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Dependence of molar heat capacity of liquid alkanols C_3–C_5 on their structure [☆]

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Abstract

The dependence of molar heat capacities upon the molecular structure of isomeric alcohols C_3–C_5 is discussed in the liquid and ideal gas states. In general, the differences of the heat capacities for the ideal gas state are small in comparison to those for the liquid state. The larger differences for the liquid state are due to steric effects which occur during the formation of hydrogen bonds between molecules.

Keywords: Alcohol; Alkanol; Gas; Hydrogen bond; Isomer; Liquid; Molar heat capacity

1. Introduction

Significant attention is given to the alkanols from a molecular point of view because strong hydrogen bonding is present in these compounds. Hydrogen bonding has a considerable influence on many physical properties including heat capacity of the liquid. While the isobaric heat capacity of a pure compound in the ideal gas state can be computed from the spectral data, experimental measurements are necessary to obtain reliable results for the liquid state.

The temperature dependence of liquid heat capacity has been measured reliably for all the isomers of propanol, butanol, and several 1-alkanols [1]. For other isomeric alcohols, there are accessible either no data, very unreliable data, or data available from mixing measurements and often at one temperature only. Six of the

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eight existing isomers of pentanol were recently measured [2] although in the narrow temperature region from 303 to 326 K. (The measurements for 1-pentanol was carried out only for testing of the calorimeter used and 2,2-dimethyl-1-propanol was not studied due to its high melting temperature (about 323 K).)

From a knowledge of heat capacities of the isomeric alkanols from C_3 to C_5 at 303 K one can make a comparison of differences in heat capacity values which are related to their molecular structures, where it has shown that the structure of molecules of various isomers of the same alcohol in the liquid state has a significant influence on their heat capacity values. In order to study the cause of these differences, isobaric heat capacities of the same isomer in both liquid and ideal gaseous states as well as these values for various isomers with the same number of carbon atoms have been compared.

2. Computational part

Molar heat capacity in the liquid state can be predicted from the value of molar heat capacity in the ideal gas state, vaporization enthalpy and state behavior of the liquid. The difference between heat capacity of liquid and ideal gas can be expressed by means of the formula [3]

$$C^{\mathrm{l}}_{p,\mathrm{m}} - C^{\mathrm{g}\ominus}_{p,\mathrm{m}} = -\left(\frac{\mathrm{d}\,\Delta H_{\mathrm{vap,m}}}{\mathrm{d}T}\right)_{\mathrm{sat}} + \left[V^{\mathrm{l}}_{\mathrm{m}} - T\left(\frac{\partial V^{\mathrm{l}}_{\mathrm{m}}}{\partial T}\right)_p\right]\left(\frac{\mathrm{d}p}{\mathrm{d}T}\right)_{\mathrm{sat}} \tag{1}$$

where $\Delta H_{\mathrm{vap,m}}$ is the molar enthalpy of vaporization, $V^{\mathrm{l}}_{\mathrm{m}}$ is the molar liquid volume, p denotes the saturated vapor pressure and subscript sat refers to properties on the vapor–liquid saturation curve.

There are two terms on the right side of Eq. (1). The first corresponds to the temperature dependence of the molar enthalpy of vaporization while the second expresses the $p-V-T$ behavior of a liquid. The following relationship is valid in the second term:

$$V^{\mathrm{l}}_{\mathrm{m}} - T\left(\frac{\partial V^{\mathrm{l}}_{\mathrm{m}}}{\partial T}\right)_p = \left(\frac{\partial H^{\mathrm{l}}_{\mathrm{m}}}{\partial p}\right)_T \tag{2}$$

where $H^{\mathrm{l}}_{\mathrm{m}}$ is the molar enthalpy of a liquid. The changes of the molar enthalpy of liquids with respect to pressure is very small, while the derivation of the saturated vapor pressure with respect to temperature is not great enough to make the second term in Eq. (1) comparable with the first one. Therefore, it can be expected that the first term in Eq. (1) should be a main part of the heat capacity difference.

This assumption was confirmed by means of computations. The molar volumes $V^{\mathrm{l}}_{\mathrm{m}}$ were computed from the tabulated densities [4] and for a description of the temperature dependence of the liquid molar volume, the Rackett equation was used

$$V^{\mathrm{l}}_{\mathrm{m}} = \frac{RT_{\mathrm{k}}}{p} z_{\mathrm{k}}^{1+(1-T_{\mathrm{r}})^{2/7}} \tag{3}$$

where T_k denotes the critical temperature and z_k the critical compressibility factor. To increase reliability of computations, the value of z_k was evaluated from the experimental values of liquid density ϱ at given reduced temperature T_r

$$z_k = \left(\frac{Mp}{\varrho R T_k}\right)^{1/[1+(1-T_r)^{2/7}]} \tag{4}$$

where M is the molecular mass. For evaluation of the derivation of the saturated vapor pressure with respect to temperature, the Antoine equation was used

$$\log p = A - \frac{B}{t + C} \tag{5}$$

The values of the critical properties were taken from the literature [4,5] and the constants proposed by Wichterle and Linek [6] were used in the Antoine equation (5).

To describe the temperature dependence of the enthalpy of vaporization the extended Thiessen equation proposed by Majer et al. [3] was used

$$\Delta H_{\mathrm{vap,m}} = A(1 - T_r)^{\beta} e^{-\alpha T_r} \tag{6}$$

where T_r is the reduced temperature and A, α, β are empirical constants. The values of the vaporization molar enthalpies were taken from the compilation by Majer et al. [7].

The hydrogen bonding in alcohols leads to the formation of associated complexes; dimers are the most stable among them. The molar association enthalpy was estimated by means of quantum chemistry computations as a difference

$$\Delta H_{\mathrm{ass,m}} = (\Delta H_f)_{\mathrm{dimer,m}} - 2(\Delta H_f)_{\mathrm{monomer,m}} \tag{7}$$

where $(\Delta H_f)_{\mathrm{dimer,m}}$ and $(\Delta H_f)_{\mathrm{monomer,m}}$ are enthalpies of formation of dimer and monomer respectively.

The MNDO/M method [8] was used for computation of the association enthalpy. This method is a modification of the standard MNDO method [9], where the nuclear repulsion term between the atoms, forming a hydrogen bond, is evaluated by means of a modified formula. The most stable conformations of dimer and monomer were taken into account. All the computations were carried out with complete geometry optimization.

3. Results and discussion

Temperature dependence of heat capacity of C_3, C_4 and C_5 alkanols are plotted on Figs. 1, 2 and 3. The values of measured heat capacities of the liquids at 303 K as well as these values in the ideal gas state for the same temperature are summarized in Table 1. The differences $\Delta C_{p,\mathrm{m}}^{\mathrm{l-g}} = C_{p,\mathrm{m}}^{\mathrm{l}} - C_{p,\mathrm{m}}^{\mathrm{g}\ominus}$ obtained from experimental data (denoted by subscript e) and computed using Eq. (1) (denoted by subscript c) are also presented in this table. The last column of this table (denoted II.term) contains the second term of the righthand side of Eq. (1), computed by

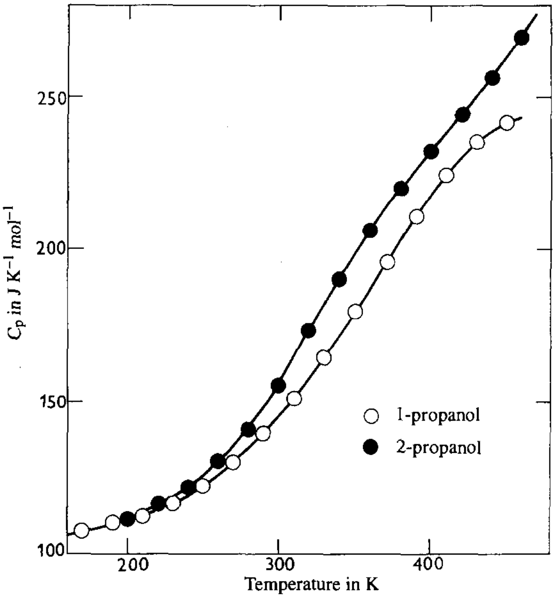

Fig. 1. Temperature dependence of the molar heat capacity of propanols

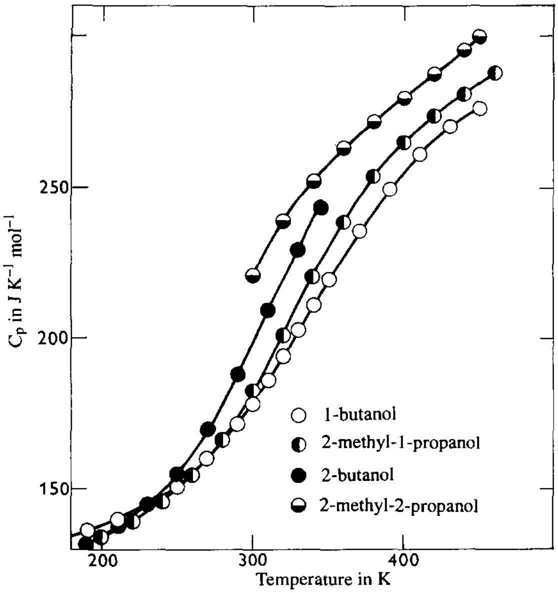

Fig. 2. Temperature dependence of the molar heat capacity of butanols.

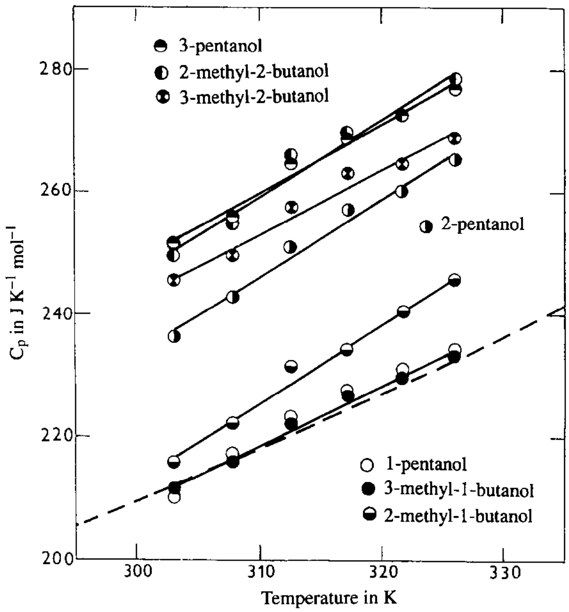

Fig. 3. Temperature dependence of the molar heat capacity of pentanols.

Table 1
Isobaric molar heat capacities (in J K^{-1} mol^{-1}) of alkanols in liquid and gas state and their differences at 303 K

Compound	$C^{l}_{p,m}$	Ref.	$C^{g}_{p,m}$	Ref.	$(\Delta C^{l-g}_{p,m})_e$	$(\Delta C^{l-g}_{p,m})_c$	II.term
1-Propanol	146.5	1	86.6	14	59.9	65.1	−0.01
2-Propanol	158.3	10	90.4	14	67.9	80.6	−0.19
1-Butanol	181.2	1	109.4	14	71.8	78.5	−0.006
2-Butanol	202.5	11	114.0	14	88.5	91.9	−0.012
2-Methyl-1-propanol	185.4	12	110.3	15	75.1	74.8	−0.008
2-Methyl-2-propanol	224.4	13	115.0	14	109.4	121.1	−0.024
1-Pentanol	212.0	1	134.4	16	77.6	85.3	−0.003
2-Pentanol	237.5	2	139.2	15	97.3	102.5	−0.005
3-Pentanol	252.1	2	138.0	15	113.9	–[a]	
2-Methyl-1-butanol	214.1	2	134.9	15	79.2	82.2	−0.004
2-Methyl-2-butanol	250.5	2	133.7	15	116.8	115.6	−0.013
3-Methyl-1-butanol	212.0	2	136.0	15	76.0	87.3	−0.003
3-Methyl-2-butanol	246.1	2	135.6	15	110.5	–[a]	

[a] Constants of the Thiessen equation (6) are not available.

means of the procedure described above. One can see from this table that this term is negligible in comparison with the first one, which was pointed out in connection with Eq. (2). Thus, the difference between liquid and gaseous heat capacities is given by the change of the molar enthalpy of vaporization with respect to

Table 2
Differences between molar heat capacities (in J K^{-1} mol^{-1}) of isomers and 1-alkanols at 303 K

Compound	$(\Delta C^{g}_{p,m})_e$	$(\Delta C^{l}_{p,m})_e$	$(\Delta C^{l}_{p,m})_c$
2-Propanol	3.8	11.8	19.3
2-Butanol	4.6	21.3	18.0
2-Methyl-1-propanol	0.9	4.2	−2.8
2-Methyl-2-propanol	5.6	43.2	48.3
2-Pentanol	4.8	25.5	22.0
3-Pentanol	3.6	40.1	–[a]
2-Methyl-1-butanol	0.5	2.1	−2.6
2-Methyl-2-butanol	−0.7	38.5	29.4
3-Methyl-1-butanol	1.6	0	2.0
3-Methyl-2-butanol	1.2	34.1	–[a]

[a] Constants of the Thiessen equation (6) are not available.

temperature. The correct evaluation of this derivation requires precise data for the molar enthalpy vaporization at various temperatures. Therefore, there is a semiquantitative agreement between experimental and calculated values for the difference $\Delta C^{l-g}_{p,m}$ in Table 1.

The experimental differences of heat capacities between isomers and 1-alkanols of liquid $(\Delta C^{l}_{l,m})_e$ and gas $(\Delta C^{g}_{p,m})_e$ are summarized in Table 2. Similar differences obtained by means of substracting of Eq. (1) for a liquid isomer and a 1-alkanol using the values of $C^{g}_{p,m}$ from Table 1 are denoted by $(\Delta C^{l}_{p,m})_e$. This table shows that the differences in the values for the gaseous heat capacity are small in comparison with the liquid state. The values calculated from Eq. (1) in the last column also show a semiquantitative correspondence with the experimental values. One finds from both tables, that the structure of alcohol molecules has a primary influence on the temperature dependence of the vaporization enthalpy.

This can be explained by means of steric effects during formation of the hydrogen bonds in liquid alcohols. The values of molar heat capacity of liquids, corresponding to various isomers of the same alkanol, increase with increasing steric crowding of molecules with respect to interaction of the –OH groups with $-CH_3$. The strength of hydrogen bonding decreases in isomers where greater steric effects are present and the number of associated molecules decreases with temperature to a greater extent in comparison with 1-alkanols. This results in lower values for the vaporization enthalpy and a greater negative slope of its value with respect to temperature, also resulting in larger values for the molar heat capacity in the liquid state.

This consideration can be demonstrated by the relation between the difference $\Delta C^{l-g}_{p,m}$ and the strength of hydrogen bonding. The values of the normal boiling temperature and the association enthalpy were used as the criteria for the strength of hydrogen bonding. The corresponding values are summarized in Table 3. There is a certain correspondence between the strength of hydrogen bonding and the difference $\Delta C^{l-g}_{p,m}$. One can see from the Figs. 4 and 5, the graphical dependences of

Table 3
Differences between molar heat capacities in liquid and gas state, enthalpies of association and vaporization at 303 K and normal boiling temperature of alkanols

Compound	$(\Delta C_{p,m}^{l-g})_e$/J K^{-1} mol^{-1}	$\Delta H_{ass,m}$/kJ mol^{-1}	$\Delta H_{vap,m}$/kJ mol^{-1}	T_{nb}/K
1-Propanol	59.9	−19.1	47.2	371.0
2-Propanol	67.9	−16.7	45.0	355.7
1-Butanol	71.8	−18.0	52.0	390.7
2-Butanol	88.5	−17.8	49.3	372.7
2-Methyl-1-propanol	75.1	−17.1	50.5	381.3
2-Methyl-2-propanol	109.4	−13.3	46.1	355.7
1-Pentanol	77.6	−18.8	56.6	411.2
2-Pentanol	97.3	−15.2	53.7	392.1
3-Pentanol	113.9	−13.1	–[a]	389.3
2-Methyl-1-butanol	79.2	−16.8	56.6	403.2
2-Methyl-2-butanol	116.8	−15.3	49.6	388.2
3-Methyl-1-butanol	76.0	−20.0	55.2	405.2
3-Methyl-2-butanol	110.5	−13.2	–[a]	385.2

[a] Constants of the Thiessen equation (6) are not available.

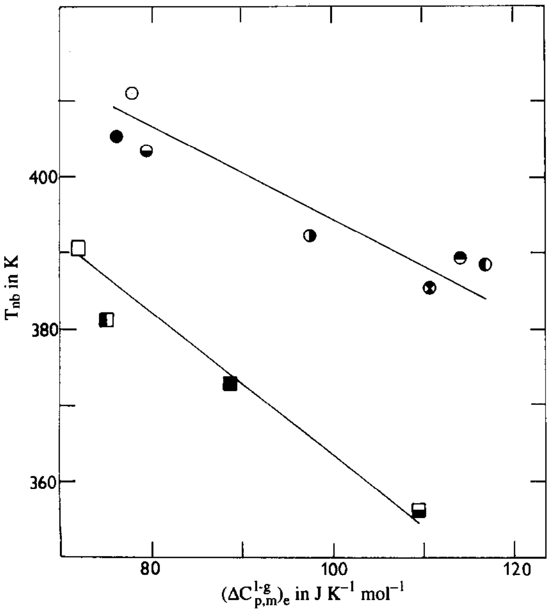

Fig. 4. Dependence of the normal boiling temperature on the difference of heat capacity in the liquid and gas state for butanols and pentanols: □, 1-butanol; ■, 2-butanol; ◧, 2-methyl-1-propanol; ⬓, 2-methyl-2-propanol; ○, 1-pentanol; ◑, 2-pentanol; ◓, 3-pentanol; ◒, 2-methyl-1-butanol; ◐, 2-methyl-2-butanol; ●, 3-methyl-1-butanol; ⊗, 3-methyl-2-butanol.

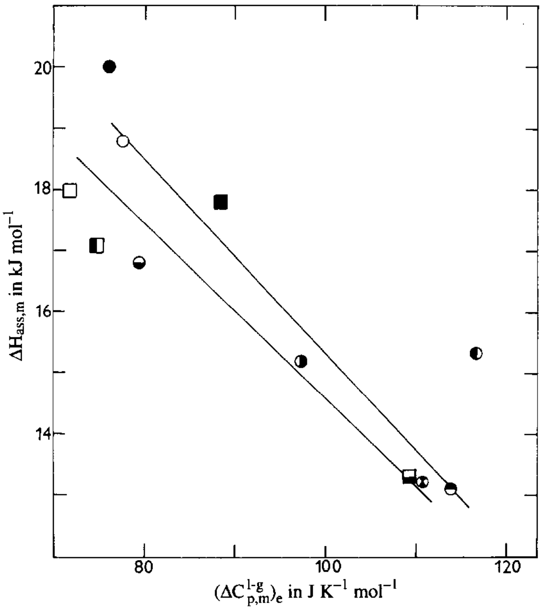

Fig. 5. Dependence of the molar association enthalpy on the difference of heat capacity in the liquid and gas state for butanols and pentanols: □, 1-butanol; ■, 2-butanol; ◧, 2-methyl-1-propanol; ⬓, 2-methyl-2-propanol; ○, 1-pentanol; ◑, 2-pentanol; ◓, 3-pentanol; ◒, 2-methyl-1-butanol; ◐, 2-methyl-2-butanol; ●, 3-methyl-1-butanol; ⊗, 3-methyl-2-butanol.

the values of the normal boiling temperature and the association enthalpy with the values of difference $C^{l}_{p,m} - C^{g\ominus}_{p,m}$.

Figure 4 shows a linear relationship between the values of the normal boiling temperature and the difference $\Delta C^{l-g}_{p,m}$ for butanols and pentanols. The dependence of the association enthalpy $\Delta H_{ass,m}$, computed by means of quantum chemistry for the difference of heat capacities in the liquid and gas state is shown in Fig. 5. A clear correlation between these two quantities (with the exception of 2-methyl-2-butanol) is evident from these figures. Greater steric effects with respect to the interaction of the hydroxyl groups with the ending methyl groups and therefore weaker hydrogen bonding evidently leads to a lower boiling temperature as well as to a higher molar heat capacity of the liquid.

4. Conclusions

The dependence of the value of the gaseous heat capacity of alcohols upon their molecular structure is small in comparison with the value for the heat capacity of the liquid. The influence of the molecular structure of an alcohol upon the value of liquid heat capacity is given mainly by the temperature dependence of enthalpy of vaporization. This dependence correlates well with the strength of the hydrogen bonding between alcohol molecules. Greater steric effects and therefore weaker hydrogen bonds are present in several isomeric alcohols in comparison with the corresponding l-alkanol. The steric effects increase with decreasing distance between the hydroxyl and methyl group in alkanol molecules. For alcohols, molecular association decreases with increasing temperature causing a larger change in the molar heat capacity in the liquid state than is observed for the gaseous state.

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