
PART 2

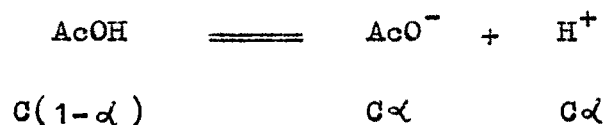
EXTENSION OF THE PRINCIPLE OF ADDITIVITY OF
VISCOSITY B COEFFICIENTS TO MIXTURES OF WEAK
ACIDS AND THEIR SALTS

2.1 INTRODUCTION

In this part, the validity of the principle of additivity of viscosity B coefficients in the mixtures of weak acids and their salts has been examined. It is rather well established that the viscosity B coefficients of the Jones-Dole's equation are additive, as already mentioned earlier in part 1 (section 1.1 and 1.2), 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 equations have been proposed, 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 the direct pH measurements conducted on such acid solutions. A satisfactory agreement between these values of α is 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.

2.2 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. Thus,



Assuming additivity of 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 .

$$\text{Therefore, } B_{\text{obs}} = (1-\alpha) B_{\text{AcOH}} + \alpha B_{\text{AcO}^- \text{H}^+} \quad (2.2.1),$$

$B_{\text{AcO}^- \text{H}^+}$ 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 by,

$$A_{\text{obs}} = (1-\alpha) A_{\text{AcOH}} + \alpha A_{\text{AcO}^- \text{H}^+} \quad (2.2.2)$$

It is interesting to note from eqs. 2.2.1 and 2.2.2 that at infinite dilution $\alpha = 1.0$ and therefore, $B_{\text{obs}} = B_{\text{AcO}^- \text{H}^+}$ and $A_{\text{obs}} = A_{\text{AcO}^- \text{H}^+}$, which one would expect. Hence, eqs. 2.2.1 and 2.2.2. are consistent.

By rearrangement of eq. 2.2.1, we obtain,

$$\alpha = \frac{B_{\text{obs}} - B_{\text{AcOH}}}{B_{\text{AcO}^- \text{H}^+} - B_{\text{AcOH}}} \quad (2.2.3)$$

so that α , the degree of dissociation at a concentration C ,

can be derived from the measured viscosity B coefficient of the acetic acid solution, B_{obs} , at the same concentration provided that the B coefficients of the "fully dissociated" acetic acid ($B_{AcO^-H^+}$) and the undissociated acid (B_{AcOH}) are known. For the general case of weak acid, HA, and its salt eq. 2.2.3 reads,

$$\alpha = \frac{B_{obs} - B_{HA}}{B_{H^+A^-} - B_{HA}} \quad (2.2.3a)$$

$B_{AcO^-H^+}$ is calculated by adding up B_{H^+} and B_{AcO^-} ; the latter are derived from viscosity studies on solution 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 0.1 M) and different stoichiometric concentrations of acetic acid (say, 0.05 M, 0.075 M, 0.1 M and 0.15M). With the above mentioned supposition that acetic acid at these concentrations

is fully undissociated* in presence of 0.1(M) sodium acetate, one would obtain from the Jones-Dole's equation,

$$\frac{\eta}{\eta_0} = 1 + [A] \sqrt{C} + [B] \cdot C + \dots \quad (2.2.4)$$

in which [A] and [B] are composite quantities, given by

$$[A] = A_{\text{AcOH}} + A_{\text{NaOAc}} \quad (2.2.5)$$

$$[B] = B_{\text{AcOH}} + B_{\text{NaOAc}} \quad (2.2.6)$$

while η and η_0 are the viscosity coefficients at the same temperature of the mixture of acetate and acetic acid, having a mean

* Taking the dissociation constant (K_a) of acetic acid at 25°C to be 1.8×10^{-5} , it follows for the ionisation equilibrium in a 0.1 M acetic acid solution which is also 0.1 M with respect to an acetate that

$$\begin{aligned} 1.8 \times 10^{-5} &= \frac{C_{\text{H}^+} \cdot C_{\text{OAc}^-}}{C_{\text{AcOH}}} \\ &= \frac{0.1x (0.1 + 0.1x)}{0.1(1-x)} = \frac{0.01x (1+x)}{0.1(1-x)} \end{aligned}$$

where x is the equilibrium degree of dissociation of the acid

$$\text{or, } 1.8 \times 10^{-5}(1-x) = 0.1x(1+x)$$

$$\text{or, } 0.1x(1 + 1.8 \times 10^{-5} + x) = 1.8 \times 10^{-5}$$

$$\text{or, } 0.1x(1 + x) \cong 1.8 \times 10^{-5}$$

whence, $x \cong 0$, i.e., $C_{\text{AcOH}} \cong 0.1 \text{ M}$, i.e., acetic acid is

practically undissociated in presence of 0.1M AcONa.

(molar) concentration C , and of water, respectively.

On obtaining $[A]$ and $[B]$ from the intercept^{and}/slope respectively of the (least-square) best fit plot of $(\frac{\eta}{\eta_0} - 1)/\sqrt{C}$ vs. \sqrt{C} (vide. eq.2.2.4), A_{AcOH} and B_{AcOH} are derived, using eqs.2.2.5 and 2.2.6, and with a knowledge of A_{NaOAc} and B_{NaOAc} from independent experiments on acetate solutions.

To calculate α according to eq.(2.2.3), 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

$$B_{obs} C + A_{obs} \sqrt{C} = \frac{\eta}{\eta_0} - 1 \quad (2.2.7)$$

where B_{obs} and A_{obs} are given by eqs. 2.2.1 and 2.2.2. On substituting A_{obs} from eq.2.2.2 in eq.2.2.7 one obtains

$$\frac{\eta}{\eta_0} - 1 = B_{obs} C + [(1-\alpha)A_{AcOH} + \alpha A_{AcO^{-}H^{+}}] \sqrt{C}$$

which, on rearrangement, becomes

$$B_{obs} = \frac{(\frac{\eta}{\eta_0} - 1)}{C} - \frac{1}{C^{3/2}} [C A_{AcOH} - C \alpha A_{AcOH} + C \alpha A_{AcO^{-}H^{+}}] \dots \quad (2.2.8)$$

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

$$B_{obs} = \frac{(\frac{\eta}{\eta_0} - 1)}{C} - \frac{1}{C^{3/2}} [C A_{AcOH} + C_{H^+}(A_{AcO^{-}H^{+}} - A_{AcOH})] \dots \quad (2.2.9)$$

Thus, B_{obs} is obtained from eq. 2.2.9 with a knowledge of A_{AcOH} and $A_{AcO^{-}H^{+}}$ ($A_{AcO^{-}H^{+}}$ is given as $A_{NaOAc} + A_{HCl} - A_{NaCl}$),

and pH (i.e., C_{H^+}) of the given solution of acetic acid.

Equation 2.2.9 may be rewritten as

$$B_{\text{obs}} c^{3/2} = \sqrt{c} \left(\frac{\eta}{\eta_0} - 1 \right) - \left[c A_{\text{AcOH}} + C_{H^+} (A_{\text{AcO}^-H^+} - A_{\text{AcOH}}) \right] \dots (2.2.10)$$

On inspection of eq.2.2.10 it is clear that at infinite dilution ($C = 0$, $C_{H^+} = C\alpha = 0$), $\alpha = 1.0$ and $\eta = \eta_0$. On such substitutions in eq. 2.2.10, both sides of the latter vanish. Hence eq.2.2.10 is also consistent.

On substituting the values of B_{AcOH} , $B_{\text{AcO}^-H^+}$ and B_{obs} , determined as described above, in eq.2.2.3 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.

2.3 EXPERIMENTAL DETAILS

The same type of viscometers, water thermostat etc., as described in section 1.3 of part 1, have been used for the present investigation.

The chemicals used, namely glacial acetic acid, propionic acid, hydrochloric acid and sodium acetate etc., 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 double distilled water of conductivity less than $3 \mu \text{ mho.cm}^{-1}$. An electrical balance, reading upto 10 μg , was used for recording weights in the preparation of solutions and measurements of density (by using a specific

gravity bottle).

The details of the experimental steps to obtain α from viscosity measurements are as follows :

(i) The viscosity B coefficients of sodium acetate and sodium propionate, determined earlier in part 1 by noting the times of flow at a number of concentrations, ranging from 0.05 to 0.5 M of each of these solutions, as well as that of water, all at 30°C, and then having recourse to the graphical plot, as mentioned (vide. eq.2.2.4), were used in the present case. The viscosity A coefficients of these compounds were also noted from the intercepts of the plots.

(ii) A series of mixtures, which were 0.1 M with respect to NaOAc and successively 0.05 M, 0.075 M, 0.1 M and 0.15 M with respect to acetic acid, were prepared and the composite constants [A] and [B] (vide. eqs.2.2.5 and 2.2.6) were determined in the same manner as above (acetic acid was considered fully undissociated in these mixtures).

(iii) From (i) and (ii), A_{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 A_{NaOAc} from (i), and noting A_{NaCl} from the literature¹, $A_{\text{AcO}^- \text{H}^+}$ was calculated from the relation,

$$A_{\text{AcO}^- \text{H}^+} = A_{\text{NaOAc}} + A_{\text{HCl}} - A_{\text{NaCl}}$$

$A_{\text{H}^+ \text{A}^-}$ for propionic acid was also calculated in the same manner.

(vi) $B_{\text{AcO}^- \text{H}^+}$ was obtained as $(B_{\text{H}^+} + B_{\text{NaOAc}} - B_{\text{Na}^+})$ 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 0.1 M acetic acid solution (and of 0.1 M propionic acid), and then using eq.2.2.9 in which the values of A_{AcOH} and $A_{\text{AcO}^- \text{H}^+}$, as obtained above, were used.

(viii) The degree of dissociation α was finally calculated, by using eq.2.2.3 from the values of B_{obs} , B_{AcOH} and $B_{\text{AcO}^- \text{H}^+}$. The α so obtained was compared with the value derived from the measured pH of 0.1 M acid solution.

2.4 RESULTS

A synopsis of results has been given in tables, 2.4.1 to 2.4.6, 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 2.4.6). The corresponding α obtained from the direct pH measurements (say, α_{pH}) is also included in the same table for the purpose of comparison.

[†] The measured A and B coefficients (and hence α values) as reported here, slightly differ from the values in the published paper enclosed in the thesis (vide. J. Indian Chem. Soc., 1981, 58, 1051), because the data reported here are obtained from the slopes and intercept of the (least-square) best-fit lines, whereas the published values refer to the eye-approximate plots.

TABLE 2.4.1

Temperature = 30°C

Viscosity of water (η_0) at 30°C = 0.7975 cp

Density of water (ρ_0) at 30°C = 0.9956 g.ml⁻¹

Solution	Molar Concentration C/M	Coefficient of Viscosity of solution η /cp	B coefficient (slope of the best fit line for the plot of η_{sp}/\sqrt{C} vs. \sqrt{C})/lit.mol ⁻¹
Sodium acetate	0.10	0.8131	
	0.20	0.8303	
	0.30	0.8494	0.1870 (B ₁)
	0.40	0.8670	
	0.50	0.8877	
Sodium propionate	0.10	0.8284	
	0.20	0.8613	
	0.25	0.8776	0.3930 (B ₂)
	0.30	0.8957	
	0.40	0.9311	
Hydrochloric acid	0.20	0.8042	
	0.40	0.8146	0.063
	0.60	0.8228	(not used
	0.80	0.8338	elsewhere)
	1.00	0.8416	

Table 2.4.1 (Contd.)

Solution	C/M Mean molar concentration	η/c_p	B coefficient/ lit.mol ⁻¹
Sodium acetate (0.1M)+Acetic acid (undisso- ciated)	0.0650	0.8215	Composite B
	0.0750	0.8258	coefficient
	0.1000	0.8316	[B ₁]
	0.1250	0.8381	0.2832
Sodium propionate (0.1M) + propionic acid (undissociated)	0.0625	0.8298	Composite B
	0.0750	0.8345	coefficient
	0.1000	0.8458	[B ₂]
	0.1250	0.8563	0.4850

TABLE 2.4.2

Solution	B coefficient	A coefficient
Sodium acetate	0.1870 (B ₁)	0.010 (A ₁)
Sodium propionate	0.3930 (B ₂)	0.006 (A ₂)
Hydrochloric acid	0.063 (not used elsewhere)	0.005

TABLE 2.4.3

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

TABLE 2.4.4

Solution	Composite B coefficient $[B_1]$ and $[B_2]$	Composite A coefficient $[A_1]$ and $[A_2]$	B coefficient of undissociated acid $B_{HA} = [B_1] - (B_1)$ and $B_{HA} = [B_2] - (B_2)$	A coefficient of undissociated acid $A_{HA} = [A_1] - (A_1)$ and $A_{HA} = [A_2] - (A_2)$
Acetic acid + Sodium acetate	0.2832	0.043	0.0962	0.033
Propionic acid + Sodium propionate	0.4850	0.047	0.092	0.041

TABLE 2.4.5

Solution / Ion	B coefficient	A coefficient	Reference
H_3O^+	0.0709	-	2
Na^+	0.0859	-	2
$NaCl$	0.0793	0.0062	1

TABLE 2.4.6

Solution	$B_{H^+A^-}$ $= B_{NaA} + B_{H_3O^+} - B_{Na^+}$	$A_{H^+A^-}$ $= A_{NaA} + A_{HCl} - A_{NaCl}$	B_{obs}	α	d_{pH}
Acetic acid (0.1M)	0.172	0.0088	0.0977	0.0197	0.0158
Propionic acid (0.1M)	0.378	0.0048	0.0962	0.0150	0.0110

2.5 DISCUSSION

The degree of dissociation for both acetic and propionic acids, as obtained from the present viscosity studies, is seen from table 2.4.6 (5th column) to be of the same order of magnitude as the values (α_{pH}) calculated from the pH of the weak acid solutions (6th column of table 2.4.6). 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 reasonable satisfaction that the kind of agreement in α values, as elaborated in the preceding paragraphs, well justifies the extension of the additivity principle of viscosity B (and, A) coefficients to mixtures of the type investigated in the present case.

2.6 REFERENCES

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