Note

THERMODYNAMICS AND ION—SOLVENT INTERACTIONS OF TRICHLOROACETIC ACID IN 50% DIOXANE—WATER

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The thermodynamics of ion-association in aqueous solutions was reviewed by Noncollas [1] in 1960. The ion-pairs of nitrates [2], halides [3—5], hydroxides [5—8], sulphates [9], acetates [2] and malonates [10] of some metal ions were studied and the thermodynamic parameters were reported. Similarly, the association data of some organic and inorganic acids [11—14] were also studied. From these studies it was concluded that the association constants may decrease or increase or may pass through a minimum with increase in temperature, but no explanation was given for the deviations observed. Hence, we have studied the thermodynamics of ion-pair formation of trichloroacetic acid in 50%(w/w) dioxane—water mixtures at different temperatures and the deviations are explained in terms of the changes in ion—solvent interactions with temperature.

EXPERIMENTAL

Trichloroacetic acid (E. Merck) was purified as reported earlier [15]. Dioxane (BDH, AR grade) was purified using the procedure of Lind and Fuoss [16], and had a specific conductance less than 1.0×10^{-8} s cm^{-1}. The conductivity water had a specific conductance less than 5×10^{-7} s cm^{-1}. The experimental arrangement was the same as reported earlier [17] and the accuracy of the measured conductances was better than ±0.05%.

RESULTS AND DISCUSSION

The molar conductances of the solutions of trichloroacetic acid (TCA) in 50% (w/w) dioxane—water mixtures at 25, 35, 45 and 55°C are given in Table 1. The dielectric constants and viscosities of dioxane—water mixtures at different temperatures were taken from the literature [18].

The conductance data were analyzed using the Fuoss—Hsia equation [19] with Fernandez-Prini coefficients [20]

$$\Lambda = \Lambda_0 - s(\alpha c)^{1/2} + E\alpha c \ln(\alpha c) + J_1(\alpha c)^{3/2} - K_A \Lambda y_\pm^2 \alpha c \qquad (1)$$

where the various symbols have their usual meaning. The activity coefficients

TABLE 1

Conductances of trichloroacetic acid in 50% (w/w) dioxane—water mixtures at different temperatures

$10^5 c$ (mole dm^{-3})	Λ (s cm^2 mole^{-1})	
	25°C	35°C
275.90	123.83	138.57
236.49	125.12	140.53
206.93	126.15	142.07
183.93	127.24	143.41
165.54	128.04	144.60
150.49	128.59	145.49
137.95	129.26	146.39
118.24	130.08	147.76
103.46	130.83	148.71
91.967	131.53	149.79
82.770	132.05	150.60
68.975	132.85	151.98
55.180	133.89	153.28
45.983	134.54	154.37
34.488	135.52	155.83

$10^5 c$ (mole dm^{-3})	Λ (s cm^2 mole^{-1})	
	45°C	55°C
162.83	166.32	187.54
139.57	168.22	190.21
122.12	169.86	191.86
108.12	171.05	193.50
97.696	172.23	194.98
88.815	173.37	196.14
81.413	174.09	197.11
69.783	175.62	199.09
61.060	176.40	200.46
54.276	177.45	201.42
48.848	178.35	202.32
40.707	179.61	204.07
30.530	181.30	206.06
24.424	182.53	207.84

$(y_\pm)$ were calculated using the equation

$$-\log y_\pm = A(\alpha c)^{1/2}/\{1 + Ba(\alpha c)^{1/2}\} \tag{2}$$

Equation (1) was solved as originally described by Justice [21] and subsequently clarified by Pethybridge and Spiers [22]. This procedure envisages the replacement of the distance of closest approach of ions (a) by the Bjerrum critical distance (q). The standard deviation (σ) values were calculated from the relation

$$\sigma = \{\Sigma(\Lambda_{exp} - \Lambda_{cal})^2/(N - 3)\}^{1/2} \tag{3}$$

TABLE 2

Association parameters obtained for trichloroacetic acid using the Fuoss—Hsia equation for $a = q$ and $a = 2q$ in 50% dioxane—water mixtures

T (°C)	$a = q$			$a = 2q$		
	Λ_0	K_A	σ	Λ_0	K_A	σ
25	139.99	42.40	0.083	139.98	46.23	0.084
35	162.02	64.23	0.123	161.97	67.60	0.136
45	188.96	79.66	0.165	188.91	83.27	0.173
55	215.77	90.83	0.214	215.70	94.49	0.225

All calculations were carried out on a TDC-12 computer and the results are given in Table 2.

For uni-univalent electrolytes Walden and Birr [23] modified Stoke's law and obtained the relation

$$\Lambda_0 \eta = 0.820(1/r_s^+ + 1/r_s^-) \tag{4}$$

or

$$(1/r_s^+ + 1/r_s^-)^{-1} = 0.820/\Lambda_0 \eta \tag{5}$$

For any electrolyte the $(1/r_s^+ + 1/r_s^-)^{-1}$ factor could be calculated from experimentally obtained Λ_0 values in various solvents and viscosities of the concerned solvents. This factor is a measure of the hydrodynamic radii of the ions and in turn it could be used to gain information about the ion—solvent interactions by assuming the applicability of Walden's rule.

The Walden products [23] along with $(1/r_s^+ + 1/r_s^-)^{-1}$ factors are presented in Table 3. The Walden products were found to decrease with increase in temperature. The solvation of ions and consequently the hydrodynamic radii would be expected to depend to some extent on the nature of the solvent and to a lesser degree on the temperature. This subject was thoroughly investigated by Walden and Birr [23] who showed that the products $\Lambda_0 \eta$ or $\lambda_0^\pm \eta$ are generally independent of temperature. However, several pronounced variations with temperature were found in systems containing hydrogen ions,

TABLE 3

Walden products, hydrodynamic radii and thermodynamic parameters

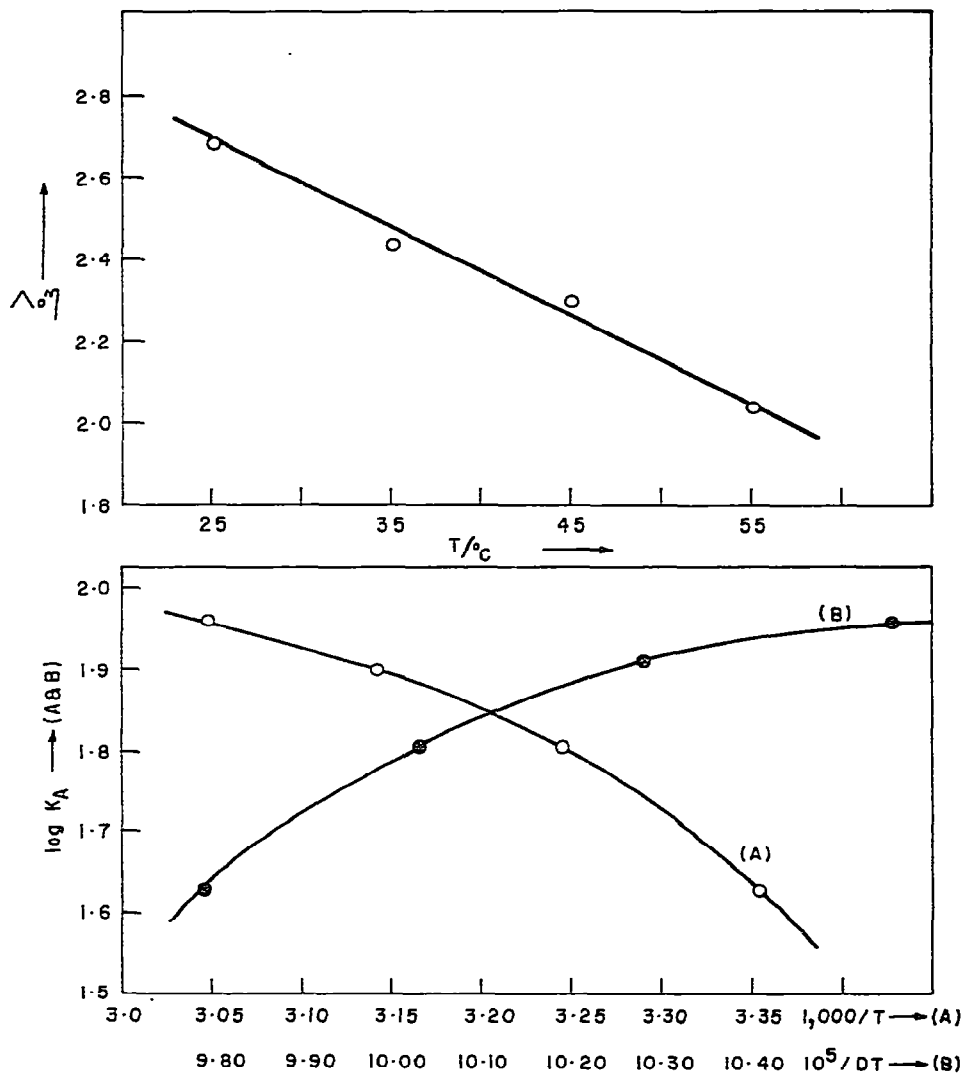| T (°C)	$\Lambda_0 \eta$	$(1/r_s^+ + 1/r_s^-)^{-1}/A$	ΔG^0 (kJ mole^{-1})	ΔH^0 (kJ mole^{-1})	ΔS^0 (J deg^{-1} mole^{-1})
25	2.681	0.306	—9.28		
35	2.430	0.337	—10.66	31.70	137.45
45	2.305	0.356	—11.57	17.54	91.48
55	2.033	0.403	—12.29	11.38	72.14

Fig. 1. Plot of $\Lambda_0\eta$ vs. temperature for trichloroacetic acid in a 50% dioxane—water mixture.

Fig. 2. Plot of log K_A vs. $1/T$ for trichloroacetic acid in a 50% dioxane—water mixture.

in highly associated or highly viscous solvents. Ions of small size or of un-symmetrical shape or those ions where the charge is distributed, would be expected to show serious departure from Walden's rule, especially when studied in solvents of widely differing polarizability and molecular volume. The structural effects of solvents on the conductance of ions in aqueous solutions are derived from a comparison of the Walden products in aqueous and non-aqueous solutions at several temperatures. In the case of large Walden products the negative temperature coefficients have been attributed to the breaking of the structure of the solvent by the addition of the electrolytes, and positive temperature coefficients to the increase in the structure of the solvent which results in the structure making character, characteristic of

the electrolyte. The $\Lambda_0 \eta$ vs. temperature plot for trichloroacetic acid in 50% dioxane—water mixtures was found to be linear with a correlation coefficient of —0.991 (Fig. 1). The negative value for the temperature coefficient suggests that trichloroacetic acid acts as a structure breaker in this solvent mixture. This decrease in the structure of the solvent may be attributed to the large size of the trichloroacetate ion.

The $(1/r_s^+ + 1/r_s^-)^{-1}$ factor is of the order of 1—3 Å for elementary ions such as Li^+, Ag^+, etc., which is in agreement with estimates of (solvated) ionic radii deduced from other data. The values calculated for trichloroacetic acid is exceptionally low, being about 0.3—0.4 Å in 50% dioxane—water mixtures. Since there is independent evidence for the high conductance of H^+ ions being mainly due to successive exchanges between solvent (water) molecules (i.e., proton jump mechanism), the inapplicability of Stoke's law and hence Walden's rule could be anticipated.

The thermodynamic parameters, viz., ΔG^0, and ΔS^0, were calculated from the association constant data at different temperatures and ΔH^0 for the temperature ranges 25—35, 35—45 and 45—55°C using the following relations

$$\Delta G^0 = -2.303 RT \log K_A \tag{6}$$

$$\Delta H^0 = 2.303 R \cdot T_1 T_2 / (T_1 - T_2) \log(K_2/K_1) \tag{7}$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0) T \tag{8}$$

The results are summarized in Table 3. It is clear from Table 3 that as the temperature increases ΔG^0 and ΔS^0 decrease. The decrease in ΔS^0 may be interpreted in terms of solute—solvent interactions. As the temperature increases from 25 to 55°C ion-solvation increases, and hence the decrease in ΔS^0.

ΔH^0 is supposed to be constant and independent of temperature range studied. In fact, ΔH^0 varied with temperature range and decreased from 31.7 for 25—35°C to 11.4 kJ mole^{-1} for 45—55°C. No concrete conclusions could be drawn from these parameters for the reasons given below.

K_A varies both with temperature and D, and since D is also a function of temperature no meaningful values of the thermodynamic parameters can be obtained. Association constants for trichloroacetic acid in 50% dioxane—water mixtures were estimated in the temperature range 25—55°C. From Fig. 2(A) it is evident that the plot of log K_A vs. $1/T$ is non-linear but a concave downward curve. Further, all the theoretical expressions for K_A contain D and T together and with the same power. Therefore the association constants are changed to the same extent and in the same manner by the change in D or T. Hence, if the non-linear trend is entirely due to changes in the dielectric constant of the solvent with temperature, then the plot of log K_A vs. $1/DT$ should be linear as predicted by the theories of ion-pair formation. However, Fig. 2(B) shows that log K_A vs. $1/DT$ plot is also non-linear; in fact a smooth curve is obtained in this case. As trichloroacetic acid in this solvent mixture acts as a structure breaker of the solvent, a change in temperature may be associated with the changes not only in the dielectric constant but also in the liquid structure of the solvent. Therefore, the temperature

coefficients of the association constants of trichloroacetic acid in 50% dioxane—water mixtures may not be useful in studying the thermodynamics of ion-pair formation in electrolyte solutions.

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