

Apparent Molal Compressibility Behaviour of Sodium Salts of Some Fatty Acids at Different Temperatures

M V KAULGUD* & K SURYA MOHAN RAO†

Department of Chemistry, Nagpur University, Nagpur 440 010

Received 9 December 1986; revised and accepted 23 April 1987

Sound velocity measurements in dilute solutions (0-0.06 *m*) of sodium salts of fatty acids from formic to caproic acids with the help of a differential phase-comparison interferometer at 5°, 15°, 20°, 25°, 30° and 45°C coupled with density measurements using buoyancy method have enabled the evaluation of precise limiting apparent molal compressibilities (ϕ_k^0) for all the salts. By subtracting the $\phi_k^0(\text{Na}^+)$ it is possible to evaluate ϕ_k^0 for all the anions. The $\phi_k^0(T)$ trends for the anions are interpreted in terms of electrostrictive and hydrophobic interaction of the anion moiety with solvent water. The ϕ_k^0 values in addition enable one to estimate the thickness of the Frank and Wen disordered B-region in water as 3 Å. The deviation constants b_k and b_v for apparent compressibility and apparent volume have been interpreted in terms of ion pair formation and cosphere overlap using Gurney's model. It has been shown that the hydration numbers cannot be easily evaluated.

Sodium salts of higher fatty acids behave as surface active agents in aqueous solutions. Measurements of densities^{1,2}, entropies of transfer³, enthalpies of dilution⁴, heats of solutions⁵ and activity and osmotic coefficients⁶ in aqueous solutions of salts have been used to throw light on solute-solvent interactions.

The apparent molal compressibility (ϕ_k) is also a useful parameter in elucidating the solute-solvent interactions. Except for the work in the authors laboratory⁸, not much work seems to have been done on compressibility behaviour of dilute solutions of sodium carboxylates. The reported measurements were carried out at high concentrations (> 0.2 *m*). These limiting apparent compressibility (ϕ_k^0) values are not considered reliable, for the following reasons: (a) extrapolations were done employing limiting law equation not applicable at higher concentrations; and (b) due to limited accuracy of measurements points at lower concentrations show considerable scatter. Hence extrapolation to infinite dilution are not unique.

Recently, Bhowmik and Mohanty⁹ have measured the apparent compressibilities in aqueous solutions of sodium salts of fatty acids (formate to valerate) at different temperatures (25-55°C). However, on account of the limited accuracy of the interferometric method of measuring sound velocities, they could not carry out measurements in really dilute solutions. Consequently, extrapol-

ations to obtain ϕ_k^0 using the limiting law are unsatisfactory for reason (a) mentioned above. They have also calculated hydration numbers from the ϕ_k^0 values.

The present work reports accurate ϕ_k^0 values and describes ϕ_k -concentration dependence of sodium salts of formic, acetic, propionic, *n*-butyric, valeric and caproic acids in low concentration region (0-0.06 *m*) at six different temperatures, 5°, 15°, 20°, 25°, 30° and 45°C obtained from sound velocity measurements using the differential phase-comparison-interferometer. This is the first systematic work on compressibility of sodium salts of fatty acids at low concentrations and different temperatures. The aim was to have a clear picture of anion-water interactions.

Materials and Methods

Sodium formate and acetate (both AR, BDH) were further recrystallised with ethanol and dried *in vacuo* for two to three days. Sodium propionate, butyrate, valerate and caproate were prepared from the respective carboxylic acid (AR) as follows: To a sample of carboxylic acid was added sodium hydroxide solution which was just a little less than required for complete neutralisation of the acid. The solution was evaporated to dryness and washed with ethanol or acetone to remove excess acid. The samples were recrystallised from ethanol or ethanol-water mixtures and dried *in vacuo* for two to three days before use.

The purity of the samples was checked by conductometric titration and it was found to be better

†Present address: Basic Research and Training Division, National Environmental Engineering Research Institute, Nagpur 440 020

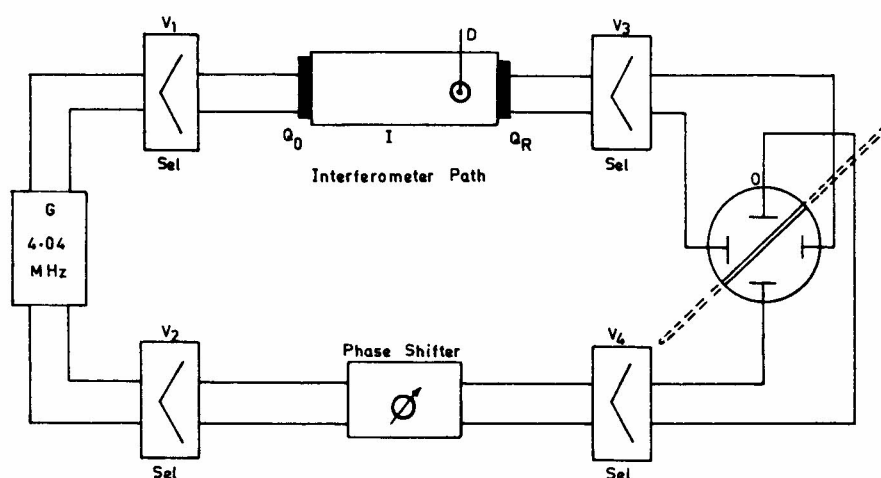


Fig. 1—Block diagram of the phase-comparison interferometer

than 99.9%, except in the case of sodium caproate where it was found to be 99.5%.

Sound velocity measurements

The sound velocities were measured differentially using a phase-comparison interferometer⁹⁻¹¹. In this method a r.f. voltage from a generator (G) (see Fig. 1) was applied to the two plates of a detector oscilloscope (O) through two different channels. One of the channels consisted of an interferometer path (I) having an oscillating crystal, (Q_0) and a receiving crystal (Q_R). In the second channel a calibrated phase shifting network was incorporated. Small changes in sound velocity caused on the addition of solute in (I) resulted in a small splitting of the Lissajous figure of the oscilloscope screen which was compensated by the fine phase shifting network.

Provided there was a travelling wave between Q_0 and Q_R the relation between phase shift and the change in velocity was given by Eq. (1)

$$\Delta U = \frac{U_0^2}{2\pi\nu l} \cdot \frac{\Delta\alpha}{57.3} \quad \dots (1)$$

where U_0 is the initial velocity of sound in solvent, l is the interferometer path length, ν is the frequency and $\Delta\alpha$ is the phase shift in degrees.

The change in velocity at any desired concentration was found by summing the sound velocity changes measured after successive additions of small quantities of solute (see Eq. 2)

$$(\Delta U)_c = \sum_{c=0}^{c=c} \Delta U_i \quad \dots (2)$$

Solutions of salts of different concentrations were prepared *in situ* in a separate stainless vessel having sound transparent windows placed in (I). Salt solutions were added using a weighing pipette. Concentrations were calculated by knowing the initial mass of water taken and the mass of the added salt solution of known molality.

The temperature in the interferometer path was maintained at the desired temperature for 2 hr with an accuracy of $\pm 0.001^\circ\text{C}$ by circulating thermostated liquid from a MK-70 cryostat (-30 to $+30 \pm 0.02^\circ\text{C}$) through copper coils placed in the path (I). A set of 20 to 25 measurements were carried out.

Accuracy in sound velocity measurements was 1, 2 and 3 cm/s for a velocity change of 1, 3 and 8 m s⁻¹ respectively. The details of measurements and accuracy obtained have been described earlier^{10,12}.

The densities were measured using a differential float density balance. With an accuracy of 5 ppm. Details have been described elsewhere¹³.

From the sound velocity and density values the apparent molal compressibility (ϕ_k) was calculated using Eq. (3)

$$\phi_k = \frac{1000}{mdd_0} (d_0\beta - d\beta^0) + \beta \cdot \frac{M_2}{d} \quad \dots (3)$$

where d_0 , d and β^0 , β are the densities and compressibilities of solvent and solution respectively, m is the molality, and M_2 is the molecular weight of the solute. The limiting apparent molal compressibility (ϕ_k^0) was obtained by extrapolating (using a least squares fit making use of a DCM 1120 microcomputer) ($\phi_k - S_k \sqrt{m}$) versus m plot to zero concentration using the well

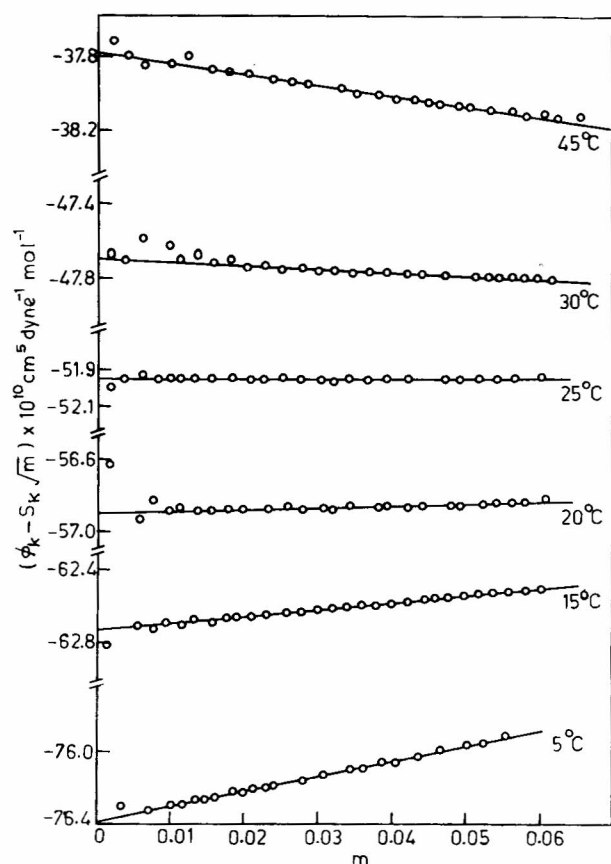


Fig. 2—Plot of $(\phi_k^0 - S_k \sqrt{m}) \times 10^{10} (\text{cm}^5 \text{dyne}^{-1} \text{mole}^{-1})$ versus molality (m) for sodium acetate at 5°, 15°, 20°, 25°, 30° and 45°C

known equation (Eq. 4), which takes into account the deviations from the Debye-Hückel theory.

$$\phi_k = \phi_k^0 + S_k \sqrt{m} + b_k m \quad \dots (4)$$

In Eq (4) S_k is the isothermal constant since adiabatic constant S_{k_s} has not been calculated but it is expected to be close to the isothermal constant.

From the extrapolated ϕ_k^0 values (obtained by least squares fit) of salts, those of the anions were obtained by subtracting the ϕ_k^0 of Na^+ ion. The ϕ_k^0 values of Na^+ ion at 15°, 30° and 45°C were taken from the work of Millero *et al.*¹⁵ Values at intermediate temperatures were obtained by interpolations.

Results and Discussion

Errors in the measurement of correct limiting parameters

Figure 2 shows plots of $(\phi_k - S_k \sqrt{m})$ versus m at different temperatures for sodium acetate. Similar plots were obtained for other salts. Slope (b_k) of the plots at different temperatures are given in Table 1 for all the salts studied presently. In Table 2 are given the corresponding deviation constants (b_v) for apparent volumes obtained¹³ from the plots of $(\phi_v - S_v \sqrt{m})$ versus

Table 1—Deviation Constants (b_k) for Apparent Molal Compressibility of Sodium Salts of Fatty Acids

Sodium salt	$b_k \times 10^{10} (\text{kg cm}^5 \text{dyne}^{-1} \text{mol}^{-2})$					
	5°	15°	20°	25°	35°	45°C
Formate	5.0	2.0	0	-1.2	-3.0	-6.3
Acetate	8.6	2.0	1.3	0.1	-1.9	-5.8
Propionate	14.8	7.6	3.3	1.0	-1.3	-4.8
Butyrate	11.7	7.2	3.2	1.1	-0.16	-6.7
Valerate	18.7	5.8	2.0	0.0	-2.2	-1.7(?)
Caproate	17.2	7.4	3.7	0.8	-1.7	-6.0

Table 2—Deviation Constants (b_v) for Apparent Molal Volumes of Sodium Salts of Fatty Acids

Sodium salt	$b_v (\text{kg cm}^3 \text{mol}^{-2})$					
	5°	15°	20°	25°	30°	45°C
Formate	0.7	0.2	0	0	-0.3	-1.2
Acetate	0.7	0.3	0.1	0	-0.2	-0.7
Propionate	1.2	0.5	0.1	0	-0.4	-1.2
Butyrate	0.6	0.1	0	-0.2	-0.4	-0.9
Valerate	-0.1	-0.34	-0.6	-0.5	-0.7	-0.9
Caproate	-0.4	-0.4	-0.5	-0.6	-0.75	-0.91

Table 3—Limiting Apparent Molal Compressibilities (ϕ_k^0) of Sodium and Fatty Acid Anions

Ion	$-\phi_{k(\text{ion})}^0 \times 10^{10} (\text{cm}^5 \text{dyne}^{-1} \text{mol}^{-1})$					
	5°	15°	20°	25°	30°	45°C
Sodium*	45.4	36.5	32.8	30.0	27.7	25.6
Formate	14.3	15.3	15.0	14.7	14.8	11.4
Acetate	33.0	26.2	24.1	22.0	20.0	12.2
Propionate	53.9	35.1	31.3	28.6	26.4	18.8
Butyrate	56.3	37.5	33.0	29.0	25.5	12.8
Valerate	60.2	35.5	32.5	28.3	24.9	11.9
Caproate	62.7	34.6	30.3	26.3	23.5	11.6

*Taken from Millero *et al.*¹⁵

m for all the salts at the same temperatures. These plots and the values of b_k and b_v clearly show that merely plotting ϕ_k (or ϕ_v) against $\sqrt{c}$ (or $\sqrt{m}$) and extrapolating to zero concentration do not give correct limiting parameters at different temperatures even from measurements at low concentrations, and much less from those at higher concentrations. This is a point which was generally overlooked by many workers in this field.

The ϕ_k^0 of the anions are given in Table 3 and are plotted graphically in Fig. 3.

Limiting apparent molal compressibilities (ϕ_k^0) and their temperature dependence

The ϕ_k^0 for fatty acid anions are all negative and become more negative with increase in chain length of

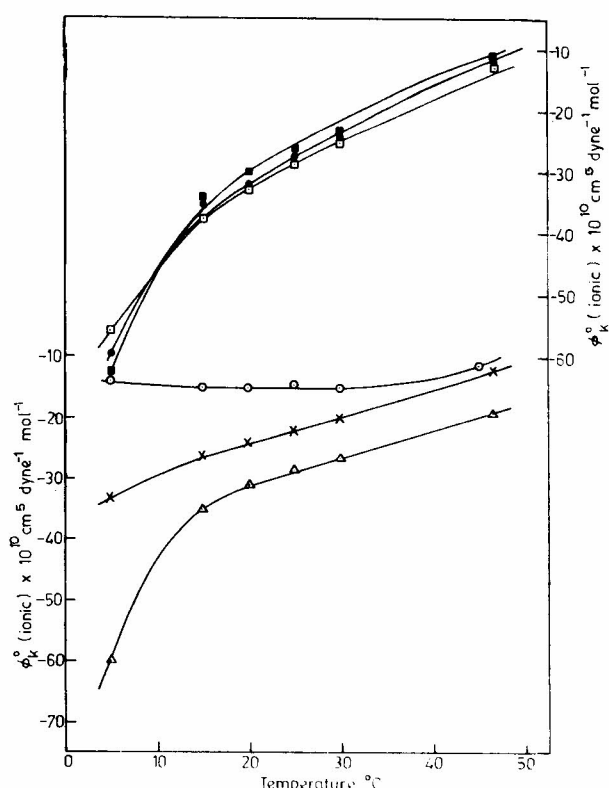


Fig. 3—Plots of limiting apparent ionic compressibility ($\phi_k^0 \times 10^{10}$, $\text{cm}^5 \text{dyne}^{-1} \text{mol}^{-1}$) against temperature for different fatty acid anions

○—○ Formate, ×—× Acetate and Δ—Δ Propionate (left hand scale); □—□ Butyrate, ●—● Valerate and ■—■ Caproate (right hand scale)

the salt. Negative ϕ_k^0 of ions in aqueous solutions are interpreted¹⁶ in terms of loss of compressibility of water due to strong electrostrictive forces in the vicinity of ions, causing electrostrictive hydration of ions. The fatty acid anions carry a negative charge centre and also possess a hydrophobic tail. As has been rightly observed by Bhowmik and Mohanty⁹, negative ϕ_k^0 for these ions manifests both electrostrictive and hydrophobic hydration effects. However, due to intrinsic limitations of their data (see above), it was not possible to visualize the nature and extent of these two hydration effects separately.

The results of ϕ_k^0 in this work obtained by adopting the extrapolation procedure making due allowance for the deviations from the Debye-Hückel theory are decidedly more reliable, and also more informative on account of the measurements at lower temperatures. The flattening off of ϕ_k^0 values after butyrate ion appears to indicate some sort of saturation effect similar to that observed by Krishnan and Friedmann¹⁸ in structure-making tendency of alcohols and alkylammonium cations.

A comparison of ϕ_k^0 value of formate ion with that of

a negative monovalent ion of similar size namely Cl^- ion is revealing (the fact that negative charge in the formate anion is slightly more diffuse does not vitiate the comparison). ϕ_k^0 values for Cl^- ion in water at 15°, 30° and 45° are -19.1 , -14.5 and $-13.4 \times 10^{-10} \text{ cm}^5 \text{dyne}^{-1} \text{mol}^{-1}$ respectively¹⁵, which are similar to those of formate ion both in magnitude and temperature dependence. This fact suggests a similarity in their mode of interaction with water, which is predominantly electrostrictive. The near constancy of $\phi_k^0(T)$ values further shows that this electrostriction is relatively insensitive to rise in temperature. It is thus reasonable to assume that formate ion also interacts with water in electrostrictive way. We assume next the validity of the Frank and Wen model¹⁹ for the interaction of ions with water resulting in three regions of water, namely A (highly electrostricted), B (partially disordered) and C (normal bulk water). The near constancy of ϕ_k^0 for formate ion means that the A-region is firmly held even at elevated temperatures and structural changes in B- and C-regions undergo such changes with rising temperature which nearly compensate each other, leaving ϕ_k^0 relatively unaffected.

The temperature variation of ϕ_k^0 for all the other fatty acid anions studied in this work (Fig. 3, Table 3) and more importantly the difference in the behaviour of consecutive members is quite interesting. At 5°C the change in ϕ_k^0 ($\Delta\phi_k^0$) in going from formate to acetate is large (18.7 units) and negative. It becomes larger and more negative in going from acetate to propionate ($\Delta\phi_k^0 \approx -21$ units). This decreasing trend in ϕ_k^0 does not continue after propionate ion, and the next member, i.e. the butyrate ion, has ϕ_k^0 more negative by only 3 units than propionate ion. Subsequent members, i.e. the valerate and caproate ions have ϕ_k^0 values only marginally more negative than the previous members (Table 3). The above features can be explained on the basis that the additional CH_2 group in acetate as compared to formate ion protrudes beyond the electrostricted A-zone into the disordered B-zone (Frank and Wen model) and imparts protection to the disordered water molecules due to hydrophobic hydration. This leads to more negative ϕ_k^0 . This view is consistent with the large negative value of entropy of ionization ($\Delta S = -22.1 \text{ eu mol}^{-1}$)²⁰ for acetate ion, which together with viscosity and conductance²¹ properties shows its structure-strengthening ability. Similar arguments can be put forth in the case of propionate ion, where the additional CH_2 group in comparison to acetate continues to be in the disordered B-zone bringing about further structural ordering in the solvent water. The $\Delta\phi_k^0$ values become much smaller after propionate ($\sim 2-4$ units) at all temperatures. This shows that the additional $-\text{CH}_2-$ groups beyond propionate now protrude into the C-zone (Frank and

Wen) model of normal bulk water, which is more structured than the disordered B-zone. Hence, the CH_2 groups have diminished chance of hydrophobic interaction with disordered solvent molecules resulting in smaller variation in ϕ_k^0 . This is consistent with lower solubilities of higher fatty acids in water. The ϕ_k^0 value at low temperature thus appears to be governed by the structural or disordered effects. The above analysis further leads to the estimation of thickness of the Frank and Wen B-region for fatty acid anions as roughly equivalent to two C – C bond lengths or about 3 Å. This is a very important outcome of the present study of ϕ_k^0 of fatty acid anions.

The large variation in ϕ_k^0 with temperature for all ions ($d\phi_k^0/dT + ve$) other than the formate ion ($d\phi_k^0/dT \approx 0$) bears further scrutiny of the mode of interaction proposed above. It can be seen that the ϕ_k^0 values for other members become less negative with increase in temperature—gradually for acetate ion and more rapidly for higher members—showing that the structural stabilisation imparted to water by the hydrophobic chain is temperature labile. It can further be observed that at sufficiently high temperature (45°C) the ϕ_k^0 values for all the anions tend towards a common limit, ($-12 \times 10^{-10} \text{ cm}^5 \text{ dyne}^{-1} \text{ mol}^{-1}$) which is not very different from that for formate ion (-11.4×10^{-10}). This important observation strongly suggests that at sufficiently high temperatures all acid anions interact with water predominantly through $-\text{COO}^-$ group, i.e. electrostrictively; and that the hydrophobic chain ceases to interact with water. This might be taken to mean that solutes tend to cluster together at higher temperatures offering only the $-\text{COO}^-$ end for interaction with water. The $\phi_k^0(T)$ results for the fatty acid anions presented here thus clearly demonstrate the operation of structural hydration effects at low temperature and electrostrictive hydration at higher temperatures.

Hydration numbers

No attempt is made in this work to calculate the hydration numbers of the acid anions using Eq. (5):

$$n_H = -\frac{\phi_k^0}{\beta^0 V^0} \quad \dots (5)$$

as is generally done by many authors, and also by Bhoumik and Mohanty⁹. Equation (5) yields physically meaningful hydration numbers only in those cases where the electrostrictive pressure exerted by the ions on the surrounding water molecules is sufficiently high ($\approx 10^7$ e.s.u.) to render the solvent molecules incompressible. In fact this has been the underlying assumption in arriving at Eq. (5)¹⁷. However, as shown by

Desnoyers *et al.*²², this condition is obtained strictly only for ions like Li^+ , Mg^{++} etc. having small diameters and hence high charge densities. The method is inapplicable in the case of ions like Cl^- , HCOO^- where the electrostatic pressure would be of the order of $\sim 5 \times 10^5$ e.s.u. so that the compressibility of the hydrated water cannot be assumed to be zero.

Viewed in the light of the above, the hydration behaviour of fatty acid anions—partly electrostrictive and partly hydrophobic—is far from fulfilling the presumption of Eq. (5). Even formate ion with a radius of about 1.35 Å fails to satisfy this equation. The hydrocarbon chain of fatty acid anion interacts with water molecules through Van der Waals forces giving rise to 'soft hydration' (hydrophobic hydration), which is qualitatively different from the hard electrostrictive hydration. It is thus not very correct to extend Eq. (5) to ions studied in this work. Values of n_H derived by earlier workers⁹ are thus not correct and hence do not reflect the correct physical picture of ion-solvent interaction. The proper procedure to arrive at n_H would be to first subtract the electrostrictive part of ϕ_k^0 (-12 units, see above) from the measured values to obtain ϕ_k^0 due to hydrophobic interaction followed by use of two different and well-founded equations to calculate (n_H)-electrostriction and (n_H)-hydrophobic, separately from the above division of ϕ_k^0 . Such equations do not exist. Further theoretical work in this direction is very much called for.

Also no attempt has been made in this work to calculate incremental $\Delta\phi_k^0$ per CH_2 group, for the simple reason that the present results show that this is not constant but varies according to whether it is close to the COO^- group or farther away from it.

Deviation constants b_v and b_k

The b_v -values decrease with increase in the size of anions. Also db_v/dT is negative. These features are exhibited by other electrolytes (e.g. NaCl) and the size effect is similar to that shown by tetraalkylammonium ions²³. However, the db_v/dT for tetra-salts (Bu_4NBr) shows positive values.

Positive deviations of b_k at lower temperatures can be interpreted in terms of ion-pair formation²³, reflecting the structural compatibility of hydration cospheres of cation and anions. The negative b_v -values for valerate and caproate at 5°C can be understood as the combined effect of ion-pair formation ($+ve$ b_v) and overlap of hydration cospheres of the chain leading to $-ve$ b_k -values. As discussed by Desnoyers *et al.*²⁴ such overlap of cospheres in the case of species with long hydrocarbon chain takes place to offset the thermodynamically unfavourable hydrophobic hydration of such species. The observed small b_v -values

are a net result of these two opposing effects. At higher temperatures thermal agitation renders the weak ion-pair formation less probable and gives way to anion-anion interaction leading to increased overlap of cospheres, and consequent release of bulky ice-like hydration water into bulk as normal water having smaller volume. This explains the uniformly negative b_v -values for all members at 45°C and their near constancy points to the tendency of anions to cluster together in such a way that they interact with water only through COO^- groups.

The b_k -values (Table 1) can also be interpreted in a similar way as above. Positive b_k -values are to be understood as release of water from the incompressible electrostricted sheaths around the ions into the more compressible bulk water due to ion-pair formation. Rapid increase of b_k in the series at 5°C from a value of 5 units for formate to 18.7 units for valerate should then mean additional release of the less compressible hydrophobically hydrated water into the bulk on account of increased overlap of cosphere due to anion-anion interaction. Since the hydrophobic hydration melts off with increase in temperature this leads to a gradual decrease in b_k with increase in temperature for all the members. At 45°C all members tend to have the same (–ve) value of b_k indicating cluster formation due to anion-anion interactions, thereby achieving an economy of the number of structured water molecules per molecule of the dissolved solute. Since individual ionic contributions to b_k are not yet available, it is not possible to evaluate and interpret ionic b_k individually.

It can be concluded that the precise measurements of ϕ_k^0 of fatty acid anions over an extended temperature range including low temperatures enable a clear distinction between electrostrictive and hydrophobic interaction of water and the charge centre and hydrocarbon tail respectively. The trends in ϕ_k^0 have been used to arrive at the thickness of the Frank and Wen B-region, which is about 3 Å wide. Convergence of ϕ_k^0 values for

all members to approximately the same negative value at high temperature suggests exclusive interaction between charge centre and water only implying that the hydrocarbon chains tend to form clusters. The deviation constants b_v and b_k show trends which indicate ion-pair formation, at low temperature going over into anion-anion interaction at elevated temperature corroborating results of ϕ_k^0 .

Acknowledgement

One of us (K S M R) is thankful to the UGC, New Delhi for the award of a junior research fellowship.

References

- 1 Watson G M & Felsing W A, *J Am Chem Soc*, **63** (1941) 410.
- 2 Sakurai M, *Bull Chem Soc (Japan)*, **46** (1973) 1596.
- 3 Snell H & Greyson H, *J Phys Chem*, **74** (1970) 2148.
- 4 Lindenbaum S, *J Phys Chem*, **74** (1970) 3027.
- 5 Ahluwalia J C & Chawla B, *J Soln Chem*, **6** (1975) 383.
- 6 Diamond R M, *J Phys Chem*, **45** (1966) 2513.
- 7 Worley J D & Klotz I M, *J Phys Chem*, **45** (1966) 2868.
- 8 Kaulgud M V & Rao K S M, *Indian J Chem*, **13** (1975) 616.
- 9 Bhowmik S & Mohanty R K, *Indian J Chem*, **25A** (1986) 416.
- 10 Kaulgud M V, *Acustica*, **15** (1965) 377.
- 11 Kaulgud M V, *Z Phys Chem (Neue Folge)*, **47** (1963) 24.
- 12 Kaulgud M V, Rao K S M & Pandya G H, *Indian J Pure Appl Phys*, **15** (1978) 459.
- 13 Kaulgud M V, Rao K S M & Dole H G, *Indian J Chem*, **16A** (1978) 955.
- 14 Rao K S M, Ph D Thesis, Nagpur University 1978.
- 15 Millero F J, Ward G K, Lipple L K & Hoff E V, *J Phys Chem*, **78** (1974) 1636.
- 16 Corey V B, *Phys Rev*, **64** (1943) 350.
- 17 Passynski A, *Acta Physicochim*, **8** (1938) 385.
- 18 Krishnan C V & Friedman H L, *J Phys Chem*, **73** (1979) 1572.
- 19 Frank H S & Wen W Y, *Discu Faraday Soc*, **24** (1957) 133.
- 20 Coetzee J F, *Solute-solvent interactions* (Marcel-Dekker, New York) 1969.
- 21 Gurney R W, *Ionic process in solutions* (McGraw Hill, New York) 1953.
- 22 Desnoyers J E, Verrall R E & Conway B E, *J Chem Phys*, **43** (1965) 243.
- 23 Millero F J, *Chem Rev*, **71** (1971) 147.
- 24 Desnoyers J E, Perron M, Arel G & Jolicoeur C, *J Phys Chem*, **73** (1969) 3346.

