Decarboxylation of Hydrogencarbonatopentaamminecobalt(III) in Aquo-organic Solvent Media[†]

Anadi C. Dash,* Neelamadhab Dash, Prafulla K. Das and Jyotsnamayee Pradhan
Department of Chemistry, Utkal University, Bhubaneswar-751004, India

The decarboxylation of hydrogencarbonatopentaamminecobalt(III) has been investigated in aqueous, 99% D_2O and aquo-organic solvent media (0–70 wt.% of cosolvent) at $15 \leqslant t/°C \leqslant 40$ ($I = 0.02$ mol dm^{-3}), using methanol, propan-2-ol, *tert*-butyl alcohol, ethylene glycol, acetone, acetonitrile, DMSO and ethylene carbonate as cosolvents. The solvent isotope effects on rate ($k_{H_2O}/k_{D_2O} = 1.0$ at 15–35 °C) and activation parameters ($\Delta H^{\neq} = 77.7 \pm 1.0$, 77.8 ± 0.9 kJ mol^{-1} and $\Delta S^{\neq} = 16 \pm 3$, 16 ± 3 J K^{-1} mol^{-1} for aqueous and 99% D_2O media, respectively) were negligible.

The decarboxylation rate constant increased with increasing mole fraction (X_{org}) of the cosolvent and the effect was pronounced at relatively high values of X_{org} for the dipolar aprotic cosolvents. This was attributed to a greater degree of destabilisation of the initial state as compared to the transition state with increasing mole fraction of the cosolvent. The ln k_s *vs.* $1/\varepsilon_s$ plots (k_s is the rate constant and ε_s the bulk relative permittivity) showed marked dependence on the nature of the cosolvents; the gradients of such plots generally increased with increasing dipole moment of the cosolvent molecules, indicating thereby that the solvation of the initial state and the transition state of the substrate is governed by the ion–dipole interactions between the water and cosolvent molecules. The relative transfer free energy of activation, $[\Delta\Delta G_t^{\neq}]_{(s \leftarrow w)}$, decreased linearly with X_{org} for all mixed-solvent media, indicating that the preferential solvation effect is not significant. The activation enthalpy and entropy *vs.* X_{org} plots displayed extrema suggesting that these thermodynamic parameters are sensitive to the structural changes in the bulk solvent phase. The solvent effects on $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are mutually compensatory.

Previous studies from our laboratory and elsewhere have dealt with the solvolytic aquation of halogenoaminecobalt(III) complexes in mixed-solvent media.[2,3] It is believed that such reactions undergo a dissociative interchange mode of ligand substitution at the cobalt(III) centre. The solvation of the ionic leaving groups strongly affects the reactivities of the substrates. Invariably the solvolysis rate decreases with increasing amount of non-aqueous component in the aquo-organic solvent media. The variation of rates and activation parameters was interpreted in terms of electrostatic and non-electrostatic medium effects, as well as solvent structural effects. In continuation of our work, we now report on the effect of solvent on the decarboxylation of the hydrogen-carbonatopentaamminecobalt(III) ion.

It has been established by Harris *et al.*[4] that the decarboxylation of $(NH_3)_5CoCO_3^+$ is acid catalysed. However, the rate is independent of the acidity of the medium once the carbonato complex is fully protonated [pK of $(NH_3)_5CoCO_3H^{2+} = 6.7$ at 25 °C, $I = 0.5$ mol dm^{-3}].[5] The decarboxylation of the hydrogencarbonato complex occurs with retention of a Co—O bond.[6] This is a typical reaction in which the leaving group is essentially a non-dipolar molecule (CO_2). Hence this reaction provides an opportunity to examine the medium effects on the differential solvation of the like charged initial state and the transition state for which there is likely to be little perturbation around the $(NH_3)_5Co^{3+}$ moiety, *i.e.* at a site several atoms away from the reaction site. Besides, there is currently wide interest in understanding the molecular dynamics of processes in mixed-solvent media of low water content which are of relevance to chemistry, biology and physiology. One such reaction of biochemical importance is the reversible hydration of CO_2.[7] From these considerations, investigation of the medium effects on the decarboxylation of the model carbonato complex was considered worthwhile.

In the present work we report a thorough study of the decarboxylation of $(NH_3)_5CoCO_3H^{2+}$ in mixed aquo-organic solvent media using dipolar protic and aprotic cosolvents. In contrast to the retarding effects of aquo-organic solvent media on the rates of aquation of halogenoamine-cobalt(III) substrates, we observed appreciable acceleration of the rate of decarboxylation of this hydrogencarbonato complex in all mixed-solvent media, the effect being relatively more significant for dipolar aprotic cosolvents.

Experimental

$[Co(NH_3)_5CO_3]NO_3 \cdot H_2O$, the carbonatopentaammine-cobalt(III) nitrate, was prepared by the published method[4] and recrystallised from water. The purity of the sample was further checked by Co and NH_3 analyses. (Found: Co, 20.6; NH_3, 29.3%. Calc. for $[(NH_3)_5CoCO_3](NO_3) \cdot H_2O$: Co, 20.7; NH_3, 29.9%.) The UV–VIS spectrum displayed λ_{max} at 505 nm with $\varepsilon = 94.0$ dm^3 mol^{-1} cm^{-1} [literature data,[4] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 505 (94)].

AnalaR-grade (purity $> 99\%$) solvents[‡] were stored over molecular sieve (4A) and distilled before use. AnalaR-grade ethylene carbonate (purity $> 99.5\%$) was used without further purification. Water from a deioniser was redistilled from alkaline permanganate. D_2O (99.4%) was procured from BARC, Trombay, India. Solvent mixtures were prepared in wt.%. The UV–VIS spectra were recorded on a double-beam UV–VIS Hitachi spectrophotometer.

Kinetics

The rate of decomposition of the carbonato complex was followed at 510 nm using a HITECH SF 51 stopped-flow spectrophotometer equipped with a fully computerised data

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[†] This paper is part 14 of a series entitled Effect of Solvent on the Reactions of Coordination Complexes; Part 13 is ref. 1.

[‡] Abbreviations: methanol, MeOH; propan-2-ol, Pr^{i}OH; ethylene glycol, EG; *tert*-butyl alcohol, Bu^{t}OH; acetone, AC; acetonitrile, AN; dimethylsulphoxide, DMSO; ethylene carbonate, EC.

acquisition and display system. The cell compartment and the reaction mixtures loaded in Hamilton syringes were thermostatted to $\pm 0.1\,°C$ by circulating water from a thermostatic liquid circulator C-85 D through a cooler FC-200 (HITECH, UK). Equal volumes of thermostatted solutions of complex and $HClO_4$, both in the same solvent composition and loaded separately in syringes, were mixed under air pressure using a pneumatic drive mechanism. Final concentrations of the complex and $HClO_4$ in the reaction mixture were $(1-2) \times 10^{-3}$ mol dm^{-3} and ca. 2×10^{-2} mol dm^{-3}, respectively. The exponential decrease of the absorbance with time, displayed as a voltage output was fitted to the relationship $(A_t - A_\infty) = (A_0 - A_\infty)\exp(-k_s t)$ where the terms have their usual meaning, by a computer programme available for the Apple II GS computer interface.

The mean value of the first-order rate constant and its standard deviation for a given solvent composition was computed from at least seven runs. The rate measurements were made at five temperatures from 15 to 35 °C ($\Delta T = 20\,°C$ at 5 °C intervals) for all solvent systems, except for ethylene carbonate–water for which the working temperatures were 15 °C (for wt.% EC of 0–40) and 20–40 °C (for wt.% EC of 0–70) owing to the limited solubility of EC in water.

The activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) were calculated by fitting the rate data to eqn. (1)

$$\ln k_s/T = (\ln k_B/h + \Delta S^{\neq}/R) - \Delta H^{\neq}/RT \qquad (1)$$

where k_B and h denote the Boltzmann constant and Planck's constant, respectively. The left-hand side of eqn. (1) was weighted inversely as its variance, which was calculated from the known variances of k_s and T.

Results and Discussion

### Decarboxylation of $(NH_3)_5CoCO_3H^{2+}$ in Aqueous and D_2O Media

The rate and activation parameters for the decarboxylation of $(NH_3)_5CoCO_3H^{2+}$ in water and D_2O (ca. 99%) are collected in Table 1. The first-order rate constant is also independent of $[H^+]$ in the range 0.005–1.0 mol dm^{-3} indicating thereby that the hydrogencarbonato complex has little propensity for further protonation. The values of the rate and activation parameters (except for $\Delta S^{\neq}$) reported by Harris et al.[4] for the fully aqueous medium [$k = 1.25$ s^{-1} at 25 °C, $\Delta H^{\neq} = 71.4 \pm 2.1$ kJ mol^{-1}, $\Delta S^{\neq} = -2 \pm 4$ J K^{-1} mol^{-1}, $I = 0.5$ mol dm^{-3} ($NaClO_4$)] compare satisfactorily with those reported in this work. The comparatively low value of $\Delta S^{\neq}$ reported by Harris et al.[4] might be due to the high ionic strength maintained in their study. The observed solvent isotope effect on the rate ($k_{H_2O}/k_{D_2O} = 1.0$, $15 \leqslant t/°C \leqslant 35$) and the activation parameters [$\Delta X^{\neq}$ (D_2O) $\approx \Delta X^{\neq}$ (H_2O), $X = H, S$ (see Table 1)] further indicates that the differential

Table 1 Rate and activation parameters for the decarboxylation of $[Co(NH_3)_5CO_3H]^{2+}$ in fully aqueous and 99% D_2O media[a]

$T/°C$[b]	k_{H_2O}/s^{-1}	k_{D_2O}/s^{-1}	k_{H_2O}/k_{D_2O}
15.0	0.34 ± 0.03	0.342 ± 0.008	0.99 ± 0.09
20.0	0.63 ± 0.03	0.62 ± 0.02	1.02 ± 0.06
25.0	1.10 ± 0.05	1.11 ± 0.06	0.99 ± 0.07
30.0	1.92 ± 0.06	1.94 ± 0.13	0.99 ± 0.07
35.0	3.10 ± 0.10	3.09 ± 0.07	1.00 ± 0.04
40.0	5.10 ± 0.25	—	—
	$\Delta H^{\neq}/kJ$ mol^{-1}	$\Delta S^{\neq}/J$ K^{-1} mol^{-1}	
H_2O	77.7 ± 1.0	16 ± 3	
D_2O	77.8 ± 0.9	16 ± 3	

[a] $[HClO_4] = 0.02$ mol dm^{-3}. [b] $\pm 0.1\,°C$.

solvation effects of D_2O and H_2O are not significant. A two-step mechanism involving the zwitterionic intermediate which decarboxylates via rate-determining C—O bond breaking [see reaction (I)] is consistent with our observations.

Reaction (1)

transition state
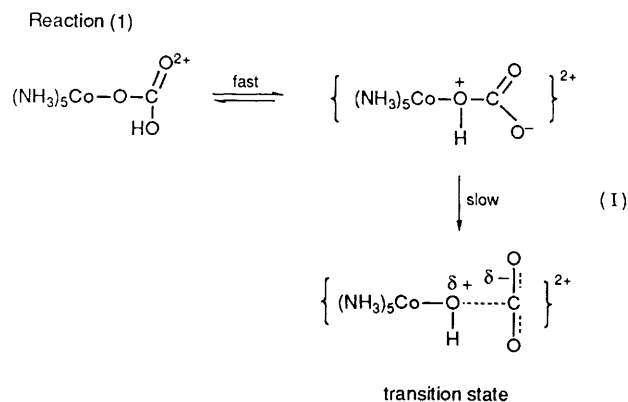
This mechanism is equivalent to that proposed for the decarboxylation of the protonated hydrogencarbonate.[8]

Variation of Rate Constant with Solvent Composition

The rate data for different aquo-organic solvent media at 15–40 °C are collected in Table 2. The protic cosolvents exert comparable rate acceleration over the composition range studied. The rate acceleration due to the dipolar aprotic cosolvents is much stronger. Using the thermodynamic cycle as depicted in Scheme 1, the activation free energy ($\Delta G_s^{\neq}$) for the mixed solvent (s) is given by eqn. (2)

$$\Delta G_s^{\neq} = \Delta G_g^{\neq} + \Delta G_{solv,\,t.s.}^0 - \Delta G_{solv,\,i.s.}^0 \qquad (2)$$

Scheme 1
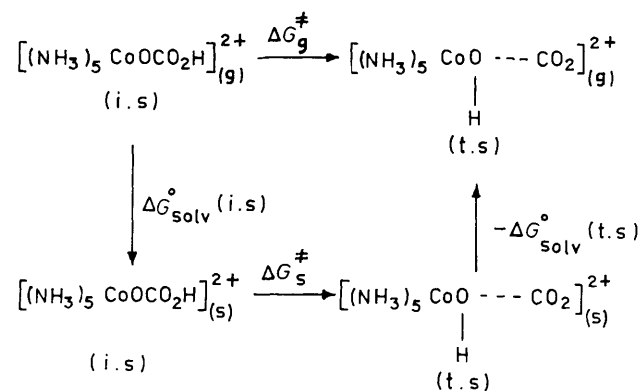
where $\Delta G_s^{\neq}$ is the activation free energy in the gas phase and $\Delta G_{solv,\,t.s.}^0 - \Delta G_{solv,\,i.s.}^0$ denotes the difference in the free energy of solvation of the like charged transition state and the initial state. Thus the rate variation with solvent composition [$k_s = (k_\beta T/h)\exp(-\Delta G_s^{\neq}/RT)$] is attributed to the effect of the differential solvation of the initial [$(NH_3)_5CoOCO_2H^{2+}$] and transition $\{[(NH_3)_5CoOH\cdots CO_2]^{2+}\}$ states.

The electrostatic contribution to the free energy of solvation of an ion i (i = i.s. or t.s.), $[\Delta G_{solv,\,i}^0]_{el}$, is inversely dependent on the bulk relative permittivity (ε_s) of the medium.[9] The plots of $\ln k_s$ vs. $1/\varepsilon_s$,[10] and $\ln k_s$ vs. X_{org} at a fixed ε_s ($= 62.5$) at 25 °C are shown in Fig. 1. The non-linearity in such plots indicates the importance of the non-electrostatic contribution to the solvation free energy. Note that the order of variation of the rate constant with respect to the cosolvents is

Table 2 Rate data for decarboxylation of $[Co(NH_3)_5CO_3H]^{2+}$ in mixed-solvent media with various wt.% organic solvent at different temperatures

organic solvent	$T/°C$	k_s/s^{-1} [a]							
		5 wt.%	10 wt.%	20 wt.%	30 wt.%	40 wt.%	50 wt.%	60 wt.%	70 wt.%
MeOH	15.0	0.38 ± 0.01	0.37 ± 0.03	0.41 ± 0.01	0.43 ± 0.01	0.46 ± 0.01	0.55 ± 0.04	0.59 ± 0.03	0.68 ± 0.02
	20.0	0.67 ± 0.05	0.64 ± 0.03	0.69 ± 0.04	0.73 ± 0.04	0.85 ± 0.02	0.91 ± 0.04	1.09 ± 0.05	1.29 ± 0.07
	25.0	1.13 ± 0.08	1.15 ± 0.09	1.21 ± 0.09	1.31 ± 0.09	1.46 ± 0.05	1.69 ± 0.15	1.93 ± 0.06	2.24 ± 0.12
	30.0	2.09 ± 0.07	1.86 ± 0.10	2.19 ± 0.07	2.33 ± 0.09	2.56 ± 0.09	2.96 ± 0.07	3.24 ± 0.11	3.72 ± 0.12
	35.0	3.59 ± 0.17	3.46 ± 0.18	3.88 ± 0.15	4.13 ± 0.21	4.39 ± 0.35	4.90 ± 0.15	5.42 ± 0.12	6.11 ± 0.12
		(0.029)	(0.059)	(0.123)	(0.194)	(0.273)	(0.360)	(0.457)	(0.569)
Pr^iOH [b]	15.0	0.30 ± 0.02	0.32 ± 0.02	0.34 ± 0.04	0.36 ± 0.02	0.39 ± 0.02	0.44 ± 0.03	0.49 ± 0.03	0.61 ± 0.07
	20.0	0.54 ± 0.04	0.55 ± 0.04	0.64 ± 0.04	0.72 ± 0.05	0.73 ± 0.07	0.77 ± 0.05	0.96 ± 0.04	1.10 ± 0.05
	25.0	0.95 ± 0.04	0.98 ± 0.07	1.15 ± 0.10	1.21 ± 0.09	1.27 ± 0.09	1.34 ± 0.12	1.56 ± 0.06	1.86 ± 0.07
	30.0	1.67 ± 0.08	1.70 ± 0.08	2.00 ± 0.12	2.15 ± 0.14	2.32 ± 0.08	2.23 ± 0.15	3.00 ± 0.17	3.36 ± 0.16
	35.0	3.15 ± 0.24	3.10 ± 0.12	3.66 ± 0.22	4.08 ± 0.18	4.26 ± 0.18	4.56 ± 0.27	4.68 ± 0.27	5.40 ± 0.13
		(0.015)	(0.032)	(0.070)	(0.114)	(0.166)	(0.230)	(0.309)	(0.411)
Bu^tOH	15.0	0.36 ± 0.05	0.37 ± 0.05	0.38 ± 0.04	0.36 ± 0.04	0.42 ± 0.06	0.47 ± 0.05	0.40 ± 0.03	—
	20.0	0.67 ± 0.05	0.66 ± 0.03	0.67 ± 0.03	0.68 ± 0.04	0.68 ± 0.02	0.75 ± 0.05	0.80 ± 0.07	—
	25.0	1.17 ± 0.04	1.19 ± 0.03	1.21 ± 0.04	1.24 ± 0.05	1.23 ± 0.03	1.32 ± 0.02	1.40 ± 0.12	—
	30.0	1.87 ± 0.11	1.89 ± 0.10	1.88 ± 0.08	1.91 ± 0.08	2.07 ± 0.11	2.33 ± 0.13	2.40 ± 0.08	—
	35.0	3.03 ± 0.10	3.13 ± 0.10	3.25 ± 0.15	3.45 ± 0.10	3.82 ± 0.10	4.00 ± 0.18	4.50 ± 0.11	—
		(0.013)	(0.026)	(0.057)	(0.094)	(0.139)	(0.196)	(0.267)	
EG	15.0	0.30 ± 0.05	0.36 ± 0.06	0.37 ± 0.09	0.40 ± 0.05	0.46 ± 0.05	0.39 ± 0.05	0.44 ± 0.04	0.54 ± 0.05
	20.0	0.63 ± 0.04	0.64 ± 0.05	0.68 ± 0.09	0.73 ± 0.03	0.79 ± 0.06	0.81 ± 0.04	0.88 ± 0.06	1.01 ± 0.03
	25.0	1.10 ± 0.15	1.18 ± 0.04	1.19 ± 0.03	1.20 ± 0.03	1.31 ± 0.06	1.34 ± 0.02	1.51 ± 0.05	1.71 ± 0.05
	30.0	1.99 ± 0.13	1.90 ± 0.14	1.99 ± 0.03	2.11 ± 0.09	2.22 ± 0.19	2.37 ± 0.04	2.67 ± 0.14	2.94 ± 0.09
	35.0	3.27 ± 0.16	3.38 ± 0.12	3.60 ± 0.32	3.68 ± 0.21	3.84 ± 0.12	3.95 ± 0.14	4.31 ± 0.07	5.10 ± 0.06
		(0.015)	(0.031)	(0.068)	(0.111)	(0.162)	(0.225)	(0.303)	(0.404)
AC	15.0	0.40 ± 0.01	0.44 ± 0.01	0.47 ± 0.02	0.55 ± 0.03	0.65 ± 0.03	0.94 ± 0.07	1.20 ± 0.03	—
	20.0	0.63 ± 0.05	0.66 ± 0.07	0.80 ± 0.03	0.88 ± 0.07	1.14 ± 0.09	1.71 ± 0.09	2.17 ± 0.12	—
	25.0	1.19 ± 0.07	1.19 ± 0.08	1.32 ± 0.06	1.75 ± 0.07	2.23 ± 0.09	3.02 ± 0.11	3.89 ± 0.12	—
	30.0	2.02 ± 0.08	2.13 ± 0.14	2.26 ± 0.10	2.96 ± 0.24	3.67 ± 0.12	5.18 ± 0.29	6.56 ± 0.35	—
	35.0	3.54 ± 0.27	3.49 ± 0.32	3.85 ± 0.18	5.30 ± 0.44	6.70 ± 0.52	9.63 ± 0.80	10.80 ± 0.60	—
		(0.016)	(0.033)	(0.072)	(0.117)	(0.171)	(0.237)	(0.317)	
AN	15.0	0.33 ± 0.08	0.39 ± 0.06	0.46 ± 0.04	0.55 ± 0.05	0.65 ± 0.04	0.88 ± 0.06	1.18 ± 0.07	—
	20.0	0.64 ± 0.03	0.69 ± 0.03	0.81 ± 0.06	0.94 ± 0.06	1.20 ± 0.04	1.49 ± 0.10	2.06 ± 0.08	—
	25.0	1.09 ± 0.06	1.18 ± 0.05	1.49 ± 0.05	1.73 ± 0.12	2.18 ± 0.10	2.82 ± 0.23	3.53 ± 0.19	—
	30.0	1.89 ± 0.13	2.02 ± 0.08	2.46 ± 0.09	2.82 ± 0.21	4.11 ± 0.27	5.06 ± 0.39	6.37 ± 0.49	—
	35.0	3.22 ± 0.29	3.50 ± 0.12	4.23 ± 0.21	4.71 ± 0.19	6.76 ± 0.35	8.36 ± 0.51	10.1 ± 0.5	—
		(0.023)	(0.046)	(0.099)	(0.158)	(0.226)	(0.305)	(0.396)	
DMSO	15.0	0.36 ± 0.02	0.40 ± 0.03	0.38 ± 0.03	0.46 ± 0.05	0.57 ± 0.04	0.79 ± 0.04	1.17 ± 0.14	1.84 ± 0.11
	20.0	0.64 ± 0.05	0.66 ± 0.06	0.71 ± 0.07	0.83 ± 0.06	0.98 ± 0.09	1.43 ± 0.06	2.08 ± 0.08	3.04 ± 0.15
	25.0	1.17 ± 0.03	1.22 ± 0.05	1.37 ± 0.06	1.51 ± 0.06	1.86 ± 0.07	2.71 ± 0.15	3.54 ± 0.15	5.12 ± 0.21
	30.0	2.04 ± 0.08	2.19 ± 0.05	2.40 ± 0.09	2.68 ± 0.05	3.22 ± 0.07	4.54 ± 0.20	5.78 ± 0.25	8.82 ± 0.28
	35.0	3.31 ± 0.29	3.73 ± 0.22	3.93 ± 0.44	4.20 ± 0.39	5.56 ± 0.50	7.75 ± 0.50	9.56 ± 0.50	15.4 ± 1.4
		(0.012)	(0.025)	(0.055)	(0.090)	(0.135)	(0.188)	(0.257)	(0.350)
EC	15.0	0.29 ± 0.05	0.42 ± 0.04	0.45 ± 0.05	0.56 ± 0.10	0.67 ± 0.04	—	—	—
	20.0	0.64 ± 0.05	0.74 ± 0.06	0.83 ± 0.09	1.00 ± 0.05	1.15 ± 0.05	1.42 ± 0.12	1.74 ± 0.11	2.45 ± 0.16
	25.0	1.10 ± 0.04	1.29 ± 0.06	1.37 ± 0.06	1.70 ± 0.09	2.05 ± 0.13	2.63 ± 0.05	3.16 ± 0.21	4.35 ± 0.12
	30.0	1.93 ± 0.12	2.05 ± 0.14	2.50 ± 0.09	2.96 ± 0.09	3.65 ± 0.16	4.54 ± 0.18	5.61 ± 0.21	7.14 ± 0.29
	35.0	3.30 ± 0.18	3.45 ± 0.15	4.02 ± 0.12	5.01 ± 0.17	5.82 ± 0.17	7.53 ± 0.44	9.30 ± 0.45	11.5 ± 0.6
	40.0	5.19 ± 0.27	5.22 ± 0.25	6.46 ± 0.48	7.56 ± 0.35	9.72 ± 0.23	11.5 ± 0.9	14.7 ± 1.4	17.4 ± 1.1
		(0.010)	(0.022)	(0.049)	(0.080)	(0.120)	(0.169)	(0.234)	(0.323)

[a] Values given in parentheses are mole fractions. [b] Values of k_s/s^{-1} for 2, 8 and 15 wt.% Pr^iOH at 25 °C are 0.92 ± 0.08, 0.97 ± 0.08, 1.07 ± 0.10, respectively.

$Bu^tOH < Pr^iOH < MeOH < EG < AC < AN \ll DMSO < EC$ for any value of $\varepsilon_s^{-1} \geqslant 2.0$. The dipole moment of the cosolvent molecules also varies in the same order except for the alcohols ($\mu/D\dagger$ = 1.70, 1.66, 1.66, 2.28, 2.69, 3.44, 3.90 and 4.87 for MeOH, Pr^iOH, Bu^tOH, EG, AC, AN, DMSO and EC, respectively).[10,11] This might indicate that solvation (and hence the rate) is at least partly governed by the ion–dipole interactions between the substrate and the cosolvent molecules.

An attempt was made to correlate the rate constant with Dimorth and Richardt's solvatochromic solvent polarity parameter E_T (ref. 10, p. 188). The normalized values of E_T (E_T^N) for the mixed-solvent media used here decrease with increasing mole fraction (X_{org}) of the cosolvent. The plots of $\ln k_s$ vs. E_T^N (see Fig. 2) are non-linear. A similar trend has been reported for the solvolysis reactions of several inorganic and organic substrates including halogenoaminecobalt(III) complexes in mixed-solvent media.[12] The non-linearity in $\ln k_s$ vs. E_T^N plots might be due to either (i) preferential solvation of the initial state and transition state of the reactant[12] or (ii) preferential solvation of the probe solute used for the evaluation of E_T. An attempt is made here to analyse the rate dependence on solvent composition in terms of a simplified preferential solvation model proposed by Marcus (ref. 10, p.
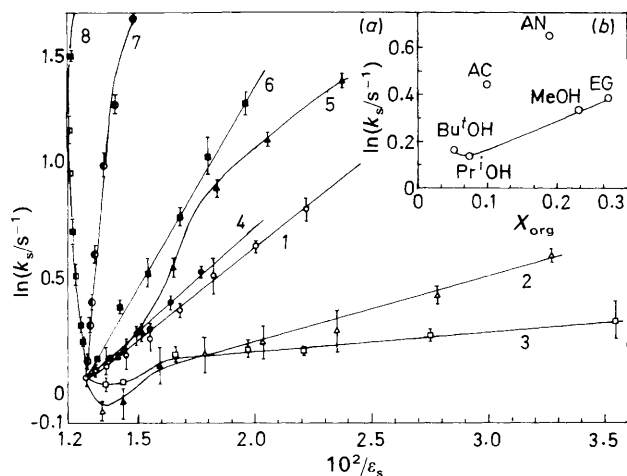
$\dagger$ 1 D $\approx 3.335 \times 10^{-30}$ C m.

Fig. 1 (a) $\ln(k_s/s^{-1})$ vs. $10^2/\varepsilon_s$ plots at $25\,°C$ for mixed-solvent media: 1, MeOH; 2, Pr^{i}OH; 3, Bu^{t}OH; 4, EG; 5, AC; 6, AN; 7, DMSO; 8, EC. (b) $\ln(k_s/s^{-1})$ vs. X_{org} plot at $25\,°C$ for $\varepsilon_s = 62.5$

206) and discussed at length in our earlier papers on the solvolysis of some halogenoaminecobalt(III) complexes in mixed-solvent media.[2,13] Based on this model, the activation free energy of transfer, $[\Delta\Delta G_t^{\neq}]_{s\leftarrow w} = (\Delta G_s^{\neq} - \Delta G_w^{\neq})$, where transfer of the reactant takes place from water (w) to the mixed solvent (s), is given by eqn. (3)

$$[\Delta\Delta G_t^{\neq}]_{s\leftarrow w} = X_{org}[\Delta G_{t,\,t.s.}^0 - \Delta G_{t,\,i.s.}^0]_{org\leftarrow w}$$
$$+ \Delta g R T X_{org}(1 - X_{org}) \quad (3)$$

where $\Delta g = g_{t.s.} - g_{i.s.}$ (i.e. the difference of the preferential solvation parameter for the transition state and the initial state) and $[\Delta G_{t,\,t.s.}^0 - \Delta G_{t,\,i.s.}^0]_{org\leftarrow w}$ denotes the relative transfer free energy for the transfer of the transition state and initial state from water to the pure organic cosolvent. Note that $[\Delta\Delta G_t^{\neq}]_{s\leftarrow w}$ $\{k_s/k_w = \exp[(-\Delta\Delta G_t^{\neq}]_{s\leftarrow w}/RT\}$ varies linearly with X_{org} in accord with eqn. (4)

$$[\Delta\Delta G_t^{\neq}]_{s\leftarrow w} = a_i X_{org} + \delta_i \quad (4)$$

where the constants a_i and δ_i are sensitive to the nature of the cosolvent. The values of δ_i are only marginally different from zero, being statistically insignificant for most solvent systems at various temperatures (see Table 3). It is thus evident that the preferential solvation of the transition and initial states must be similar (i.e. $\Delta g = g_{t.s.} - g_{i.s.} = 0$) in all mixed-solvent media at all temperatures. The negative values of a (Table 3)

Fig. 2 $\ln(k_s/s^{-1})$ vs. E_T^N plot at $25\,°C$ for MeOH–water ($\bigcirc$), Pr^{i}OH–water ($\triangle$), AC–water ($\pmb{\mathbb{O}}$), AN–water ($\bullet$) and DMSO–water ($\square$) media

indicate that the initial state is destabilised to a greater extent than the transition state ($[\Delta G_{t,\,i.s.}^0]_{org\leftarrow w} > [\Delta G_{t,\,t.s.}^0]_{org\leftarrow w}$) when transfer takes place from water to pure organic cosolvent.

The transfer chemical potential data[14] for an analogous substrate, $(NH_3)_4CoCO_3^+$, suggest that MeOH–water and Pr^{i}OH–water media destabilise this substrate relative to water. The substrate used here $[(NH_3)_5CoOCO_2H^{2+}]$ is strongly hydrophilic and its interaction with the solvent is likely to be greater than that of $(NH_3)_4CoCO_3^+$. The solvent cospheres of both the initial and transition states are populated by both H_2O and the molecules of the cosolvent owing to favourable electrostatic interactions and hydrogen-bonding effects. The values of the Savage–Wood group interaction parameters indicate that while interaction between alkyl groups will lead to a negative free energy change, favouring the solvation of the initial and transition states by the organic cosolvents, the interactions between the alkyl groups and OH and NH in the solvent cospheres of the substrate will destabilise it in the mixed-solvent media.[15–17] This led us to believe that both the initial state and the transition state of the reactant will be destabilised by the mixed-solvent media. The observed rate acceleration is, however, attributed to greater destabilising effects of the mixed-solvent media on the compact initial state as compared to those on the expanded transition state.

The transition state for the decarboxylation reaction is associative in nature. As such, the principles of additivity,

$$[\Delta G_{t,\,t.s.}^0]_{s\leftarrow w} = [\Delta G_{t,\,(NH_3)_5CoOH^{2+}} + \Delta G_{t,\,CO_2}^0]_{s\leftarrow w}$$

Table 3 Calculated values of $-a_i/kJ\,mol^{-1}$ and $\delta_i/kJ\,mol^{-1}$ for various solvents at different temperatures

medium	$-a_i/kJ\,mol^{-1}$ ($\delta_i/kJ\,mol^{-1}$)[a]				
	15 °C	20 °C	25 °C	30 °C	35 °C
MeOH–H$_2$O	2.39 ± 0.15	3.18 ± 0.20	3.41 ± 0.11	3.20 ± 0.22	2.64 ± 0.08
	(0.17 ± 0.05)	(0.14 ± 0.06)	(0.18 ± 0.02)	(0.01 ± 0.07)	(-0.22 ± 0.08)
Pr^{i}OH–H$_2$O	4.03 ± 0.13	4.24 ± 0.29	3.91 ± 0.21	4.39 ± 0.38	3.30 ± 0.04
	(0.32 ± 0.03)	(0.35 ± 0.07)	(0.32 ± 0.06)	(0.34 ± 0.08)	(-0.12 ± 0.10)
Bu^{t}OH–H$_2$O	1.40 ± 0.80	1.68 ± 0.41	1.48 ± 0.20	2.79 ± 0.32	3.97 ± 0.17
	(-0.18 ± 0.13)	(-0.04 ± 0.06)	(-0.14 ± 0.03)	(0.17 ± 0.05)	(0.09 ± 0.03)
EG–H$_2$O	2.58 ± 0.62	2.78 ± 0.15	2.52 ± 0.21	2.82 ± 0.14	2.73 ± 0.19
	(0.01 ± 0.15)	(-0.01 ± 0.04)	(-0.01 ± 0.05)	(0.07 ± 0.03)	(-0.09 ± 0.05)
AC–H$_2$O	8.69 ± 0.49	10.0 ± 0.7	10.4 ± 0.5	10.1 ± 0.8	10.0 ± 0.6
	(-0.22 ± 0.07)	(0.10 ± 0.13)	(0.11 ± 0.05)	(0.17 ± 0.14)	(-0.15 ± 0.12)
AN–H$_2$O	7.70 ± 0.23	7.59 ± 0.13	7.78 ± 0.25	8.58 ± 0.39	8.08 ± 0.45
	(0.09 ± 0.06)	(0.15 ± 0.03)	(0.11 ± 0.05)	(0.23 ± 0.07)	(0.05 ± 0.10)
DMSO–H$_2$O	11.8 ± 0.5	11.9 ± 0.4	11.1 ± 0.4	10.9 ± 0.5	11.4 ± 0.6
	(0.15 ± 0.11)	(0.26 ± 0.09)	(0.06 ± 0.06)	(0.08 ± 0.10)	(-0.03 ± 0.10)
EC–H$_2$O[b]	14.1 ± 2.6	10.0 ± 0.5	10.7 ± 0.6	10.5 ± 0.8	10.6 ± 0.7
	(0.02 ± 0.21)	(-0.17 ± 0.08)	(-0.10 ± 0.10)	(-0.18 ± 0.13)	(-0.22 ± 0.11)

[a] Values given in parentheses are for δ_i. [b] At $40.0\,°C$, $a = -10.7 \pm 1.0\,kJ\,mol^{-1}$ and $\delta = -0.10 \pm 0.14\,kJ\,mol^{-1}$ for EC–H$_2$O.
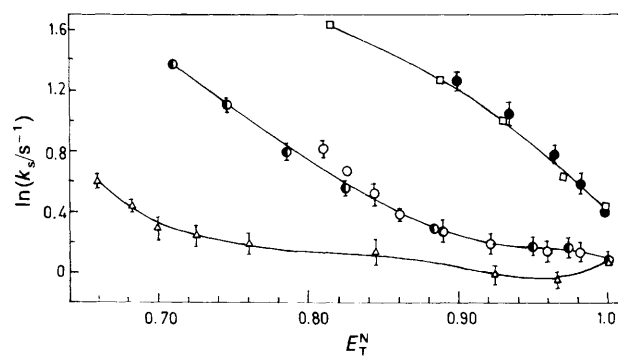
are not applicable in assessing the importance of the transfer free energy of CO_2 on $[\Delta\Delta G_t^{\ne}]_{s\leftarrow w}$. $[\Delta G_{t,\,CO_2}^0]_{s\leftarrow w}^{298.2\,K}$ for MeOH–water media (molar scale) calculated from the available solubility data[18] is negative at all X_{MeOH} and decreases with increasing X_{MeOH}. This is in keeping with the fact that the observed rate acceleration with increasing X_{MeOH} is at least partly due to the enhanced solvational stabilisation of CO_2 in this mixed-solvent medium relative to water.

From the relation

$$[\Delta G_{t,\,i.s.}^0]_{s\leftarrow w} = \alpha[\Delta G_{t,\,(NH_3)_5CoOH^{2+}}^0 + \Delta G_{t,\,CO_2}^0]_{s\leftarrow w}$$
$$+ (1 - \alpha)[\Delta G_{t,\,i.s.}^0]_{s\leftarrow w}$$

where α is a measure of the degree of C—O bond breaking in the transition state, eqn. (5) is obtained

$$\frac{1}{\alpha}[(\Delta\Delta G_t^{\ne} - \alpha\Delta G_{t,\,CO_2}^0)_{s\leftarrow w}]$$

$$= (\Delta G_{t,\,(NH_3)_5CoOH^{2+}}^0 - \Delta G_{t,\,i.s.}^0)_{s\leftarrow w} \quad (5)$$

The left-hand side of eqn. (5) decreases steadily with increasing X_{MeOH} up to 0.35 for any value of α in the range 0.5–1.0. Fig. 3 depicts the trend in the variation of the left-hand side of eqn. (5) with X_{MeOH} for different chosen values of α from which it is evident that the initial state [i.e. $(NH_3)_5CoCO_3H^{2+}$] is relatively more destabilised than the final product cobalt(III) complex [i.e. $(NH_3)_5CoOH^{2+}$] when both are transferred from water to MeOH–water at the same composition. The limited data indicate that the solubility of CO_2 in EG–water at 25 °C (1 atm.) decreases from 0.0316 to
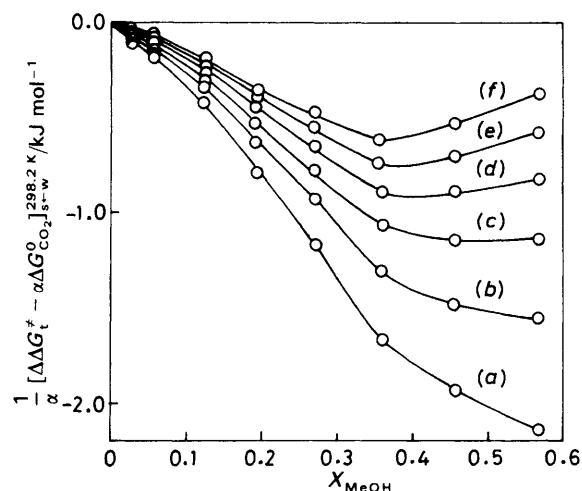

Fig. 3 $(1/\alpha)[\Delta\Delta G_t^{\ne} - \alpha\Delta G_{CO_2}^0]_{s\leftarrow w}/kJ\ mol^{-1}$ vs. X_{MeOH} plot at 25 °C: $\alpha = 0.5$ (a), 0.6 (b), 0.7 (c), 0.8 (d), 0.9 (e), 1.0 (f)

0.0295 mol dm^{-3} when X_{EG} increases from 0.02 to 0.06. The solubility data for CO_2 in other mixed-solvent media used in this study are not available. However, the solubility of CO_2 in water,[18] acetone,[20] and DMSO[20] at 25 °C follow the trend: acetone > DMSO $\gg$ water. This might indicate that the observed rate-enhancing effect of AC–water and DMSO–water media is partly due to the solvational stabilisation of CO_2.

Table 4 Mole fractions (X_{org}) at which extrema in the plots of $\Delta H^{\ne}$ (or $\Delta S^{\ne}$) vs. X_{org} are observed for the solvolysis of halogenoaminecobalt(III) complexes and the decarboxylation of $(NH_3)_5CoCO_3H^{2+}$ in mixed-solvent media

| complex | X_{org}^{max} | | | $(X_{org}^{min})^a$ | | | | |
	MeOH	Pr^{i}OH	Bu^{t}OH	EG	AC	DMSO	EC	AN
1		0.03–0.07 0.04, 0.07 (0.11)	0.06					
2			0.025 (0.1 plt)				ca. 0.05	
3			0.02–0.03 (ca. 0.10 plt)					
4	0.2–0.3	0.05–0.15 (0.2 plt)	0.045–0.075			0.15		
5		(0.03), (0.1)	(0.05–0.06)					
6			0.04					
7		(0.05) (0.1 plt)	(0.03–0.04) (0.07–0.1)					
8	0.1							
9				0.07				
10	0.06 (0.28–0.45)			(0.11)	(0.07), (0.17)			
11	(0.05)	0.1 (0.3 plt)	0.1–0.15					
12	0.2 (0.03), (0.12)	0.17 (0.12)	(0.02–0.06)	(0.01)	(0.07–0.23 plt)			
13			(0.04–0.06)					
14			0.04–0.11 (0.16)					
15		0.05, 0.15 (0.1)						
16		0.07–0.10	0.02					0.02–0.04 (ca. 0.2 plt)
17	0.05–0.35	0.12	(0.015)		(0.035)	0.05–0.15 (0.3 plt)	(0.025)	0.22

^{a} Values in parentheses are for X_{org}^{min}; plt; plateau. 1, $(NH_3)_5CoCl^{2+}$;[16,17] 2, trans-Co(en)$_2$Cl$_2^+$;[18,19] 3, cis-Co(en)$_2$Cl$_2^+$;[20] 4, trans-Co(py)$_4$Cl$_2^+$;[21] 5, trans-Co(en)$_2$ClN$_3^+$;[22] 6, cis-Co(en)$_2$ClN$_3^+$;[23] 7, cis-Co(en)$_2$ClCNS$^+$;[24] 8, cis-Co(en)$_2$(bzmH)Br^{2+};[25] 9, cis-Co(en)$_2$(imH)Cl^{2+};[26] 10, cis-Co(en)$_2$(tzNH$_2$)Br^{2+};[27] 11, cis-Co(en)$_2$(ethanolamine)Cl^{2+};[2] 12, cis-Co(en)$_2$(cyclohexylamine)Cl^{2+};[1,11] 13, cis-Co(en)$_2$(2-aminopropan-2-ol)Cl^{2+};[28] 14, trans-Co(4EtPy)$_4$Cl$_2^+$;[29] 15, trans-Co(4MePy)$_4$Cl$_2^+$;[30] 16, cis-Co(en)$_2$NH$_3$Br^{2+};[31] 17, $(NH_3)_5CoOCO_2H^{2+}$ (this work).
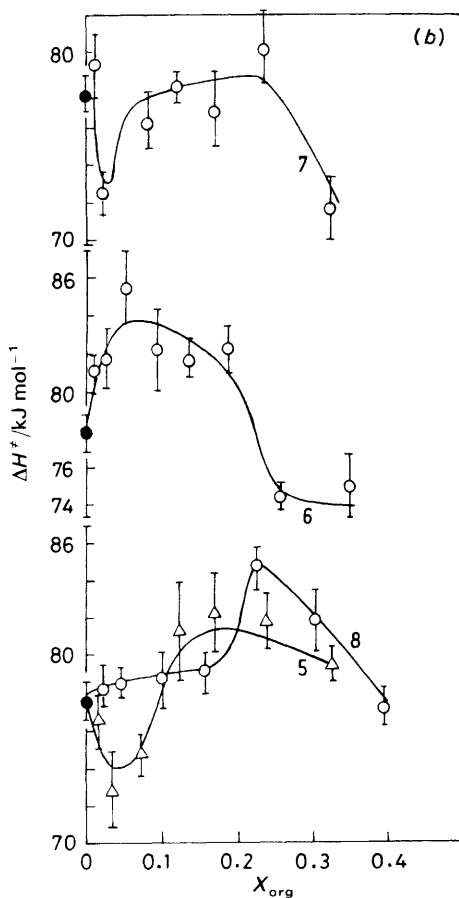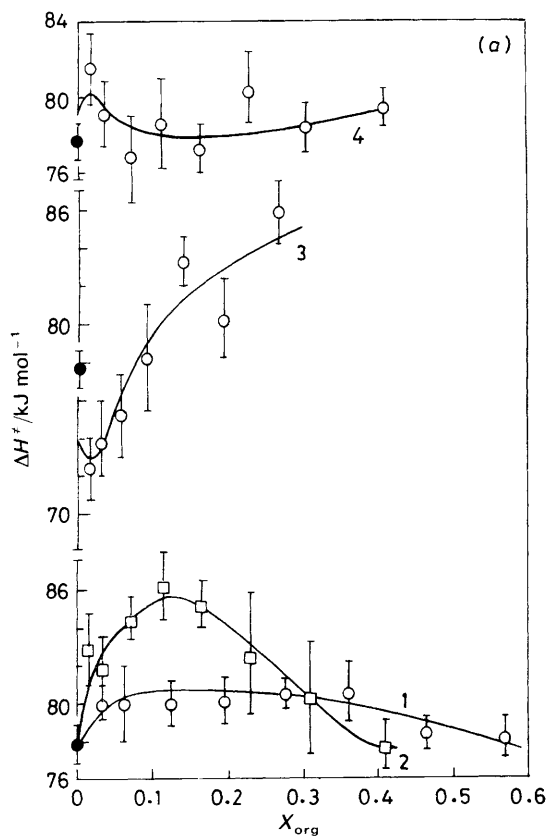
Fig. 4 (a) $\Delta H^{\neq}$/kJ mol^{-1} vs. X_{org} plot: 1, MeOH; 2, Pr^{i}OH; 3, Bu^{i}OH; 4, EG. (b) $\Delta H^{\neq}$/kJ mol^{-1} vs. X_{org} plot: 5, AC; 6, DMSO; 7, EC; 8, AN

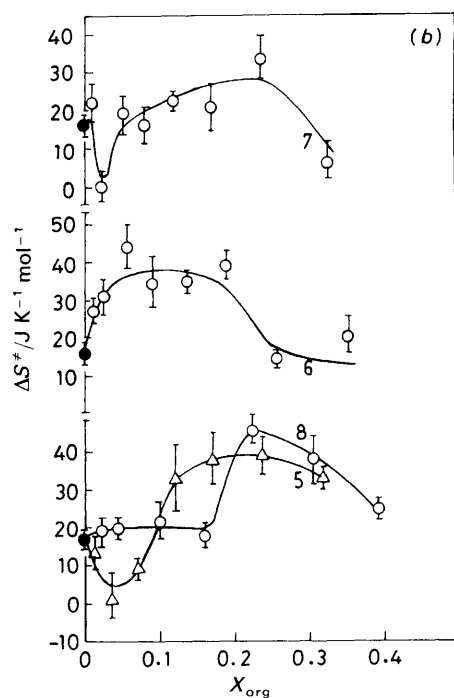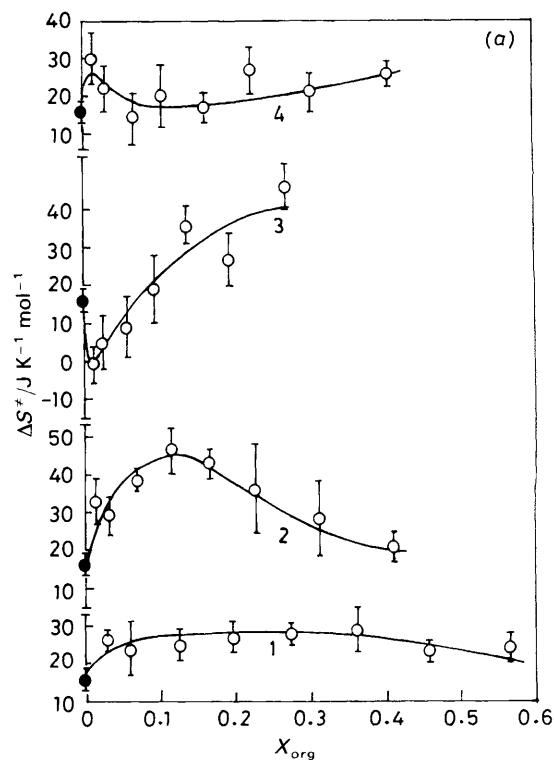**Fig. 5** (a) $\Delta S^{\neq}$/J K^{-1} mol^{-1} vs. X_{org} plot: 1, MeOH; 2, Pr^{i}OH; 3, Bu^{i}OH; 4, EG. (b) $\Delta S^{\neq}$/J K^{-1} mol^{-1} vs. X_{org} plot: 5, AC; 6, DMSO; 7, EC; 8, AN

Variation of Activation Parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) with Solvent Composition

The activation enthalpies (Fig. 4) and entropies (Fig. 5) show distinct non-linear variation with solvent composition for all mixed-solvent systems except for MeOH–H$_2$O and EG–H$_2$O for which the trend is subdued by the experimental errors in these thermodynamic parameters. The mole fractions (X_{org}) at which extrema are exhibited in the plots of $\Delta H^{\neq}$ (or $\Delta S^{\neq}$) vs. X_{org} (Table 4) also closely agree with those reported for the solvolytic reactions of halogenoaminecobalt(III) complexes[1,2,13,21–36] in the corresponding mixed-solvent

media. Note that the extrema are observed for the decarboxylation reaction for which the effects of differential solvation of the initial and transition states in highly aqueous binaries are likely to be minimal. We submit that this is due to variation of the solvational components of the activation parameters with solvent structure which is modified with the addition of the cosolvent to water.[37–39]

In contrast with all other media, $\Delta H^{\neq}$ (or $\Delta S^{\neq}$) for AN–H$_2$O remained virtually independent of composition up to $X_{AN} = 0.15$ and then increased to attain a sharp maximum at $X_{AN} = 0.225$, indicating a pronounced change in solvent structure around $X_{AN} \approx 0.2$. This is consistent with the suggestion of Esteal *et al.*[40] that a pronounced structural change due to breakdown of the water structure sets in around $X_{AN} \approx 0.15$–0.2 after the hydrogen-bonded water network becomes saturated with weakly interacting acetonitrile molecules. Studies of the thermodynamic and transport properties of the DMSO–water system have led to the generally accepted conclusion that the DMSO–H$_2$O interaction due to hydrogen bonding is at its maximum in the range of X_{DMSO} of 0.3–0.4.[39–41] Strikingly, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ tend to attain plateau minima in the range of X_{DMSO} of 0.25–0.35.

The variations of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ with solvent composition are mutually compensatory, as is evident from the linearity in the plot of $\Delta H^{\neq}$/kJ mol^{-1} *vs.* $\Delta S^{\neq}$/J K^{-1} mol^{-1} (not shown) which satisfactorily accommodates all data points.

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