

HEAT CAPACITIES OF MONOMER MODELS OF SOME HYDROPHILIC POLYMERS IN AN AQUEOUS SOLUTION FROM 20° TO 60°C

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Dedicated to Professor E. Erdős on the occasion of his 60th birthday.

The apparent molar heat capacities of propionic and isobutyric acids and of 2-hydroxyethyl pivalate and 2-(2'-hydroxyethoxy)ethyl pivalate in a dilute aqueous solution were determined with a DASM-1 m calorimeter. Moreover, the apparent specific volumes of these compounds in the aqueous solution and their molar heat capacities in the bulk liquid state were also determined. In the range 20°–60°C the apparent heat capacity in the aqueous solution is temperature-independent, or (in the case of propionic acid) increases slightly with temperature. The apparent heat capacities measured at 25°C were compared with values estimated using various reported additivity schemes. Good agreement was observed for both acids; the other two compounds with more complicated molecules showed significant deviations from additivity.

In the last decade, great attention has been devoted to the thermodynamic properties of dilute aqueous solutions of organic compounds, especially those modelling various structural units of biological polymers. The objective consisted in relating the solution behaviour of these macromolecules, and in particular their conformational changes, with the interaction between their individual components and the aqueous environment. Lately, aqueous solutions of synthetic bioanalogue polymers have also aroused increasing interest; their thermodynamic interaction with water is one of the input parameters decisive for their applicability in medicine. Here too the investigation of polymers should keep pace with that of low-molecular weight model compounds.

Among the measurable thermodynamic properties – activity, enthalpy and volume changes, thermal expansion, compressibility and heat capacity, particularly the latter seems to be a sensitive indicator of the interaction between dissolved compounds and water, and predominantly of changes in the intermolecular structure of liquid water caused by the presence of a dissolved compound. The recent progress in the calorimetric technique and construction of new sensitive apparatuses^{1,2} make possible measurements of the apparent heat capacities of compounds dissolved in water, both at sufficient dilution (so that extrapolation to zero concentration is feasible) and depending on temperature. In this respect, the DASM-1 scanning calorimeter

according to Privalov¹ is especially promising, as it allows measurements to be made between 0° and 100°C. This study reports the apparent heat capacities and apparent specific volumes of propionic and butyric acids, 2-hydroxyethyl pivalate and 2-(2'-hydroxyethoxy)ethyl pivalate in dilute aqueous solutions at temperatures between 20° and 60°C, and the heat capacities of these compounds in the bulk liquid state between 0° and 100°C. The structure of the compounds under investigation resembles that of unit of some hydrophilic polymers: polyacrylic acid, polymethacrylic acid, poly (2-hydroxyethyl methacrylate) and poly [2-(2'-hydroxyethoxy)ethyl methacrylate]. As a preliminary for a comparison between the low-molecular weight models and polymers, intended in our further work, the measured data are confronted with estimates obtained by using various reported additivity schemes.

EXPERIMENTAL

Materials

Propionic acid, reagent grade (Lachema, Czechoslovakia) was distilled twice with a small amount of added KMnO_4 ; $n_D^{20} = 1.3865$ (ref.³ 1.3865), $\rho^{20} = 993.4 \text{ kg m}^{-3}$ (ref.³ 993.36). Isobutyric acid (Lachema) chromatographically pure, $\rho^{25} = 946.25 \text{ kg m}^{-3}$ (ref.⁴ 945.1). Esters: 2-hydroxyethyl and 2-(2'-hydroxyethoxy)ethyl pivalates were identical with those reported in ref.⁵. Their purity according to GLC was higher than 99%, the water content was below 1%.

Measuring Procedures

The heat capacities of pure compounds sealed in hermetic aluminium pans were determined with a DSC-2 Perkin-Elmer (USA) apparatus connected with 4 1/2 digit A/D converter and tape puncher. Within the given temperature range, each time the base lines with empty pans, and lines with sample and sapphire single crystal for calibration were measured successively. The specific heat capacity values were obtained for each integer Kelvin by using a Wang 2 200 C calculator after correction of primary data to base line, to dynamic constants of the apparatus and to the different masses of the aluminium pans.

The apparent specific volumes of compounds in dilute solutions were calculated from the densities of solutions determined by using a DMA 02C densitometer⁶. The temperature was measured by means of a calibrated thermometer with an accuracy higher than 0.05 K; its oscillations during the measurement were checked with a thermistor having a sensitivity higher than 0.005 K. The densitometer was calibrated with water and air.

The apparent heat capacities of compounds in dilute aqueous solutions were measured by using a differential adiabatic scanning microcalorimeter¹ DASM-1 m, SKB-Poustchino USSR. Two gold measuring cells in the form of a low flat cylinder, each 1 cm^3 in volume, provided with platinum filling capillaries, 1 mm in diameter, were placed in an adiabatic double jacket surrounded with a massive metallic isothermal thermostat cooled to 273 K by means of semiconductor cooling batteries. Each of the cell was provided on one of its bases with a vacuum-deposited electrical resistance heating connected in a symmetrical dc resistance bridge. Between the other two bases of the cells, there were uniformly distributed approximately 100 Cu-Constantan thermocouples for indication of the temperature differences between the cells and connected to the input of a compensation amplifier. The difference in the heat capacities of the two cells

was compensated for by the current of the amplifier in the diagonal of the bridge. The magnitude of the compensation current in this connection was proportional to the compensation power and was recorded with an X-Y recorder. The constant heating rate was controlled by the constant heating power from an independent current source.

In order to increase the accuracy of measurement and to computerize it the output signal of the calorimeter was amplified with a Keithley 148 nanovoltmeter and recorded on a punched tape using a 4 1/2 digit A/D converter.

The measurements were carried out with a constant overpressure of c. 100 kPa in order to reduce the danger of bubble formation. First, the base line was recorded with both cells filled with redistilled water; after that, one cell was filled with a dilute aqueous solution of the measured compound, and the measurement was carried out in the same regime. At the end, the calorimeter was calibrated under the same conditions using calibration heating and constant current from a Takeda Riken 6120 DC-standard.

RESULTS

The results of measurements of the temperature dependence of molar (or apparent molar) heat capacities are given in Table I and Figs 1a-d. An analysis of the reproducibility and sources of errors showed that the heat capacities of the bulk liquid samples were reliable within $\pm <1\%$, the main part of uncertainty being an error due to the nonzero vapour phase volume.

The apparent specific volumes, ϕ_v , of compounds in dilute aqueous solutions were calculated from measured water and solution densities ρ_1 , ρ_{soln} , using the expression

$$\phi_v = [1/(\rho_{\text{soln}} \cdot w_1) - 1/\rho_1]/g_2 \quad (1)$$

in which w_1 is the weight fraction of solvent in solution, g_2 is the ratio of masses of the dissolved compound and solvent. Four to six solutions were taken for the measurement each time, in the range 0.5–2 wt.% at 4–5 temperatures in the temperature range 290–330 K. No significant dependence on concentration was observed for these compounds within the given concentration range. The temperature dependences could be described in terms of a linear equation, the constants of which for the individual compounds are listed in Table I. We believe that the apparent molar volumes are reliable within $\pm <1\%$.

The apparent molar heat capacities, ϕ_c , were calculated using the expression²

$$\phi_c = M_2(c_1\phi_v/v_1 - P/\dot{T}m_2), \quad (2)$$

where M_2 is the molar mass of the dissolved compound, c_1 , v_1 are the specific heat capacity and the specific volume of water respectively, ϕ_v is the apparent specific volume of the dissolved compound. \dot{T} is the heating rate, P is the compensation power, m_2 is the mass of the dissolved compound in the measuring cell, $m_2 = Vg_2 \cdot \rho_{\text{soln}}/(1 + g_2)$, and V is the volume of the measuring cell.

Even though the reproducibilitites of measurements of the heating rates, power calibration constants and measurements without exchange of the sample were better than $\pm 0.5\%$, it is estimated that the reliability of measurement ϕ_c does not exceed $\pm 3\%$, mainly because of the lower reproducibility of filling of calorimetric cells. In order to rule out systematic errors, the apparent specific heat capacities of urea were measured in an aqueous solution with $w_2 0.007$, at two heating rates (1 and 2 K/min). The value measured at 297.3 K, $\phi_c = 1.445 \text{ J K}^{-1} \text{ g}^{-1}$, was in complete agreement with the most recent reported data².

The measurements were performed each time at two rates of temperature increase (1 and 2 K per min), at two compositions of solution ($w_2 0.005 - 0.02$). The results were independent of both factors within the limits of experimental error. The range of measurements was 291 K - 370 K; calculation using Eq. (2) could of course provide reliable ϕ_c values only in the range 290 K - 330 K in which the apparent volumes were measured.

TABLE I

Constants of polynomials expressing the temperature dependence of measured quantities ($Y = A_0 + A_1 \cdot T + A_2 \cdot T^2 + \dots$) and standard deviations σ of the latter

Compound	A_0	$A_1 \cdot 10^3$	$A_2 \cdot 10^6$	σ
C_p^* , liquid state (270-370 K), in $\text{JK}^{-1} \text{ mol}^{-1}$				
Propionic acid	129.7	-126.3	748.6	0.19
Isobutyric acid	130.1	-81.56	854.1	0.22
2-Hydroxyethyl pivalate	15.79	1.337	-1.197	0.69
2-(2'-Hydroxyethoxy)ethyl pivalate	63.18	228.8	-2.571	0.67
ϕ_c , aqueous solution (290-330 K), in $\text{JK}^{-1} \text{ mol}^{-1}$				
Propionic acid	71.47	1.028	-1.400	0.15
Isobutyric acid	178.5	986.7	-1.545	0.15
2-Hydroxyethyl pivalate	560.8	35.1	-	0.84
2-(2'-Hydroxyethoxy)ethyl pivalate	675.8	-22.2	-	2.6
ϕ_v , aqueous solution (290-330 K), in $\text{m}^3 \text{ kg}^{-1}$				
Propionic acid	574.7	1.136	-	-
Isobutyric acid	592.3	1.229	-	-
2-Hydroxyethyl pivalate	705.4	848	-	-
2-(2'-Hydroxyethoxy)ethyl pivalate	620.0	1.038	-	-

DISCUSSION

It is known that the heat capacity of liquid water is roughly twice that of ice. This unusually large difference is generally regarded as reflecting the destruction of hydrogen bonds with increasing temperature. The structure of hydrogen bonds in liquid water compared with that appearing in crystalline ice is considerably disturbed and has a much lower cooperativity; this is why the former structure also lacks the

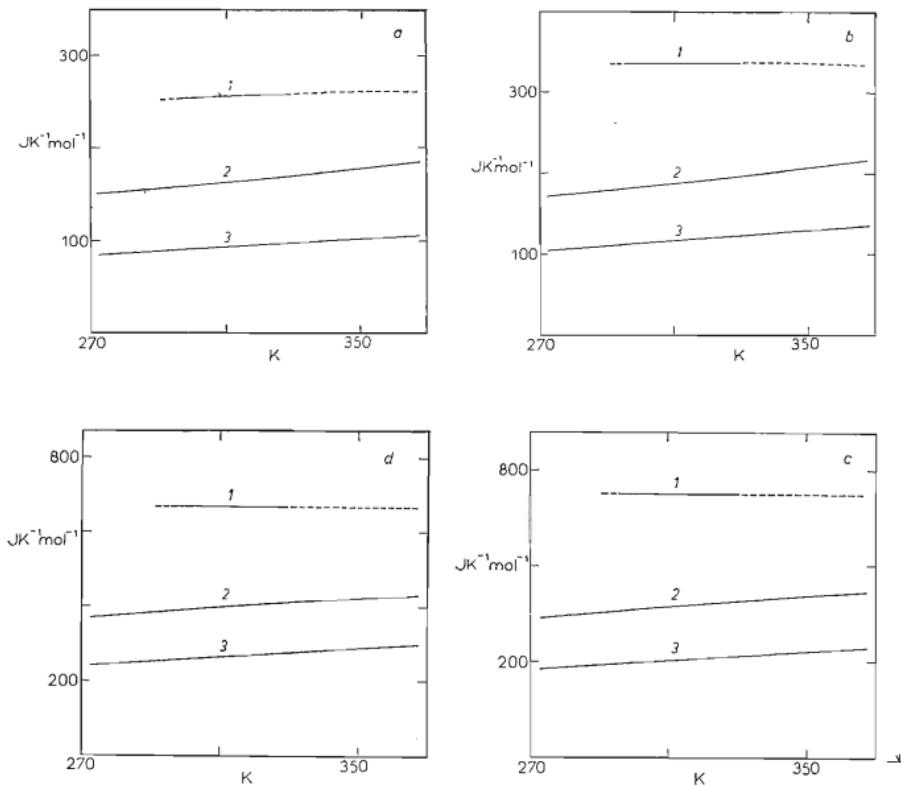


FIG. 1

Temperature dependences of heat capacities: 1 apparent molar heat capacity in aqueous solution, 2 molar heat capacity in bulk liquid state, 3 molar heat capacity in ideal gas state (calculated using ref.⁸). Broken part of curve 1 — ϕ_v values extrapolated beyond the measured temperature range substituted into Eq. (2). Data for (a) propionic acid, (b) isobutyric acid, (c) 2-hydroxyethyl pivalate, (d) 2-(2'-hydroxyethoxy)ethyl pivalate

high heat stability of the latter. The gradual disordering in liquid water on heating leads to a higher energy consumption.

It can be regarded as proven that in dilute aqueous solutions of organic compounds with aliphatic or aromatic groups, additional hydrogen bonds between molecules of water are formed in the immediate surroundings of these groups. This ordering process is reflected in a negative contribution to the entropy and enthalpy of mixing. The high positive values of excess heat capacity indicate that also hydrogen bonds induced by the presence of alkyl chains are readily broken by heating. The compound containing a sufficient number of hydrocarbon groups has then a much higher apparent heat capacity in the dilute aqueous solution ϕ_c , than the heat capacity of the same compound in the bulk liquid state, $C_{p2}^*(l)$ (ref.⁷). This general experience is also confirmed by our results shown in Figs 1a-d. For the sake of illustration, the temperature dependences of heat capacity in the ideal gas state, $C_{p2}^*(g)$, estimated by the method of group contributions⁸ are also plotted in these figures. The heat capacity in the ideal gas state includes the contributions of translational, rotational and internal modes of the thermal motion of molecules. The difference $C_{p2}^*(l) - [C_{p2}^*(g) - R]$ reflects a thermal change in the cohesion energy of the dissolved compound in the bulk liquid state. Analogically, the difference $\phi_c - [C_{p2}^*(g) - R]$ describes a temperature change in the interaction energy released in the absorption of gas solute in liquid water with formation of an infinitely dilute solution. The latter difference is more than twice the former, which demonstrates an extremely strong effect of breaking of the additional water structure on the heat capacity.

In a great majority of cases, the reported values of partial or apparent heat capacity of organic nonelectrolytes in an aqueous solution are related only to 25°C. On the other hand, however, Roux, Perron and Desnoyers⁹⁻¹¹ report the heat capacities of some compounds both in the aqueous solution and in the bulk liquid state at several temperatures (mainly 10°C, 25°C, 40°C). The heat capacity in the bulk liquid state increases for all compounds under investigation with the exception of methyl-diethyl amine, the temperature dependence of which has an unpronounced maximum. According to the behaviour of heat capacity in the aqueous solution and its difference from that in the liquid state, the compounds investigated so far can be divided into several groups: 1) both ϕ_c and $\phi_c - C_{p2}^*$ decrease with increasing temperature for 2-propanol, 2-methyl-2-propanol, ethyl acetate, 2-butoxyethanol, methyldiethyl amine and triethyl amine; 2) ϕ_c is virtually independent of temperature, $\phi_c - C_{p2}^*$ decreases with temperature; this group comprises 2-ethoxyethanol, butanone and the compounds measured by us, *viz.*, isobutyric acid, 2-hydroxyethyl pivalate and 2-(2'-hydroxyethoxy)ethyl pivalate (Figs 1b-d); 3) the behaviour of propionic acid seems still exceptional as according to our measurements its ϕ_c in water slightly increases with temperature, but the difference $\phi_c - C_{p2}^*$ slightly decreases (Fig. 1a); 4) in the case of bis(2-ethoxyethyl) ether, ϕ_c and C_{p2}^* increase with temperature in the same way, so that their difference is temperature-independent. Interpretation of such various

types of behaviour and their correlation with the molecular structure of dissolved compounds will be possible only on the basis of a much more extensive assembly of data.

An effort to correlate a large amount of data available for 25°C with molecular structure has led to the construction of a number of additive schemes^{9,12-14} which make possible an estimate of the apparent heat capacity in the aqueous solution from structural contributions. Since these schemes may prove to be very useful when comparing the heat capacities of hydrophilic polymers with those of their low-molecular weight models, we checked their applicability in the case of compounds investigated by us. The applied schemes and structural units (atoms, bonds, groups) whose contributions were summed up to yield ϕ_c are reviewed in Table II. Some contributions had to be obtained by adjustment using the existing data on ϕ_c ; this mainly concerns contributions related to the ester group —COO— which are missing in most of the schemes. The adjustment was performed with data on methyl acetate and ethyl acetate⁹ (data for other simple esters were not available). To make the individual schemes comparable with each other, the adjustment was performed also in those cases where some value in the original set has already been reported^{9,14}.

The ϕ_c values obtained by various methods of estimation are compared with the measured ones in Table III; in addition to the compounds investigated by us, methyl acetate and ethyl acetate are also included. The Table shows that in the case of propionic and isobutyric acids all procedures with the exception of the method of atomic contributions lead to a good estimate. With esters, there is a striking discrepancy in the case of the method of atomic contributions, and to a minor extent also in the case of the method of bond contributions. Obviously, a correction adequately reflecting mutual interaction between the individual elements of the —COO— group should be added to the sum of contributions of the individual atoms or bonds forming the group. The good agreement achieved using all these schemes of group contributions for methyl and ethyl acetate was of course obtained forcibly by adjustment of the contribution related to —COO—.

With 2-hydroxyethyl and 2-(2'-hydroxyethoxy)ethyl pivalates, the values obtained from group schemes are significantly higher in most cases than experimental ones. The particularly large deviations which appeared if the G1 method was used (Nichols and coworkers) can partly be explained through the influence of the tert-butyl group. By using data in Table V, ref.¹², the authors of the method point out that the substitution of n-butyl with tert-butyl leads to a decrease in ϕ_c by some 30 J K⁻¹ mol⁻¹; this effect, however, cannot be adequately described by scheme G1, because contributions of all CH_i groups (*i* in the range 0–3) can be expressed as

$$\phi_c(CH_i) = \phi_c(C) + i\phi_c(H), \quad (3)$$

where $\phi_c(C)$ and $\phi_c(H)$ are constants. The validity of this equation was also assumed

TABLE II
Additive contributions used in the estimation (A-G4) of apparent heat capacities

Scheme	Type of contributions	Contributions taken from authors	Adjusted contributions (J K ⁻¹ mol ⁻¹)
A	atomic (Guthrie ¹³)	C ₄ , C ₃ , H _C , O ₂ , O ^a	—
B	bond (Guthrie ¹³)	C—C, C—H, CO—C, CO—O, C—O, O—H	—
G1	group (Nichols and coworkers ¹²)	$\begin{array}{c} \\ -\text{CH}_3, -\text{CH}_2-, -\text{CH}-, -\text{C}-, -\text{O}- \\ \\ -\text{OH}, -\text{COOH} \end{array}$	$-\text{COO}-; -12 \pm 4^b$
G2	group (Roux and coworkers ¹¹)	$\begin{array}{c} \\ -\text{CH}_3, -\text{CH}_2-, -\text{H}, -\text{O}-, -\text{OH} \end{array}$	$-\text{COO}-; -52 \pm 5^b$
G3	group (Guthrie ¹³)	$\begin{array}{c} \text{CH}_3(X), \text{CH}_2(\text{C})(\text{CO}), \text{CH}_2(\text{C})(\text{O}), \\ \text{CH}(\text{C})_2(\text{CO}), \text{C}(\text{C})_3(\text{CO}), \text{CO}(\text{O})(\text{C}), \text{O}(\text{C})_2, \\ \text{OH}(\text{C}), \text{OH}(\text{CO})^d \end{array}$	$-\text{COOH}; -15 \pm 2^c$ $\text{O}(\text{CO})(\text{C}); +78 \pm 5^b$
G4	group (Cabani ¹⁴)	see G1; $(-\text{O}-; -\text{OH})^e; \text{A}_z^f$	$-\text{COO}-; +4 \pm 5^b$

^a Digit in the subscript gives the number of bound adjacent atoms; letter in the subscript denotes the kind of bound atom. ^b Adjusted so as to adequately describe data for methyl acetate, ethyl acetate, ref. ⁹. ^c Adjusted so as to adequately describe our data for propionic and isobutyric acid. ^d Symbols in brackets denote immediate neighbours of the group. ^e Contribution originating in the interaction between the two given groups separated by two carbon atoms. ^f Constant contribution per molecule.

when scheme G2 was used. Guthrie's method (G3), where Eq. (3) does not hold and the group contributions are moreover distinguished with respect to the character of immediate neighbours, very adequately describes ϕ_c of pivalic acid and of its N-methyl amide (Table I, ref.¹³). On the contrary, the deviation found with 2-(2'-hydroxyethoxy)ethyl pivalate was a significant one. A possible explanation can be seen in the mutual influence of three polar groups separated by ethylene groups; in methods G1, G2, G3 such an interaction is not considered. Let it be added that it can be seen from Table I, ref.¹³ that Guthrie's scheme G3 leads to very good predictions for a number of 2-alkoxyethanols and dialkoxyethanes where mutual influence between two polar groups in the molecule could be assumed; this agreement was also checked for data on bis(2-ethoxyethyl)ether⁹ containing three ether groups.

In the scheme of Cabani and coworkers, interaction contributions are defined of pairs of hydrophilic groups which are separated by one or several carbon atoms. Hence, in this scheme the agreement between our data could be improved, at least formally, by introducing contributions of the interaction between —COO— and —O—, or between —COO— and —OH not indicated by the authors. To obtain these two parameters, data on only two pivalates under study are available, so that their introduction was abandoned.

The analysis described in this study suggests that additive schemes may become a useful tool for the correlation of data on new compounds with molecular structure, if sufficient data are available to check the reliability of the scheme and if caution is observed throughout the procedure.

TABLE III

Experimental and estimated ϕ_c values (in $\text{JK}^{-1} \text{mol}^{-1}$) at 25°C ; methods of estimation denoted as in Table II

Compound	Exp. value	Estimate					
		A	B	G1	G2	G3	G4
Propionic acid	253.3	231	255	252	251	265	254
Isobutyric acid	336.6	313	340	342	339	351	348
Methyl acetate	298.2 ^a	246	270	302	304	303	304
Ethyl acetate	396.6 ^a	328	355	392	392	393	391
2-Hydroxyethyl pivalate	552.6	517	542	604	578	560	607
2-(2'-Hydroxyethoxy)ethyl pivalate	667.3	639	659	727	682	686	717

^a Ref.⁹.

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