

Thermodynamic & Transport Properties of Aqueous Solutions of Fluoro-, Chloro-, Bromo-, & Iodoacetic, Propionic & Butyric Acids

M. V. KAULGUD & G. H. PANDYA

Department of Chemistry, Nagpur University, Nagpur 10

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Thermodynamic properties associated with the ionization of a series of halogen substituted fatty acids (fluoro-, chloro-, bromo-, and iodo- acetic, propionic and butyric acids) have been analysed in the light of Frank and Wen model [*Disc. Faraday Soc.*, 24 (1957), 133] of the effect of ions on water structure. It is found out that the acid anions cause a breakdown in water structure. The extent of this structure breaking depends upon the number of substituted halogen atoms but not on the size of the halogen atom. The same conclusion is also derived for the anions of trichloroacetic acid and trifluoroacetic acid by plotting the experimentally measured temperature coefficient of viscosity B -parameter against the temperature coefficient of Walden product. The values of equivalent conductance (λ°) for these and fully fluorinated higher fatty acids, viz. pentafluoropropionic acid and heptafluorobutyric acid, also corroborate the above conclusions. Spectroscopic results too indicate the structure breaking character of these acid anions.

EXTENSIVE measurements have been carried out in this laboratory¹ on the sound velocity and compressibility in aq. solutions of the halogenated organic acids over a wide range of concentrations and temperatures. For an adequate interpretation of these results in terms of solute-solvent interaction it is helpful to analyse the thermodynamic and transport properties of these systems. In doing so, reliance has been placed on the Frank and Wen² model of the effect of ions on the structure of water in which the existence of three solvent regions A, B and C around a given ion, representing highly electrostricted, partially broken down and normal water respectively has been postulated. Use has also been made of the work of King³ on the interpretation of thermodynamics of ionization of proteins and fatty acids in terms of the orientation of water molecules about the polar groups. Structure making and structure breaking ions show significant differences in the entropies of ionization. Yet another approach for recognizing the structure making or breaking effect of the ions is to consider the temperature coefficient of the Walden product $\Delta(\lambda^\circ\eta^\circ)/\Delta T$ and of the viscosity B -coefficient $\Delta B/\Delta T$, where B is obtained by applying the well known Jones-Dole equation to viscosity measurements. For structure forming ions the former is positive and the latter quantity is negative and vice versa for structure breaking ions. This result emerges⁴ from simple consideration of the effect of temperature on the bulk water and the nature of water in the ionic cosphere. Kay⁵ used this idea to distinguish between the structure-making and structure-breaking ions by plotting $\Delta(\lambda^\circ\eta^\circ)/\Delta T$ against $\Delta B/\Delta T$ (Fig. 1).

Materials and Methods

The reported⁶ thermodynamic data (Table 1) on the ionization of halogenated fatty acids in aq.

solutions have been analysed in this paper. In order to support the conclusions drawn from the present analysis of the thermodynamic data, we have measured the viscosity (using Ostwald type viscometer, accuracy 0.2%) and conductivity (using a Philips PR 9500 bridge in conjunction with a Jones type conductance cell having the cell constant 2.20) of two representative acids, trichloroacetic and trifluoroacetic acids, at 15° and 25°. Measurements of conductance were also done for the aq. solutions of pentafluoropropionic acid ($\text{CF}_3\text{CF}_2\text{COOH}$) with a view to evaluating the equivalent conductance at infinite dilution of the acid anion.

Results and Discussion

Results of the measurements of viscosity B -coefficient, λ° and the Walden product for CF_3COO^-

TABLE 1* — THE ENTROPIES OF IONIZATION OF FATTY ACIDS IN AQ. SOLUTIONS AT 25°

Acid	Mol. formula	ΔS° cal mole ⁻¹ deg ⁻¹	$(\Delta S^\circ)_1$ cal mole ⁻¹ deg ⁻¹
Acetic	CH_3COOH	-22.1	—
Propionic	$\text{C}_2\text{H}_5\text{COOH}$	-22.9	-0.8
<i>n</i> -Butyric	$\text{C}_3\text{H}_7\text{COOH}$	-24.3	-2.2
Fluoroacetic	CH_2FCOOH	-16.5	+5.6
Difluoroacetic	CHF_2COOH	-6.0	+16.0
Trifluoroacetic	CF_3COOH	-1.0	+21.1
Chloroacetic	CH_2ClCOOH	-16.9	+5.2
Dichloroacetic	CHCl_2COOH	-6.0	+16.1
Trichloroacetic	CCl_3COOH	-2.0	+20.1
Bromoacetic	CH_2BrCOOH	-17.4	+4.7
Dibromoacetic	CHBr_2COOH	-8.0	+14.1
Tribromoacetic	CBr_3COOH	-2.0	+20.1
Iodoacetic	CH_2ICOOH	-19.3	+2.8

*Taken from ref. 6.

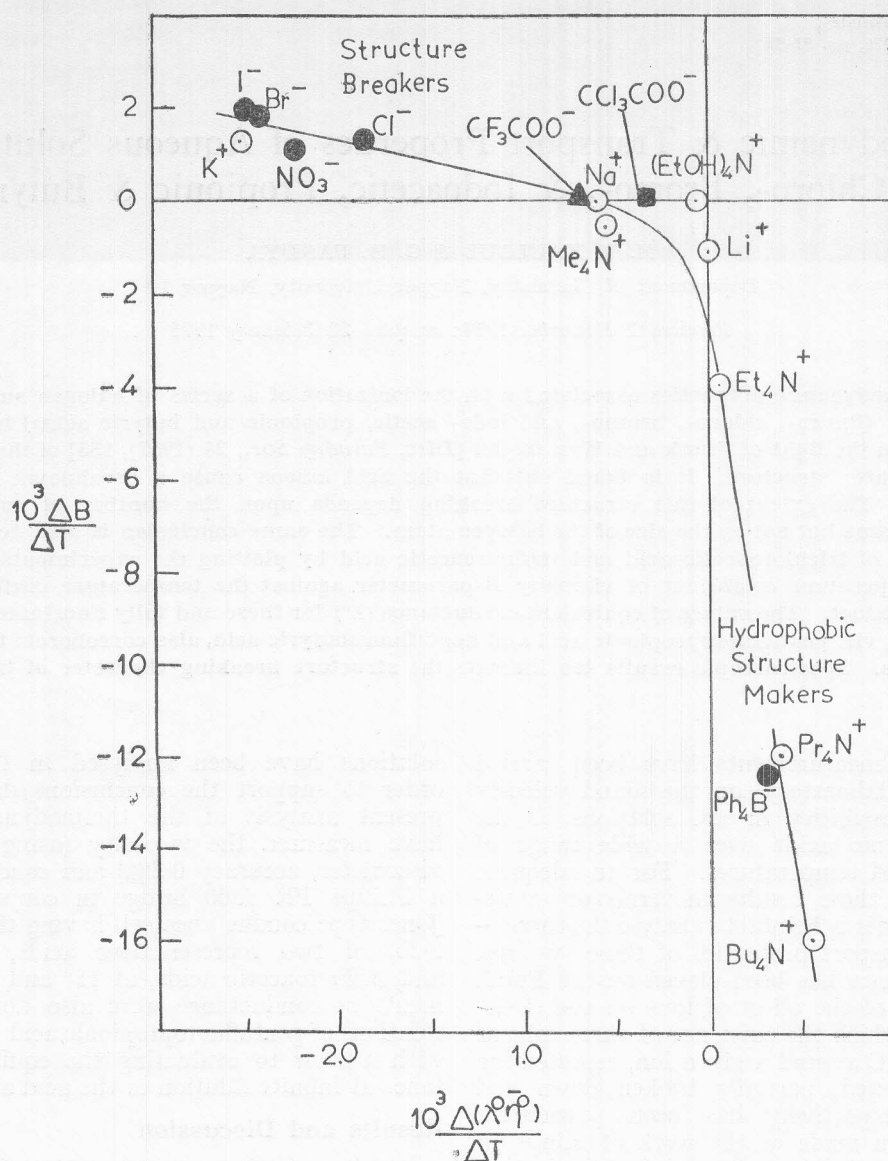


Fig. 1 — A comparison of the temperature dependence of viscosity B -coefficient and limiting ionic conductance-viscosity product for aq. solutions (reproduced from Kay⁴)

and CCl_3COO^- ions are given in Table 2. Table 3 shows λ^0 values for some aliphatic acid anions and their fully fluorinated analogues. The entropies of ionization given in Table 1 can yield information on the relative effects of various acid anions on the surrounding water molecules. On the basis of a large negative entropy of ionization of acetic acid coupled with the transport properties⁷ of the acetate ion showing acetate to be a net structure forming ion, one can easily throw light on the behaviour of other acid anions by considering the entropy change $(\Delta S^\circ)_1$ for the following reaction:



where R.COOH represents either the halogen substituted or long chain fatty acid. The entropy change $(\Delta S^\circ)_1$ for reaction (1) can be easily computed, and the values are given in Table 1.

Positive values of $(\Delta S^\circ)_1$ for halogen substituted acids, clearly point out that the anions of these acids behave like structure breakers causing disorder in the neighbouring water molecules. This may be due to the diminished charge density on the carboxyl group on account of the inductive effect exerted by the electronegative halogen atoms or due to dipole-dipole interaction between C-X ($\text{X} = \text{halogen}$) bonds and water dipoles or both. The data in Table 1 show that successive substitution of a given halogen atom in the acid leads to an increase in the value of $(\Delta S^\circ)_1$. This indicates increasing disorder caused by the corresponding anion (mono-, di- and tri-fluoroacetic acids, etc., and also chloro and bromo acids). It is noteworthy that increase in the size of the halogen atom has little or no effect on $(\Delta S^\circ)_1$ showing that the group moments C-X ($\text{X} = \text{F, Cl, Br, I}$), which are all about

TABLE 2 — VISCOSITY B -COEFFICIENTS AND WALDEN PRODUCTS FOR THE ACID ANIONS CF_3COO^- AND CCl_3COO^-

Temp. C°	B -Coefficient	λ°	$\lambda^\circ \eta^\circ$
$\text{CF}_3\text{COO}^-; \Delta(\lambda^\circ \eta^\circ)/\Delta T = -0.674$			
15	0.15	29.4	33.45
25	0.15	30.2	26.88
$\text{CCl}_3\text{COO}^-; \Delta(\lambda^\circ \eta^\circ)/\Delta T = -0.335$			
15	0.22	34.4	39.14
25	0.23	40.2	35.79

TABLE 3 — LIMITING EQUIVALENT CONDUCTIVITIES (λ°) OF ACID ANIONS IN WATER AT 25°C

Acid anion	λ°	Ref.
CH_3COO^-	40.9	10
CF_3COO^-	40.0	11
$\text{CH}_3\text{CH}_2\text{COO}^-$	35.8	10
$\text{CF}_3\text{CF}_2\text{COO}^-$	40.0*	—
$\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-$	32.6	10
$\text{CF}_3\text{CF}_2\text{CF}_2\text{COO}^-$	29.0	11

*Present work.

1.4 ± 0.1 D (ref. 8) must be playing a decisive role in the interaction with solvent water than the size of halogen atom. Our measurements of temperature coefficient of Walden product and of viscosity B -coefficient for CCl_3COO^- and CF_3COO^- when plotted on the Kay⁵ plot (Fig. 1) clearly show that these ions fall in the region of structure breaking ions (Fig. 1), thus corroborating the conclusion drawn earlier. Further, the fact that the entropy of ionization of the trifluoro-, trichloro- and tribromo-acetic acids are very low shows that vis-à-vis the dissociated ion, the undissociated acid molecules behave similarly, viz. they too act as structure breakers.

It is also observed that the increase in chain length of a hydrophobic chain results in enhanced structure making as revealed by negative (ΔS°)₁ values (Table 1). One would therefore expect that the increase in chain length of a halogen substituted acid (pentafluoropropionic acid and heptafluorobutyric acid) should cause the reverse effect, i.e. introduce more structural disorder. Since the free energy and entropy of ionization for these acids were not available, it was not possible to justify this statement without additional proof. A clue can be obtained if one examines the values of λ° for the acid anions which are fully fluorinated and compares them with λ° values for the corresponding hydrogen acid. These values obtained partly from the present study and partly from literature are given in Table 3.

Table 3 shows that the values of $\lambda_{\text{FA}}^\circ$ and $\lambda_{\text{HA}}^\circ$ are not very divergent. This is rather surprising because due to the frictional drag of solvent, $\lambda_{\text{FA}}^\circ$ ought to be less than $\lambda_{\text{HA}}^\circ$. The experimental results ($\lambda_{\text{HA}}^\circ \approx \lambda_{\text{FA}}^\circ$) can be reconciled only by

supposing that fluorinated acid anions are merely bare ions devoid of bulky hydration cosphere, whereas the alkyl chain acid anions (HA^-) are able to stabilize the structure of water (hydrophobic hydration) and the entire entity as such takes part in the electrolytic conductance. Thus it is obvious that HA^- anions stabilize water structure while the FA^- anions break down water structure, a conclusion which is adequately borne out by the thermodynamic results.

The most direct evidence for the effect of ions on the structural integrity of water in ionic solutions comes from the effect of dissolved ions on the IR spectra of solutions. It has been shown⁹ that the values of $\Delta\nu_3$ [where $\Delta\nu_3$ is the shift in frequency of $\nu_{\text{O-H}}$ (HDO in D_2O salt solution) from $\nu_{\text{O-H}}$ (HDO in pure D_2O)] for a number of salts having common cation (Na^+) gave large negative values of $\Delta\nu_3$ for the alkyl chain carboxylate anions, indicating thereby that owing to their hydrophobic long chain they reinforce water structure around them causing enhanced hydrogen bond strength in native water structure. These anions having negative $\Delta\nu_3$ values thus act as structure makers. The anions CCl_3COO^- and CF_3COO^- show positive $\Delta\nu_3$ values which are not as large as those of nitrate, bromide or iodide or other structure breaker anions, nevertheless the positive sign of $\Delta\nu_3$ makes it clear that CF_3COO^- and CCl_3COO^- anions are structure breakers.

Thus the thermodynamic and transport properties of aqueous solutions of halogenated organic acids indicate that the acid anions are not very effective structure promoters and in the limit of maximum halogen substitution might even act like structure breakers. The undissociated molecules of highly halogenated acids also exhibit similar behaviour.

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