Kinetic Solvent and Temperature Effects in the Neutral Methanolysis of Chloromethyl Trichloroacetate in Acetonitrile–Methanol Solutions

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The kinetic behaviour of the neutral methanolysis of chloromethyl trichloroacetate in acetonitrile–methanol solutions over a wide temperature range has been studied. The kinetic data were compared with the available data for the neutral hydrolysis of chloromethyl dichloroacetate in acetonitrile–water solutions. It is suggested that the methanolysis of chloromethyl trichloroacetate takes place by the general base-catalysed $B_{AC}3$ mechanism, methanol acting as a general base catalyst. In contrast to the marked concentration dependence of $\Delta C_p^{\ddagger}$ found in the case of the neutral ester hydrolysis, it seems that for the neutral methanolysis $\Delta C_p^{\ddagger}$ remains almost unchanged over the methanol concentration range used. The difference in behaviour is interpreted in terms of the structural properties of the two solvent systems acetonitrile–methanol and acetonitrile–water.

Solvent effects on hydrolysis reactions have usually been explained in terms of the unique structural properties of liquid water. However, the relation between the nature of the medium and the reaction rate is often complex owing to the many possible interactions between the medium and the initial and the transition states of the reaction. Of the thermodynamic activation parameters the heat capacity of activation ($\Delta C_p^{\ddagger} = \mathrm{d}\Delta H^{\ddagger}/\mathrm{d}T$) has proved to be a most valuable probe for studying solvent effects on those reactions where the transition state of the rate-limiting step is more polar than the initial state.[1–23] In water-rich solutions of organic cosolvents, $\Delta C_p^{\ddagger}$ is shown to go first through a minimum value at some mole fraction x_w of water when a water-structure-making cosolvent, such as an alcohol, is added, but to go through a maximum when a water-structure-breaking cosolvent, such as acetonitrile, is added to water.

For both alcohols and water there is an appreciable degree of structure associated with hydrogen-bonding.[24–28] However, the structure of liquid methanol, the most water-like of the alcohols, consists primarily of long, winding hydrogen-bonded chains with roughly linear hydrogen bonds rather than the three-dimensional hydrogen-bonded network typical of liquid water and ice. The aim of this work was to study solvent effects caused by added acetonitrile for the methanolysis of chloromethyl trichloroacetate over a wide temperature range and to compare the kinetic data with those observed for the neutral hydrolysis of chloromethyl dichloroacetate[6] as an example of ester hydrolysis in $MeCN-H_2O$ solutions.

Experimental

Chloromethyl trichloroacetate was prepared by chlorinating methyl trichloroacetate with gaseous chlorine,[29] and was purified by careful fractional distillation (Todd apparatus). The solvent mixtures were prepared by diluting a known weight of methanol (E. Merck AG, getrocknet, pro analysi) with acetonitrile (Fluka AG, puriss.) to a known volume in a volumetric flask. Acetonitrile was purified as described by Coetzee.[30] According to Karl-Fischer water titration, methanol and purified acetonitrile contained less than 0.01 and 0.05% water, respectively. The solutions were stored over molecular sieves and the rate coefficients for the parallel runs, determined during the course of the experimental work, indicated that the water content of the stock solutions did not increase during storage. The initial ester concentrations were about 10^{-4}M. The temperature was stable to within about ±0.01 K.

Table 1. Temperature range (T/K), number of data points (N), first-order rate coefficients (k/s^{-1}), activation enthalpies ($\Delta H^{\ddagger}/\mathrm{J\ mol^{-1}}$), activation entropies ($\Delta S^{\ddagger}/\mathrm{J\ mol^{-1}\ K^{-1}}$), and heat capacities of activation ($\Delta C_p^{\ddagger}/\mathrm{J\ mol^{-1}\ K^{-1}}$), calculated from equation (1) in its three-parameter form, for the neutral methanolysis of chloromethyl trichloroacetate in acetonitrile–methanol solutions with the mole fraction x_m of methanol at 298.15 K

x_m	T	N	10^3k	$\Delta H^{\ddagger}$	$-\Delta S^{\ddagger}$	$-\Delta C_p^{\ddagger}$
1.000	273—328	11	2.673	27 410 ± 30	202.2 ± 0.1	99 ± 4
0.940	273—328	9	2.228	26 570 ± 80	206.6 ± 0.3	101 ± 10
0.891	278—328	17	1.931	25 600 ± 90	211.0 ± 0.3	102 ± 12
0.842	273—328	10	1.598	25 260 ± 80	213.7 ± 0.3	84 ± 10
0.790	273—328	10	1.318	24 990 ± 80	216.2 ± 0.3	90 ± 10
0.736	273—328	10	1.053	24 430 ± 70	220.0 ± 0.2	88 ± 8
0.694	273—328	10	0.878	23 820 ± 110	223.6 ± 0.4	83 ± 15
0.647	273—328	10	0.700	23 310 ± 60	227.1 ± 0.2	75 ± 7
0.562	273—328	10	0.540	22 630 ± 90	231.6 ± 0.3	83 ± 11
0.487	273—328	11	0.291	21 710 ± 50	239.8 ± 0.2	47 ± 6
0.380	273—328	10	0.146	20 310 ± 140	250.2 ± 0.5	106 ± 17

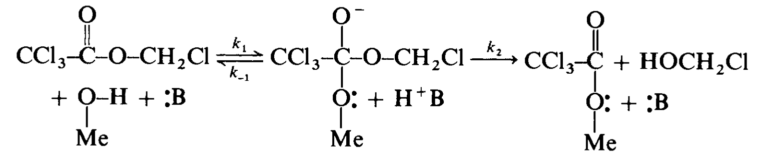
The reactions were followed conductometrically as described earlier;[12] the concentration of hydrogen chloride was measured. The rate coefficients were calculated by the Guggenheim method.[31] The standard deviations of the rate coefficients were, in general, less than 0.05%, but were sometimes about 0.1%. The thermodynamic activation parameters were calculated from an extended Arrhenius equation (1) by the method of Clarke and

$$\ln k = \mathrm{A} + \mathrm{B}/T + \mathrm{C}\ln T + \mathrm{D}T + \mathrm{E}T^2 + \ldots \quad (1)$$

Glew[32] after an orthogonalization procedure up to the five-parameter form. According to the Student t-test only the first three parameters of equation (1) were significant at the 99.9% or higher level, and in the following treatment equation (1) is used in its three-parameter form. The kinetic data for the neutral methanolysis of chloromethyl trichloroacetate in MeCN–MeOH solutions at 298.15 K are given in Table 1.

Discussion

Mechanism.—In neutral or slightly acidic solutions the hydrolysis of esters with electronegative substituents often takes place by the neutral ester hydrolysis mechanism, $B_{AC}3$.[33–36] In



$$\mathrm{CCl_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2Cl} + \underset{\mathrm{Me}}{\mathrm{O\text{-}H}} + :\mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CCl_3\text{-}\overset{O^-}{\underset{\underset{Me}{O:}}{C}}\text{-}O\text{-}CH_2Cl} + \mathrm{H^+B} \xrightarrow{k_2} \mathrm{CCl_3\text{-}\overset{O}{\overset{\|}{\underset{\underset{Me}{O:}}{C}}}} + \mathrm{HOCH_2Cl} + :\mathrm{B} \tag{2}$$

$$k_2, k_{-1} \gg k_1$$

$$\mathrm{ClCH_2OH} \xrightarrow[\text{fast}]{\text{MeOH}} \mathrm{MeOCH_2OH + HCl} \xrightarrow{\text{MeOH}} \mathrm{CH_2(OMe)_2 + H_2O}$$

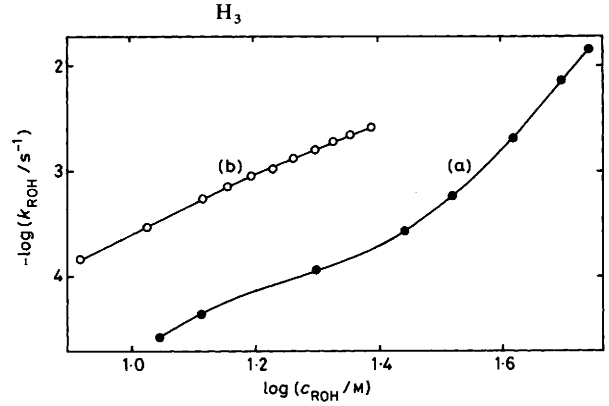


Figure 1. Plots of log k_{ROH} *versus* log c_{ROH} for (a) the hydrolysis of chloromethyl dichloroacetate in acetonitrile–water solutions (R = H)[6] and (b) the methanolysis of chloromethyl trichloroacetate in acetonitrile–methanol solutions (R = Me) at 298.15 K

the case of α-halogenoalkyl esters, nucleophilic displacement of the α-halogen is also possible.[8,35–37] These mechanisms can be distinguished experimentally: it is typical of neutral ester hydrolysis that the values of activation enthalpy ($\Delta H^\ddagger$) and activation entropy ($\Delta S^\ddagger$) are especially low, 37—50 kJ mol^{-1} and −150 to −180 J mol^{-1} K^{-1}, respectively, in water at 298 K.[6,13,16,33–35,38,39] For S_N solvolysis of α-halogenoalkyl acetates in water at 298 K, $\Delta H^\ddagger$ is usually about 40 kJ mol^{-1} and $\Delta S^\ddagger$ about 140 J mol^{-1} K^{-1} more positive than the aforementioned values for the $B_{\mathrm{AC}}3$ mechanism.[8,17,35,37]

For the methanolysis of chloromethyl trichloroacetate in methanol or in its solutions in acetonitrile the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are even lower (Table 1) than those typical of $B_{\mathrm{AC}}3$ hydrolysis of esters. In the case of alcoholysis, experimental data for reactions which take place by the $B_{\mathrm{AC}}3$ mechanism are scarce. The uncatalysed methanolysis of 2,4-dinitrophenyl acetate is considered to take place by the $B_{\mathrm{AC}}2$ mechanism because of the low value of $\Delta S^\ddagger$ (−126.7 J mol^{-1} K^{-1}).[40] Often the hydrolysis of phenyl esters is found to proceed by nucleophilic catalysis, *i.e.* by the B_{AC}N mechanism.[41] For the solvolysis of t-butyl chloride at 298 K, on the other hand, the values of $\Delta H^\ddagger$ are 97.2 and 104.1 kJ mol^{-1} and of $\Delta S^\ddagger$ 51.0 and −13.0 J mol^{-1} K^{-1} in water and methanol, respectively.[42] On this basis it is now concluded that the methanolysis of chloromethyl trichloroacetate takes place by the $B_{\mathrm{AC}}3$ mechanism rather than by S_N solvolysis of chlorine. According to the neutral ester hydrolysis mechanism[33–36] there must be at least two methanol molecules in the transition state of the rate-limiting step, the first adding to the carbonyl group of the ester and the other acting as a general base catalyst. In the case of chloromethyl trichloroacetate, the mechanism can be written in the form of equation (2). This mechanism is in accord with the reaction path proposed by Johnson[43] for the general base-catalysed ethanolysis of ethyl trifluoroacetate.

Solvent Effects on Kinetic Data.—The rate coefficients $k_{\mathrm{h}}/10^{-3}$ s^{-1} of the neutral hydrolyses of chloromethyl chloroacetate and dichloroacetate in water at 298 K are 0.1082 and 14.6, respectively.[13,34] The additional chlorine in the acyl group thus causes a 135-fold increase in rate. On this basis and by neglecting the possible steric effects of the third chlorine it can be estimated that the rate coefficient for the $B_{\mathrm{AC}}3$ hydrolysis of chloromethyl trichloroacetate is about 2 s^{-1}, *i.e.* about 750 times the value for its methanolysis (Table 1). The relatively small reactivity of methanol may be a result of the lack of strong intermolecular forces in alcohols as compared with water. Alcohols also possess lower basicity, ionizing power, and polarity than water, *e.g.* the values of the relative permittivity (ε_r) at 298 K for methanol and water are 32.6 and 78.5, respectively.[44,45] In the light of the values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for the methanolysis of the present ester in methanol (Table 1) and, for example, the respective values of 39.2 kJ mol^{-1} and −148.7 J mol^{-1} K^{-1} for the hydrolysis of chloromethyl dichloroacetate in water,[13] the retarded rate of methanolysis is primarily an entropy effect although the activation enthalpy of methanolysis is more favourable.

Acetonitrile retards the neutral methanolysis of chloromethyl trichloroacetate (Table 1). This retardation is small when compared with the rate-lowering effect caused by acetonitrile in the case of the neutral ester hydrolysis.[6,7,17] Thus, *e.g.* for the reaction of chloromethyl dichloroacetate in MeCN–H$_2$O solutions at 298 K there is an almost 540-fold decrease in the rate coefficients when x_{w} is changed from 1.00 to 0.418, and the plot of log k_{h} *versus* log c_{w} is linear only for the most water-rich solutions, with slope 6.8 (Figure 1).[6] For the methanolysis of chloromethyl trichloroacetate in MeCN–MeOH solutions, on the other hand, there is only about an 18-fold decrease in the rate coefficients when the mole fraction x_{m} of methanol is decreased from 1.00 to 0.380 (Table 1). In this case the plot of log k_{m} *versus* log c_{m} is linear over almost the whole composition range, with slope 2.5, and the plot is nearly parallel with that found in the aforementioned case of chloromethyl dichloroacetate in the most acetonitrile-rich water solutions (Figure 1). Attempts to correlate reaction rates with the macroscopic properties of the system, such as permittivity, have often failed; more information can be obtained by examining the influence of the water structure on reaction rates in terms of changes in activation parameters. It is, however, worthy of mention that the dielectric properties of MeCN–MeOH solutions remain almost unchanged over the whole composition profile, while in the case of MeCN–H$_2$O solutions the permittivity of the medium decreases markedly with decreasing water concentration, the value of ε_r at 298 K for pure acetonitrile being 36.0.[44]

It is typical of the hydrolyisis of an apolar substrate in aqueous solutions that with decreasing water concentration both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ first decrease, showing a minimum which is often followed by a maximum.[5–22,37] The positions of the extrema are often thought to represent changes in water

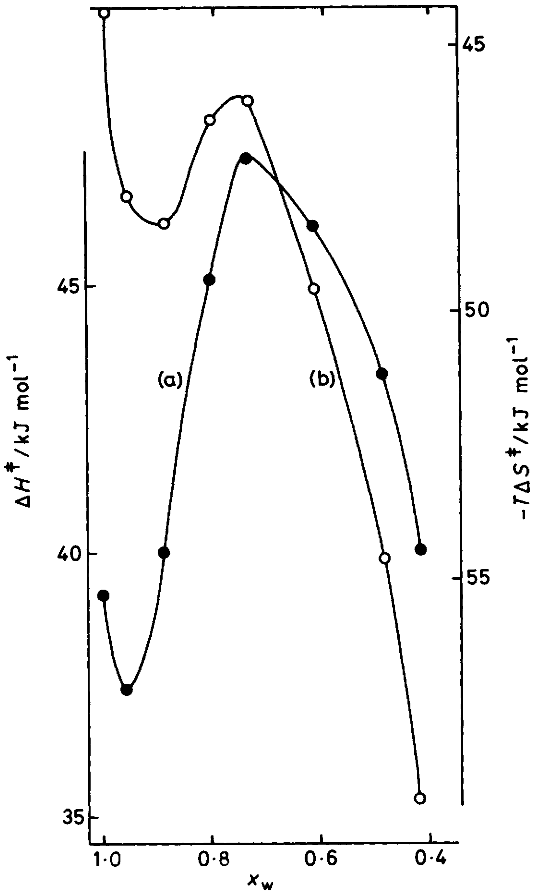


Figure 2. Plots of (a) $\Delta H^\ddagger$ and (b) $T\Delta S^\ddagger$ *versus* x_w for the hydrolysis of chloromethyl dichloroacetate in acetonitrile–water solutions at 298.15 K as recalculated from the data of Cleve[6]

Table 2. Maximum and minimum values of $\Delta C_p^\ddagger$ at the mole fraction x_w of water, estimated from the plots of $\Delta C_p^\ddagger$ *versus* x_w for hydrolysis reactions in acetonitrile–water solutions

Substrate	Mechanism	Maximum $\Delta C_p^\ddagger$/J mol^{-1} K^{-1}	Maximum x_w	Minimum $\Delta C_p^\ddagger$/J mol^{-1} K^{-1}	Minimum x_w
$CHCl_2CO_2CH_2Cl$[a]	$B_{AC}3$	−120	0.9	−265	0.6
CF_3CO_2Me[b]	$B_{AC}3$	−170	0.85	−220	0.65
$CH_2ClCO_2CHClCCl_3$[c]	$B_{AC}3$	−185	0.85	−305	0.6
AcOCHClMe[d]	S_N	−114	0.9		
Me_3CCl[e]	S_N	−160	0.85		

[a] According to the data in Figure 4. [b] Ref. 7. [c] Ref. 6. [d] Ref. 17. [e] Ref. 2.

structure. As an example, the plots of $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ *versus* x_w for neutral hydrolysis of chloromethyl dichloroacetate in $MeCN-H_2O$ solutions are shown in Figure 2. It can be seen that in the most water-rich solutions and in solutions where $x_w < 0.7$ the entropy of activation controls the kinetics; at $0.8 > x_w > 0.95$ the enthalpy of activation is more dominant. In comparison with the complicated dependence of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ on cosolvent content in Figure 2, the plots of $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ *versus* x_m for the neutral methanolysis of chloromethyl trichloroacetate in MeCN–MeOH solutions show quite a monotonic decrease with increasing acetonitrile content (Figure 3). In this case the entropy of activation decreases much more rapidly than the enthalpy of activation over the whole composition range studied. The differences in the dependence of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ found between neutral ester hydrolysis and methanolysis may be understood as reflecting the simpler structural properties of methanol and methanolic solutions than those of water and aqueous solutions.

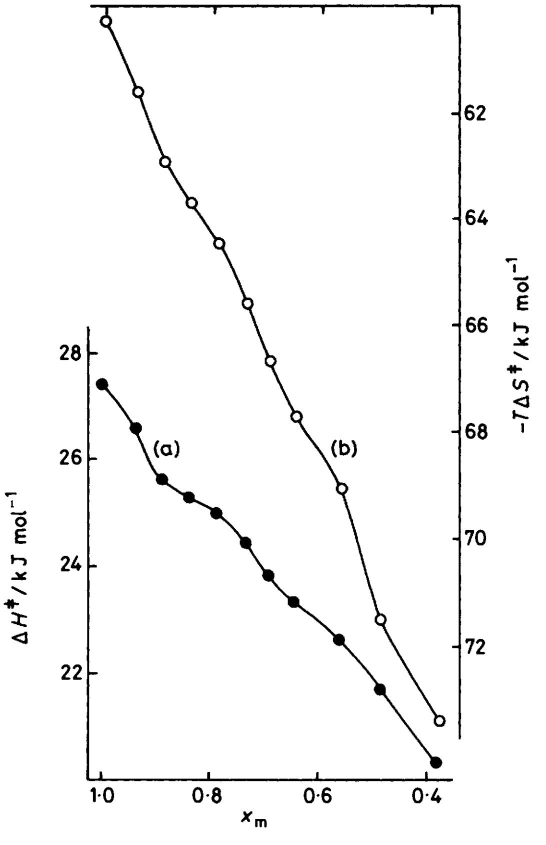


Figure 3. Plots of (a) $\Delta H^\ddagger$ and (b) $T\Delta S^\ddagger$ *versus* x_m for the methanolysis of chloromethyl trichloroacetate in acetonitrile–methanol solutions at 298.15 K

Most ionogenic solvolytic reactions in alcohols, water, and aqueous solutions do not follow the Arrhenius equation exactly, but usually have a negative heat capacity of activation.[1–22,34,35,38,39,46–48] For the $B_{AC}3$ hydrolysis of carboxylic esters the values of $\Delta C_p^\ddagger$ in water are *ca.* −200 J mol^{-1} K^{-1}, while for the neutral alcoholysis of chloromethyl trichloroacetate the values -99 ± 4 and -61 ± 32 J mol^{-1} K^{-1} have been determined in methanol (Table 1) and ethanol,[49] respectively. The more positive values of $\Delta C_p^\ddagger$ found for the alcoholyses are in accord with the smaller amount of structure in alcohols than in water.

Because the heat capacity of activation as a real rate parameter of ionogenic solvolytic reactions is determined mainly by the solvation differences between the initial and transition states, it is a sensitive indicator of changes in solvent structure.[23] As an indication of the water-structure-breaking ability of acetonitrile, $\Delta C_p^\ddagger$ is shown first to increase and to have a maximum, located in the mole fraction range of water from 0.9 to 0.8 independent of reaction mechanism (Table 2). Thus, the cosolvent is mainly responsible of the existence of a maximum (or a minimum), but the substrate has an effect on the exact position of an extremum. When acetonitrile concentration is high enough, a maximum in $\Delta C_p^\ddagger$ is followed by a minimum (Table 2, Figure 4). It has been shown that several structural regions exist in the whole composition profile of $MeCN-H_2O$ solutions.[50] It seems that acetonitrile first weakens the water structure by occupying the cavities in the hydrogen-bonded

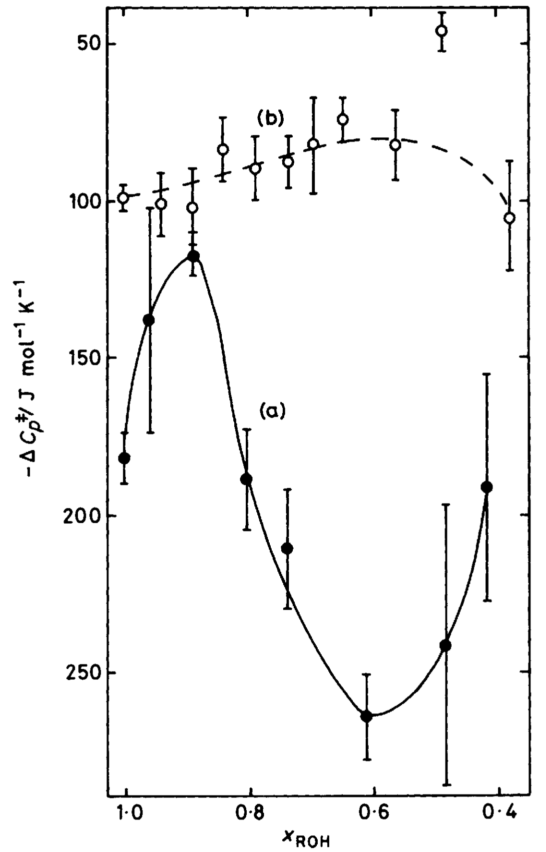


Figure 4. Plots of $\Delta C_p^{\ddagger}$ *versus* x_{ROH} for (a) the hydrolysis of chloromethyl dichloroacetate in acetonitrile–water solutions (R = H) as recalculated from the data of Cleve,[6] and (b) the methanolysis of chloromethyl trichloroacetate in acetonitrile–methanol solutions (R = Me)

network of water. The maximum occupancy is reached at x_w about 0.85, *i.e.* at about the mole fraction of water where $\Delta C_p^{\ddagger}$ also has maximum value. When $0.85 > x_w > 0.45$, MeCN–H_2O mixtures are considered to have a microheterogeneous structure which contains globules where water exists in a very ordered state. Thus, the $\Delta C_p^{\ddagger}$ minimum found in MeCN–H_2O solutions, *e.g.* at x_w about 0.6 for the neutral hydrolysis of chloromethyl dichloroacetate, is located near the middle of the aforementioned water concentration range where the relative proportion of the acetonitrile-rich disordered phase is thought to exceed that of the water-rich globules. It seems, however, that the nature of the two 'microphases' in MeCN–H_2O solutions is more simple than that found, for example, in the case of 2-butoxyethanol–water solutions. In the last-mentioned system $\Delta C_p^{\ddagger}$ is highly temperature dependent near the mole fraction 0.98 of water, owing to the pseudo-microphase transitions which take place near this 'magic' mole fraction.[11,15,51] An interesting feature of the two systems MeCN–H_2O and 2-butoxyethanol–water is that both exhibit phase separation: the first shows an upper critical solution temperature at about 272 K at x_w close to 0.62,[50] while there is a closed miscibility gap for the latter system with a lower critical solution temperature which varies from 341.55 to 322.98 K when x_w goes from 0.983 37 to 0.967 08.[52]

In contrast to the marked changes in $\Delta C_p^{\ddagger}$ found for neutral ester hydrolysis in MeCN–H_2O solutions, the plot of $\Delta C_p^{\ddagger}$ *versus* x_m for the methanolysis of chlormethyl trichloroacetate in MeCN–MeOH solutions shows quite a monotonic course (Figure 4). Within the limits of experimental accuracy, $\Delta C_p^{\ddagger}$ now remains almost unchanged over the whole range of acetonitrile concentrations studied. This is in accord with the structural properties of the solvent system in question. In view of the relatively marked decrease in viscosity observed when acetonitrile is added to methanol and of the viscosity data and tracer diffusion coefficients determined for MeCN–EtOH solutions, it seems that strong dipole–dipole interactions between the unlike molecules largely determine the properties of MeCN–MeOH solutions.[44,53]

In conclusion, the difference in concentration dependence of $\Delta C_p^{\ddagger}$ found between MeCN–MeOH and MeCN–H_2O solutions may be understood in terms of the lack of a strong hydrogen-bonded network structure in the former system. In MeCN–MeOH solutions, dipole–dipole interactions cause the disruption of methanol–methanol hydrogen bonds, resulting in only a negligible effect on $\Delta C_p^{\ddagger}$. In aqueous acetonitrile solutions the weakening of the water structure by the occupancy of the cavities by acetonitrile, followed by a progressive disruption of the water structure, together with the tendency for segregation of water and acetonitrile molecules, causes the marked changes in $\Delta C_p^{\ddagger}$ with increasing acetonitrile concentration.

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