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Osmotic Coefficients of Aqueous Solutions of Some Alkyl Acetates at the Freezing Point of the Solvent

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Summary. The osmotic coefficients of aqueous solutions of some alkyl acetates (methyl, ethyl, 1-propyl, 1-butyl, 2-methyl-1-propyl, 2-butyl, and 2-methyl-2-propyl acetate) up to saturation were determined by freezing point measurements. The relations for the dependence of the osmotic coefficients, the activity coefficient of the solute, and the excess *Gibbs* energies of solution as well as the respective partial molar functions of solute and solvent on molality are given in analytical form; the regression coefficients are correlated with the *McMillan-Mayer* virial coefficients. In addition, the difference in the *Gibbs* free energy of solvation for the solvent in solution relative to the pure solvent was calculated and is discussed in terms of the lattice theory for water. The hydrophobic effect is explained on the basis of fluctuation theory, and the aggregation numbers of the solute molecules as well as the excess solvent molecules in the surroundings of the solute molecules were estimated.

Keywords. Alkyl acetates; Water; Activity coefficients; Excess *Gibbs* free energy; Hydrophobic hydration.

Osmotische Koeffizienten wäßriger Lösungen einiger Alkylacetate beim Gefrierpunkt des Lösungsmittels

Zusammenfassung. Die osmotischen Koeffizienten wäßriger Lösungen einiger Alkylacetate (Methyl-, Ethyl, 1-Propyl-, 1-Butyl-, 2-Methyl-1-propyl-, 2-Butyl- und 2-Methyl-2-propylacetat) im Bereich von verdünnten bis gesättigten Lösungen wurden durch Gefrierpunktsmessungen ermittelt. Die Ausdrücke für die Abhängigkeit der osmotischen Koeffizienten, des Aktivitätskoeffizienten des gelösten Stoffs und der *Gibbs*schen Zusatzenergie der Lösung sowie der entsprechenden partiellen molaren Funktionen des Lösungsmittels und des gelösten Stoffs von der Molalität werden in analytischer Form angegeben; die Regressionskoeffizienten werden mit den *McMillan-Mayer*schen Virialkoeffizienten korreliert. Zusätzlich wurde die *Gibbs*sche freie Lösungsenergie für das Lösungsmittel in der Lösung im Vergleich zum reinen Lösungsmittel berechnet; sie wird im Kontext der Gitterenergie des Wassers diskutiert. Der hydrophobe Effekt wird auf der Basis der Fluktuationstheorie erklärt, die Aggregationszahlen der gelösten Moleküle sowie der überschüssigen Lösungsmoleküle in der Umgebung der gelösten Moleküle wurden abgeschätzt.

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Introduction

In view of the increasing biological and technological applications of alkyl acetates, some of the physico-chemical properties of these solutes in water have been the subject of many investigations in the past in order to obtain a deeper insight into the solute-solute and solute-solvent interactions in such systems [1, 2]. As is well known, esters are polar compounds that are attracted to each other in the pure state by a combination of dipole-dipole interactions between polar CO_2 groups and by dispersion forces between nonpolar hydrocarbon groups. In aqueous solution, esters are fairly hydrophobic solutes and can interact only by hydrogen bonding between the polar groups and the water molecules and by hydrophobic hydration.

The aim of this study was to obtain information on the effect of the structure of the alkyl chain on some of the thermodynamic properties of the investigated systems.

Results and Discussion

The practical osmotic coefficient ϕ for aqueous solutions of alkyl acetates was calculated from the freezing point depression θ using the relation

$$\phi = 0.5377\frac{\theta}{b} + 2.3 \times 10^{-4}\,\frac{\theta^2}{b} \tag{1}$$

which enables the calculation of ϕ to the third decimal place when the molality b ($\mathrm{mol \cdot kg^{-1}}$) is of the order to $1\,\mathrm{mol \cdot kg^{-1}}$ [3]. The practical molal osmotic coefficients are given in Table 1 and shown in Figs. 1 and 2. The calculated values of the osmotic coefficients of aqueous solutions of methyl, ethyl, and 1-propyl acetate are accurate to within 1%, whereas the others are accurate to 2%. From Table 1 and Figs. 1 and 2 it can be seen that the molal osmotic coefficients decrease with increasing molality and that their values depend on the structure of the alkyl chain.

According to the *McMillan-Mayer* theory of solutions [4] which proposes a formal separation of the excess thermodynamic functions into contributions arising from pairs, triplets *etc.* of the solute particles in a definite media, the dependence of the osmotic coefficients on molality for the system investigated may be given by Eq. (2) where g_{22} and g_{222} are the viral coefficients which characterize the contributions to the excess *Gibbs* free energy due to pair and triplet interactions among alkyl acetate molecules in aqueous solution and R is the gas constant. The values of the viral coefficients g_{22} and g_{222} for the investigated system are given in Table 2.

$$\phi = 1 + \frac{g_{22}}{\mathrm{R}T}b + \frac{2g_{222}}{\mathrm{R}T}b^2 \tag{2}$$

From Table 2 it can be seen that the viral coefficients are negative and that their absolute values increase with increasing chain length for *n*-alkyl acetates, whereas for isomeric butyl acetates the values of g_{22} depend on the structure of the alkyl chain. Thus, the lowest value was obtained for tertiary butyl acetate. The negative values of virial coefficients g_{22} and g_{222} may be ascribed to dipole-dipole interactions of solute molecules and to hydrophobic interactions [5].

Table 1. Practical molal osmotic coefficient, molal activity coefficient of solute, excess *Gibbs* free energy, and partial molal excess *Gibbs* free energy of solute and solvent at the freezing point of the solvent

$\frac{b}{\mathrm{mol \cdot kg^{-1}}}$	ϕ	γ_2	$\frac{-G^{\mathrm{ex}}}{\mathrm{J \cdot kg^{-1}}}$	$\frac{-\bar{G}_2^{\mathrm{ex}}}{\mathrm{J \cdot mol^{-1}}}$	$\frac{\bar{G}_1^{\mathrm{ex}}}{\mathrm{J \cdot mol^{-1}}}$
Methyl acetate					
0.5523	0.987	0.976	14	55	0.29
0.9548	0.974	0.953	47	109	1.03
1.4724	0.952	0.918	124	194	2.90
1.9704	0.925	0.879	245	293	6.00
2.4770	0.894	0.834	423	412	10.8
3.1052	0.847	0.773	735	584	19.4
3.5965	0.805	0.723	1058	737	28.7
4.0280	0.764	0.677	1408	886	38.9
Ethyl acetate					
0.0870	0.975	0.950	5.2	117	0.09
0.1685	0.955	0.910	18.7	214	0.31
0.2156	0.945	0.890	30.1	265	0.49
0.2338	0.941	0.882	35.1	284	0.57
0.3225	0.926	0.851	64.0	367	0.98
0.4272	0.913	0.821	106.9	448	1.52
0.4868	0.908	0.808	134.6	485	1.83
0.5741	0.905	0.792	179.0	528	2.24
0.6492	0.905	0.783	219.7	555	2.53
0.7633	0.910	0.776	284.6	577	2.81
0.7803	0.911	0.775	294.4	579	2.83
1-Propyl acetate					
0.0202	0.992	0.984	0.4	35	0.006
0.0418	0.984	0.968	1.5	73	0.028
0.0650	0.975	0.951	3.7	114	0.067
0.0842	0.968	0.937	6.2	148	0.112
0.1078	0.958	0.920	10.2	189	0.184
0.1263	0.951	0.907	14.0	222	0.252
0.1408	0.946	0.897	17.4	247	0.314
0.1507	0.942	0.890	19.9	265	0.359
0.1584	0.939	0.885	22.0	278	0.397
0.1624	0.937	0.882	23.2	285	0.417
0.1907	0.926	0.863	31.9	335	0.575
1-Butyl acetate					
0.0038	0.995	0.991	0.0	22	0.001
0.0123	0.985	0.970	0.4	70	0.008
0.0169	0.974	0.950	1.2	117	0.022
0.0205	0.973	0.947	1.3	124	0.024
0.0217	0.961	0.924	2.8	179	0.051
0.0314	0.960	0.922	3.0	185	0.054
0.0389	0.951	0.907	4.3	222	0.078
0.0450	0.944	0.893	5.8	257	0.104
0.0495	0.938	0.883	7.0	282	0.126

Table 1 (*continued*)

$\frac{b}{\text{mol}\cdot\text{kg}^{-1}}$	ϕ	γ_2	$\frac{-G^{\text{ex}}}{\text{J}\cdot\text{kg}^{-1}}$	$\frac{-\bar{G}_2^{\text{ex}}}{\text{J}\cdot\text{mol}^{-1}}$	$\frac{\bar{G}_1^{\text{ex}}}{\text{J}\cdot\text{mol}^{-1}}$
2-Butyl acetate					
0.0080	0.989	0.978	0.2	51	0.004
0.0137	0.981	0.962	0.6	87	0.011
0.0241	0.966	0.935	1.8	153	0.033
0.0318	0.955	0.915	3.2	202	0.058
0.0403	0.944	0.893	5.2	256	0.093
0.0489	0.931	0.872	7.6	311	0.137
0.0590	0.917	0.848	11.1	375	0.199
0.0671	0.906	0.829	14.3	427	0.258
2-Methyl-1-propyl acetate					
0.0035	0.994	0.987	0.0	28	0.001
0.0133	0.976	0.954	0.7	108	0.013
0.0208	0.962	0.928	1.8	169	0.032
0.0269	0.951	0.908	3.0	220	0.053
0.0317	0.943	0.893	4.1	258	0.074
0.0384	0.931	0.871	5.9	309	0.106
0.0445	0.920	0.852	8.1	362	0.145
0.0481	0.913	0.842	9.4	392	0.170
2-Methyl-2-propyl acetate					
0.0061	0.979	0.960	0.3	94	0.005
0.0142	0.952	0.908	1.6	219	0.028
0.0206	0.930	0.869	3.3	317	0.059
0.0284	0.904	0.825	6.2	437	0.112
0.0360	0.878	0.783	10.0	554	0.180
0.0469	0.841	0.728	16.9	722	0.305
0.0482	0.837	0.721	17.9	742	0.322
0.0579	0.804	0.675	25.9	893	0.467
0.0619	0.790	0.657	29.5	953	0.532

The molal activity coefficient of solute γ_2 was calculated using *Bjerrum*'s equations [6]:

$$d((1-\phi)b) + b\,\mathrm{d}\ln\gamma_2 = 0 \tag{3}$$

Considering Eq. (2), the following expression for the molal activity coefficient of solute can be obtained:

$$\ln\gamma_2 = \frac{2g_{22}}{\mathrm{R}T}b + \frac{3g_{222}}{\mathrm{R}T}b^2 \tag{4}$$

The values of γ_2 for the systems investigated are given in Table 1. The average relative standard error of the activity coefficient is less than 2%. The dependence of γ_2 on molality is similar to that observed for the molal osmotic coefficients.

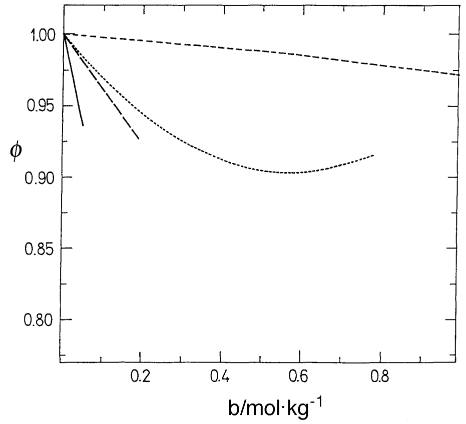

Fig. 1. Dependence of the practical molal osmotic coefficient on the molality of *n*-alkyl acetates at the freezing point of the solvent (– – –: methyl, - - - - -: ethyl, — — —: propyl, ——: 1-butyl acetate)

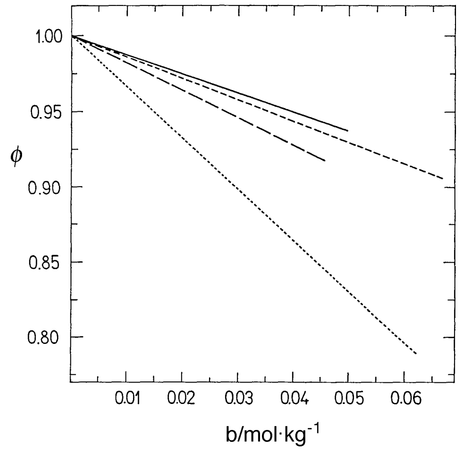

Fig. 2. Dependence of the practical molal osmotic coefficient on the molality of isomeric butyl acetates at the freezing point of the solvent (—: 1-butyl, – – –: 2-butyl, — — —: 2-methyl-1-propyl-, - - - - -: 2-methyl-2-propyl acetate)

Table 2. Values of the virial coefficients g_{22} and g_{222} for aqueous solutions of some alkyl acetates at the freezing points of the solvent

Solute	$\dfrac{-g_{22}}{\mathrm{J \cdot kg \cdot mol^{-2}}}$	$\dfrac{-g_{222}}{\mathrm{J \cdot kg^{2} \cdot mol^{-3}}}$
Methyl acetate	40.5±0.4	11.49±0.06
Ethyl acetate	709±1	−289±1
1-Propyl acetate	878±10	
1-Butyl acetate	2850±60	
2-Methyl-1-propyl acetate	4070±80	
2-Butyl acetate	3180±30	
2-Methyl-2-propyl acetate	7700±40	

To represent the deviation from ideality of the investigated solutions, the excess *Gibbs* free energy of solution per kg of solvent, G^{ex} ($\text{J} \cdot \text{kg}^{-1}$), was calculated making use of Eqs. (2) and (4) [7]:

$$G^{\text{ex}} = b\text{R}T(1 - \phi + \ln\gamma_2) = g_{22}b^2 + g_{222}b^3 \tag{5}$$

The calculated values of G^{ex} are given in Table 1; their relative standard error, calculated from Eq. (5), considering only the standard error of the virial coefficient, is 2%. The values of G^{ex} are negative. Furthermore, the excess *Gibbs* free energy of solution can also be given by Eq. (6) where n_i is the number of moles of component i ($i = 1$: solvent, $i = 2$; solute) and $\bar{G}_i^{\text{ex}}$ is the partial molal excess *Gibbs* free energy of component i as defined by Eq. (7).

$$G^{\text{ex}} = n_1\bar{G}_1^{\text{ex}} + n_2\bar{G}_2^{\text{ex}} \tag{6}$$

$$\bar{G}_i^{\text{ex}} = \left(\frac{\partial G^{\text{ex}}}{\partial n_i}\right)_{T,P,n_j \neq n_i} \tag{7}$$

Thus, the partial molal excess *Gibbs* free energy of solute and solvent, respectively, are calculated from

$$\bar{G}_2^{\text{ex}} = \text{R}T\ln\gamma_2 = 2g_{22}b + 3g_{222}b^2 \tag{8}$$

and

$$\bar{G}_1^{\text{ex}} = M_1 b\text{R}T(1 - \phi) = -M_1 \cdot g_{22}b^2 - 2 \cdot M_1 \cdot g_{222}b^3 \tag{9}$$

where M_1 ($\text{kg} \cdot \text{mol}^{-1}$) is the molar weight of solvent. The partial molal excess *Gibbs* free energy of solute and solvent calculated by means by Eqs. (8) and (9) are given in Table 1. Their average relative errors are 2%. The $\bar{G}_2^{\text{ex}}$ values are negative and follow the same order as those of G^{ex}, in contrast to the $\bar{G}_1^{\text{ex}}$ values which are positive and small and tend to increase with increasing molality.

Some information about the solvation ability of the solvent was obtained from the approach of *Ben Naim* [8]. According to this theory, the difference in the solvation *Gibbs* free energy of a solvent molecule in solution ΔG_1^{*1} relative to the pure solvent $\Delta G_{\text{w}}^{*\text{p}}$, $\Delta\Delta G_1^*$ ($\text{J} \cdot \text{molecule}^{-1}$), is given by

$$\Delta\Delta G_1^* = \Delta G_1^{*1} - \Delta G_{\text{w}}^{*\text{p}} = kT\ln\left(\frac{C_1^0 a_1}{C_1}\right) \tag{10}$$

where k is the *Boltzmann* constant, C_1^0 is the number density of pure solvent in pure solvent ($\text{molecules} \cdot \text{cm}^{-3}$), C_1 is the number density of solvent in solution, and a_1 is the activity of solvent in solution. The term C_1^0/C_1 was obtained from the respective densities of solvent [9] and solution by extrapolation of density data down to the freezing point of the solvent [2]. The value of $\ln a_1$ was calculated from

$$\ln a_1 = -bM_1\phi \tag{11}$$

The calculated values of $\Delta\Delta G_1^*$ ($\text{J} \cdot \text{mol}^{-1}$) for the investigated systems are given in Table 3 at rounded molalities and at the freezing point of the solvent. The values of $\Delta\Delta G_1^*$ for isomeric butyl acetates are within experimental error equal to that of 1-butyl acetate. From Table 3 it follows that the values of $\Delta\Delta G_1^*$ are positive and increase with increasing molality and chain length of the *n*-alkyl acetate molecule.

Table 3. Dependence of $\Delta\Delta G_1^*$ on molality for aqueous solutions of some alkyl acetates at the freezing point of the solvent

$\frac{b}{\text{mol} \cdot \text{kg}^{-1}}$	$\frac{\Delta\Delta G_1^*}{\text{J} \cdot \text{mol}^{-1}}$			
	Methyl acetate	Ethyl acetate	1-Propyl acetate	1-Butyl acetate
0.01	1.2	1.5	1.9	8.6
0.02	2.3	3.1	3.8	10.9
0.03	3.5	4.6	5.7	13.1
0.04	4.7	6.2	7.6	15.4
0.06	7.0	9.3	11.4	17.7
0.08	9.4	12.4	15.2	
0.10	11.7	15.5	19.0	
0.15	17.0	23.2		

The data for $\Delta\Delta G_1^*$ for alkyl acetates are substantially lower than the corresponding data for water in aqueous solutions of *D*-glucose [8] and aqueous solutions of *D*-mannitol and *D*-sorbitol [10].

According to *Ben Naim* [8] it is not possible to state categorically whether the observed effects are due to direct solute-solvent interactions or from indirect changes of the structure of the solvent environment induced by the addition of the solute. Since the *Gibbs* free energy of solvation of water in pure water at 0°C is negative [8] ($\Delta G_\text{w}^{*\text{p}} = -27.792\,\text{kJ} \cdot \text{mol}^{-1}$), from the values obtained for $\Delta\Delta G_1^*$ we may conclude that the addition of alkyl acetate to water makes the solvation *Gibbs* free energy of water molecules in solution less negative relative to the corresponding value of the pure solvent molecule. The major reason for this is probably the overall weakening of the average binding energy of the water molecule with its surroundings when alkyl acetate is added to the solvent. The observed $\Delta\Delta G_1^*$ values are in accordance with the number of methylene groups in *n*-alkyl acetate, *i.e.* $\Delta\Delta G_1^*$ at a definite molality increases with increasing chain length. On the contrary, for isomeric butyl acetates the $\Delta\Delta G_1^*$ values in the molality range studied are the same in spite of their different structure.

Recently, on the basis of the fluctuation theory of *Kirkwood* and *Buff* [11], *Liu* and *Rukenstein* [12] were able to explain the hydrophobic effect as an aggregation process which drives nonpolar solute molecules to aggregate, whereas solvent molecules in the surroundings of solute molecule are in excess. According of this theory, the dimensionless parameter N_{22}, as a measure of the aggregation number representing the total excess of solute molecules in the surroundings of a solute molecule at infinite dilution, is given by

$$N_{22} = \rho_{\text{m},2}\beta R\text{T} + \frac{V_1^0}{V_2^0}(1 + K_2) - \frac{2\bar{V}_{2,0}}{V_2^0} \qquad (12)$$

where $\rho_{\text{m},2}$ is the density of the pure solute ($\text{mol} \cdot \text{cm}^{-3}$), β is the isothermal compressibility of the solvent, V_1^0 and V_2^0 are the molar volumes of solvent and solute, $\bar{V}_{2,0}$ is the partial molal volume of the solute at infinite dilution, and K_2 is given by

$$\left(\frac{\partial \ln \gamma_{2,x}^{*}}{\partial x_2}\right)_{P,T}^{\infty} = -K_2 \tag{13}$$

where $\gamma_{2,x}^{*}$ is the activity coefficient of the solute defined according to the symmetric convention for normalization [13]. On the other hand, the excess solvent molecules in the surroundings of a solute molecule at infinite dilution, H_{12}^{∞}, is given by

$$H_{12}^{\infty} = \rho_{\mathrm{m},1}(\beta \mathrm{R}T - \bar{V}_{2,0}) \tag{14}$$

where $\rho_{\mathrm{m},1}$ is the density of the pure solvent ($\mathrm{mol} \cdot \mathrm{cm}^{-3}$). The molal activity coefficients of solute, given in Table 1, are defined by the unsymmetrical convention for normalization and on a molality scale. Their values were multiplied by the factor of $(1+M_1 b)$, and from them the slope of the limiting activity coefficients $(\partial \ln \gamma_{2,x}/\partial x_2)_{P,T}^{\infty}$ was obtained [13].

In Table 4, besides the values of the limiting derivative of the activity coefficient of solute, the volume of pure solute, the limiting partial molal volumes of solute, the total excess solute molecules, and the excess solvent molecules are given. The molal and partial molal volume of solute were obtained by extrapolation of published values [2] down to the freezing point of the solvent. In the calculation of N_{22} and H_{12}^{∞}, the products $\rho_{\mathrm{m},2}\beta \mathrm{R}T$ or $\rho_{\mathrm{m},1}\beta \mathrm{R}T$ were not taken into account since the isothermal compressibility of water is small ($\beta = 5.0885 \cdot 10^{-5}\,\mathrm{bar}^{-1}$ at 273.15 K [14]), and so the products $\rho_{\mathrm{m},1}\beta \mathrm{R}T = 0.064$ and $\rho_{\mathrm{m},2}\beta \mathrm{R}T$ range from 0.009 for 2-methyl-2-propyl acetate to 0.015 for methyl acetate.

From Table 4 it can be seen that the parameter N_{22} increases with increasing chain length in the *n*-alkyl acetate molecule. The negative value for methyl acetate has no physical meaning. It seems that the relatively small molecule of methyl acetate is completely solvated as a monomeric unit by water molecules *via* hydrogen bonding and that its size fits the dimension of the cavities in the water structure [15]. In contrast, the isomeric butyl acetates showed a substantial difference in degree of aggregation. The lowest value of N_{22} was calculated for

Table 4. Limiting derivatives K_2, molar volume of solute V_2^0 partial molar volume of solute at infinite dilution $\bar{V}_{2,0}$, total excess of solute molecules N_{22}, and excess solvent molecules H_{12}^{∞} at the freezing point of the solvent

Solute	K_2	$V_2^0[2]$ / $\mathrm{mol} \cdot \mathrm{cm}^{-3}$	$\bar{V}_{2,0}[2]$ / $\mathrm{mol} \cdot \mathrm{cm}^{-3}$	N_{22}	$-H_{1,2}^{\infty}$
Methyl acetate	1.0	77.2	69.9	−1.3	3.8
Ethyl acetate	34	95.3	86.1	4.8	4.7
1-Propyl acetate	42	112.2	101.8	5.1	5.6
1-Butyl acetate	138	128.8	116.9	18	6.4
2-Methyl-1-propyl acetate	198	130.2	117.5	26	6.5
2-Butyl acetate	155	130.3	118.0	20	6.5
2-Methyl-2-propyl acetate	376	130.8	118.2	50	6.5

1-butyl acetate and the highest one for 2-methyl-2-propyl acetate. Similarly, from the work of *Liu* and *Ruchenstein* [12] it follows that the parameter N_{22} increases with increasing chain length in the *n*-alkane molecule and that N_{22} depends on the structure of the chain in isomeric alkanes. Furthermore, from Table 4 it can be seen that the absolute value of H_{12}^{∞} increases with increasing chain length in the *n*-alkyl acetate molecule as was observed by *Liu* and *Ruckenstein* [12] for the *n*-alkane molecule, whereas for isomeric butyl acetates these values are constant. Similarly, from the data given in Table 4 it follows that the value of $\Delta\Delta G_1^*$ does not depend on the structure of the isomeric butyl acetate. Thus, from the thermodynamic properties of the investigated solutions, such as the activity coefficient of solute and solvent and the partial molar volume of solute, the degree of aggregation of solute molecules as well as the excess of solvent molecules in the surroundings of the solute molecule can be obtained. From the above results it may be deduced that the non-ideal behaviour of these solutions may be ascribed to hydrophobic hydration as well as to hydrogen bonding of solute molecules with water molecules.

Experimental

Materials

Methyl, ethyl 1-propyl, 1-butyl, 2-methyl-1-propyl, and 2-methyl-2-propyl acetate (Fluka A.G.) 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 293.15 and 298.15 K and their densities at 298.15 K. The values obtained are presented in Table 5 together with literature values. From the purified compounds and doubly distilled water, solutions were prepared on a molality scale ($\mathrm{mol \cdot kg^{-1}}$). The molality range measured depends on the water solubility of the investigated ester: $4.0\,\mathrm{mol \cdot kg^{-1}}$ for methyl, $0.8\,\mathrm{mol \cdot kg^{-1}}$ for ethyl, $0.2\,\mathrm{mol \cdot kg^{-1}}$ for propyl, and approximately $0.05\,\mathrm{mol \cdot kg^{-1}}$ for butyl acetates.

Freezing point measurements

The freezing point depression of the solutions was measured with a Knauer cryoscopic unit Model 7312400000 equipped with a strip chart recorder (Knauer Model 733.41). The solvent and the solution were supercooled to the same temperature. The formation of ice crystals was initiated by internal vibrations, and the freezing point depression was recorded as the difference in resistance on the thermistor (Δr, arbitrary scale) between solvent and solution. The reproducibility of Δr measurements was better than 1% of the measuring scale.

The instrument was calibrated using sodium chloride solutions. For these solutions the freezing point depression was calculated by the *Lagrange* interpolation method using known values of the weight fraction *versus* freezing point depression for sodium chloride solutions, θ (Ref. [16]). The following calibration curve was obtained (standard error: 0.26).

$$\Delta r = (132.72 \pm 0.29)\theta - (1.825 \pm 0.067)\theta^2 \tag{15}$$

The values of the constants in Eq. (15) were obtained from eighteen different sodium chloride solutions ranging from 0.0244 to $1.7617\,\mathrm{mol \cdot kg^{-1}}$ corresponding to freezing point depressions from 0.087 to 6.057 K. The relative standard deviation of θ was estimated to be 0.3%. Thus, from the known Δr value of the investigated solution, the freezing point depression could be calculated *via* Eq. (15); so for methyl acetate at $b = 4.0279\,\mathrm{mol \cdot kg^{-1}}$, $\theta = 5.70\,\mathrm{K}$; ethyl acetate, $b = 0.7803\,\mathrm{mol \cdot kg^{-1}}$, $\theta = 1.30\,\mathrm{K}$; propyl acetate: $b = 0.1907\,\mathrm{mol \cdot kg^{-1}}$, $\theta = 0.33\,\mathrm{K}$.

Table 5. Experimental densities and refractive indices of pure alkyl acetates compared with literature data

Solute	$\rho_0/g\cdot\mathrm{cm}^{-3}$ (298 K)		n_D (293 K)	n_D (298 K)	n_D (293 K)	n_D (298 K)
	Exptl.	Lit.	Exptl.		Lit.	
Methyl acetate		0.9279^{a}				
	0.92701	0.92709^{b}	1.3615	1.3591	1.3614^{a}	1.3589^{a}
Ethyl acetate		0.89455^{a}				
	0.89431	0.89437^{b}	1.3724	1.3698	1.37239^{a}	1.36978^{a}
1-Propyl acetate		0.88303^{a}				
	0.88250	0.88250^{b}	1.3842	1.3822	1.38442^{a}	1.3828^{a}
1-Butyl acetate		0.87636^{a}				
	0.87648	0.87614^{b}	1.3941	1.3918	1.3942^{a}	1.3918^{a}
2-Methyl-1-propyl acetate		0.8677^{a}				
	0.86583	0.86617^{b}	1.3901	1.3879	1.39018^{a}	1.3880^{a}
2-Butyl acetate		0.8694^{a}				
	0.86530	0.86537^{b}	1.3891	1.3870	1.38941^{a}	1.3875^{a}
2-Methyl-2-propyl acetate		0.8593^{c}				
	0.86061	0.86057^{b}	1.3864	1.3838	1.3862^{c}	1.3840^{c}

^{a}Ref. [9]; ^{b}Ref. [2]; ^{c}Ref. [18]

Density measurements

The density of the purified alkyl acetates (ρ_0, $\mathrm{g\cdot cm^{-3}}$), was measured with a vibrating tube digital densimeter (Model DMA 601, Anton Paar, Graz, Austria) calibrated with air and water at 298.15 K [17]. The thermal stability of the measuring cell was controlled by an A. Paar digital thermometer (DT 10020) to better than ±0.01 K. The accuracy of the density measurements was estimated as $2\cdot 10^{-5}\,\mathrm{g\cdot cm^{-3}}$.

Refractive index measurements

The refractive index was measured with an Abbé refractometer (Carl Zeiss, Jena, Model 32G 110e) with a precision of $1\cdot 10^{-4}$. All measurements were performed at 293.15 and 298.15 K and at a wave length of 589 nm.

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