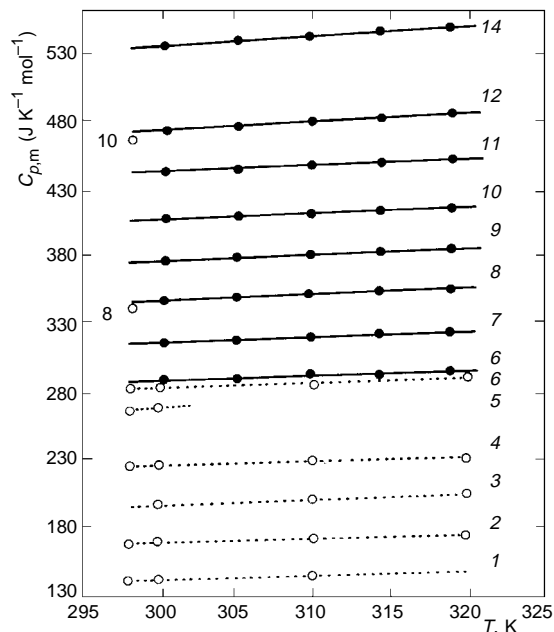

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Temperature dependences of the $C_{p,m}$ data for n-alkyl acetates. A comparison of our experimental (●) and literature[3,4] (○) data. Numbering of curves corresponds to the code of compounds

the methylene group contribution to $C_{p,\mathrm{m}}$ slightly increases with the chain length in the acetate homologous series and can be hardly averaged by a single value of 29.79 J K^{-1} mol^{-1} as it follows from the group contribution method. A similar dependence of the –CH$_2$–

TABLE III
Parameters in Eq. (1) correlating heat capacities of acetates with temperature

Acetate[a]	a	$10^2 \cdot b$, K^{-1}	s^b, J K^{-1} mol^{-1}
6	21.43	4.40	0.06
7	24.90	4.37	0.06
8	24.64	5.69	0.10
9	28.88	5.42	0.07
10	33.53	5.11	0.07
11	36.18	5.62	0.05
12	33.14	7.86	0.10
14	39.94	8.08	0.05

[a] For numbering of acetates see Table I. [b] Standard error of the estimate $s = [\Sigma(C_{p,\mathrm{m}}^{\mathrm{exp}} - C_{p,\mathrm{m}}^{\mathrm{calc}})^2/(N - N_{\mathrm{p}})]^{0.5}$ where the superscripts exp and calc denote the experimental and calculated $C_{p,\mathrm{m}}$ values, N is the total number of heat capacity points and $N_{\mathrm{p}} = 2$ is the number of coefficients in Eq. (1).
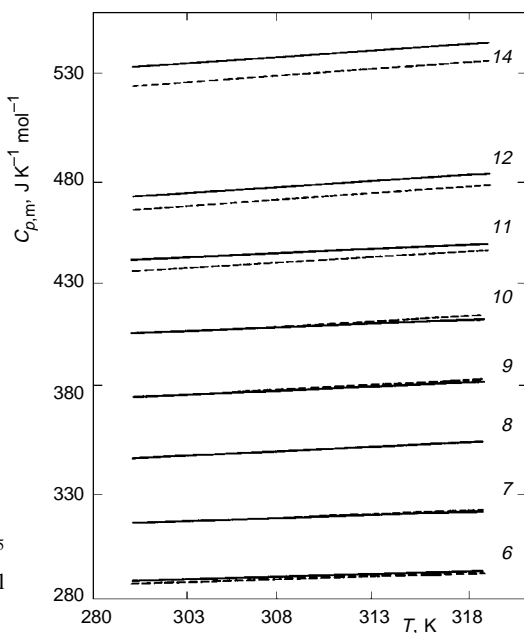

FIG. 2
Experimental (———) and predicted[5] (– – – –) molar heat capacities for n-alkyl acetates

increment on the number of carbon atoms in the chain has also been observed for other homologous classes of compounds, such as methyl alkanoates[10]. Bearing in mind that the group contribution values for homologous series are usually based on experimental measurements for only a few low-molecular-weight derivatives, they may not contain information that is vital for the successful representation of higher-molecular-weight homologues. As a consequence, the group additivity method exhibits progressively increasing deviations with chain increasing length.

Additional $C_{p,m}$ data of high accuracy that span a larger n in different homologous series are needed before a detailed re-evaluation of group contribution values can be made. However, until these data become available, the evidence given here suggests that the group contribution values provide a first estimate that should be viewed with some caution when applied to higher acetate homologues.

REFERENCES

1. Poling B. E.: Fluid Phase Equilib. *116*, 102 (1996).
2. Chickos J. S., Hosseini S., Hesse D. G.: Thermochim. Acta *249*, 41 (1995).
3. Zabransky M., Ruzicka V., Jr., Majer V., Domalski E. S.: *Heat Capacity of Liquids: Critical Review and Recommended Values*, Vol. I, II. J. Phys. Chem. Ref. Data, Monograph *6*, ACS, Washington D.C. 1996.
4. Deshpande D. D., Patterson D., Andreolli-Ball L., Costas M., Trejo L. M.: J. Chem. Soc., Faraday Trans. *87*, 1133 (1991).
5. Ruzicka V., Jr., Domalski E. S.: J. Phys. Chem. Ref. Data *22*, 597 (1993).
6. *TRC, Thermodynamic Tables; Non-Hydrocarbons*. Thermodynamic Research Center, The Texas A&M University System College Station, Suppl. No. 76, December 31, 1996.
7. Meyer E. F., Awe M. J., Wagner R. E.: J. Chem. Eng. Data *25*, 371 (1980).
8. Shigley J. W., Bonhorst C. W., Liang C. C., Althouse P. M., Triebold H. O.: J. Am. Oil Chem. Soc. *32*, 213 (1955).
9. Svoboda V., Zabransky M.: Collect. Czech. Chem. Commun. *56*, 2786 (1991).
10. Fuchs R.: J. Chem. Thermodyn. *11*, 959 (1979).