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Thermodynamics of Solution of Some Alkyl Acetates in Water

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Summary. The temperature dependence of the solubility of methyl acetate (MeOAc), ethyl acetate (EtOAc), 1-propyl acetate (1-PrOAc), 1-butyl acetate (1-BuOAc), 2-methyl-1-propyl acetate (*iso*-BuOAc), 2-butyl acetate (*sec*-BuOAc), and 2-methyl-2-propyl acetate (*tert*-BuOAc) in water in the temperature range from 298.2 to 318.2 K was determined. The experimental solubility data together with some literature values are presented as a function of temperature and given in analytical form. The solubilities of the investigated compounds at 298.2 K were correlated with the number of carbon atoms in the solute molecule. The standard thermodynamic functions for solubility, *i.e.* *Gibbs* free energy, enthalpy, heat capacity, and entropy, were calculated. The *Gibbs* free energy is positive and increases linearly with the number of carbon atoms, whereas the enthalpy and entropy are negative. The standard thermodynamic functions were converted to thermodynamic quantities for hydration. The *Gibbs* free energies of hydration of alkyl acetates, which are negative, are compared with the *Gibbs* free energy of hydration of some *n*-alkanes, 1-alcohols, and 1-alkylamines. The standard thermodynamic functions of hydration were analyzed using a modified version of the theoretical approach developed by *Lee* and *Graziano* [1].

Keywords. Alkyl acetates; Water; Standard thermodynamic functions of solution; Thermodynamic functions of hydration.

Introduction

Solute-solvent interactions are fundamental to the understanding of the solution process and to questions of solubility and solubilization. In addition, many biological processes of living organisms are a series of chemical events followed by interactions of the molecules and ions in aqueous solution. Water is unusual as a solvent, particularly for nonpolar solute molecules. Unlike simpler solvents, the insertion of a nonpolar or polar solute in water is strongly energetically unfavourable, as can be deduced from the large and negative entropy of solution at room temperature which is accompanied by a large and positive heat capacity [2]. These properties define hydrophobic hydration, which results from hydrogen bonding and the ordering of water molecules around the solute molecule. Thus, transfer of a nonpolar or polar compound from the gas phase to water has many peculiar thermodynamic implications [3].

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Alkyl acetates are important technological and biological compounds. The presence of the polar ester group with a dipole moment of 1.9 D [4] provides the necessary energetic interactions with water molecules to solubilize alkyl acetates. On the other hand, the nonpolar region of the ester molecule plays an important role in the hydrophobic hydration process. The water molecules interact with the alkyl chain through *van der Waals* forces. The thermodynamics of solution of alkyl acetates have been investigated in the past [5–8]. Although the *Gibbs* free energy of solution of some acetates is known (see *e.g.* Ref. [8]), there are few systematic data on the enthalpy or entropy of solution. We therefore set out to determine the *Gibbs* free energy, enthalpy, entropy, and heat capacity of solution of some alkyl acetates in water.

Results and Discussion

The experimental results are summarized in Table 1, where for each compound the solubilities determined in water as a function of temperature are given. From Table 1 it can be seen that the solubility of the investigated alkyl acetates decreases with increasing temperature except for MeOAc. The solubility data of Table 1, together with some literature values, are represented as a function of temperature as

$$x_2 = a_0 + a_1(T - T_0) + a_2(T - T_0)^2 + a_3(T - T_0)^3 \qquad (1)$$

where a_0, a_1, a_2, and a_3 are empirical constants (Table 2), $T_0 = 298.2$ K, and T is the absolute temperature. In Figs. 1 and 2, the dependence of x_2 on temperature is

Table 1. Solubility of alkyl acetates in water in the temperature range from 298.2 to 318.2 K and experimental error of the estimation

	$x_2 \cdot 10^4$				
	298.2 K	303.2 K	308.2 K	313.2 K	318.2 K
MeOAc	710.3±3.5	701.3±1.6	706.8±1.3	702.6±1.7	713.5±2.0
EtOAc	161.21±0.73	153.58±0.49	147.56±0.33	142.76±0.22	137.04±0.31
1-ProAc	38.52±0.06	36.44±0.11	34.90±0.11	33.71±0.12	32.43±0.02
1-BuOAc	9.289±0.009	8.783±0.047	8.351±0.040	7.819±0.029	7.582±0.059
iso-BuOAc	9.842±0.028	9.458±0.020	9.082±0.026	8.697±0.087	8.538±0.045
sec-BuOAc	12.93±0.10	12.27±0.04	11.54±0.05	11.01±0.03	10.61±0.04
tert-BuOAc	11.14±0.15	10.76±0.08	9.99±0.17	9.46±0.12	8.70±0.14

Table 2. Regression coefficients (Eq. (1)) of alkyl acetates together with the regression correlation coefficient r and the standard error of the estimate s

	$a_0 \cdot 10^3$	$-a_1 \cdot 10^5$	$a_2 \cdot 10^7$	$-a_3 \cdot 10^9$	r	$s \cdot 10^5$
MeOAc	70.90±0.26	9.5±3.7	50.12±0.88	−9.7±7.2	0.894	81
EtOAc	16.149±0.030	15.79±0.29	24.7±1.4	13.8±4.0	0.992	22
1-ProAc	3.838±0.031	4.75±0.16	11.64±0.80	11.6±1.4	0.994	10
1-BuOAc	0.909±0.024	1.21±0.12	3.81±0.60	3.43±0.96	0.949	6.6
iso-BuOAc	1.000±0.023	1.37±0.12	3.67±0.63	2.31±1.23	0.954	6.2
sec-BuOAc	1.24±0.036	1.72±0.17	3.88±0.88	3.05±1.42	0.963	8.9
tert-BuOAc	1.149±0.011	1.795±0.059	3.41±0.30	2.42±0.61	0.997	2.6

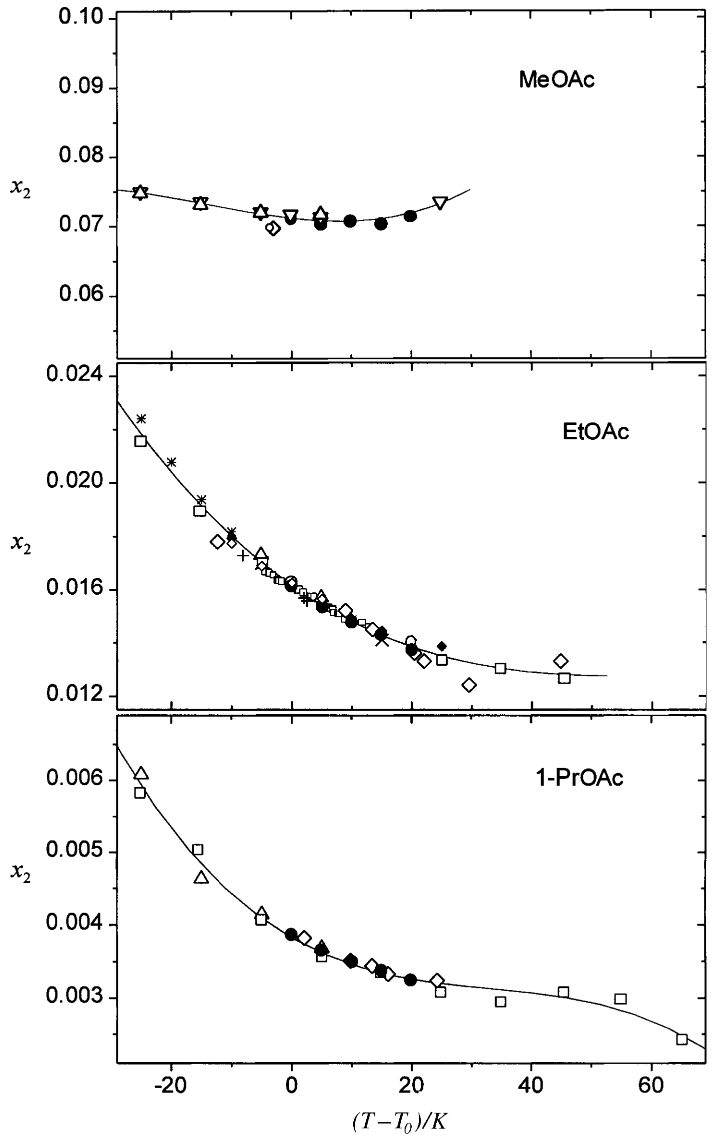

Fig. 1. Solubility of MeOAc, EtOAc, and 1-PrOAc in water as a function of temperature; •: data from Table 1, Δ: Rayman [31], ◇: *Skrzecz* [32], ∇: *Hill* [33], ∘: *Beregovykh* [34], □: *Stephenson* [17], □: *Altshuller* [35], ∗: *Merriman* [36], ◆: *Schlesinger* [37], ×: *Beech* [38], ○: *Richon* [39], +: *Griswold* [40], ◇: *Gayler* [41]

given; the curves are drawn on the basis of empirical constants. From these graphs it is apparent that the solubility data given in Table 1 are in good agreement with published ones. In selecting literature values we included only primary solubility data which do not differ by more than 3% for MeOAc, EtOAc, and 1-PrOAc and 7% for isomeric butyl acetates from our data at the relevant temperature. The differences in the observed solubilities of various alkyl acetates presented in Figs. 1 and 2 may be ascribed to the different experimental techniques employed to achieve equilibrium between water and the organic phase and to different

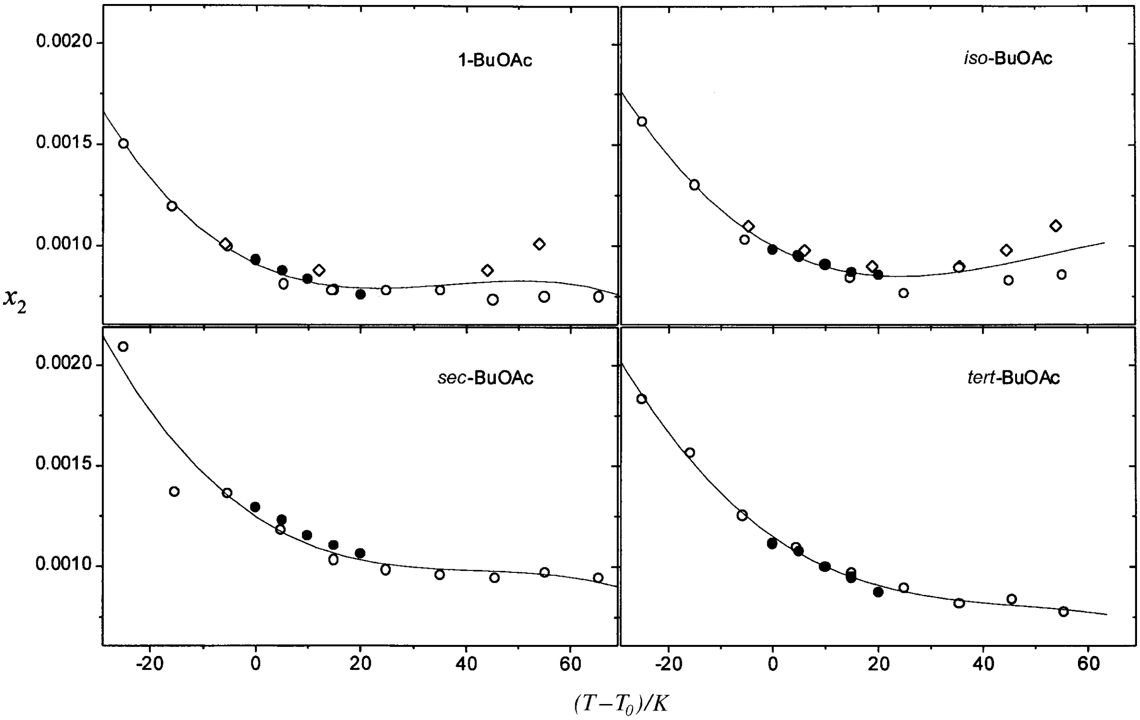

Fig. 2. Solubility of isomeric butyl acetates in water as a function of temperature; •: data from Table 1, ○: *Stephenson* [17], ◇: *Skrzecz* [32]

analytical procedures used for the determination of alkyl acetates in a saturated aqueous solution.

Some correlations between the structural features of a solute molecule and its solubility have been reported, including the number of carbon atoms n [9, 10], molar volume V_2^0 [9], molecular surface areas S [11, 12], molecular refraction R_M [13], and dipole moment μ [9]. Thus, for example, the solubility of hydrocarbons [14] or polynuclear aromatic hydrocarbons [10] has been successfully correlated with the number of carbon atoms using either a linear or parabolic equation.

The correlation between the solubility of the investigated 1-alkyl acetates, *i.e.* $\ln x_2$ and the number of carbon atoms in the solute molecule n, is linear and decreases with n as can be seen from the correlation equation $\ln x_2 = (-1.41 \pm 0.01) \cdot n + (-1.29 \pm 0.04)$ with a standard deviation of $s = 0.05$ and a linear correlation coefficient of $r = 0.99994$ at 298.2 K. In the calculation, the data for the solubility for 1-*Pe*OAc at 298.2 K were obtained from the IUPAC Solubility Data Series [15], and those for 1-*He*OAc as an average from Refs. [16–18].

For the solubility process, *i.e.* for the transfer of a mole of alkyl acetate from the pure liquid to the saturated aqueous solution (Eq. (2)), the standard thermodynamic functions for solubility, *i.e.* the *Gibbs* free energy ΔG_θ^0, enthalpy ΔH_θ^0, and heat capacity $\Delta C_{p,\theta}^0$, were calculated using a non-empirical procedure given by *Clarke* and *Glew* [19] in the form of Eq. (3) where R is the gas constant,

a_2 the activity of the solute in a saturated aqueous solution, *i.e.* $a_2 = x_2 f_2$ (f_2: mole fraction activity coefficient), $b_0 = -\Delta G_\theta^0/\theta$, $b_1 = \Delta H_\theta^0/\theta$, and $b_2 = \Delta C_{p,\theta}^0$.

$$\text{Compound}_{(l)} \rightleftharpoons \text{Compound}_{(aq)} \tag{2}$$

$$R \ln a_2 = b_0 + b_1 u_1 + b_2 u_2 \tag{3}$$

The corresponding independent variables are defined as $u_1 = x\sum_{n=1}^{\infty}(-x)^{n-1} \equiv x/(1+x)$ and $u_2 = x^2 \sum_{n=1}^{\infty}\frac{n}{n+1}(-x)^{n-1} \equiv \ln(1+x) - x/(1+x)$, where $T_0 = \theta = 298.2\,\mathrm{K}$ and $x = (T - T_0)/T_0$. The activity coefficients for the investigated solutes were taken from Ref. [20]. Since the activity coefficients are determined at the freezing point of the solvent, their temperature dependence was calculated using the corresponding excess enthalpy of solution h^E of MeOAc, EtOAc and 1-BuOAc, and partial molar excess enthalpy of solute at infinite dilution $h^{E\infty}$ [5] to obtain the relative partial molar enthalpy of solute $\bar{L}_2$ in the form

$$\bar{L}_2 = \frac{b'(1-x_2)^2}{(a'x_2 + b')^2} - h^{E\infty} \tag{4}$$

where the correlation coefficients a' and b' are taken from Ref. [5]. $\bar{L}_2$ for 1-PrOAc was obtained from the interpolated values of a' and b' for EtOAc and 1-BuOAc as $a' = -63.4 \cdot 10^{-4}\,\mathrm{mol \cdot J^{-1}}$ and $b' = -1.04 \cdot 10^{-4}\,\mathrm{mol \cdot J^{-1}}$, respectively [5]. To extend the temperature range of the solubility data given in Table 1 in which the activity coefficients of solute f_2 and relative partial molal enthalpy of solute $\bar{L}_2$ are determined, we included in our analysis of standard thermodynamic functions *via* Eq. (3) the calculated solubility data in intervals of 5 K from Eq. (1). Thus, we used the temperature range from 283 to 323 K for MeOAc (below its normal boiling point) and between 293 and 333 K for the other acetates. In the calculation of the temperature dependence of solubility, an extrapolation of the activity coefficients was used which does not exceed by more than 25% which is acceptable for a nonelectrolyte solution. For isomeric butyl acetates we used the value of $\bar{L}_2$ for 1-BuOAc, since the molar excess enthalpy of solute at infinite dilution does not depend on the structure of the alkyl chain [5]. So, the difference of $R \ln a_2$ of these compounds due to the temperature correction of f_2 does not exceed 2% over the whole temperature range studied. In calculating the standard thermodynamic function of 1-*Pe*OAc we used the IUPAC values [15], and for 1-*He*OAc the standard *Gibbs* free energy was calculated as an average from the data of Refs. [16–18]. For both compounds we assumed that the activity coefficients of these solutes are close to unity at very low mole fractions.

The calculated standard thermodynamic functions for the solubility of some alkyl acetates in water at 298.2 K are compiled in Table 3. The uncertainties of the thermodynamic functions were calculated from the relation

$$R\left(\frac{\mathrm{d}x_2}{x_2} + \frac{\mathrm{d}f_2}{f_2}\right) = \mathrm{d}b_0 + u_1\mathrm{d}b_1 + u_2\mathrm{d}b_2 \tag{5}$$

where $\mathrm{d}f_2$ is the standard deviation of the solute activity coefficient [20] and $\mathrm{d}b_0$, $\mathrm{d}b_1$, and $\mathrm{d}b_2$ are the uncertainties of the respective parameters from which the relevant errors of standard thermodynamic functions were calculated.

Table 3. Standard thermodynamic functions for the solubility of alkyl acetates at 298.2 K; the values in parentheses were estimated calorimetrically [5]

	$\frac{\Delta G_\theta^0}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{-\Delta H_\theta^0}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{-\Delta S_\theta^0}{\mathrm{J\cdot mol^{-1}K^{-1}}}$	$\frac{\Delta C_{p,\theta}^0}{\mathrm{J\cdot mol^{-1}K^{-1}}}$
MeOAc	8.16±0.04	8.27±0.01 (8.83)	55.1±0.1	29±0.8
EtOAc	11.21±0.06	11.24±0.08 (9.81)	75.3±0.3	173±0.3
1-ProAc	14.50±0.08	9.84±0.23	82±1	190±5
1-BuOAc	17.81±0.21	9.16±0.69 (9.93)	90±3	328±28
iso-BuOAc	17.77±0.19	9.22±0.65	90±3	316±26
sec-BuOAc	17.24±0.21	9.49±0.75	90±3	221±19
tert-BuOAc	18.02±0.08	7.88±0.27	87±1	128±4
1-*Pe*OAc[a]	20.54±0.17	13.0±1.1	113±4	427±35
1-*He*OAc[b]	24.11±0.28			

[a] Calculated from the values of solubility in the IUPAC Solubility Data Series using a polynomial regression of 2nd order [15]; [b] calculated from the average and standard deviation of the values of solubility at 298.2 K from Refs. [16–18]

The *Gibbs* free energy for the dissolution process (Eq. (2)) is positive, and their values increase almost linearly with increasing number of carbon atoms in the molecule of 1-alkyl acetate ($r = 0.9996$). The values for isomeric butyl acetates are close together, the difference between the lowest value for *sec*-BuOAc and the highest value for *tert*-BuOAc being only 5%. The ΔH_θ^0 values are negative and close to the calorimetric ones [5] for MeOAc, EtOAc, and 1-BuOAc. These values are given in parentheses in Table 3. The ΔH_θ^0 values for the lower members of the alkyl acetates do not show any trend with increasing molecular weight of the solute, except for 1-*Pe*OAc as has also been observed previously [5]. The standard entropies for the dissolution process (Eq. (2)) are negative, and their values decrease almost linearly with increasing number of carbon atoms in the molecule of 1-alkyl acetate ($r = 0.978$). Again, the standard entropies for isomeric butyl acetates are close together; the least negative value is obtained for *tert*-BuOAc. The values of the heat capacity of 1-alkyl acetates are positive and increase with increasing number of carbon atoms ($r = 0.983$), whereas the data for isomeric butyl acetates depend on the structure of the alkyl chain. Thus, for example, the lowest value was obtained for *tert*-BuOAc and the highest for 1-BuOAc.

Considering the hydration process as the transfer of a molecule from a fixed position in an ideal gas phase to a fixed position in liquid water at constant pressure, temperature, and composition, and neglecting the difference in volume of the two phases, the *Ben-Naim* standard *Gibbs* free energy change [21] corresponds to the work of coupling the solute with water. Thus, the *Ben-Naim* standard state [22] implies that all the entropy change associated with the gas-to-liquid transfer is due to solvent reorganization because the solute molecule has a fixed position. Thermodynamic functions of the transfer of the solute from ideal gas at $P = 1.013 \cdot 10^5\,\mathrm{Pa}$ to saturated water solutions $(\Delta X_\theta^0(ig \rightarrow aq), X : G, H, S)$ was calculated using ΔG_θ^0, ΔH_θ^0, vapour pressure of the solute at 298.2 K (P_s^{298}), and heat of vaporization $(\Delta H_{\mathrm{vap}}^{298})$ at 298.2 K. Thermodynamic functions $\Delta X_\theta^0(ig \rightarrow aq)$, based on the mole fraction scale, can be converted to the thermodynamic quantities of solvation by the following transformations where the

Table 4. Vapour pressure, heat of vaporization, and standard thermodynamic functions of hydration of alkyl acetates corrected to *Ben-Naim* standardization at 298.2 K

	$\frac{P_s^{298}}{\text{kPa}}$	$\frac{\Delta H_{\text{vap}}^{298}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{-\Delta G_\theta^*}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{-\Delta H_\theta^*}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{-\Delta S_\theta^*}{\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}}$
MeOAc	28.83[a]	32.30[a]	12.83	38.6	86
EtOAc	12.60[a]	35.62[a]	11.83	43.4	106
1-ProAc	4.50[a]	39.83[a]	11.11	47.8	123
1-BuOAc	1.66[a]	43.64[a]	10.29	50.7	136
iso-BuOAc	2.39[a]	39.2[a]	9.38	45.5	121
sec-BuOAc	3.2[a]	38[c]	9.25	45.4	121
tert-BuOAc	5.5[c]	38.03[b]	7.06	42.7	120
1-*Pe*OAc	0.60[b]	43[c]	9.66	55	152
1-*He*OAc	0.185[b]		9.19		

[a] [42]; [b] [43]; [c] calculated from the *Clausius-Clapeyron* equation (T_b: boiling point of compound) according to $\ln(P_s^{298}/P_s^{T_b}) = -\Delta H_{\text{vap}}^{298}/R \cdot (1/298K - 1/T_b)$

Ben-Naim thermodynamic quantities are denoted by a superscript asterisk, V_1^0 is the molar volume of the solvent at $1.013 \cdot 10^5$ Pa, and α_1^0 is the coefficient of thermal expansion of the solvent at constant pressure.

$$\Delta G_\theta^* = \Delta G_\theta^0(ig \rightarrow aq) - RT\ln(RT/PV_1^0) \tag{5}$$

$$\Delta H_\theta^* = \Delta H_\theta^0(ig \rightarrow aq) - RT(T\alpha_1^0 - 1) \tag{6}$$

$$\Delta S_\theta^* = \Delta S_\theta^0(ig \rightarrow aq) + R\ln(RT/PV_1^0) - R(T\alpha_1^0 - 1) \tag{7}$$

The values of the standard thermodynamic functions (Table 3) corrected to the *Ben-Naim* standardization are given in Table 4. In the calculation, the value of $\alpha_1^0 = 257.2 \cdot 10^{-6}\,\text{K}^{-1}$ was used [23]. From Table 4 it can be seen that the ΔG_θ^* values of the alkyl acetates investigated are negative. The dependence of ΔG_θ^* on the number of carbon atoms in the 1-alkyl chain of the solute molecule, shown in Fig. 3, is linear with a constant slope of (0.73±0.04) $\text{kJ} \cdot \text{mol}^{-1}$ on the carbon atom. In the same figure, the *Gibbs* energies of hydration of some *n*-alkanes (from methane to 1-octane) [22], 1-alkanols (from methanol to 1-pentanol) [24], and 1-alkylamines (from methyl amine to butyl amine) [21] are presented for comparison. The *Gibbs* free energies of hydration for both monofunctional compounds (1-alkanols and 1-alkylamines) are negative, whereas the values of ΔG_θ^* for *n*-alkanes are positive. The effect of the length of the alkyl chain on ΔG_θ^* is similar in all reported kinds of organic compounds. The values of ΔH_θ^* and ΔS_θ^* for alkyl acetates investigated are negative and decrease with the molecular weight of the 1-alkyl acetate. For the isomeric butyl acetates they increase with the branching of the alkyl chain. Figure 4 shows the dependence of ΔH_θ^* and ΔS_θ^* on the number of carbon atoms in the 1-alkyl chain. In this figure, data for some *n*-alkanes [25], 1-alkanols [24], and 1-alkylamines [21] are included. From Fig. 4 it can be seen that ΔH_θ^* values for some 1-alkyl acetates are between the values for polar compounds (1-alkanols and 1-alkylamines) and for *n*-alkanes. The values of ΔS_θ^*, shown in Fig. 4, are similar to those of 1-alkanols and 1-alkylamines.

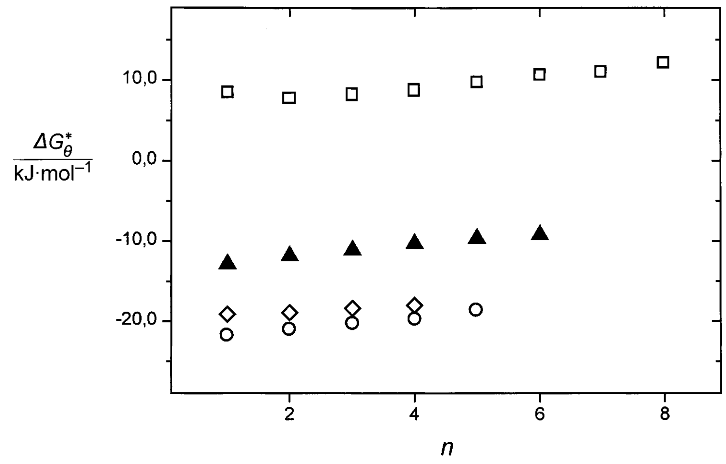

Fig. 3. *Gibbs* free energy of hydration of some 1-alkyl acetates (▲), 1-alkylamines (◇) [21], 1-alcohols (○) [24], and *n*-alkanes (□) [22] in water at 298.2 K as a function of the number of carbon atoms in the alkyl chain

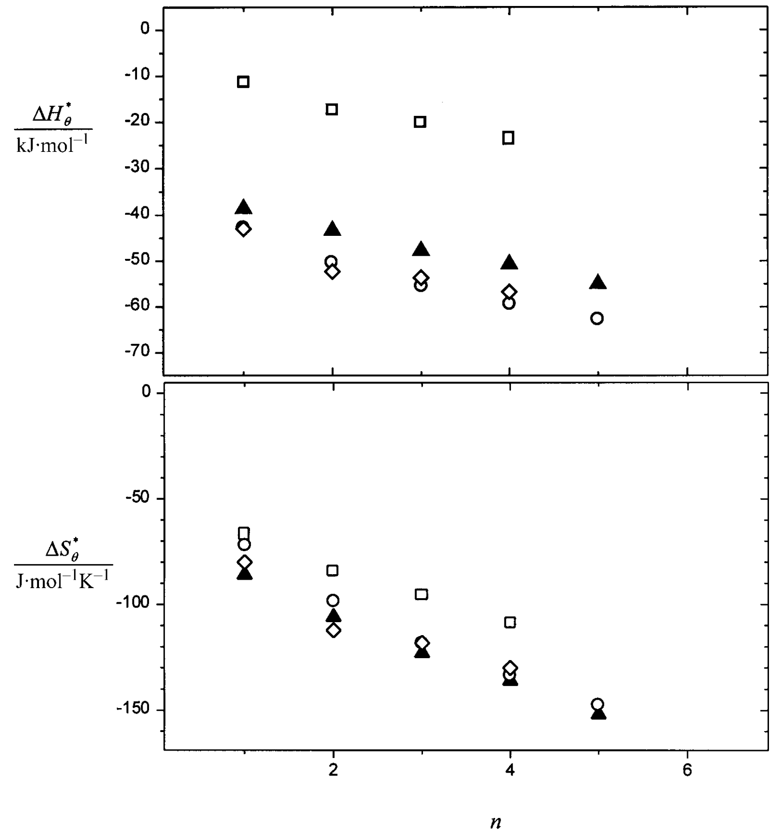

Fig. 4. Hydration enthalpies and entropies of some 1-alkyl acetates (▲), 1-alkylamines (◇) [21], 1-alcohols (○) [24], and *n*-alkanes (□) [25] in water at 298.2 K as a function of the number of carbon atoms in the alkyl chain

The hydration thermodynamics of the investigated alkyl acetates were analyzed by a theoretical approach developed by *Muller* [26] and later modified by *Lee* and *Graziano* [1]. According to this theory, the hydration entropy change may be given as a sum [24]:

$$\Delta S_\theta^* = \Delta S_x + \Delta S^h \tag{9}$$

ΔS_x represents the entropy contribution due to the excluded volume effect, and ΔS^h represents the entropy contribution due to the reorganization of H-bonds. By the assumption that ΔS_x can be calculated from the *Gibbs* free energy of cavity creation, $\Delta \bar{G}_c$, the ΔS_x value was calculated as

$$\Delta S_x = -\Delta \bar{G}_c / T \tag{10}$$

The *Gibbs* free energy required to create a cavity in water was calculated by the scaled particle theory [27] according to Eq. (11) where $y = \pi \sigma_1^3 C_1/6$ is the ratio of the hard sphere volume to the molar volume of the solvent, $C_1 = N_\mathrm{A}/V_1^0$ is the number density of the solvent, N_A is *Avogadro*'s number, and σ_1 and V_1^0 are the hard sphere diameter and molar volume of the solvent. The diameter of the cavity to be created is σ_2, and $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ is the radius of the sphere which excludes the centres of surrounding solvent molecules. The necessary molecular parameters are given in Tables 3 and 4 of Ref. [18].

$$\begin{aligned}\Delta \bar{G}_c = RT\Bigg(&6\frac{y}{1-y}\left(2\left(\frac{\sigma_{12}}{\sigma_1}\right)^2 - \frac{\sigma_{12}}{\sigma_1}\right) \\ &+ 18\left(\frac{y}{1-y}\right)^2\left(\left(\frac{\sigma_{12}}{\sigma_1}\right)^2 - \frac{\sigma_{12}}{\sigma_1} + \frac{1}{4}\right) - \ln(1-y)\Bigg)\end{aligned} \tag{11}$$

The calculated $\Delta \bar{G}_c$ values are compiled in Table 5. As was expected, they are large and positive and increase linearly with the *van der Waals* volume of the 1-alkyl acetate; for the isomeric butyl acetates, they are nearly constant (to 0.02%). As has been shown previously, the application of the scaled particle theory leads to the conclusion that the work of cavity creation is larger in water than in common organic solvents because the excluded volume effect is exaggerated by the small size of the water molecule [28, 29].

Table 5. The *Gibbs* free energy of cavity formation ($\Delta \bar{G}_c$) and entropy contributions from the excluded volume effect (ΔS_x) and for the reorganization of H-bonds (ΔS^h) at 298.2 K

	$\Delta \bar{G}_c$ / $\mathrm{kJ \cdot mol^{-1}}$	$-\Delta S_x$ / $\mathrm{J \cdot mol^{-1} K^{-1}}$	ΔS^h / $\mathrm{J \cdot mol^{-1} K^{-1}}$
MeOAc	36.5	122	36
EtOAc	41.3	138	33
1-ProAc	45.7	153	30
1-BuOAc	49.9	167	32
iso-BuOAc	49.9	167	46
sec-BuOAc	49.9	167	46
tert-BuOAc	49.9	167	48
1-*Pe*OAc	53.9	181	28
1-*He*OAc	57.7	194	

The ΔS^h values were evaluated by means of Eq. (9). The calculated values of ΔS_x and ΔS^h are collected in Table 5. From the values of ΔS_x and ΔS^h it can be seen that the excluded volume effect determines the sign of the hydration entropies of the alkyl acetates. In contrast, the ΔS^h values are positive and depend on the length and structure of the alkyl chain. The ΔS^h values given in Table 5 are much higher than for higher members of the 1-alcohol series at 298.2 K [24].

Similarly, the hydration enthalpy of nonpolar molecules is made up of two parts [29, 1] where E_a accounts for the direct solute-water *van der Waals* interaction energy which is not related to reorganization of H-bonds, and ΔH^h accounts for the enthalpy contribution due to reorganization of H-bonds of water molecules in the hydration shell.

$$\Delta H_\theta^* = E_a + \Delta H^h \tag{12}$$

According to this approach E_a is also considered as the sum of two parts:

$$E_a = E_a(vdW) + E_a(\text{H-bond}) \tag{13}$$

$E_a(vdW)$ is the *van der Waals* contribution due to the nonpolar moiety and identical to that of the corresponding alkyl chain; it can be estimated from the group additivity analysis given by *Jorgenson* [30]. E_a(H-bond) is the H-bond contribution due to the functional group. The value of ΔH^h in Eq. (12) can be calculated by an assumption which takes into account that H-bond reorganization is a compensating process, not affecting the hydration *Gibbs* free energy change:

$$\Delta H^h = T \cdot \Delta S^h \tag{14}$$

Therefore, E_a(H-bond) may be calculated by means of Eqs. (12)–(14).

Applying this model to alkyl acetates, we calculated the values of ΔH^h, E_a, $E_a(vdW)$, and E_a(H-bond) which are collected in Table 6. The values of ΔH^h are positive and depend on the molecular weight of the solute; for the isomeric butyl acetates, they are practically constant. On the contrary, the E_a values are negative and decrease with increasing molecular weight of the solute. For the isomeric butyl acetates, they decrease with increasing branching of the alkyl chain. Values of $E_a(vdW)$ for alkyl acetates were calculated by means of a group additivity analysis of *Jorgensen*'s results for aliphatic hydrocarbons [30]. These values, collected in

Table 6. *van der Waals* interaction energy (E_a) enthalpy contribution due to the reorganization of H-bonds (ΔH^h) and *van der Waals* enthalpy contribution due to the nonpolar moiety ($E_a(vdW)$) and to the H-bond term (E_a(H-bond)) at 298.2 K

	$-E_a$ / $\text{kJ} \cdot \text{mol}^{-1}$	ΔH^h / $\text{kJ} \cdot \text{mol}^{-1}$	$-E_a(vdW)$ / $\text{kJ} \cdot \text{mol}^{-1}$	$-E_a(\text{H-bond})$ / $\text{kJ} \cdot \text{mol}^{-1}$
MeOAc	49.3	10.7	20.2	29.1
EtOAc	53.1	9.7	27.4	25.7
1-ProAc	56.8	9.1	34.6	22.2
1-BuOAc	60.2	9.5	41.8	18.4
iso-BuOAc	59.3	13.8	32.7	26.6
sec-BuOAc	59.2	13.8	32.7	26.5
tert-BuOAc	57.0	14.2	36.0	21.0
1-*Pe*OAc	63.9	8.7	49.0	14.6

Table 6, are negative, like those calculated for 1-alcohols [24]. The E_a(H-bond) values are negative and decrease almost linearly with increasing molecular weight of the solute molecule, which means that the ester group is not involved in the same number of H-bonds with water molecules. For 1-alcohols, E_a(H-bond) values are constant for the lower members of the homologous series and amount to $-31.0\,\mathrm{kJ \cdot mol^{-1}}$ [24].

The total hydration *Gibbs* free energy is given by Eq. (15) [24] from which follows that there is a balance of three contributions: the direct *van der Waals* interaction energy, the direct solute-water H-bond energy, and the excluded volume effect due to solute insertion into liquid water. The independence of ΔG^* values from the number of carbon atoms in the molecule of solute (see Fig. 3) for 1-alcohols and 1-alkylamines may be explained by the constant value of E_a(H-bond) and a compensation of $E_a(vdW)$ and $\Delta\bar{G}_c$. For the first four members of the 1-alkyl alkylamines we obtained E_a(H-bond) values between 35.5 and $28.6\,\mathrm{kJ \cdot mol^{-1}}$, so a slight dependence on the molecular weight of the solute was observed.

$$\Delta G_a^* = E_a + T\Delta S_x = E_a(vdW) + E_a(\text{H-bond}) + \Delta\bar{G}_c \qquad (15)$$

In conclusion, on the basis of standard thermodynamic functions of solution, especially of the large and positive heat capacity and of the thermodynamic functions of hydration, it may be concluded that the investigated solutes are essentially hydrophobically hydrated and that the solute molecule affects the ordering of water molecules around the solute.

Experimental

Methyl, ethyl, 1-propyl, 1-butyl, 2-methyl-1-propyl, 2-methyl-2-propyl, 1-pentyl, 1-hexyl (Fluka AG), and 2-butyl acetate (Aldrich) were purified by distillation under reduced pressure and then stored over 4 Å molecular sieves in a well-closed container. The purity of the compounds was checked by measurement of their refractive indices at 293.2 and 298.2 K and their densities at 298.2 K. The values obtained are given in Refs. [18] and [20].

Solubility measurements

The experimental procedure has been described previously [18]. Each value of solubility, expressed as a mole fraction x_2, is based on at least three measurements. The relative standard deviations were derived and gave reproducibilities in the case of volumetric analysis better than 1% whereas in the case of HPLC analysis (2-methyl-2-propyl acetate) the reproducibilities were between 2 and 3%.

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