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Salting-Out of Some Alkyl Acetates in Aqueous Sodium Chloride Solutions

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Summary. Solubilities 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 (*ter*-BuOAc), 1-pentyl acetate (1-*Pe*OAc) and 1-hexyl acetate (1-*He*OAc) in water and in aqueous sodium chloride solutions at concentrations ranging up to $1.0\,\mathrm{mol\cdot dm^{-3}}$ were determined at 25.0°C by analyzing the saturated aqueous or salt solutions. Solubility ratios of alkyl acetates in pure water and in aqueous sodium chloride solution were calculated and found to be linearly dependent on the concentration of sodium chloride. The solubility ratios were also calculated by the approach of the scaled particle theory and according to the theories of *McDevit* and *Long*, *Cross*, *Conway et al.*, and *Aveyard*. All these theories, except that of *Conway*, correctly predict the order of magnitude of the experimental results, but do not discriminate between isomeric butyl acetates. The theoretical values obtained from the scaled particle and *Aveyard* theories coincide well with the experimental values, especially for the higher alkyl acetates. The purely electrostatic theory of *Conway et al.* not even predicts the salting-out effect for the alkyl acetates investigated.

Keywords. Alkyl acetates; Solubility; Water; Sodium chloride solutions; *Setchenov* coefficient.

Introduction

The solubility of nonpolar and polar solutes in aqueous electrolyte solutions has been a subject of considerable experimental and theoretical interest in the past [1]. Most of the experimental work has been concentrated on slightly soluble nonpolar nonelectrolytes. The recent interest in salt effects in biological systems has pointed to the need for more data on the interactions of salts with small polar molecules.

The solubility of some alkyl acetates in water and aqueous salt solutions have been the subject of many investigations [2–4]. In an extended study, *Cross* and *McTigue* [5] have determined the relative activity coefficients of some alkyl acetates in concentrated sodium chloride solutions beyond $1.0\,\mathrm{mol\cdot dm^{-3}}$ using the distribution technique. In the present work, experimental and predicted solubilities of some alkyl acetates in relatively dilute sodium chloride solutions calculated according to the scaled particle [6], *McDevit-Long* [7], and *Aveyard* [8] theories and the electrostatic approach of *Conway et al.* [9] are considered in order to

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clarify the various factors which influence the solubility of alkyl acetates in aqueous sodium chloride solutions.

Results and Discussion

In Table 1 the solubilities of some alkyl acetates in water and in aqueous sodium chloride solutions are given. From the collected data it can be seen that the solubility of an alkyl acetate in water or in aqueous sodium chloride solution depends on the structure of the alkyl chain and the concentration of sodium chloride, and that the solubility decreases with increasing molecular weight of the alkyl acetate or increases with increasing branching for isomeric butyl acetate. The data are in good agreement with published ones. So, for example, *Altshuller* [2] determined the solubility of ethyl acetate in water at 25.0°C and found a value of 8.01 g/100 g of solvent, which is in good agreement with the value 8.014 g/100 g of solvent calculated from the data given in Table 1. The solubility data of ethyl acetate in sodium chloride solutions given by *Altshuller* show a linear dependence of solubility on the concentration of sodium chloride solution, so their data can be compared with those in Table 1. For the solubility of ethyl acetate in 0.15 $\mathrm{mol \cdot dm^{-3}}$ sodium chloride solution, a value of 6.996 weight percent was calculated which is in good agreement with the value given in Table 1. For the solubility of ethyl acetate in water at 25.0°C, *Tewari* [4] gives a value of 0.726 $\mathrm{mol \cdot dm^{-3}}$ which is lower than our value (0.839 $\mathrm{mol \cdot dm^{-3}}$) calculated from the data in Table 1. *Tewari* also determined the solubility of 1-propyl and 1-butyl acetate in water and gave values of 0.200 $\mathrm{mol \cdot dm^{-3}}$ for propyl acetate and 0.0577 $\mathrm{mol \cdot dm^{-3}}$ for 1-butyl acetate. From the data collected in Table 1, values of 0.209 $\mathrm{mol \cdot dm^{-3}}$ and 0.0511 $\mathrm{mol \cdot dm^{-3}}$ can be obtained for the solubility of the two alkyl acetates in water at 25.0°C.

The solubility of a nonelectrolyte in aqueous salt solution at low salt concentrations, c_s ($\mathrm{mol \cdot dm^{-3}}$), is given by Eq. (1) [10] where $\frac{y_2}{y_2^0}$ is the ratio of the molar activity coefficients, $\frac{c_2^0}{c_2}$ is the ratio of the molar concentrations of a nonelectrolyte in water and in aqueous salt solution, respectively, k_s is the salting coefficient, a characteristic value for the given salt-nonelectrolyte pair which can be related to the standard *Gibbs* free energy of transfer of the solute from water to the aqueous electrolyte solution [11], and k_i is the nonelectrolyte self-interaction parameter. If the concentrations c_2 and c_2^0 are relatively low, the last term in Eq. (1) is usually omitted [10]. Since Eq. (1) is valid only at low salt concentrations, the k_s values for alkyl acetates were obtained from Eq. (2).

$$\log\frac{y_2}{y_2^0} = \log\frac{c_2^0}{c_2} = k_s c_s + k_i(c_2 - c_2^0) \tag{1}$$

$$k_s = -\left(\frac{\mathrm{d}(\log c_2)}{\mathrm{d}(c_s)}\right)_{c_s \to 0} \tag{2}$$

The calculated values of coefficient k_s for the investigated systems are given in Table 2 from which it can be seen that the *Setchenow* constants are positive, meaning that sodium chloride depresses the solubility of alkyl acetates in aqueous

Table 1. Solubilities of some alkyl acetates in water and aqueous sodium chloride solutions together with densities of saturated solutions at 25.0°C

c_s / $\text{mol}\cdot\text{dm}^{-3}$	w_2 / %	ρ / $\text{g}\cdot\text{cm}^{-3}$	c_s / $\text{mol}\cdot\text{dm}^{-3}$	w_2 / %	ρ / $\text{g}\cdot\text{cm}^{-3}$
	MeOAc			*sec*-BuOAc	
0	23.925±0.139	1.00050	0	0.8276±0.0065	0.99684
0.15	21.877±0.033	1.00568	0.15	0.7507±0.0045	1.00299
0.50	18.422±0.039	1.01809	0.50	0.6130±0.0038	1.01671
0.75	16.604±0.040	1.02587	0.75	0.5405±0.0038	1.02693
1.00	14.834±0.033	1.03593	1.00	0.4538±0.0019	1.03677
	EtOAc			*ter*-BuOAc	
0	7.419±0.036	0.99654	0	0.7139±0.0099	0.99671
0.15	6.920±0.040	1.00822	0.15	0.6697±0.0099	1.00292
0.50	5.850±0.036	1.02170	0.50	0.5272±0.0134	1.01702
0.75	5.348±0.015	1.02468	0.75	0.4440±0.0053	1.02694
1.00	4.676±0.038	1.04086	1.00	0.3744±0.0041	1.03675
	1-PrOAc			1-PeOAc	
0	2.1451±0.0048	0.99653	0	0.1604±0.0029	0.99705[a]
0.15	1.9696±0.0051	1.00263	0.15	0.1468±0.0038	1.00321[a]
0.50	1.6610±0.0035	1.01665	0.50	0.1124±0.0015	1.01730[a]
0.75	1.4665±0.0022	1.02649	0.75	0.0962±0.0019	1.02725[a]
1.00	1.2999±0.0065	1.03656	1.00	0.0826±0.0017	1.03711[a]
	1-BuOAc			1-*He*OAc	
0	0.5959±0.0006	0.99682	0	0.04151±0.0005	0.99705[a]
0.15	0.5470±0.0023	1.00296	0.15	0.03836±0.0013	1.00321[a]
0.50	0.4523±0.0031	1.01715	0.50	0.02822±0.0011	1.01730[a]
0.75	0.3927±0.0018	1.02732	0.75	0.02320±0.0010	1.02725[a]
1.00	0.3432±0.0040	1.03677	1.00	0.01974±0.0008	1.03711[a]
	iso-BuOAc				
0	0.6312±0.0018	0.99679			
0.15	0.5912±0.0022	1.00291			
0.50	0.4872±0.0010	1.01680			
0.75	0.4285±0.0024	1.02706			
1.00	0.3643±0.0010	1.03677			

[a] Density of water or sodium chloride solution

Table 2. Salting coefficient for some alkyl acetates in aqueous sodium chloride solution at 25.0°C

Solute	k_s / $\text{dm}^3\cdot\text{mol}^{-1}$
MeOAc	0.185±0.004
EtOAc	0.178±0.004
1-PrOAc	0.201±0.002
1-BuOAc	0.224±0.001
iso-BuOAc	0.225±0.005
sec-BuOAc	0.241±0.006
ter-BuOAc	0.269±0.007
1-*Pe*OAc	0.283±0.007
1-*He*OAc	0.312±0.009

salt solutions. Their values increase almost linearly for 1-alkyl acetates, with the exception of methyl acetate, with increasing chain length with a slope of 0.0026±0.0003, whereas for isomeric butyl acetates their values depend on the structure of the alkyl chain. The value of k_s obtained for ethyl acetate is in good agreement with the published value of 0.189 [3].

In order to predict the salting effect of alkyl acetate in aqueous sodium chloride solution, the scaled particle theory given by *Masterton* and *Lee* was used [6]. According to this theory [12, 13], *Shoor* and *Gubbins* derived the following expression for log c_2 [14]:

$$-\log c_2 = \frac{\bar{g}_2^h}{kT \ln(10)} + \frac{\bar{g}_2^s}{kT \ln(10)} + \log kT \sum_{j=1}^{4} C_j \tag{3}$$

$\bar{g}_2^h$ is the free energy change required to create a cavity large enough to accommodate a nonelectrolyte molecule, $\bar{g}_2^s$ is the free energy change which takes into account the interaction between the solute molecule and the surrounding solvent molecules, C_j is the number density of species j, k is the *Boltzmann* constant, and T is the absolute temperature. In subsequent calculations we use the subscript 1 to represent the solvent (water), 2 for the nonelectrolyte, 3 for the cation (Na^+), and 4 for the anion (Cl^-).

Following the accepted theory of solubility [6], the *Setchenow* coefficient k_s is given as a sum of three terms where k_α is the cavity term, k_β is the interaction term, and k_γ transforms k_s from a molar to a mole fraction scale (Eq. (4)). For a 1:1 electrolyte, k_γ can be calculated from Eq.(5) [6] where $V_{\phi,s,0}$ is the apparent molar volume of the salt at infinite dilution, M_1 is the molecular weight of water, and ρ_1 is the density of pure water. For aqueous sodium chloride solutions at 25.0°C the value $V_{\phi,s,0} = 16.628\,\mathrm{cm^3 \cdot mol^{-1}}$ [15], and $\rho_1 = 0.9970474\,\mathrm{g \cdot cm^{-3}}$ [16] were used to calculated k_γ. The calculated value of k_γ amounts to $0.0085\,\mathrm{dm^3 \cdot mol^{-1}}$. This term is very small for simple inorganic electrolytes.

$$k_s = k_\alpha + k_\beta + k_\gamma \tag{4}$$

$$k_\gamma = \left(\frac{\mathrm{d}\log \Sigma C_j}{\mathrm{d}c_s}\right)_{c_s \to 0} = \frac{1}{\ln(10)}\left(\frac{2M_1}{\rho_1} - V_{\phi,s,0}\right) \tag{5}$$

The interaction parameter k_β was calculated from Eq.(6) [6] where N_A is *Avogadro's* number, μ_1 the dipole moment of water, ε_j/k the energy parameter, and σ_j the diameter of species j. In calculating the term k_β the diameter of the water molecule σ_1 is taken to be 0.275 nm [12]. The hard-sphere diameter of the solute

Table 3. Parameters for the scaled particle theory of water and sodium chloride ions at 25.0°C

	$\frac{\sigma}{\mathrm{nm}}$	$\frac{\varepsilon/k}{\mathrm{K}}$	$\frac{\alpha \cdot 10^{24}}{\mathrm{cm^3}}$
H_2O	0.275[a]	85.3[a]	1.45[c]
Na^+	0.190[b]	147.5[d]	0.21[b]
Cl^-	0.362[b]	225.6[d]	3.02[b]

[a] Ref. [12]; [b]Ref. [36]; [c]Ref. [37]; [d]Ref. [20]

molecule, σ_2, was calculated from *de Ligny's* relation [17] based on *Bondi's van der Waals* volume $V_{2,w}$ [18] (Eq. 7).

$$
\begin{aligned}
k_\beta &= \left(\frac{\mathrm{d}(\bar{g}\,^s_2/\mathrm{k}T\ln(10)}{\mathrm{d}c_s}\right)_{c_s\to 0} \\
&= -\frac{4\pi N_A}{9T\ln(10)}\left(\frac{\varepsilon_2}{k}\right)^{1/2}\left(\left(\frac{\varepsilon_3}{k}\right)^{1/2}(\sigma_2+\sigma_3)^3+\left(\frac{\varepsilon_4}{k}\right)^{1/2}(\sigma_2+\sigma_4)^3\right) \\
&\quad +\frac{4\pi N_A\rho_1}{9TM_1\ln(10)}V_{\phi,s,0}\left(\frac{\varepsilon_1}{k}\right)^{1/2}\left(\frac{\varepsilon_2}{k}\right)^{1/2}(\sigma_1+\sigma_2)^3+\frac{32\pi N_A\rho_1\mu_1^2V_{\phi,s,0}\alpha_2}{3kTM_1\ln(10)(\sigma_1+\sigma_2)^3}
\end{aligned}
\tag{6}
$$

$$
\sigma_2=\left(\frac{6\cdot V_{2,w}}{\pi\cdot N_A}\right)^{1/3} \tag{7}
$$

The polarizability of alkyl acetate, α_2, was calculated from the *Lorentz-Lorenz* relation using the refractive indices and densities of alkyl acetates given in Table 8 and in Ref. [19]. The energy parameter ε_2/k, given in Table 4, was evaluated from the *Mavroyannis-Stephen* theory [20] using the polarizability and diameter of the investigated nonelectrolyte solutes. The parameters for the scaled particle theory of water and ions at 25.0°C are given in Table 3, those for alkyl acetates in Table 4.

The hard-sphere diameters for some alkyl acetates have been estimated by *Cross* and *McTigue* [5] from the correlation between the hard-sphere diameter and the limiting apparent molar volume of some nonpolar solutes. Values of 0.512 nm (MeOAc), 0.548 nm (EtOAc), 0.573 nm (ProAc), and 0.590 nm (BuOAc) were obtained. These values are close to the values listed in Table 4.

The calculated values of k_β for the investigated alkyl acetates are compiled in Table 5 from which it can be seen that the interaction parameter k_β is negative and that its absolute value increases almost linearly with increasing molecular weight of the 1-alkyl acetates, whereas the values for isomeric butyl acetates are the same.

Table 4. Hard-sphere diameters, energy parameters, polarizabilities and *van der Waals* volumes for some alkyl acetates at 25.0°C

Solute	σ_2 / nm	ε_2/k / K	$\alpha_2\cdot 10^{24}$ / cm^3	V_w / $\mathrm{cm}^3\cdot\mathrm{mol}^{-1}$
MeOAc	0.514	145.3	7.0	42.74
EtOAc	0.552	147.6	8.9	52.97
1-PrOAc	0.585	149.0	10.7	63.20
1-BuOAc	0.615	149.4	12.6	73.43
iso-BuOAc	0.615	150.2	12.6	73.42
sec-BuOAc	0.615	149.9	12.6	73.42
ter-BuOAc	0.615	149.5	12.5	73.41
1-*Pe*OAc	0.643	150.0	14.4	83.66
1-*He*OAc	0.668	152.2	16.4	93.89

The term for the free energy of cavity formation, k_α, was calculated from Eq.(8) [6]:

$$k_\alpha = \left(\frac{\mathrm{d}(\bar{g}_2^{h}/\mathrm{k}T\ln(10))}{\mathrm{d}c_s}\right)_{c_s\to 0} = \left(\frac{\mathrm{d}\log(1-\tau_3)}{\mathrm{d}c_s} + \frac{\mathrm{d}A}{\mathrm{d}c_s}\right)_{c_s\to 0} \tag{8}$$

A is defined as

$$A = \frac{3\tau_1\sigma_2}{\ln(10)(1-\tau_3)}\left(1 + \frac{\tau_2\sigma_2}{\tau_1} + \frac{3\tau_1\sigma_2}{2(1-\tau_3)}\right) \tag{9}$$

and τ_n as

$$\tau_n = \frac{\pi}{6}\sum_{1}^{4} C_j\sigma_j^n \tag{10}$$

In the calculation of k_α, the terms involving C_2 were neglected. The calculated values of k_α are compiled in Table 5 from which it can be seen that the values of k_α are positive, meaning that the free energy change for cavity formation becomes more positive as the concentration of salt increases. Thus, the values of k_α of 1-alkyl acetates increase linearly with increasing molecular weight, whereas for isomeric butyl acetates these values are the same.

The salting coefficient, $k_{s(\mathrm{cal})SPT}$, given in Table 5, was calculated by adding k_α, k_β and k_γ (see Eq. (4)). Since the limiting apparent molar volume of sodium chloride is relatively small, the contribution of k_γ to the sum $k_\alpha + k_\beta$ is negligible. Thus, the sign of the salting coefficient depends upon the relative magnitudes of k_α and k_β. As has been shown previously [6], both k_α and k_β increase in absolute magnitude with increasing size of the nonelectrolyte molecule and with the concentration of sodium chloride, as was also observed for the investigated alkyl acetates.

In view of the various approximations of the scaled particle theory and the uncertainties of the parameters used, the calculated values of the salting coefficient given in Table 5 are of the correct order of magnitude (see Table 2). The calculated

Tabel 5. Interaction parameters (k_β) cavity formation parameters (k_α) and calculated salting coefficients ($k_{s(\mathrm{cal})SPT}$) of some alkyl acetates at 25.0°C

Solute	$\frac{-k_\beta}{\mathrm{dm}^3\cdot\mathrm{mol}^{-1}}$	$\frac{k_\alpha}{\mathrm{dm}^3\cdot\mathrm{mol}^{-1}}$	$\frac{k_{s(\mathrm{cal})SPT}}{\mathrm{dm}^3\cdot\mathrm{mol}^{-1}}$
MeOAc	0.141	0.342	0.210
EtOAc	0.163	0.388	0.234
1-PrOAc	0.184	0.432	0.257
1-BuOAc	0.204	0.473	0.278
iso-BuOAc	0.204	0.473	0.278
sec-BuOAc	0.204	0.473	0.278
ter-BuOAc	0.204	0.473	0.278
1-*Pe*OAc	0.223	0.512	0.298
1-*He*OAc	0.243	0.550	0.315

values of $k_{s\,(\mathrm{cal})\,SPT}$ are from 31% for ethyl acetate to 1% for hexyl acetate higher than the experimental ones.

The *McDevit-Long* theory of the salt effect of an electrolyte on the activity of nonpolar solutes [7] has been frequently used to interpret the solubility of nonelectrolytes in an electrolyte solution. In this approach the magnitude of the salt effect is related to the volume change which occurs when salt and water are mixed. Their resulting relation is Eq. (11) [7] where $\bar{V}_{2,0}$ and $\bar{V}_{s,0}$ are the partial molar volumes of nonelectrolyte and salt in aqueous solution at infinite dilution, V_s is the molar volume of pure (liquid) electrolyte, β_0 is the compressibility of pure water, and R is the gas constant.

$$k_s = \frac{\bar{V}_{2,0}(V_s - \bar{V}_{s,0})}{\ln(10)\mathrm{R}T\beta_0} \tag{11}$$

In calculating the salting coefficient, the partial molar volumes of the investigated compounds at infinite dilution were taken from Ref. [19], whereas those of 1-pentyl and 1-hexyl acetate were obtained by extrapolation of the linear relation between the partial molar volume of 1-alkyl acetate at infinite dilution and the corresponding molar volume given in Ref. [19]. The intrinsic volume of sodium chloride ($V_s = 26.9\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$) was taken from Ref. [21], the partial molar volume of sodium chloride at infinite dilution from Ref. [15], and the compressibility of pure water ($\beta_0 = 4.53 \cdot 10^{-10}\,\mathrm{Pa}^{-1}$) from Ref. [22]. The calculated salting coefficients $k_{s(\mathrm{cal})MD}$ are given in Table 6. From this Table it can be seen that, although the sequence of salting coefficients coincides with that found experimentally except for isomeric butyl acetates (see Table 2), the calculated values are higher by a factor of 1.6 (methyl acetate) to 2.2 (1-butyl acetate).

Cross [23] has expanded the *McDevit*-Long theory of nonelectrolyte activity coefficients in aqueous salt solutions so that it may be applied to concentrated electrolyte solutions. According to this theory, the relative mole fraction activity coefficient, f_{rel}, is given by Eq. (12) where r_n is the distance of closest approach to

Table 6. Partial molar volumes of some alkyl acetates at infinite dilution at 25.0°C and salting coefficients using the *McDevit-Long*, *Cross*, and *Aveyard* theories

Solute	$\bar{V}_{2,0}$ / $\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$	$k_{s(\mathrm{cal})MD}$ / $\mathrm{dm}^3 \cdot \mathrm{mol}^{-1}$	$k_{s(\mathrm{cal})C}$ / $\mathrm{dm}^3 \cdot \mathrm{mol}^{-1}$	$k_{s(\mathrm{cal})A}$ / $\mathrm{dm}^3 \cdot \mathrm{mol}^{-1}$
MeOAc	72.23[a]	0.287	0.114	0.176
EtOAc	88.87[a]	0.354	0.134	0.202
1-PrOAc	105.12[a]	0.418	0.155	0.225
1-BuOAc	121.17[a]	0.482	0.174	0.246
iso-BuOAc	121.43[a]	0.483	0.174	0.248
sec-BuOAc	121.73[a]	0.485	0.175	0.249
ter-BuOAc	121.27[a]	0.483	0.174	0.249
1-*Pe*OAc	136.50[b]	0.543	0.192	0.267
1-*He*OAc	152.16[b]	0.605	0.210	0.286

[a] Ref. [19]; [b]obtained from the extrapolation procedure

Table 7. Relative molar activity coefficients ($\log y_{\mathrm{rel}}$) calculated from Eq. (10) and experimental values for some alkyl acetates at 25.0°C

$c_s/\mathrm{mol\cdot dm^{-3}}$		$\log y_{\mathrm{rel}}$			
Solute		0.150	0.500	0.750	1.000
MeOAc	exp.	0.0366	0.1059	0.1478	0.1925
	cal.	0.0159	0.0548	0.0840	0.1136
EtOAc	exp.	0.0251	0.0924	0.1301	0.1816
	cal.	0.0180	0.0639	0.1006	0.1333
1-PrOAC	exp.	0.0344	0.1024	0.1523	0.2004
	cal.	0.0235	0.0761	0.1151	0.1558
1-BuOAc	exp.	0.0345	0.1110	0.1684	0.2225
	cal.	0.0262	0.0855	0.1292	0.1754
iso-BuOAc	exp.	0.0258	0.1038	0.1552	0.2216
	cal.	0.0263	0.0857	0.1294	0.1755
sec-BuOAc	exp.	0.0397	0.1218	0.1721	0.2439
	cal.	0.0263	0.0859	0.1298	0.1760
ter-BuOAc	exp.	0.0251	0.1229	0.1933	0.2633
	cal.	0.0262	0.0853	0.1291	0.1750
1-*Pe*OAc	exp.	0.0358	0.1457	0.2091	0.2711
	cal.	0.0288	0.0943	0.1427	0.1935
1-*He*OAc	exp.	0.0316	0.1588	0.2397	0.3056
	cal.	0.0315	0.1032	0.1561	0.2117

the nonelectrolyte molecule, and $\bar{r}_h$ is the distance of closest approach to the average solvated ion present in solution.

$$\lim_{n_n\to 0}(\log f_{\mathrm{rel}}) = \frac{\bar{V}_{2,0}c_s(V_s-\bar{V}_{s,0})}{\ln(10)\mathrm{R}T\beta} \cdot \left(1-\frac{c_s}{2}(V_s-\bar{V}_{s,0})-\frac{c_s^2}{3}(V_s-\bar{V}_{s,0})^2-\dots\right)\frac{\bar{r}_h}{\bar{r}_h+r_n} \qquad (12)$$

In the calculation of the relative mole fraction activity coefficient from Eq. (12) we used only the first two terms in parentheses. The following parameters were used: r_n values were calculated from the molar volumes of alkyl acetate ($V_2^0 = 4/3N_A\pi r_n^3$), the value of $\bar{r}_h = 0.243\,\mathrm{nm}$ was taken from Ref. [23], and $\beta(\mathrm{bar}^{-1})$ values were calculated for the different salt solutions from the relation $\beta = \beta_0 - a_1\cdot c_s + a_2\cdot c_s^{3/2}$, where $a_1 = -5.91\cdot 10^{-6}$ and $a_2 = 1.04\cdot 10^{-6}$ as given in Ref. [24]. After conversion of the relative mole fraction activity coefficient to the molar concentration scale [25], values of the relative molar activity coefficients ($\log y_{\mathrm{rel}}$) were obtained as shown in Table 7 together with experimental ones. From Table 7 it is apparent that an increasing size of the hydrocarbon segment in the alkyl acetate leads to higher activity coefficients calculated from Eq. (12). Since the ion-dipole and dipole-dipole forces involving the polar part of the ester molecule are approximately constant in solutions of sodium chloride, the hydrophobic part of the ester molecule must play an important

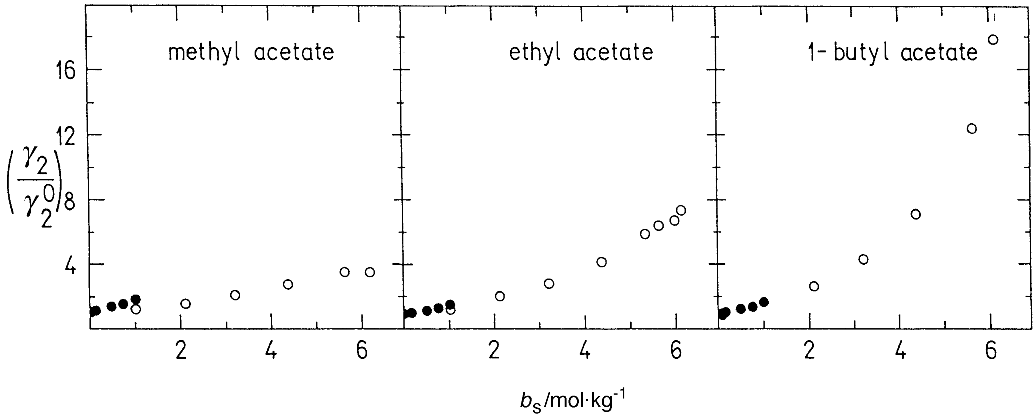

Fig. 1. Ratio of molal activity coefficients for some 1-alkyl acetates at 25.0°C; ●: this work, ○: *Cross* and *McTigue*

role as has been shown previously [26]. From this Table it is also evident that the experimental relative molar activity coefficients are higher than those calculated by Eq. (12) except for some solutes at the lowest concentration of sodium chloride (2-methyl-1-propyl and 2-methyl-2-propyl). The salting coefficient $k_{s(\mathrm{cal})C}$ was calculated from a linear plot of $\log y_{\mathrm{rel(cal)}}$ vs. c_s. The results obtained are compiled in Table 6. The salting coefficients $k_{s(\mathrm{cal})C}$ are lower by a factor of 1.3 to 1.6 than those determined experimentally, whereas their sequence follows the experimental values except for isomeric butyl acetates.

In an extended study, *Cross* and *McTigue* [5] have determined the ratio of molal activity coefficients for some 1-alkyl acetates at 25.0°C in concentrated sodium chloride solutions beyond $1.0\,\mathrm{mol}\cdot\mathrm{kg}^{-1}$ using the distribution technique. Figure 1 shows as an example the ratio of experimental molal activity coefficients, $\frac{\gamma_2}{\gamma_2^0}$ for some investigated alkyl acetates as a function of the molality of the sodium chloride solution together with the corresponding values determined by *Cross* and *McTigue*. From this figure it may be seen that both experimental techniques coincide except for methyl acetate. It is interesting to note that *Cross* and *McTigue* were able to interpret the experimental data on the basis of Eq. (12) only for methyl acetate in sodium chloride solution, whereas for higher homologues of 1-alkyl acetate (up to 1-pentyl acetate) their ratios of the relative molal activity coefficients are lower than the experimental ones.

A simple approach to the salting coefficients of nonpolar and polar solutes by strongly solvated salts has been developed by *Aveyard* based on the desorption of ions from the interface in the region of low dielectric constant [8]. The salting coefficient may be calculated in terms of the surface tension increment caused by the addition of salt to the solvent. For calculation of the salting coefficient the molar volumes of solvent and solute as well as the osmotic coefficient of the salt solution must be known. The following simple expression for a 1,1-electrolyte ($\nu = 2$) and a nonpolar solute was obtained for the salting coefficient:

$$k_s = \frac{0.74 \cdot 6 \cdot \nu}{\ln(10)} (V_1^0)^{1/3} (V_2^0)^{2/3} \phi \tag{13}$$

V_1^0 and V_2^0 are the molar volumes of solvent and nonelectrolyte solute ($\mathrm{m}^3 \cdot \mathrm{mol}^{-1}$), ϕ is the molal osmotic coefficient of the aqueous salt solution at $c_s = 1.0\,\mathrm{mol} \cdot \mathrm{dm}^{-3}$, and the factor of 0.74 arises from the approximation that the solvent and solute in their pure state consist of close-packed spherical molecules. For a polar nonelectrolyte the salt effect can only be estimated if the differences in the surface tension of the salt solution, an appropriate polar nonelectrolyte, and a pure solvent are known. Since the investigated alkyl acetates are slightly polar compounds [27], we used Eq. (13) for the calculation of salting coefficients. In this calculation the value of 0.937 [25] was used for the molal osmotic coefficient. The values of salting coefficient $k_{s(\mathrm{cal})A}$ obtained are given in Table 6. From the collected data it can be seen that Eq. (13) satisfactorily describes the salting coefficients of the investigated compounds (less than 10% deviation).

Finally, according to the electrostatic theory of *Conway et al.* [9], considering the dielectric saturation effect near the ion and the primary hydration of the ion, the following equations result [9]:

$$\frac{c_2^0 - c_2}{c_2^0} = \frac{n_s c_s}{c_1^0} + N_A c_s \left(\frac{4\pi (z_i e_0)^2 (\alpha_{o,1} - \alpha_{o,2})}{\varepsilon^2 \mathrm{k} T \bar{r}_h} \right) \tag{14}$$

$$\frac{\Delta c_2}{c_2^0} = k_s c_s \tag{15}$$

n_s is the solvation number of the electrolyte, c_1^0 is the molar concentration of pure water, z_i the charge number of an ion i, e_0 the electron charge, $\alpha_{o,1}$ and $\alpha_{o,2}$ the orientation polarization of water and nonelectrolyte, respectively, $\bar{r}_h$ is the radius of the primary hydration sheath, and ε is the dielectric constant of the solvent. The first term of Eq. (14), which is supposed to be nonelectrolyte independent, gives a salting-out contribution which considers the strong ion-solvent interaction present in the primary solvation shell of the ion where dielectric saturation effects are significant. The second term of Eq. (14) leads either to a salting-out or salting-in contribution depending on the difference of orientation polarization of water and the nonelectrolyte. For calculation of the salting coefficient we used the following values: for the solvation number of sodium chloride $n_s = 4.4$ [28], for the dielectric constant of water $\varepsilon = 78.304$ [16], for the radius of the primary hydration sheath, $\bar{r}_h = 0.243\,\mathrm{nm}$ [23], and the orientation polarization of water and nonelectrolyte $\alpha_{o,i}$ was calculated from Eq. (16) [38].

$$\alpha_{o,i} = \frac{\mu_i^2}{3\mathrm{k}T} \tag{16}$$

For the dipole moment of the water molecule in aqueous solution, a value of $\mu_1 = 1.77\,\mathrm{D}$ [39], was used, whereas for the investigated alkyl acetates we used dipole moments determined in benzene solution based on the *Debye* relation [27, 29]. Since for benzene solutions the dielectric constant of benzene is within 1.3% equal to the square of the refractive index of benzene, the dipole moments obtained are within experimental error equal to the *Onsager* value [25]. The dipole moments range from 1.82 D for EtOAc to 1.92 for *ter*-BuOAc [27, 29]. The difference of orientation polarization ($\alpha_{o,1} - \alpha_{o,2}$) in Eq. (14) is negative, except for MeOAc, and consequently the salting coefficients are also negative. The first term of Eq.

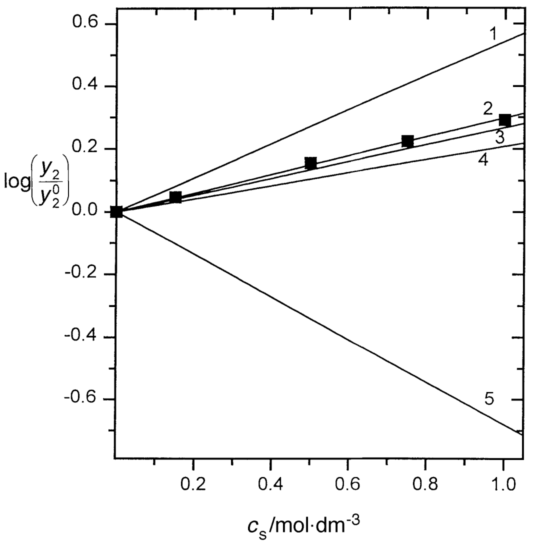

Fig. 2. Dependence of log $\left(\frac{y_2}{y_2^0}\right)$ for 1-*Pe*OAc on molar salt concetration at 25.0°C; ■: experimental values, —: calculated value (1: *McDevit* and *Long*, 2: *Masterton* and *Lee*, 3: *Aveyard*, 4: *Cross*, 5: *Conway*)

(14) is relatively small and amounts to $0.079\,\mathrm{dm}^3\cdot\mathrm{mol}^{-1}$. The only positive value for the salting coefficient is obtained for MeOAc. Its value of $0.484\,\mathrm{dm}^3\cdot\mathrm{mol}^{-1}$ is too high by a factor of 2.6.

Figure 2 compares, as an example, the experimental solubility values of 1-*Pe*OAc with those calculated by the theoretical models. The close similarity between the experimental results and those calculated by the approach of *Masterton* and *Lee* [6] is an indication that the positive change of the standard *Gibbs* free energy accompanying the formation of 1 mol of cavities in the aqueous electrolyte solvent, relative to pure water, is the primary factor determining the solubility results. The energy of cavity formation is influenced not only by the magnitude of the nonelectrolyte molecule, but also by its ability to interact with its ions. This theory, contrary to other approaches, has the great advantage that the required molecular parameters are readily available and that in the past it has been successfully applied to many systems containing polar [30] and nonpolar nonelectrolyte solutes [31] as well as for systems containing tetraalkyl ammonium ions [11]. Furthermore, this theory can be obtained as a special case of the perturbation theory [32, 33]. On the other hand, the *Aveyard* approach [8] which is based on the desorption of ions from the interface gives a relatively satisfactory description of the investigated nonelectrolyte solutes. In this theory, contrary to the scaled particle theory, the contribution to cavity transfer is taken to be zero. So, the surface activity of the nonelectrolyte molecule must play an important role. The deficiency of this method is that the parameter required, *i.e.* the difference in the surface tension of the salt solution, the polar nonelectrolyte, and that of the pure solvent, is not available for most common cases. Among the semi-empirical approach of *McDevit* and *Long* [7], the extended version of *Cross* [23], and the purely electrostatic approach of *Conway et al.* [9], the *Cross* relation gives values which are closer to the experimental ones than those calculated by the other two theories. In the electrostatic theory, the orientation polarizability of the solvent and nonelectrolyte molecules as well as effects concerning the primary and secondary hydration sheaths are the predominant factors accounting for the salting-out effect (see Eq. (14)). These effects cannot explain the observed salting-out effect of the investigated highly polarizable nonelectrolyte solutes. It seems that preferential solvation phenomena which take place in mixtures of polar molecules are primarily responsible for the observed differences between the calculated and experimental values. None of these methods can be considered as fully satisfactory because of unacceptable errors in the evaluation of salting coefficients or because of the difficulty in finding the parameters required for the calculation.

Experimental

Methyl, ethyl, 1-propyl, 1-butyl, 2-methyl-1-propyl, 2-methyl-2-propyl, 1-pentyl, 1-hexyl (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 20.0°C and 25.0°C and their densities at 25.0°C. The values obtained for 1-pentyl and 1-hexyl acetate are presented in Table 8 together with literature values, whereas those of the other compounds investigated are given in Ref. [26]. Sodium chloride (Carlo Erba, RPE) was dried to constant weight at 105°C. Aqueous sodium chloride solutions in the concentration range from 0.15 to 1.00 $\mathrm{mol\cdot dm^{-3}}$ were prepared with doubly distilled water.

Solubility measurements

Solubility measurements of alkyl acetates were performed as follows: 100 $\mathrm{cm^3}$ of water or salt solution, contained in a stoppered *Erlenmeyer* flask, were shaken with a slight excess of alkyl acetate for five hours in a thermostatted water bath at 25.00±0.03°C. To achieve separation of the two phases the mixture was left for a period of eighteen hours in the water bath. A certain amount of aqueous phase (g) was then removed and the dissolved alkyl acetate determined either by acidimetric titration after saponification of alkyl acetate [34] or in the case of 2-methyl-2-propyl, 1-pentyl, and 1-hexyl acetate with an HPLC system. A 4-channel degassing unit (X-act, Jour Research, Knauer; Marathon-XT autosampler (Spark, Holland); Eurospher 80-C18 (300×4.6 mm) column (Knauer GmbH, Germany); Knauer UV/Vis detector was used. Each solubility value of alkyl acetate, expressed as a weight fraction w_2 (%), is based on at least three measurements. The molar concentration of the salt solution was taken to be that before addition of alkyl acetate.

Table 8. Experimental densities and refractive indices of pure 1-pentyl and 1-hexyl acetate compared with literature data

Solute	$\rho_0/(\mathrm{g\cdot cm^{-3}})$(25°C)		n_D(20°C)	n_D(25°C)	n_D(20°C)	n_D(25°C)
	Exptl.	Lit.	Exptl.		Lit.	
1-*Pe*OAc	0.87222	0.8719[a]	1.40249	1.40004	1.4028[a]	–
1-*He*OAc	0.86836	0.8681[a]	1.40909	1.40673	1.4096[a]	1.4068[b]

[a] Ref. [16]; [b] Ref. [29]

Density measurements

The densities of the purified alkyl acetates (ρ_2, $\text{g} \cdot \text{cm}^{-3}$) and saturated alkyl acetate – salt solutions (ρ, $\text{g} \cdot \text{cm}^{-3}$) were measured with a vibrating tube digital densimeter (model DMA 601, Anton Paar, Graz, Austria) calibrated with air and water at 25°C [35]. 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 $2.10^{-5}\,\text{g} \cdot \text{cm}^{-3}$.

Refractive index measurements

The refractive index was measured with a Schmidt-Haeusch refractometer, model DUR-W2, with a precision of 1.10^{-6}. All measurements were performed at 20°C and 25°C and at a wavelength of 589 nm.

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