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Enthalpies of transfer of monomethyl esters of dicarboxylic acids from water to aqueous–alcoholic solvent mixtures

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Abstract

Enthalpies of transfer of sodium salts of monomethyl esters of oxalic, malonic, succinic, adipic, fumaric, maleic, *o*-phthalic, isophthalic, and terephthalic acids from water to water–methanol and water–*tert*-butyl alcohol mixtures have been determined by calorimetry. Using literature data for the enthalpies of transfer for the sodium ion, based on extra thermodynamic TATB and TPTB assumptions, the enthalpies of transfer of the monoester anions were calculated. The results are discussed in terms of ion–solvent and solvent–solvent interactions.

Keywords: Aqueous–alcoholic solvent mixtures; Calorimetry; Dicarboxylic acid, monomethylester, sodium salt; Enthalpy of transfer; Ion–solvent interactions; Solvent–solvent interactions

1. Introduction

Calorimetric investigations of aliphatic carboxylic acids [1,2], sodium salts of carboxylic acids (C_1–C_4, C_{10}) [3,4] and potassium salts of *p*-halobenzoic acids [2,5] in water and water–*t*-BuOH mixtures have been described. Enthalpies of solution, ΔH_s°, and transfer functions, ΔH_t°, of these compounds show the extrema of the dependence of ΔH_s° and ΔH_t° on x_2. The position and magnitude of the extrema depend on the number of $-CH_2-$ groups in the aliphatic carboxylic acid, or on the size of the substituent in *p*-halobenzoic acid. However, relatively few thermodynamic investigations have dealt with the monoesters of the dicarboxylic acids. These interesting compounds have been widely used in the past for the study of the effects of salt and

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medium on the kinetics of their basic hydrolysis [6–9]. Interpretation of kinetic measurements of a homogeneous reaction carried out in a mixed binary solvent is based on the thermodynamic transfer functions of the reactants and activated complex [7–10].

The present study is a part of our investigation of monoesters of dicarboxylic acids and its aim was to obtain the transfer enthalpies of a series of sodium salts of monoesters and the monoester anions.

2. Experimental

The sodium salts of monoesters of dicarboxylic acids were prepared according to the literature [11–14]. Their purities were checked by elemental analysis. Methanol (MeOH) and *t*-butanol (*t*-BuOH) (Merck reagent grade) were distilled prior to use. The enthalpies of solution were measured using an isoperibolic calorimeter (VUT, Brno, Czechoslovakia) using the procedure described in a previous paper [15]. The time for which the measured process proceeded, 40 s, was sufficiently short for isoperibolic conditions to be obeyed. Neutral hydrolysis under these conditions was not observed. The enthalpies of solution were measured in a 2×10^{-3}–10^{-2} mol dm^{-3} concentration range of investigated compounds. They were found to be independent of compound concentration within experimental error and so were taken as the standard values. The experimental values of enthalpies of solution are averages of 3–6 independent measurements. The standard deviations of measured ΔH_s° values are given for each reported value.

3. Results and discussion

The standard enthalpies of solution of the sodium salts of the monomethyl esters in water–MeOH and water–*t*-BuOH mixtures of various compositions are summarized in Table 1. The transfer enthalpies of the corresponding anions, $\Delta H_t^\circ(\text{ester}^-)$ were calculated from the values of ΔH_t° (salt), obtained from ΔH_s° (salt), and literature data on the transfer enthalpies of sodium ion, $\Delta H_t^\circ(\text{Na}^+)$, in water–MeOH [16] and water–*t*-BuOH mixtures [2]. The values of the transfer enthalpies summarized in Table 2 show a remarkable difference between the behavior of aromatic and aliphatic monoester ions. The standard enthalpies of transfer for monomethyl ester ions of *o*-phthalic, isophthalic, and terephthalic acids increased regularly with increasing concentrations of *t*-BuOH. The same character of the transfer functions has been observed for *p*-substituted benzoic acids [2]. On the other hand, the dependencies $\Delta H_t^\circ(\text{ester}^-) = \text{f}(x_2)$ for the monoester ions of aliphatic dicarboxylic acids pass through the extrema. Fig. 1 illustrates the dependencies for selected monoester anions. The sharpness of the maxima for the aliphatic esters varied with the number of hydrophobic $-CH_2-$ groups. Similar variations in the transfer functions of the aliphatic carboxylic acid ions, $\Delta H_t^\circ(\text{RCOO}^-)$, were observed (see Table 3). Values of the transfer function of RCOO^- were evaluated from $\Delta H_s^\circ(\text{RCOONa})$ [4] and from dissociation enthalpies of

Table 1
Enthalpies of solution, ΔH_s°/(kJ mol^{-1}), of sodium salts of monomethyl esters of I-*o*-phthalic, II-terephthalic, III-*i*-phthalic, IV-maleic, V-fumaric, VI-oxalic, VII-malonic, VIII-succinic, and IX-adipic acid, in H_2O, H_2O–MeOH, and H_2O–*t*-BuOH at 298.2 K

Ester	MeOH/mol%				
	0	4.7	10.0	16.0	22.9
I	2.1 ± 0.2	6.9 ± 0.5	11.4 ± 0.2	16.8 ± 0.2	18.0 ± 0.5
II	8.5 ± 0.1	13.4 ± 0.4	18.5 ± 0.5	21.4 ± 0.1	21.1 ± 0.1
III	8.9 ± 0.2	13.8 ± 0.3	19.3 ± 0.2	21.6 ± 0.2	21.3 ± 0.2
IV	− 3.2 ± 0.2	0.7 ± 0.1	4.2 ± 0.2	7.8 ± 0.2	9.5 ± 0.3
V	5.8 ± 0.2	9.7 ± 0.1	14.0 ± 0.2	17.0 ± 0.2	18.0 ± 0.1
VI	8.9 ± 0.1	11.8 ± 0.2	14.6 ± 0.2	17.1 ± 0.2	19.1 ± 0.2
VII	− 4.2 ± 0.1	0.8 ± 0.1	3.7 ± 0.1	7.0 ± 0.1	8.6 ± 0.1
VIII	1.9 ± 0.1	5.1 ± 0.1	9.1 ± 0.1	12.2 ± 0.1	13.1 ± 0.4
IX	− 10.0 ± 0.2	− 4.3 ± 0.2	0.9 ± 0.2	6.0 ± 0.1	8.4 ± 0.2
Ester	*t*-BuOH/mol%				
	0	2.1	4.6	7.6	11.3
I	2.1 ± 0.2	11.4 ± 0.1	24.0 ± 0.2	26.5 ± 0.1	23.6 ± 0.1
II	8.5 ± 0.1	16.3 ± 0.1	29.5 ± 0.3	27.5 ± 0.3	22.5 ± 0.1
III	8.9 ± 0.2	17.3 ± 0.2	29.6 ± 0.3	28.5 ± 0.1	24.2 ± 0.1
IV	− 3.2 ± 0.2	1.3 ± 0.2	9.3 ± 0.1	14.6 ± 0.2	17.7 ± 0.2
V	5.8 ± 0.2	11.8 ± 0.1	21.2 ± 0.2	23.5 ± 0.2	22.6 ± 0.3
VI	8.9 ± 0.1	12.9 ± 0.2	19.1 ± 0.1	23.4 ± 0.2	23.8 ± 0.1
VII	− 4.2 ± 0.1	2.1 ± 0.1	10.6 ± 0.2	15.1 ± 0.1	16.8 ± 0.7
VIII	1.9 ± 0.1	6.4 ± 0.2	14.8 ± 0.5	20.9 ± 0.4	20.8 ± 0.3
IX	− 10.0 ± 0.2	− 1.5 ± 0.1	9.5 ± 0.1	15.5 ± 0.4	15.7 ± 0.2

Table 2
Enthalpies of transfer ΔH_t°/(kJ mol^{-1}) of monomethyl esters of dicarboxylic acid ions in H_2O–MeOH and H_2O–*t*-BuOH mixtures at 298.2 K. Symbols I*–IX* are ions of the monomethyl esters of dicarboxylic acids listed in Table 1

Ester	MeOH/mol%				*t*-BuOH/mol%			
	4.7	10.0	16.0	22.9	2.1	4.6	7.6	11.3
I*	5.6	8.2	10.9	10.6	7.1	7.4	11.9	15.7
II*	5.7	8.9	9.1	7.3	5.5	6.5	6.5	8.2
III*	5.7	9.3	8.9	7.1	5.7	6.0	7.4	9.8
IV*	4.7	6.3	7.2	7.4	2.3	− 2.0	5.3	15.1
V*	4.7	7.1	7.4	6.9	3.8	0.9	5.2	11.0
VI*	3.7	4.6	4.4	4.9	1.8	− 5.3	2.0	9.1
VII*	5.8	6.8	6.4	7.5	4.1	0.3	6.8	15.2
VIII*	4.0	6.1	6.5	5.9	2.3	− 1.6	5.5	12.0
IX*	6.5	9.8	12.2	13.1	6.3	5.0	13.0	19.9

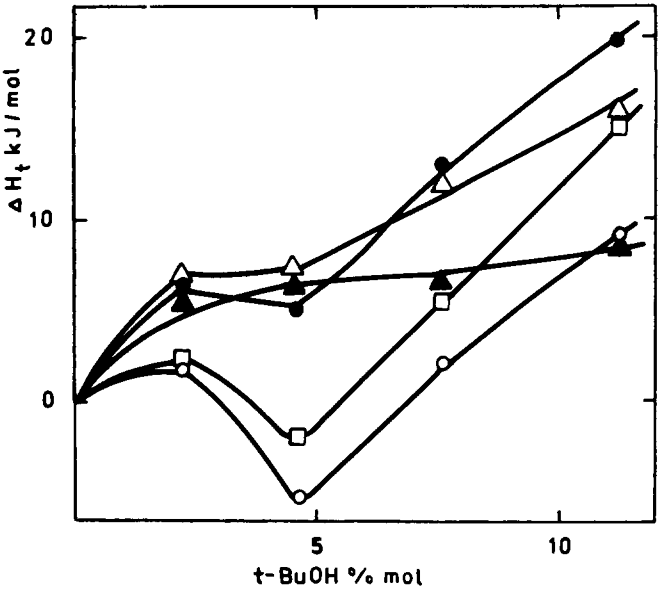

Fig. 1. Enthalpies of transfer of some monomethyl ester anions as a function of *t*-BuOH mole fraction: ○-oxalic, ●-adipic, △-*o*-phthalic, ▲-terephthalic, and □-maleic acids.

Table 3

Enthalpies of transfer $\Delta H_t^\circ/(\mathrm{kJ\ mol^{-1}})$, of aliphatic carboxylic acid ions in H_2O–*t*-BuOH mixtures at 298.2 K

	t-BuOH/mol%			
	2	4	6	10
$HCOO^-$	0.2	−5.4	−8.6	2.9
CH_3COO^-	0.7(1.8)	−3.5(−2.2)	−5.5(−4.0)	8.4(7.5)
$CH_3CH_2COO^-$	0.9(2.0)	−2.6(−1.0)	−2.6(−2.5)	11.0(10.5)
$CH_3(CH_2)_2COO^-$	1.2	0.2	0.8	14.5

Values of ΔH_t° were evaluated from ΔH_s°(RCOONa) published in Ref. [4] and values in parentheses were interpolated from graph in Ref. [2].

acetic and propionic acids in water and water–*t*-BuOH mixtures [1, 2]. As can be seen from Table 3, good agreement was found for transfer enthalpies of $\Delta H_t^\circ(CH_3COO^-)$ and $\Delta H_t^\circ(CH_3CH_2COO^-)$ estimated by the two different methods.

Because many factors influence the values of the transfer functions, the dependence of ΔH_t°(ester$^-$) on the mole fraction of the cosolvent is difficult to explain. Choudhury and Ahluwalia [4] considered the effects of hydrophobic and hydrophilic parts of the molecule separately. While the hydrophobic part of the solute modifies the solvent–solvent interactions, the hydrophilic part participates in solute–solvent interactions and the nature of the hydrophobic and hydrophilic portions of the solute influences the value of transfer enthalpy. Juillard used the fluctuating cage model [17], according to which the anions are more easily accommodated in the clathrate-like structure of water–cosolvent mixture than in pure water, but increasingly less so as their size increases. A similar trend for $\Delta H_t^\circ(\text{anion}) = f(x_2)$ for monovalent inorganic anions was found in water–*n*-propanol [18] and water–*i*-propanol [19] mixtures. The shapes and the sizes of ions are supposed to determine their ability to fill the vacant holes in the fluctuating structure.

Different trends of $\Delta H_t^\circ(\text{anion}) = f(x_2)$ were observed in water–MeOH mixtures. According to thermodynamic [20], kinetic [8], and theoretical studies [21], the methanol molecules can replace the water molecules in the solvation sphere of ions, and hydrophobic solvation is weaker in comparison with that resulting from alcohol molecules with large alkyl groups. $\Delta H_t^\circ(\text{ester}^-)$ values are positive for all monoester anions and their values are higher than those of small inorganic anions [15]. The term of cavity formation is dominant in the resulting value of $\Delta H_t^\circ(\text{ester}^-)$ in the whole cosolvent region investigated.

The pair interaction coefficients h_{EN} were estimated using the method of Desnoyers et al. [22]. The values of h_{EN} change from approximately 300 for the monomethyl ester of oxalic acid to approximately 600 J kg mol^{-2} for the monomethyl ester of adipic acid in water–MeOH mixtures. In water–*t*-BuOH mixtures the values of h_{EN} change, from approximately 800 for monomethyl ester of oxalic acid to approximately 1700 J kg mol^{-2} for the monomethyl ester of adipic acid. The value of h_{EN}, in water–*t*-BuOH mixtures evaluated from published data [4, 5] for all sodium salts of C_1–C_4 aliphatic carboxylic acids is approximately 450; for potassium benzoate it is 1000 and for potassium *p*-iodobenzoate 1500 J kg mol^{-2}. The positive values of the h_{EN} coefficient for investigated compounds suggest that the ions interact only weakly with MeOH and *t*-BuOH molecules in water-rich regions.

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