

Validity of The Principle of Additivity of Viscosity B Coefficients in The Mixtures of Weak Acids and Their Salts

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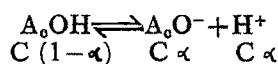
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The principle of additivity of viscosity B (and A) coefficients has been extended to mixtures of weak acids and salts. On this basis, equations giving the degree of dissociation (α) of the weak acid solutions have been developed in terms of various A and B coefficients. The α calculated from viscosity measurements is compared with the values obtained from the direct pH measurements on weak acid solutions.

It is well established that the viscosity B coefficients of Jones-Dole's equation are additive in the sense that the B coefficient differences between pairs of salts, having common anions, are constant in dilute solutions and independent of the nature of the anion¹ (cf. Kohlrausch's law of independent migration of ions). An attempt has been made in the present study to extend such additivity principle to a mixture of components each of which is characterised by a specific B coefficient. The particular systems investigated are of the general type, weak acid + salt combinations, and we have proposed equations, by way of invoking such "extended" additivity, that lead to the evaluation of an important property of weak acid solutions, namely the degree of dissociation, α , from viscosity measurements. The latter, thus obtained, is compared with the value of α derived from direct pH measurements carried on such acid solutions. A satisfactory agreement between these values of α will be taken to justify the extension of the above additivity to mixtures. The following equations are derived for acetic acid, but should equally apply to any combination of weak acid and the corresponding salt.

Theory and working formulae: Let α be the degree of dissociation of acetic acid solution at a concentration C mol. litre⁻¹ and at a given temperature.



Assuming additivity of the viscosity B coefficients at concentration C, one may write,

$$C B_{\text{obs}} = C(1-\alpha) B_{\text{ACOH}} + \alpha C B_{\text{H}^+} + \alpha C B_{\text{ACO}^-}$$

where B_{ACOH} is the B coefficient of acetic acid "molecule" i.e., the undissociated acetic acid and B_{obs} the observed B coefficient at concentration C.

Therefore, $B_{\text{obs}} = (1-\alpha) B_{\text{ACOH}} + \alpha B_{\text{ACO}^-}$... (1), B_{ACO^-} being the B coefficient of the "fully dissociated" acetic acid.

By analogy, the viscosity A coefficient (Grüneisen effect), as observed in the above acetic acid

solution, is given as,

$$A_{\text{obs}} = (1-\alpha) A_{\text{ACOH}} + \alpha A_{\text{ACO}^-} \quad \dots (2)$$

It is interesting to note from eqs. (1) and (2) that at infinite dilution $\alpha = 1.0$ and therefore $B_{\text{obs}} = B_{\text{ACO}^-}$ and $A_{\text{obs}} = A_{\text{ACO}^-}$, which one would expect. Hence, eqs. (1) and (2) are consistent.

By rearrangement of eq. (1), we obtain

$$\alpha = \frac{B_{\text{obs}} - B_{\text{ACOH}}}{B_{\text{ACO}^-} - B_{\text{ACOH}}} \quad \dots (3)$$

so that α , the degree of dissociation at a concentration C, can be derived from the measured viscosity B coefficient of acetic acid solution, B_{obs} , at the same concentration provided that the B coefficients of the "fully dissociated" acetic acid (B_{ACO^-}) and the undissociated acid (B_{ACOH}) are known.

For the general case of weak acid, HA, and its salt eq. (3) reads,

$$\alpha = \frac{B_{\text{obs}} - B_{\text{HA}}}{B_{\text{H}^+} - B_{\text{HA}}} \quad \dots (3a)$$

B_{ACO^-} is calculated by adding up B_{H^+} and B_{ACO^-} ; the latter are derived from viscosity studies on solutions of strong acids and acetates.

B_{ACOH} is obtained through an approximation. On the assumption that acetic acid is undissociated in presence of a dilute solution of an acetate, B_{ACOH} will be given by the difference between the viscosity B coefficient of a mixture of acetate and acetic acid, (B), an experimental quantity, and that of the acetate. Such a method is based on an extension of the principle of additivity of B coefficients (and A coefficients) to a mixture as mentioned above.

For the purpose, viscosity measurements are conducted on a number of mixtures of sodium acetate (at a given concentration, say 0.1M) and different stoichiometric concentrations of acetic acid (say, 0.05M, 0.075M, 0.1M and 0.15M). With the above mentioned supposition that acetic acid at these concentrations is fully undissociated

in presence of 0.1M sodium acetate, one would obtain from the Jones-Dole's equation,

$$\frac{\eta}{\eta_0} = 1 + (A) \sqrt{C} + (B) C \quad \dots (4)$$

in which (A) and (B) are composite quantities, given by

$$(A) = \Delta_{\text{ACOH}} + \Delta_{\text{NaOA}_0} \quad \dots (5)$$

and

$$(B) = B_{\text{ACOH}} + B_{\text{NaOA}_0} \quad \dots (6)$$

while η and η_0 are the viscosity coefficients at the same temperature of the mixture of acetate and acetic acid, having a mean (molar) concentration C, and of water, respectively.

On obtaining (A) and (B) from the intercept and slope respectively of the graphical plot of

$\left(\frac{\eta}{\eta_0} - 1\right) / \sqrt{C}$ vs \sqrt{C} [vide. eq.(4)], Δ_{ACOH} and B_{ACOH} are derived, using eqs. (5) and (6) and with a knowledge of Δ_{NaOA_0} and B_{NaOA_0} from independent experiments on acetate solutions.

To calculate α according to eq.(3) one requires a knowledge of B_{obs} as well. The Jones-Dole's equation, as applied to an acetic acid solution at a stoichiometric concentration C, reads,

$$B_{\text{obs}} C + A_{\text{obs}} \sqrt{C} = \frac{\eta}{\eta_0} - 1 \quad \dots (7)$$

where B_{obs} and A_{obs} are given by eqs. (1) and (2).

On substituting A_{obs} from eq. (2) in eq. (7) one obtains

$$\frac{\eta}{\eta_0} - 1 = B_{\text{obs}} C + \left[(1 - \alpha) \Delta_{\text{ACOH}} + \alpha \Delta_{\text{ACO}^- \text{H}^+} \right] \sqrt{C}$$

which, on rearrangement, becomes

$$B_{\text{obs}} = \frac{\left(\frac{\eta}{\eta_0} - 1\right)}{C} - \frac{1}{C^{3/2}} \left[C \Delta_{\text{ACOH}} - C \alpha \Delta_{\text{ACOH}} + C \alpha \Delta_{\text{ACO}^- \text{H}^+} \right] \quad \dots (8)$$

Remembering that $C \alpha = C_{\text{H}^+}$, the hydrogen ion concentration of the solution, it follows,

$$B_{\text{obs}} = \left[\frac{\eta}{\eta_0} - 1 \right] \frac{1}{C} - \frac{1}{C^{3/2}} \left[C \Delta_{\text{ACOH}} + C_{\text{H}^+} (\Delta_{\text{ACO}^- \text{H}^+} - \Delta_{\text{ACOH}}) \right] \quad \dots (9)$$

Thus, B_{obs} is obtained from eq. (9) with a knowledge of Δ_{ACOH} and $\Delta_{\text{ACO}^- \text{H}^+}$ ($\Delta_{\text{ACO}^- \text{H}^+}$ is given as $\Delta_{\text{NaOA}_0} + \Delta_{\text{HCl}} - \Delta_{\text{NaCl}}$), and pH (i.e., C_{H^+}) of the given solution of acetic acid.

Eq. (9) may be rewritten as

$$B_{\text{obs}} C^{3/2} = \sqrt{C} \left(\frac{\eta}{\eta_0} - 1 \right) - \left[C \Delta_{\text{ACOH}} + C_{\text{H}^+} (\Delta_{\text{ACO}^- \text{H}^+} - \Delta_{\text{ACOH}}) \right] \quad \dots (10)$$

On inspection of eq. (10) it is clear that at infinite dilution ($C=0$, $C_{\text{H}^+} = C \alpha = 0$), $\alpha = 1.0$ and $\eta = \eta_0$.

On such substitution in eq. (10), both sides of the latter vanish. Hence eq. (10) is also consistent.

On substituting the values of B_{ACOH} , $B_{\text{ACO}^- \text{H}^+}$ and B_{obs} , determined as described above, in eq. (3) α is calculated and then the value is compared with the one obtained by direct pH and hence C_{H^+} ($= C \alpha$) measurement of the given acetic acid solution.

Materials : An Ubbelohde type (three necked) all-glass viscometer was used for the determination of viscosities. The flow time was recorded by means of a stop watch reading up to 0.1 of a second. The average (of at least four observations) flow time for water through the capillary of the viscometer was 502.6 sec. The temperature of study was maintained at $30.0 \pm 0.05^\circ$ by the use of a water-thermostat provided with a solid state relay unit and an electrical contact thermometer.

The chemicals used, namely glacial acetic acid, propionic acid, hydrochloric acid and sodium acetate were of AnalaR grade (B.D.H. and E. Merck) while sodium propionate was prepared from the acid and anhydrous sodium carbonate (AnalaR), followed by crystallisation (twice) from water.

The solutions were prepared in deionised water of conductivity less than $3 \mu \text{ mho.cm}^{-1}$. An electrical balance, reading upto $10 \mu \text{g}$, was used for recording weights in the preparation of solutions and measurements of density (by using a specific gravity bottle).

Experimental

(i) The viscosity B coefficients of sodium acetate and sodium propionate were determined by noting the time of flow at a number of concentrations, ranging from 0.05M to 0.5M, of each of these solutions as well as that of water, all at 30° , and then having recourse to the graphical plot [viz. eq. (4)] in each case. The viscosity A coefficients of these compounds were also noted from the intercepts of the plots.

(ii) A series of mixtures, which were 0.1M with respect to NaOAc and successively 0.05M, 0.075M, 0.1M and 0.15M with respect to acetic acid, were prepared and the composite constants (A) and (B) [vide. eqs. (5) and (6)] were determined in the same manner as above (acetic acid was considered fully undissociated in these mixtures).

(iii) From (i) and (ii), Δ_{ACOH} and B_{ACOH} for the undissociated acetic acid were derived.

(iv) The steps (ii) and (iii) were repeated for propionic acid and sodium propionate.

(v) A and B for hydrochloric acid were determined as in (i) above by studying viscosity of its solutions. Next, by using the measured Δ_{NaOA_0} from (i) and noting Δ_{NaCl} from the literature¹ $\Delta_{\text{ACO}^- \text{H}^+}$ was calculated from the relation,

$$\Delta_{\text{ACO}^- \text{H}^+} = \Delta_{\text{NaOA}_0} + \Delta_{\text{HCl}} - \Delta_{\text{NaCl}}$$

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TABLE 1—VISCOSITY DATA FOR SOLUTIONS

Temperature=30°
Viscosity of water (η_0) at 30°=0.7975 cp
Density of water (ρ_0) at 30°=0.9956 g cm⁻³

Solution	Molar concentration/M	\sqrt{C}	Coefficient of viscosity of solution/cp η	$\eta Sp/\sqrt{C}$ $(\eta Sp/\eta_0 - 1)$	B coefficient (Slope of linear plot of $\eta Sp/\sqrt{C}$ vs \sqrt{C})
Sodium acetate	0.1	0.3162	0.8131	0.0620	0.180 (B ₁)
	0.2	0.4472	0.8303	0.0920	
	0.3	0.5477	0.8494	0.1190	
	0.4	0.6324	0.8670	0.1380	
	0.5	0.7071	0.8877	0.1600	
Sodium propionate	0.1	0.3162	0.8284	0.1230	0.984 (B ₁)
	0.2	0.4472	0.8613	0.1790	
	0.25	0.5000	0.8776	0.2010	
	0.30	0.5477	0.8957	0.2250	
	0.40	0.6324	0.9311	0.2650	
Hydrochloric acid	0.2	0.4472	0.8042	0.0190	0.063 (not used elsewhere)
	0.4	0.6324	0.8146	0.0340	
	0.6	0.7745	0.8228	0.0410	
	0.8	0.8944	0.8388	0.0510	
	1.0	1.0000	0.8416	0.0560	
Mean molar concentration					
Sodium acetate (0.1M) + Acetic acid (undissociated)	0.0650 0.0750 0.1000 0.1250	0.2549 0.2738 0.3162 0.3535	0.8215 0.8258 0.8316 0.8381	0.1180 0.1295 0.1353 0.1437	Composite B coefficient (B) 0.285
Sodium propionate (0.1M) + Propionic acid (undissociated)	0.0625 0.0750 0.1000 0.1250	0.2500 0.2738 0.3162 0.3535	0.8298 0.8345 0.8458 0.8563	0.1620 0.1700 0.1920 0.2090	Composite B coefficient (B) 0.488

A_H⁺A⁻ for propionic acid was also calculated in the same manner.

(vi) B_{AcO-H⁺} was obtained as (B_{H⁺} + B_{NaOAc} - B_{Na⁺}) in which B_{H⁺} and B_{Na⁺} were the literature values¹ while B_{NaOAc} was the measured value from (i). B for fully dissociated propionic acid was obtained in the same way.

(vii) B_{obs} was next determined by measuring the viscosity as well as the pH of a 0.1M acetic acid solution (and of 0.1M propionic acid) and then using eq. (9) in which the values of A_{AcOH} and A_{AcO⁻H⁺}, as obtained above, were used.

(viii) The degree of dissociation α was finally calculated, by using eq. (3) from the values of B_{obs}, B_{AcOH} and B_{AcO⁻H⁺}. The α so obtained was compared with the value derived from the measured pH of 0.1M acid solution.

Results and Discussion

A Synopsis of results has been given in Tables, 1 to 6, covering the determination of various A and B coefficients as well as the hydrogen ion concentration of the solutions and finally, the degree of dissociation (α) of the weak acid solutions studied (Table 6). The corresponding α obtained from the direct pH measurements (say, α_{pH}) is also included for the sake of comparison in the same Table.

The degree of dissociation for both acetic and propionic acids, as obtained from the present viscosity studies, is seen from Table 6 (5th column) to

TABLE 2—VISCOSITY MEASUREMENTS ON SALT SOLUTIONS AND STRONG ACID, HCl

Solution	B coefficient B ₁	A coefficient A ₁
Sodium acetate	0.180	0.012
Sodium propionate	0.984	0.008
Hydrochloric acid	0.063	0.005
(not used elsewhere)		

TABLE 3—VISCOSITY AND pH MEASUREMENTS ON WEAK ACID SOLUTIONS

Solution	$(\frac{\eta}{\eta_0} - 1)/C$	pH	C _{H⁺} = 10 ^{-pH} /g ion. litre ⁻¹
Acetic acid (0.1M)	0.2031	2.80	0.00158
Propionic acid (0.1M)	0.2270	2.96	0.00110

TABLE 4—VISCOSITY MEASUREMENTS ON MIXTURES OF WEAK ACIDS AND SALTS

Solution	Composite B coefficient (B)	Composite A coefficient (A)	* B coefficient of undissociated acid B _{HA} = (B) - B ₁	** A coefficient of undissociated acid A _{HA} = (A) - A ₁
Acetic acid + Sodium acetate	0.285	0.043	0.105	0.031
Propionic acid + Sodium propionate	0.488	0.046	0.103	0.038

* B₁ ≡ B_{NaA}; ** A₁ ≡ A_{NaA}.

TABLE 5—DATA TAKEN FROM LITERATURE^{1,2}

Solution/Ion	B coefficient	A coefficient
H ₂ O ⁺	0.0709 ²	—
Na ⁺	0.0859 ²	—
NaCl	0.0798 ¹	0.0062 ¹

able satisfaction that the kind of agreement in α values, as elaborated in the preceding paragraph, well justifies the extension of additivity principle of viscosity B (and, A) coefficients to mixtures of the type investigated in the present case.

TABLE 6—DERIVED QUANTITIES

Solution	B coefficient of fully dissociated acid $B_{H^+A^-} = B_{NaA} + B_{H_2O^+} - B_{Na^+}$	A coefficient of fully dissociated acid $A_{H^+A^-} = A_{NaA} + A_{HCl} - A_{NaCl}$	$B_{obs} = \left[\frac{\eta}{\eta_0} - 1 \right] / C$ $-\frac{1}{C^{3/2}} \left[\frac{C A_{HA} - C_{H^+}}{A_{H^+A^-} - A_{HA}} \right]$	$\alpha = \frac{B_{obs} - B_{HA}}{B_{H^+A^-} - B_{HA}}$	αpH
Acetic acid (0.1M)	0.165	0.0107	0.106	0.020	0.0158
Propionic acid (0.1M)	0.869	0.0067	0.108	0.017	0.0110

be of the same order of magnitude as the values (αpH) calculated from the pH of the weak acid solutions (6th column of Table 6). Furthermore, the relative strengths of these acids also turn out in the right order i.e., acetic > propionic from these viscosity experiments. The percent error in α in both the cases is about the same and in the same direction (error positive).

Taking into view the approximate nature of the treatment as well as the simplifying assumptions introduced at a number of steps to obtain the various A and B coefficients, it can be said with reason-

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NOTES

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Viscosity B Coefficient of Phenols and Benzyl Alcohol

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THE viscosity B coefficient of Jones-Dole's equation is known to be sensitive to the nature of solute-solvent interactions, i.e. it is related to the modification of micro-viscosity of the solvent in the neighbourhood of the solute particle as compared to the bulk viscosity. A structure-making solute is expected to have a positive B coefficient in the given solvent whereas a structure-breaker may have a less positive or altogether negative B coefficient¹. However, a large solute may always possess a positive B coefficient (irrespective of the nature of its interaction with the solvent) due to the "obstruction effect", i.e., a bending of the solvent streamlines round a large solute particle. The sign and magnitude of the temperature coefficient, $\frac{dB}{dT}$,

rather than B, therefore, often provides a better index of solute-solvent interactions. This observation is attributed to an increased thermal mobility of water molecules at higher temperatures which causes the structure-promotion by a solute more difficult (i.e., B is rendered less positive) so that $\frac{dB}{dT}$ becomes negative. A structure-breaker, on the other hand, exerts a less disruptive influence on the structure of the solvent (which is already broken) at an elevated temperature, and hence the corresponding $\frac{dB}{dT}$ is positive. These considerations are obviously independent of the size of the solute particle.

In the present study, viscosity B coefficient of phenol, resorcinol, *p*-cresol and benzyl alcohol has been determined in aqueous medium at temperatures 30, 35 and 40°. The magnitude and sign of $\frac{dB}{dT}$ at 35° is also ascertained for each solute. The B coefficients were obtained by having recourse to a graphical technique based on Jones-Dole's equation,

$$\text{namely, } \frac{\eta}{\eta_0} = 1 + A\sqrt{C} + BC \quad \dots (1)$$

where η_0 and η are the respective viscosity coefficients, at the same temperature, of pure water and the solution of molar concentration C, while A and B are empirical constants, sensitive to solute-solute interactions (Grüneisen effect) and solute-solvent interactions.

A rearrangement of eq. (1) leads to

$$\frac{\eta}{\eta_0} - 1 = A + B\sqrt{C} \quad \dots (2)$$

so that a plot of $\frac{\eta}{\eta_0} - 1$ vs \sqrt{C} gives a straight

line of slope B and intercept A.

An Ubbelohde type of viscometer with an average flow time of 502 sec for 10 ml of water (at 30°) was used for viscosity determinations. AnalaR grade materials, whenever available, have been used; otherwise, the purest grade available has been further purified. The solutions were prepared in deionised water of conductivity less than 3 μ mho cm^{-1} . The temperatures of study have been kept constant within $\pm 0.05^\circ$ by the use of a water thermostat provided with an electrical contact thermometer along with a solid-state relay unit.

The results have been entered in Table 1. That the B coefficient of phenol at lower temperatures (e.g. 30°) is higher than that of resorcinol, but lower than the value for *p*-cresol, is consistent with a corresponding change in the net content of hydrophobic (e.g. methyl) and hydrophilic (e.g. hydroxyl) groups in these compounds. An increase in the former (as in *p*-cresol) is expected to lead to an increase in the B coefficient in aqueous medium, due to structure-promotion in water through what is known as "hydrophobic hydration"². Resorcinol, with a higher content of structure-breaking hydroxyl groups, has the lowest B (at 30°). Aliphatic compounds, belonging to a particular homologous series (e.g. the carboxylates), also exhibit a similar increase in B coefficient with the lengthening of the hydrophobic carbon chain³. However, the B values for phenols are found, on comparison with those for aliphatic carboxylates, surprisingly small for six-carbon solutes (intermediate between the values for two- and three-carbon carboxylates³); this low contribution of a phenyl group may have arisen from the inability of water molecules to accommodate themselves inside the benzene ring for spatial restrictions. Such a partial loss of structure-making (i.e. "ordering") influence of methylene groups, induced by "aromaticity", is in line with the general higher water-solubilities of aromatic compounds as compared to the open-chain analogues, having the same number of carbon atoms (i.e., due to a lower "negentropy" effect of the aromatic compounds on water structure).

A positive $\frac{dB}{dT}$ at 35° for resorcinol, whereas the negative values for phenol and *p*-cresol (the latter having it more negative), are also in agreement with the generalisations made in the introductory

TABLE-1

Solution	Molar concentration/M (C)	Coefficient of viscosity of solution/cp, η at			B coefficient (slope of linear plot of $\frac{\eta - \eta_0}{\eta_0 \sqrt{C}}$ vs \sqrt{C}) at			$\frac{dB}{dT}$ at 35°
		30°	35°	40°	30°	35°	40°	
		Viscosity of water (η_0) at 30°=6.7975 cp 35°=6.7194 cp 40°=6.6529 cp		Density of water (ρ_0) at 30°=0.9956 g cm ⁻³ 35°=0.9940 g cm ⁻³ 40°=0.9922 g cm ⁻³				
Phenol	0.025	-	0.7235	0.6565	0.230	0.213	0.192	-0.0037
	0.05	0.8104	0.7280	0.6592				
	0.08	0.8177	0.7311	0.6627				
	0.10	0.8228	0.7348	0.6664				
	0.15	-	0.7432	0.6758				
	0.20	0.8434	-	-				
Resorcinol	0.05	0.7994	-	-	0.189	0.216	0.244	+0.0054
	0.05	0.8060	0.7288	0.6620				
	0.10	0.8140	0.7374	0.6706				
	0.15	-	0.7458	0.6786				
	0.20	-	0.7538	0.6867				
	0.25	-	0.7625	0.6954				
<i>p</i> -cresol	0.05	0.8503	-	-	0.366	0.326	0.295	-0.0065
	0.075	0.8081	0.7380	0.6683				
	0.10	0.8101	0.7432	0.6740				
	0.12	0.8163	0.7484	0.6797				
Benzyl alcohol	0.025	-	0.7244	0.6576	0.222	0.272	0.260	-
	0.05	-	0.7296	0.6626				
	0.075	0.8140	0.7345	0.6670				
	0.10	0.8200	0.7397	0.6712				
	0.15	0.8309	0.7512	0.6816				
	0.20	0.8406	-	-				
0.30	0.8529	-	-					

part. Consequent of these opposite signs of $\frac{dB}{dT}$, B of phenol, at a high enough temperature such as 40°, is rendered lower than that of resorcinol.

The B coefficient of benzyl alcohol, a molecular isomer of *p*-cresol, exhibits a somewhat erratic temperature-dependence (an increase in B with temperature followed by a small drop beyond 35°; the $\frac{dB}{dT}$ at 35° for benzyl alcohol is, therefore, not quoted in Table 1), eventhough the values are close to those for *p*-cresol. This perhaps results from a partial overlapping of the structure-making and structure-breaking spheres of influence of the hydrophobic methylene and hydrophilic hydroxy

groups, situated in close proximity in the side-chain, -CH₂OH, in benzyl alcohol. This gets a qualitative support from similar observations reported for the enthalpy of transfer of methanol from water to heavy water (as compared to that for higher alcohols)⁴, as well as the reported heats of transport of α -alanine and β -alanine in aqueous medium⁵.

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Viscosity B coefficients of Alkyl Carboxylates

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ABSTRACT

Viscosity B coefficients of aqueous solutions of sodium carboxylates namely sodium formate, acetate, propionate, n - butyrate, n - pentanoate, and trichloroacetate have been determined at 30°C, 35°C and 40°C by studying the relative viscosity of these solutions and the subsequent use of Jones - Dole's equation. The temperature coefficient dB/dT , for each solution has also been obtained graphically from these data. The results have been interpreted in terms of the effect on "local" structure of water of these largely hydrophobic solutes. An attempt has been made, in this context, to correlate the B coefficient with the corresponding heat of transport, a thermal diffusion parameter.

I. INTRODUCTION :

In an attempt to elucidate the effect of alkyl carboxylates on structure of water, the viscosity B-coefficients of the former in aqueous solutions have been measured at a number of temperatures between 30°C and 40°C, and the sign and magnitude of the temperature coefficient, dB/dT , is also ascertained. The latter, it may be noted in passing, is often regarded as a better (or, at least a supplementary) index of structure - making or-breaking ability of a large solute than the corresponding B coefficient itself owing to the "obstruction effect" of the solute¹.

It has been recently pointed out² that the viscosity B coefficient, as an index of solute - solvent interactions, is analogous to the corresponding heat of transport, \hat{Q} , a quantity introduced by thermodynamics of thermal diffusion³. The latter is directly related to the "local" changes in entropy density of the solvent, brought about by the presence of a solute in its neighbourhood as compared to that at infinite distance. Hence, the analogy between B and \hat{Q} .

II. EXPERIMENTAL METHODS :

The solutes of the present study have been the organic electrolytes such as the sodium salts of formic, acetic, propionic, n-butyric, n-pentanoic and trichloroacetic acids. Except for the acetate, which is readily available commercially, the other salts have been prepared in the laboratory from the pure acids and anhydrous Na_2CO_3 and then purified by crystallisation (twice) from water.

The B coefficients at 30°C, 35°C, 40°C ($\pm 0.05^\circ\text{C}$ in each case) were determined by having recourse to a graphical technique based on Jones Dole's equation⁴, i.e., by plotting η_{sp} / \sqrt{C} against \sqrt{C} , and noting B from the slope of such linear plots. The intercept on the Y-axis gives the corresponding A coefficients (not recorded in table 1).

A suspended level Ubbelohde type (three necked, all-glass) viscometer was used for viscosity experiments. It was fitted in the thermostatic bath in reproducible positions with metallic holders to ensure verticality. The viscometer was exhaustively cleaned and rinsed with filtered solvents. The average flow-time for water(10 ml.) through the capillary of the viscometer was 502 ± 0.1 sec. (at 30°C). The accuracy of the viscosity and relative viscosity determinations has also been ascertained and the proportional error was found to lie within $\pm 0.15 - 0.20$ %.

The densities of the solutions were measured by means of specific gravity bottle, taking care to fill the bottle at the appropriate temperature (of the experiment), by placing the same in a water thermostat and allowing sufficient time for attainment of thermal equilibrium, and then taking the weight quickly.

III. RESULTS :

Table 1 records the viscosity B coefficients at different temperatures as well as the corresponding

temperature coefficients, dB/dT . The B coefficients are obtained, as mentioned above, from the slopes of the (least - square) best fit linear plots of η_{sp}/\sqrt{C} vs. \sqrt{C} . The corresponding dB/dT values are also calculated in a similar way i.e., from the slope of the best fit line for the plot of B vs. T assuming a linear variation of B with temperature. With the appropriate treatment of errors, the standard deviations (not recorded in table 1) for each B and dB/dT were calculated and the confidence limits at 95% confidence were found out, using these standard deviations, and given in parenthesis below each B and dB/dT .

The heat of transport (\hat{Q}) values for the present solutes in aqueous solutions, wherever available from literature³, have also been recorded in the last column of table 1 for the purpose of correlation between viscosity and thermal diffusion parameters of the solutes studied.

Table - 1

Solution	B coefficient (slope of best fit line for the plot of η_{sp}/\sqrt{C} vs. \sqrt{C} , $\eta_{sp} = \frac{\eta - \eta_0}{C}$)			dB/dT (slope of best fit line for the plot of B vs. T)	\hat{Q} / K.J. mol ⁻¹ in 0.01 m aqueous solution taken from literature ³ at 25°C
	30°C	35°C	40°C		
Sodium formate	0.191 (± 0.029)	0.199 (± 0.012)	0.209 (± 0.021)	+ 0.0018 (± 4.5 x 10 ⁻⁴)	-
Sodium acetate	0.187 (± 0.017)	0.186 (± 0.021)	0.178 (± 0.021)	-	8.73
Sodium propionate	0.393 (± 0.026)	0.370 (± 0.023)	0.345 (± 0.014)	- 0.0048 (± 6.4 x 10 ⁻⁴)	10.50
Sodium n-butyrate	0.503 (± 0.013)	0.426 (± 0.042)	0.397 (± 0.046)	- 0.0106 (± 3.0 x 10 ⁻³)	11.71
Sodium n-pentanoate	0.606 (± 0.048)	0.530 (± 0.052)	0.455 (± 0.049)	- 0.0151 (± 3.3 x 10 ⁻³)	13.48 *
Sodium tri-chloroacetate	0.553 (± 0.037)	0.596 (± 0.021)	0.670 (± 0.018)	+ 0.0117 (± 4.3 x 10 ⁻³)	11.84

* (The value is for the 5 - carbon carboxylate, sodium neopentanoate)

IV. DISCUSSION :

Among the sodium salts of the simple carboxylic acids, a regular increase in viscosity B coefficient, especially at lower temperatures such as 30°C, is observed with molecular weight and hence size of the solute (vide. column 2 of table 1). This is consistent with the structure forming effect of the hydrophobic methylene group, and the general observation that the structure promotion in water is directly correlated with the length of the carbon chain \bar{l} of the solute^{5,6}. Some irregularity exhibited by the acetate (B being less than B of both formate and propionate) may well be due to a partial overlapping of the spheres of influence on water structure of the hydrophobic methyl and the hydrophilic carboxylate groups, situated in close proximity in acetate. This gets a qualitative support from similar observations reported for the enthalpy of transfer of methanol from water to heavy water (as compared to that for higher alcohols)⁵, as well as the reported heats of transport of α - alanine and β - alanine in aqueous medium⁷.

On inspection of dB/dT values (column 5 of table 1), this trend becomes even more clear. Whereas it is positive for the formate (a net structure - breaker), the acetate has almost a zero temperature coefficient in the temperature range 30 - 35°C (beyond which a small fall with temperature is observed, such rather erratic variations in B with temperature for the

acetate promoted us not to quote the corresponding dB/dT in table 1), and dB/dT becomes progressively more negative (which is indicative of a greater structure - promoting ability) as one moves on to n - pentanoate through propionate and butyrate. The earlier contention that dB/dT is a better criterion than B to characterise the effect of solute on the solvent structure, gets a support from the results obtained for the trichloroacetate. Thus, the very considerable increase in B from acetate to trichloroacetate at all temperatures investigated may well have arisen from a concomitant increase in the size of the solute, i.e., from the "obstruction effect" of the solute as mentioned above, even though the corresponding dB/dT is seen to be positive (column 5 of table 1) ; the trichloroacetate, therefore, appears to be a net structure - breaker in water. This is in agreement with the known structure - disruptive influence of the chlorine groups in aqueous solutions³.

A direct correlation between the heat of transport, \hat{Q} values (at 25°C), and the B coefficients, obtained at any given temperature, say 30°C, of the sodium carboxylates (vide. columns 2 and 6 of table 1) corroborates what has been said above regarding these parameters as measures of the nature of solute - solvent ("local") interactions.

The results obtained in this study, and explained as above, add to the evidence in favour of the theory of hydrophobic hydration in aqueous solutions of these largely hydrophobic (mixed) solutes^{3,8}.

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