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Thermodynamics of Transfer of Some Alkyl Acetates from Water to Water–Ethanol Mixtures

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Summary. 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), 2-methyl-2-propyl acetate (*tert*-BuOAc), 1-pentyl acetate (1-*Pe*OAc), and 1-hexyl acetate (1-*He*OAc) in 2.5, 5.0, 7.5, and 10.0 weight per cent of ethanol in water were determined at 298.2 K. The solubility of the same compounds, except for *tert*-BuOAc, 1-*Pe*OAc, and 1-*He*OAc, was determined as a function of temperature at 10.0 weight per cent of ethanol in water. From the solubility measurements the standard *Gibbs* energy (ΔG_t^0), enthalpy (ΔH_t^0), and entropy (ΔS_t^0) of transfer were determined. The calculated thermodynamic functions show that the predominant factors in the transfer of alkyl acetate molecules are the transfer of the cavity and the hydrophobic interaction of the nonpolar alkyl chain. Scaled particle theory calculations were used to determine the thermodynamics of cavity transfer, which were combined with the experimental total transfer quantities to obtain the corresponding interaction transfer quantities. It was found that the *Gibbs* energy of interaction for the transfer is negative, whereas the enthalpy and entropy of interaction for the transfer are positive; almost complete compensation of enthalpy and entropy components occurs.

Keywords. Alkyl acetates; Ethanol–water mixtures; Solubility; Standard thermodynamic functions of transfer.

Introduction

A knowledge of the thermodynamics of transfer of some polar and nonpolar solutes from pure water to an aqueous organic mixture is necessary for a clear understanding of the interactions in many aqueous ternary systems, especially in the field of complex biological systems. The properties of aqueous solutions of monohydric alcohols are of interest in many fields because of their high solubility in water, in spite of the fact that these solutions often show abnormalities in their physico-chemical properties. For monohydric alcohols in dilute solutions, such behaviour can be attributed in a general way to the bifunctional nature of the solute molecule. The hydroxyl group, which either acts as a proton donor or acceptor, can form a hydrogen bond with the water molecule and a hydrophobic hydrocarbon group. So, these mixtures are of high interest from the structural point of view [1].

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In a previous work, thorough research was carried out on the thermodynamics of solution of some alkyl acetates in water [2]. The aim of that work was to characterize the thermodynamic behaviour of these systems, especially with regard to hydrophobic interaction, which drives slightly polar alkyl acetate molecules toward aggregation in aqueous solutions [3]. The present work presents thermodynamic functions of transfer of some alkyl acetates from pure water to dilute aqueous ethanol solutions. In the literature only a few data are known for the solubility of alkyl acetates in these low-percentage ethanol water mixtures [4–7]. On the other hand, the alkyl acetate molecule can be used as a structural probe to investigate the hydrophobic effect, one of the most important forces that govern the structure and interaction of all biological molecules [8].

Results and Discussion

The experimental results together with some data from the literature [4–7] are given in Tables 1 and 4. From Table 1 it is evident that the solubility of each alkyl acetate, expressed as its mole fraction x_2 increases with increasing ratio of the mole fraction of ethanol to the mole fraction of water, x_3/x_1. The data of *Yoshio Kumagae et al.* [7] are close to ours (better than 2%), whereas those of *Acre et al.* [4] are about 40% higher than ours. The solubility of an alkyl acetate may be given by the linear relation of Eq. (1), where a_0 and a_1 are empirical constants given in Table 2.

$$x_2 = a_0 + a_1 \cdot \frac{x_3}{x_1} \tag{1}$$

The standard *Gibbs* energy change ΔG_t^0, accompanying the transfer of alkyl acetate from the standard state in water (ΔG_w^0) to the standard state in a water–ethanol solution (ΔG_s^0), can be obtained using Eq. (2) [9], where $x_{2,w}/x_{2,s}$ is the ratio of the mole fraction of alkyl acetate in saturated water and saturated water–ethanol solution, R is the gas constant, and T is the absolute temperature.

$$\Delta G_t^0 = \Delta G_s^0 - \Delta G_w^0 = RT \ln\left(\frac{x_{2,w}}{x_{2,s}}\right) \tag{2}$$

ΔG_t^0 is the *Gibbs* energy of transfer of solute at infinite dilution from the reference solvent water to the solvent s based on the standard state of the hypothetical ideal solution of unit mole fraction. In the calculation of ΔG_t^0 it was assumed that the activity coefficients of the alkyl acetates in the corresponding states of saturated solutions and in the respective solvents are likely to be more or less equal due to the relatively low mole fraction of ethanol [10]. Hence, the ratio of the activity coefficient is assumed to be one. The values of ΔG_t^0 and their errors are given in Table 3. The uncertainty of the values of ΔG_t^0 was calculated from the relation

$$\mathrm{d}\Delta G_t^0 = RT\left(\left(\frac{\mathrm{d}x_{2,w}}{x_{2,w}}\right)^2 + \left(\frac{\mathrm{d}x_{2,s}}{x_{2,s}}\right)^2\right)^{1/2}$$

using the corresponding errors of the solubility determination from Table 1 for $\mathrm{d}x_{2,w}$ and $\mathrm{d}x_{2,s}$. The respective errors of ΔG_t^0 are less than $0.04\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$ for the compound analyzed by the volumetric procedure and $0.1\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$ for

Table 1. Solubility of some alkyl acetates in water [2] and aqueous ethanol solutions together with densities of saturated solutions at 298.2 K

$\frac{x_3}{x_1} \cdot 10^3$	$x_2 \cdot 10^3$	$\frac{\rho}{\mathrm{g \cdot cm^{-3}}}$	$\frac{x_3}{x_1} \cdot 10^3$	$x_2 \cdot 10^3$	$\frac{\rho}{\mathrm{g \cdot cm^{-3}}}$
MeOAc			*iso*-BuOAc		
0.0	71.03±0.35[a]	1.00050[a]	0.0	0.9842±0.0028[a]	0.99679[a]
10.0	79.13±0.34	0.99621	10.0	1.0764±0.0038	0.99221
20.6	91.64±0.95	0.99146	20.6	1.1869±0.0072	0.98832
31.7	102.08±0.65	0.98807	31.7	1.2860±0.0051	0.98409
			43.5	1.3858±0.0030	0.98049
EtOAc			*sec*-BuOAc		
0.0	16.121±0.073[a]	0.99654[a]	0.0	1.293±0.010[a]	0.99684[a]
10.0	17.149±0.045	0.99268	10.0	1.403±0.008	0.99227
20.6	18.162±0.039	0.98842	20.6	1.520±0.003	0.98817
31.7	19.129±0.044	0.98503	31.7	1.627±0.016	0.98443
43.5	20.599±0.040	0.98147	43.5	1.775±0.003	0.98058
EtOAc (literature values)			*tert*-BuOAc		
0.0	22[c]		0.0	1.114±0.015[a]	0.99671[a]
22	26[c]		10.0	1.234±0.008	0.99225
32.9	26[c]		20.6	1.358±0.017	0.98806
0	15.8[d]		31.7	1.479±0.011	0.98404
28.2	18.7[d]		43.5	1.621±0.017	0.98040
1-PrOAc			1-*Pe*OAc		
0.0	3.852±0.006[a]	0.99653[a]	0.0	0.2223±0.0046[a]	0.99705[b]
10.0	4.115±0.007	0.99219	10.0	0.2481±0.0037	0.99249[b]
20.6	4.386±0.012	0.98806	20.6	0.2718±0.0054	0.98817[b]
31.7	4.634±0.007	0.98425	31.7	0.2995±0.0026	0.98419[b]
43.5	4.966±0.009	0.98031	43.5	0.3307±0.0050	0.98043[b]
1-BuOAc			1-*He*OAc		
0.0	0.9289±0.0009[a]	0.99682[a]	0.0	0.0519±0.0007[a]	0.99705[b]
10.0	1.0242±0.0061	0.99209	10.0	0.0570±0.0037	0.99249[b]
20.6	1.1090±0.0067	0.98806	20.6	0.0644±0.0020	0.98817[b]
31.7	1.2081±0.0021	0.98500	31.7	0.0720±0.0002	0.98419[b]
43.5	1.3048±0.0090	0.98078	43.5	0.0797±0.0010	0.98043[b]

[a] Data taken from Ref. [2]; [b] density of water–ethanol solutions taken from Ref. [27]; [c] Ref. [4]; [d] Ref. [7]

compounds analyzed by HPLC. From the data it can be seen that ΔG_t^0 values are small and negative and decrease almost linearly with the mole fraction of ethanol for the investigated alkyl acetates ($r > 0.993$). It is believed that the small *Gibbs* energy change, and hence the low solubility, arises from the small size of the water molecules [8].

The variation of ΔG_t^0 of EtOAc with the mole fraction of ethanol and some other cosolvents like aqueous dimethyl sulfoxide, dioxane, and acetonitrile mixtures [11] are interesting. At this low cosolvent mole fraction ($x_3 < 0.044$) it is

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

	$a_0 \cdot 10^3$	$a_1 \cdot 10^2$	r	$s \cdot 10^5$
MeOAc	70.40±0.91	100.0±4.7	0.9978	111
EtOAc	16.101±0.091	10.07±0.35	0.9982	12.0
1-ProAc	3.856±0.012	2.529±0.048	0.9995	1.6
1-BuOAc	0.933±0.003	0.860±0.013	0.9997	0.44
iso-BuOAc	0.987±0.005	0.931±0.020	0.9993	0.68
sec-BuOAc	1.292±0.006	1.094±0.023	0.9993	0.80
tert-BuOAc	1.116±0.003	1.158±0.011	0.9999	0.37
1-*Pe*OAc	0.222±0.001	0.247±0.004	0.9996	0.13
1-*He*OAc	0.0512±0.0004	0.065±0.002	0.9990	0.06

Table 3. Standard *Gibbs* energy of transfer (ΔG_t^0), *Gibbs* energy of cavity formation (ΔG_s^0 (cav)), *Gibbs* energy of transfer of cavity (ΔG_t^0 (cav)), and *Gibbs* energy of interaction for transfer (ΔG_t^0 (int)) as a function of mole fraction of the cosolvent at 298.2 K

	$x_3 \cdot 10^2$	$\frac{-\Delta G_t^0}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta G_i^0 \text{ (cav)}}{\text{kJ} \cdot \text{mol}^{-1}}$ $i = \text{w,s}$	$\frac{-\Delta G_t^0 \text{ (cav)}}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{-\Delta G_t^0 \text{ (int)}}{\text{kJ} \cdot \text{mol}^{-1}}$
MeOAc	0	0.0	36.45 (w)[a]	0	0.00
	0.91	0.267±0.017	36.37 (s)	0.08	0.14
	1.83	0.631±0.027	36.30 (s)	0.15	0.38
	2.76	0.899±0.020	36.26 (s)	0.19	0.56
EtOAc	0	0.0	41.25 (w)[a]	0	0.00
	0.98	0.153±0.013	41.15 (s)	0.10	0.01
	1.98	0.295±0.013	41.07 (s)	0.18	0.02
	3.01	0.424±0.013	41.02 (s)	0.23	0.05
	4.08	0.608±0.012	40.99 (s)	0.26	0.15
1-PrOAc	0	0.0	45.72 (w)[a]	0	0
	0.99	0.164±0.005	45.60 (s)	0.11	0.00
	2.01	0.322±0.007	45.51 (s)	0.20	0.02
	3.06	0.458±0.004	45.45 (s)	0.26	0.05
	4.14	0.630±0.006	45.41 (s)	0.31	0.13
1-BuOAc	0	0.0	49.92 (w)[a]	0	0
	0.99	0.242±0.015	49.79 (s)	0.13	0.07
	2.01	0.439±0.015	49.69 (s)	0.23	0.11
	3.07	0.652±0.004	49.62 (s)	0.30	0.21
	4.16	0.842±0.017	49.57 (s)	0.35	0.30
1-*Pe*OAc	0	0.0	53.91 (w)[a]	0	0
	0.99	0.273±0.063	53.78 (s)	0.14	0.08
	2.02	0.498±0.071	53.66 (s)	0.25	0.15
	3.07	0.739±0.055	53.58 (s)	0.33	0.26
	4.16	0.985±0.063	53.53 (s)	0.39	0.40

(*continued*)

Table 3 (*continued*)

	$x_3 \cdot 10^2$	$\frac{-\Delta G_t^0}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{\Delta G_i^0\,(\text{cav})}{\text{kJ} \cdot \text{mol}^{-1}}$ $i = \text{w,s}$	$\frac{-\Delta G_t^0\,(\text{cav})}{\text{kJ} \cdot \text{mol}^{-1}}$	$\frac{-\Delta G_t^0\,(\text{int})}{\text{kJ} \cdot \text{mol}^{-1}}$
1-*He*OAc	0	0.0	57.73 (w)[a]	0	0
	0.99	0.234±0.164	57.58 (s)	0.15	0.03
	2.02	0.537±0.085	57.46 (s)	0.28	0.16
	3.07	0.696±0.036	57.37 (s)	0.36	0.19
	4.16	1.112±0.092	57.31 (s)	0.43	0.49
iso-BuOAc	0	0.0	49.92 (w)[a]	0	0
	0.99	0.222±0.010	49.79 (s)	0.13	0.05
	2.01	0.464±0.016	49.69 (s)	0.23	0.14
	3.07	0.663±0.011	49.62 (s)	0.30	0.22
	4.16	0.848±0.007	49.57 (s)	0.35	0.30
sec-BuOAc	0	0.0	49.92 (w)[a]	0	0
	0.99	0.203±0.025	49.79 (s)	0.13	0.03
	2.01	0.402±0.021	49.69 (s)	0.23	0.08
	3.07	0.571±0.032	49.62 (s)	0.30	0.12
	4.16	0.786±0.022	49.57 (s)	0.35	0.24
tert-BuOAc	0	0.0	49.91 (w)[a]	0	0
	0.99	0.254±0.037	49.79 (s)	0.13	0.08
	2.01	0.491±0.047	49.69 (s)	0.23	0.16
	3.07	0.702±0.039	49.62 (s)	0.30	0.26
	4.16	0.930±0.043	49.57 (s)	0.35	0.38

[a] Data taken from Ref. [2]

accepted that water retains or even enhances some of its three dimensional structure, and that the behaviour of the mixed solvent should resemble that of pure water, *i.e.* the formation of a large number of water–water hydrogen bonds [10, 12]. In this regard the rate of decrease of the *Gibbs* energy of transfer of EtOAc with increasing cosolvent mole fraction is negligible for water–dimethyl sulfoxide mixtures (limiting slope $0.4\,\text{kJ} \cdot \text{mol}^{-1}$) and similar for water–ethanol and water–acetonitrile (limiting slopes $14.6\,\text{kJ} \cdot \text{mol}^{-1}$ and $18.3\,\text{kJ} \cdot \text{mol}^{-1}$); for water–dioxane mixtures it is much greater (limiting slope $24\,\text{kJ} \cdot \text{mol}^{-1}$). This difference was explained by a deviation from the behaviour of binary mixtures of water and an organic solvent according to *Raoult*'s law. Thus, for example, mixtures of water and dioxane [13], water and acetonitrile [14], and water and ethanol [15] show a positive deviation from *Raoults*' law, whereas mixtures of water and dimethyl sulfoxide [16] show a large negative deviation. It is known that molecules of water and dimethyl sulfoxide interact strongly with each other [16]. Thus, ethanol, dioxane, and acetonitrile are free to solvate EtOAc, whereas solvation by dimethyl sulfoxide in water-rich solvent mixtures is hindered by or requires the disruption of very stable water–dimethyl sulfoxide bonds [11]. The same conclusion may be obtained for the transfer of 2-methyl-2-propyl acetate and *iso*-propyl acetate between water and the above mentioned mixtures [11].

Table 4. Solubility and standard *Gibbs* energy of transfer ($\Delta G^0_{t,T}$) of some alkyl acetates in water–ethanol solutions at constant x_3/x_1 ratio (0.0435) as a function of temperature

	$\frac{T}{K}$	$x_2 \cdot 10^3$	$\frac{-\Delta G^0_{t,T}}{kJ \cdot mol^{-1}}$
MeOAc	303.2	118.0±1.3	1.295±0.028
	308.2	125.5±0.8	1.480±0.017
	313.2	134.4±1.4	1.673±0.028
	318.2	144.1±1.4	1.870±0.027
EtOAc	298.2	20.599±0.040	0.609±0.012
	303.2	20.730±0.047	0.733±0.010
	308.2	20.629±0.054	0.855±0.009
	313.2	20.722±0.087	0.974±0.012
	318.2	20.966±0.019	1.089±0.006
	313	18[a]	
1-PrOAc	298.2	4.9662±0.0090	0.634±0.006
	303.2	4.9095±0.0069	0.773±0.008
	308.2	4.9367±0.0056	0.901±0.009
	313.2	4.9641±0.0069	1.019±0.010
	318.2	4.9955±0.0036	1.132±0.003
1-BuOAc	298.2	1.3048±0.0090	0.894±0.017
	303.2	1.3178±0.0018	1.071±0.014
	308.2	1.3232±0.0018	1.225±0.013
	313.2	1.3535±0.0030	1.356±0.011
	318.2	1.3773±0.0012	1.467±0.021
	303	1.3[b]	
iso-BuOAc	298.2	1.3858±0.0030	0.815±0.009
	303.2	1.3841±0.0003	0.970±0.005
	308.2	1.3917±0.0015	1.114±0.008
	313.2	1.4029±0.0020	1.245±0.026
	318.2	1.4314±0.0013	1.362±0.014
sec-BuOAc	298.2	1.775±0.003	0.876±0.020
	303.2	1.781±0.008	1.057±0.014
	308.2	1.787±0.011	1.221±0.019
	313.2	1.795±0.015	1.367±0.023
	318.2	1.822±0.002	1.495±0.010

[a] Ref. [6]; [b] Ref. [5]

The hydrophobic effect of the alkyl chain in the molecule of alkyl acetate is a characteristic feature of all such solutes possessing a bulky organic functional group and an alkyl residue [17]. According to *Parker* and co-workers [18], the water molecules around a hydrophobic solute form a hydrogen-bonded network among themselves, and the formation of such a highly ordered surface or skin contributes appreciably to the entropy of transfer of the solute. The model of hydrophobic hydration of amphiphilic solute molecules proposed by *Kundu et al.* [19] assumed that the skin phase is more compact and has a more stable structure in pure water than in a mixed solvent, because steric inhibition of the alkyl chain of ethanol and the fewer hydrogen bonding sites between the molecules discourage strong solvent–solvent

interactions when ethanol molecules are present in that phase. Therefore, compared to water in the mixed ethanol–water solvent the strength of individual hydrogen bonds in the bulk phase increases, whereas their total number decreases [1]. Hence, the sharp fall of ΔG_t^0 in water-rich compositions arises from the predominance of the *Gibbs* energy of formation of the buffer bonds, *i.e.* hydrogen bonds between ethanol and water molecules, and dispersion interactions of the alkyl chain of ester molecules and the ethyl group of ethanol. Such a behaviour can also be explained by the preferential model of solvation developed by *Skwierzynski* and *Connvers* [20]. According to their explanation it seems that at low ethanol concentrations polar ester groups are predominantly solvated by water molecules, whereas the alcohol molecules are strongly bonded to water molecules. Recent studies of *Wakisaka et al.* [21] have shown that ethanol molecules are substituted for part of the water molecules in the hydrogen bonded network of water. So, the inherent water structure is conserved, and ethanol molecules interacting with water clusters are energetically more favourable than the ethanol molecule clusters.

From the linear dependence of ΔG_t^0 with the number of carbon atoms in the 1-alkyl chain the contributions of the CH_3–CO–O– unit, Δg_t^0, and of the size of the alkyl chain at constant cosolvent composition ($x_3 = 2.0 \cdot 10^{-2}$) were estimated. The Δg_t^0 value amounts to $-158\,\mathrm{J \cdot mol^{-1}}$ for the CH_3–CO–O– unit, whereas the Δg_t^0 value for each –CH_2– group is $-61\,\mathrm{J \cdot mol^{-1}}$. In the calculation of Δg_t^0 values, the data for MeOAc were not used.

It has been found that for large-sized molecules the true interaction effect, *i.e.* $\Delta G_t^0\,(\mathrm{int})$, is a better measure of the interaction between the solute and solvent molecule [22]. According to *Treiner* [22], the standard *Gibbs* energy of transfer of solute between a reference solvent (here water) and a given solvent s is

$$\Delta G_t^0 = \Delta G_t^0\,(\mathrm{cav}) + \Delta G_t^0\,(\mathrm{int}) + RT \ln(V_w/V_s) \tag{4}$$

where

$$\Delta G_t^0\,(\mathrm{cav}) = \Delta G_s^0\,(\mathrm{cav}) - \Delta G_w^0\,(\mathrm{cav}) \tag{5}$$

and

$$\Delta G_t^0\,(\mathrm{int}) = \Delta G_s^0\,(\mathrm{int}) - \Delta G_w^0\,(\mathrm{int}). \tag{6}$$

V_w and V_s are the molar volumes of water and solvent, $\Delta G_s^0\,(\mathrm{cav})$ and $\Delta G_w^0\,(\mathrm{cav})$ are the respective *Gibbs* energies of cavity formation, and $\Delta G_s^0\,(\mathrm{int})$ and $\Delta G_w^0\,(\mathrm{int})$ are the *Gibbs* energies of interaction in solvent and water, respectively.

The reversible work of introducing a hard-sphere solute into a fluid mixture containing more than one component whose molecules have hard cores, $\Delta G_s^0\,(\mathrm{cav})$, can be obtained according to Eq. (7) where σ_s is the diameter of the solute molecule, $y_i = (\pi/6)\sum_j \rho_j \sigma_j^i$, and ρ_j and σ_j are the number density and the hard sphere diameter of the j-th component, P is the pressure of the system, and N is the *Avogadro* number.

$$\Delta G_s^0(\mathrm{cav}) = -RT\left(\ln(1-y_3) - \left(\frac{3y_2}{1-y_3}\right)\sigma_s - \left(\frac{3y_1}{1-y_3} + \frac{9y_2^2}{2(1-y_3)^2}\right)\sigma_s^2 - \frac{\pi NP\sigma_s^3}{6}\right) \tag{7}$$

For the investigated systems we used the following relations:

$$y_1 = \frac{\pi}{6}(\rho_1\sigma_1 + \rho_3\sigma_3) \tag{8}$$

$$y_2 = \frac{\pi}{6}(\rho_1\sigma_1^2 + \rho_3\sigma_3^2) \tag{9}$$

$$y_3 = \frac{\pi}{6}(\rho_1\sigma_1^3 + \rho_3\sigma_3^3) \tag{10}$$

The hard sphere diameter of water was taken as 0.275 nm, that of ethanol as 0.438 nm [24], and values for alkyl acetates were taken from Ref. [25]. The number density of the components of solution was calculated from the weight fraction of the respective component and the densities of solutions. The calculated values of ΔG_s^0 (cav) are summarized in Table 3.

From the values obtained for ΔG_s^0 (cav) it may be seen that for a definite ester the reversible work to create a cavity in the mixed solvent is smaller than in water [2] and almost linearly decreases with increasing mol% of ethanol. At a definite x_3 these values linearly increase with the increasing number of carbon atoms in the alkyl acetate. ΔG_t^0 (cav) were calculated from Eq. (5) and are given in Table 3. Since ΔG_w^0 (cav) $> \Delta G_s^0$ (cav) for the systems investigated, the ΔG_t^0 (cav) values are negative and decrease linearly with increasing mole fraction of ethanol for a particular alkyl acetate. Positive values for ΔG_t^0 (cav) were obtained for transfer of MeOAc, EtOAc, 1-PrOAc and 1-BuOAc from water to water solutions of sodium chloride [26], where ΔG_w^0 (cav) $< \Delta G_s^0$ (cav). The interaction effect, *i.e.* ΔG_t^0 (int), was calculated from Eq. (4) where the molar volume of the mixed solvent, V_s, was obtained:

$$V_s = \frac{x_1 M_1 + x_3 M_3}{d_{13}} \tag{11}$$

M_1 and M_3 are the molecular weights of water and ethanol, x_1 and x_3 are the mole fractions of water and ethanol in the mixed solvent, and d_{13} is the density of the respective water–ethanol solution [27]. The last term of Eq. (4) at the highest mole fraction of ethanol contributes about $-0.20\,\mathrm{kJ}\cdot\mathrm{mol}^{-1}$ to ΔG_t^0 (int). ΔG_t^0 (int) values are summarized in Table 3. These values are negative due to the large and negative values of ΔG_t^0 and, as can be seen from Fig. 1 for 1-alkyl acetates, decrease with the mole fraction of ethanol; in addition, they depend on the structure of the alkyl chain. The data show the difference in the *Gibbs* energy of the solute–solvent interactions between the alkyl acetate and water and between the same ester and aqueous ethanol solutions. From the same figure it can be seen that the most pronounced difference in the interaction occurs for the smallest molecule (MeOAc).

As to the isomeric butyl acetates, the highest value of ΔG_t^0 (int) at a definite mole fraction of ethanol was obtained for *sec*-BuOAc. For the transfer of MeOAc, EtOAc, 1-PrOAc, and 1-BuOAc from water to the aqueous solutions of sodium chloride, *Cross* and *McTigue* [26] have found that ΔG_t^0 (int) values are negative as a result of a large ΔG_t^0 (cav) and a smaller positive value of ΔG_t^0.

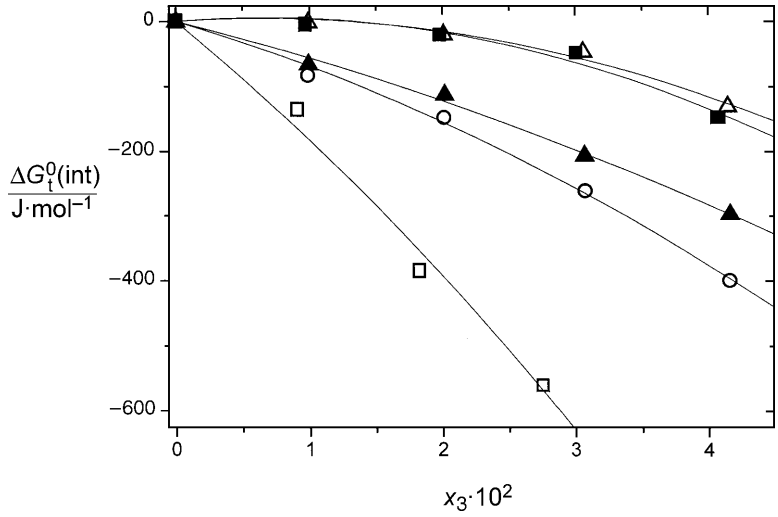

Fig. 1. Variation of ΔG_t^0 (int) of MeOAc (□), EtOAc (■), 1-ProAc (Δ), 1-BuOAc (▲), and 1-*Pe*OAc (◯) with cosolvent composition in aqueous mixtures at 298.2 K

In Table 4 and Fig. 2 the solubility of alkyl acetate, expressed as its mole fraction x_2, is given as a function of temperature at a constant ratio of $x_3/x_1 = 0.0435$. From the results collected in Table 4 where also some literature values are given [5, 6] it follows that the effect of the temperature on the solubility is relatively small and can be expressed as

$$x_2 = A_0 + A_1(T - \theta) + A_2(T - \theta)^2 \tag{12}$$

where $\theta = 298.2$ K and A_0, A_1, and A_2 are empirical constants given in Table 5 together with their relevant statistical parameters. In Table 4, the *Gibbs* energy of transfer calculated from Eq. (2) is given as a function of temperature at constant mole ratio of ethanol and water. The corresponding data for the solubility of alkyl acetate in pure water were taken from Eq. (1) in Ref. [2]. The uncertainly of the $\Delta G_{t,T}$ value was calculated from the corresponding relative error of solubility data and amounts to less than 0.04 kJ · mol^{-1}. The calculated $\Delta G_{t,T}$ values are negative and decrease with increasing temperature.

The standard thermodynamic functions of transfer, *i.e.* the *Gibbs* energy and enthalpy of transfer, were calculated by a least square method using a non-empirical procedure given by *Clarke* and *Glew* [28] in the form of Eq. (13) where $x_{2,s}$ and $x_{2,w}$ are the solubility of the solute in aqueous ethanol and aqueous solutions calculated from Eq. (12) and Eq. (1) in Ref. [2], respectively, $b_0 = -\Delta G_{t,\theta}^0/\theta$, and $b_1 = \Delta H_{t,\theta}^0/\theta$.

$$-\frac{\Delta G_{t,T}^0}{T} = -R(\ln x_{2,s} - \ln x_{2,w}) = b_0 + b_1 u_1 \tag{13}$$

The corresponding independent variable is defined as $u_1 = \delta \sum_{n=1}^{\infty} (-\delta)^{n-1} \equiv \delta/(1+\delta)$ where $\delta = (T-\theta)/\theta$. The contribution of the activity coefficient in saturated water and saturated water–ethanol solution to $-\Delta G_{t,T}^0/T$ is assumed to be zero (see Eq. (2)). The dependence of $-\Delta G_{t,T}^0/T$ on u_1 is shown in Fig. 3. The

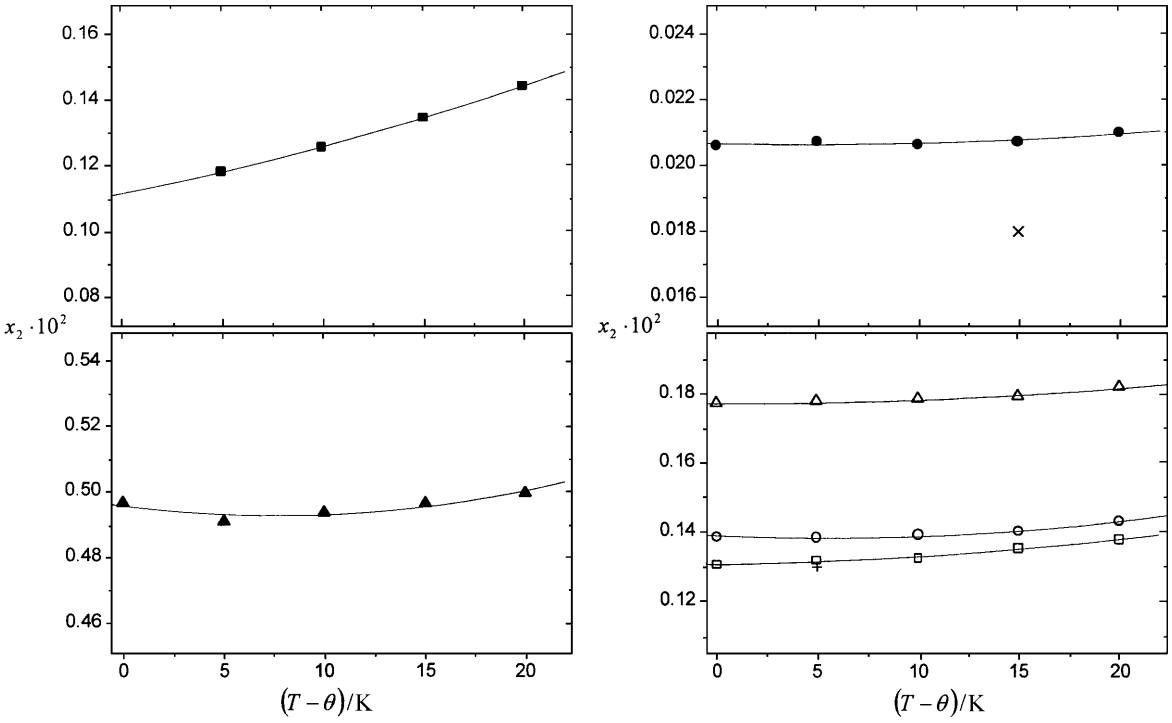

Fig. 2. Solubility of MeOAc (■), EtOAc (●), 1-PrOAc (▲), 1-BuOAc (□), *iso*-BuOAc (◯), and *sec*-BuOAc (△) in water–ethanol solutions at a ratio of $x_3/x_1 = 0.0435$ as a function of temperature; +: value from Ref. [5], ×: value from Ref. [6]

Table 5. Regression coefficients of Eq. (12) of some alkyl acetates together with the regression correlation coefficient r and the standard error s

	$A_0 \cdot 10^3$	$\frac{A_1 \cdot 10^5}{K^{-1}}$	$\frac{A_2 \cdot 10^7}{K^{-2}}$	r	$s \cdot 10^5$
MeOAc	111.42±0.35	119.0±6.5	223±25	0.999	13
EtOAc	20.645±0.090	−1.0±2.1	12±10	0.887	9.5
1-ProAc	4.957±0.018	−0.78±0.43	5.0±2.1	0.908	1.9
1-BuOAc	1.3058±0.0051	0.10±0.12	1.33±0.58	0.992	0.54
iso-BuOAc	1.3863±0.0023	−0.15±0.54	1.83±0.26	0.996	0.24
sec-BuOAc	1.7767±0.0042	−0.04±0.10	1.26±0.47	0.985	0.44

standard entropy of transfer was calculated by the *Gibbs-Helmholtz* relation where the uncertainty was estimated from the corresponding errors of coefficients b_0 and b_1. In Table 6, the standard thermodynamic functions for the transfer of alkyl acetates are given. From these results it is apparent that $\Delta G^0_{t,\theta}$ values are precise, whereas the values of $\Delta H^0_{t,\theta}$ and $T\Delta S^0_{t,\theta}$ are not. The standard *Gibbs* energies of transfer are negative and small, and their values, except for MeOAc, decrease linearly with increasing number of carbon atoms in the molecule of 1-alkyl acetate ($r = 0.909$), whereas the values for isomeric butyl acetates are close together. The difference between the lowest value for *iso*-BuOAc and the highest value

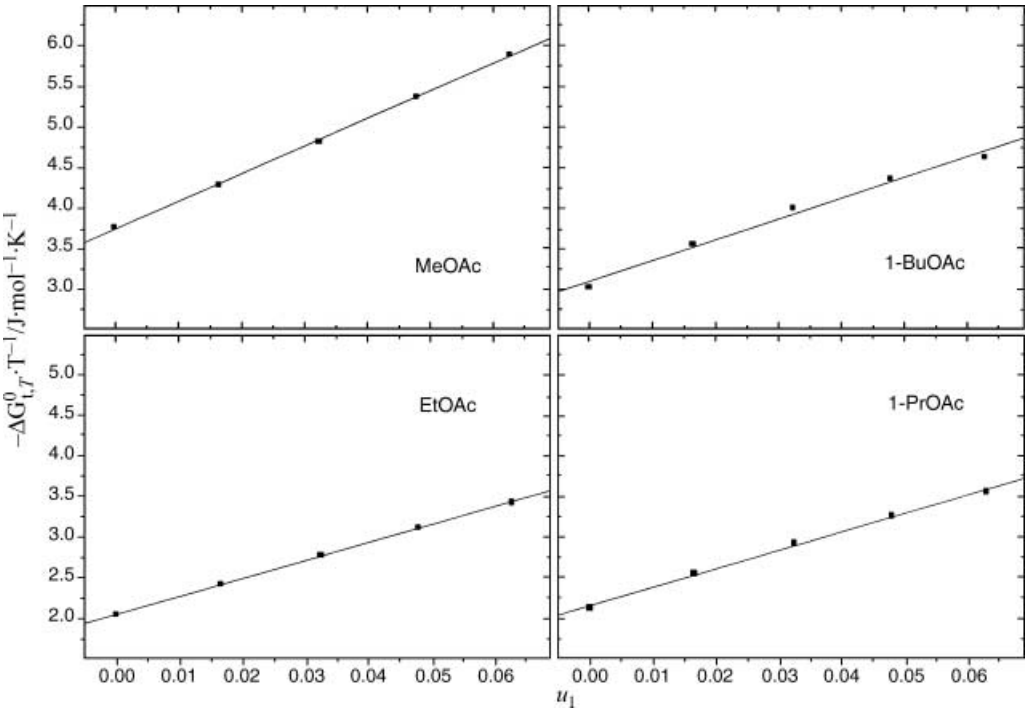

Fig. 3. The dependence of $-\Delta G^0_{t,T}/T$ on u_1

Table 6. Standard thermodynamic functions of transfer of some alkyl acetates at 298.2 K in water–ethanol solutions at constant x_3/x_1 ratio (0.0435)

	$\frac{-\Delta G^0_{t,\theta}}{kJ\cdot mol^{-1}}$	$\frac{\Delta H^0_{t,\theta}}{kJ\cdot mol^{-1}}$	$\frac{T\Delta S^0_{t,\theta}}{kJ\cdot mol^{-1}}$
MeOAc	1.113±0.019	10.07±0.45	11.18±0.47
EtOAc	0.612±0.013	6.57±0.34 (6.1[a])	7.19±0.35
1-ProAc	0.643±0.007	6.76±0.10	7.41±0.11
1-BuOAc	0.921±0.018	7.57±0.47	8.49±0.49
iso-BuOAc	0.825±0.014	7.44±0.36	8.27±0.37
sec-BuOAc	0.896±0.012	8.67±0.31	9.57±0.32

[a] calorimetric value [34]

for *sec*-BuOAc is only 10%. The $\Delta G^0_{t,\theta}$ values for 1-alkyl acetate result from about equal values of $\Delta H^0_{t,\theta}$ and $T\Delta S^0_{t,\theta}$ with a slightly higher entropy component. From this it may be concluded that enthalpies and entropies of transfer are more sensitive than the *Gibbs* energy. According to *Lee* and *Graziano* [8], any changes in the hydrogen bonding arrangement of water molecules will produce nearly or exactly compensating changes in both enthalpy and entropy. Such changes, therefore, would not produce a large *Gibbs* energy change and are connected with the large heat capacity which is characteristic of the hydrophobic effect. The $\Delta H^0_{t,\theta}$ values for 1-alkyl acetates are positive and, except for MeOAc, almost linearly increase with the increasing number of carbon atoms in the molecule ($r = 0.942$) like

$T\Delta S^0_{t,\theta}$ ($r = 0.935$). The standard enthalpy and entropy of transfer for isomeric butyl acetates depends on the structure of the alkyl chain.

As mentioned before [22, 26], it is convenient to separate the transfer parameters, *i.e.* $\Delta G^0_{t,\theta}$, $\Delta H^0_{t,\theta}$, and $T\Delta S^0_{t,\theta}$ into two contributions, the first being due to cavity transfer (ΔG^0_t (cav), ΔH^0_t (cav), and ΔS^0_t (cav)), the remainder being the difference between the solute–solvent interactions in the aqueous ethanol solution and in pure water, *i.e.* ΔG^0_t (int), ΔH^0_t (int), and ΔS^0_t (int). The expression for enthalpy of transfer, ΔH^0_t, was deduced on the basis of the relation for ΔH^0_s given in Ref. [23] similarly to the expression for the standard *Gibbs* energy of transfer (Eq. (4)) [22, 29].

$$\Delta H^0_t = \Delta H^0_t\,(\text{cav}) + \Delta H^0_t\,(\text{int}) + RT^2(\alpha^s_P - \alpha^w_P) \tag{14}$$

$T\Delta S^0_t$ (int) was calculated from the *Gibbs-Helmholtz* relation. The cavity transfer quantities were determined from the thermodynamics of cavity formation in water and in the aqueous ethanol solutions. The enthalpy of cavity formation in ethanol–water solutions, ΔH^0_s (cav), was calculated from Ref. [30] according to Eq. (15) where α^s_P is the coefficient of thermal expansion of the solution of ethanol and water.

$$\Delta H^0_s\,(\text{cav}) = \frac{\alpha^s_P RT^2}{1-y_3}\left(y_3 + \frac{3y_2\sigma_s}{1-y_3} + \frac{3y_1\sigma_s^2}{1-y_3} + \frac{9y_2^2\sigma_s^2}{(1-y_3)^2}\right) \tag{15}$$

α^s_P was calculated from the temperature dependence of the respective densities of water–ethanol solutions at $x_3/x_1 = 0.0435$ [27] as $\alpha^s_P = (-1/d)(\partial d/\partial T)_P$ and amounts to $3.15 \cdot 10^{-4}\,\text{K}^{-1} \cdot \Delta H^0_w$ (cav) was calculated from Eq. (15) using the thermal expansion coefficient of water, $\alpha^w_P = 2.57 \cdot 10^{-4}\,\text{K}^{-1}$ [31], and assuming the contributions of ethanol to y_1, y_2, and y_3 as equal to zero (Eqs. (8–10)). The calculated values of ΔH^0_s (cav) are given in Table 7 together with ΔH^0_w (cav) values. From this table it can be seen that ΔH^0_s (cav) values are positive and higher than the corresponding ΔH^0_w (cav) values in pure water. This is in accordance with *Franks*' hypothesis [12] that at low ethanol content (up to 10 mol%) the alcohol enhances the three-dimensional structure of water. Furthermore, the hydrophobic interactions between hydroxy groups determine the strength of hydrophobic interactions. Thus, the enthalpy of cavity formation must be higher in such solutions than in pure water. Both values, *i.e.* ΔH^0_s (cav) and ΔH^0_w (cav), increase linearly with increasing number of carbon atoms in the molecule. Since $\Delta H^0_s\,(\text{cav}) > \Delta H^0_w$ (cav), ΔH^0_t (cav) values are positive.

ΔS^0_s (cav) and ΔS^0_w (cav) were calculated from the *Gibbs-Helmholtz* relation; their values are given in Table 7. The values of ΔS^0_s (cav) are negative and decrease linearly with increasing number of carbon atoms in the 1-alkyl acetates. Since $\Delta S^0_w\,(\text{cav}) < \Delta S^0_s$ (cav), $T\Delta S^0_t$ (cav) values are positive and in range from 1.69 to $2.39\,\text{kJ} \cdot \text{mol}^{-1}$. From the values of ΔG^0_s (cav) given in Table 3 and ΔS^0_s (cav) given in Table 7, an unusually high entropy contribution to ΔG^0_s (cav) in water and in water–ethanol solutions can be observed; this has also been noted for water previously [26]. According to *Pierotti* [23], the cavity formation for water and water–ethanol solutions is dominated by structural changes in the solvent, accompanied by relatively small changes in the internal energy of the solvent.

Table 7. Thermodynamic functions of cavity formation in water and water–ethanol solutions and thermodynamic functions of cavity formation for the transfer of some alkyl acetates from water to water–ethanol solutions at 298.2 K

	$\frac{x_3}{x_1}$	$\frac{\Delta H_i^0\,(\mathrm{cav})}{\mathrm{kJ\cdot mol^{-1}}}$ $i = \mathrm{w,s}$	$\frac{-\Delta S_i^0\,(\mathrm{cav})}{\mathrm{J\cdot mol^{-1}\cdot K^{-1}}}$ $i = \mathrm{w,s}$	$\frac{-\Delta G_\mathrm{t}\,(\mathrm{cav})}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta H_\mathrm{t}\,(\mathrm{cav})}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{T\Delta S_\mathrm{t}\,(\mathrm{cav})}{\mathrm{kJ\cdot mol^{-1}}}$
MeOAc	0.0	5.88 (w)	103 (w)			
	0.044	7.36 (s)	97 (s)	0.22	1.48	1.69
EtOAc	0.0	6.69 (w)	116 (w)			
	0.044	8.37 (s)	109 (s)	0.26	1.68	1.94
1-ProAc	0.0	7.45 (w)	128 (w)			
	0.044	9.32 (s)	121 (s)	0.31	1.87	2.18
1-BuOAc	0.0	8.17 (w)	140 (w)			
	0.044	10.21 (s)	132 (s)	0.35	2.05	2.39
iso-BuOAc	0.0	8.16 (w)	140 (w)			
	0.044	10.21 (s)	132 (s)	0.35	2.05	2.39
sec-BuOAc	0.0	8.16 (w)	140 (w)			
	0.044	10.21 (s)	132 (s)	0.35	2.05	2.39

In Table 8, the values of thermodynamic functions of interaction for the transfer of some alkyl acetates from water to water–ethanol solution ($x_3/x_1 = 0.0435$) at 298.2 K are given, *i.e.* the difference in the thermodynamics of solute–solvent interactions between the alkyl acetates in water on the one hand and between the same ester and aqueous ethanol solution on the other hand. From this table it can be seen that both enthalpy and entropy of the transfer interaction are positive. Relatively small values of $\Delta G_\mathrm{t}^0\,(\mathrm{int})$ result in an almost complete compensation of $\Delta H_\mathrm{t}^0\,(\mathrm{int})$ by $T\Delta S_\mathrm{t}^0\,(\mathrm{int})$ except for MeOAc. Thereby, the magnitude of $T\Delta S_\mathrm{t}^0\,(\mathrm{int})$ for all 1-alkyl acetates is higher than $\Delta H_\mathrm{t}^0\,(\mathrm{int})$. In terms of *Lumry* and *Rajender*'s explanation of enthalpy–entropy compensation [32], the magnitude of an enthalpy change matched by an entropy change may be taken to indicate the degree of solvent rearrangement.

Table 8. Thermodynamic functions of the interaction for transfer of some alkyl acetates from water to water–ethanol solutions ($x_3/x_1 = 0.0435$) at 298.2 K calculated from the total transfer functions given in Table 6

	$\frac{-\Delta G_\mathrm{t}^0\,(\mathrm{int})^*}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{\Delta H_\mathrm{t}^0\,(\mathrm{int})}{\mathrm{kJ\cdot mol^{-1}}}$	$\frac{T\Delta S_\mathrm{t}^0\,(\mathrm{int})}{\mathrm{kJ\cdot mol^{-1}}}$
MeOAc	0.70	8.55	9.25
EtOAc	0.15	4.85	5.00
1-ProAc	0.15	4.85	4.99
1-BuOAc	0.38	5.48	5.48
iso-BuOAc	0.28	5.35	5.63
sec-BuOAc	0.35	6.58	6.93

From Table 8 it can be seen that ΔG_t^0 (int) values decrease with increasing size of the 1-alkyl acetate except for MeOAc ($r = 0.843$) and result from a small negative ΔG_t^0 (cav) value (Table 7) and a higher and negative $\Delta G_{t,\theta}^0$ value. Thus, the effect of increasing size of the non-electrolyte is compatible with the increase of *Gibbs* energy of cavity formation. From Table 8 it can be seen that ΔH_t^0 (int) values for 1-alkyl acetate, except for MeOAc, almost linearly increase with the size of the 1-alkyl acetate ($r = 0.868$). Thus, the energy of interaction between a molecule of ester and a molecule of water and ethanol increases due to the hydrophobic hydration of the alkyl chain, since the contribution of the polar acetate group is constant, the dipole moment of the ester group being the same for all molecules [33].

The experimentally determined thermodynamic functions of transfer of a homologous series of slightly polar molecules of alkyl acetate show a smooth transition in behaviour which is a consequence of increasing hydrophobic hydration with increasing molecular weight, *i.e.* the interaction between the alkyl side chain and solvent molecules, as can be seen in the extensive enthalpy–entropy compensation. The interactions of non-polar side chains are qualitatively similar to the interactions of non-polar molecules in the same environment.

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 K and 298.2 K and their densities at 298.2 K. The values obtained are given in Refs. [3, 25]. Absolute ethanol (Merck) was used without purification. Doubly distilled water was used to prepare the solutions.

Solubility measurements

The experimental procedure has been described previously [25]. Each solubility value of alkyl acetate, expressed as a weight fraction w_2, was based on at least three measurements, and only consistent values are reported. The relative standard deviations were derived and are reproducible in the case of volumetric analysis of saturated solutions to better than 1%; in the case of HPLC analysis (2-methyl-2-propyl, 1-pentyl, and 1-hexyl acetate) the reproducibility was between 2 and 3%.

A certain amount of saturated aqueous ethanol phase (g) was removed, and the amount of dissolved alkyl acetate was determined [25] and expressed as a weight fraction w_2. For ethanol–water solutions it was assumed that the ratio k of the weight fraction of ethanol (w_3) to water (w_1) in saturated aqueous ethanol solution was the same as in the water–ethanol solution. Thus, the weight fraction of water was calculated from according to Eq. (16).

$$w_1 = \frac{1 - w_2}{1 + k} \tag{16}$$

In calculations the subscript 1 denotes the principal solvent water, 2 the alkyl acetate, and 3 ethanol.

Density measurements

The densities of saturated solutions of alkyl acetates in ethanol–water were measured with a vibrating tube digital densimeter (model DMA 601, Anton Paar, Graz, Austria) as described before [25]. For the density of the saturated solutions of 1-*Pe*OAc and 1-*He*OAc, the density of water–ethanol at 298.2 K [27] was used due to the low solubility of these two esters.

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