

## SHORT COMMUNICATIONS

### STUDY OF MOLECULAR ASSOCIATION OF LIQUIDS BY THE APPLICATION OF THE MODIFIED LAW OF CORRESPONDING STATES

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THE law of corresponding states has been applied to the ultrasonic properties of liquids<sup>1,2</sup> and it is now established that this law is applicable to all liquids irrespective of their belonging to homologous series<sup>3</sup> or not. It has been shown that the reduced ultrasonic velocity ( $C/C_c$ ) depends more on the reduced density ( $\rho/\rho_c$ ) than on reduced temperature ( $T/T_c$ ). However, Nozdrev<sup>4</sup> connected the reduced velocity to the parameter ( $T/T_c$ ), whose contribution is much less than that of ( $\rho/\rho_c$ ) or ( $V_c/V$ ). As such, neglecting ( $T/T_c$ ) and taking ( $V_c/V$ ) alone into account, the law of corresponding states has been suitably modified and reported in a recent communication<sup>5</sup>.

The modified law of corresponding states is now extended to the study of association in liquids. Starting from the familiar equation<sup>6</sup> of Belinskaya.

$$\frac{MC^2}{T_c} = \frac{5}{3} \times \frac{RT}{T_c} + \frac{R}{v-\mu} \left[ \mu \left( \frac{V_c}{V} \right)^v - v \left( \frac{V_c}{V} \right)^\mu \right], \quad (1)$$

where all the terms have their usual significance. Equation (1) shows that  $MC^2/T_c$  is the sum of two terms.

The contribution of each term in the above expression is evaluated for all the eight liquids chosen and presented in the table. The value of the first term is shown in 3rd column and that of the second term in 4th column of table 1. A comparison of the two columns shows that the contribution of the first term is only about 0.2% of the second term in many liquids and about 0.5% in acetic acid. As such, the first term can be neglected in the range of temperatures studied and (1) is written as

$$\frac{MC^2}{T_c} = \frac{R}{v-\mu} \left[ \mu \left( \frac{V_c}{V} \right)^v - v \left( \frac{V_c}{V} \right)^\mu \right], \quad (2)$$

Putting  $v=6$  and  $\mu=2$ , valid for many liquids<sup>7</sup> and approaching the limits  $T/T_c=1$  and  $V_c/V=1$ , the ultrasonic velocity reaching its value  $C_c$  at critical temperature  $T_c$ , equation (1) further reduces to

$$\frac{MC_c^2}{T_c} = \frac{2}{3} R. \quad (3)$$

A plot of  $(MC^2/T_c)$  against  $(V_c/V)$  for each liquid is shown in figure 1. The velocities are determined by composite ultrasonic interferometer<sup>8</sup> and the densities by hydrostatic bench method<sup>9</sup>.

Since  $(MC^2/T_c)$  attains a constant value of  $(2/3 R)$  at critical temperature, all the curves, when extrapolated, merge at  $V_c/V=1$ .

#### Association factor

Association factor  $x$  for each liquid is determined by using the relation

$$\left[ \frac{(xM')C^2}{T_c} \right]_A = \left[ \frac{MC^2}{T_c} \right]_N, \quad (4)$$

where  $M'$  is the molecular weight of the associated liquid and  $M$  is that of the normal liquid. The association factor  $x$  can be written as

$$x = \left[ \frac{MC^2}{T_c} \right]_N / \left[ \frac{M'C^2}{T_c} \right]_A, \quad (5)$$

where the suffixes  $N$  and  $A$  refer to the normal and associated liquids. Here, Benzene is taken as the reference normal liquid. The velocity data for Benzene is taken from ref. 10. The values of  $(MC^2/T_c)$  evaluated for Benzene are shown in 5th column of the table for ready reference.

The association factors of all the liquids are evaluated from (5) at a common temperature and shown in 6th column of the table. Formic acid has the highest association factor, while propionic acid has the least.

Acetic acid is known as dimer with association factor of two, while formic acid is a complex molecule with association factor of four. The very high value of  $x$  for formic acid shows that its molecular aggregation is complex and this view is also su-

Table 1 Values of different terms in expression (1)

1	2	3	4	5	6
Formic acid					
0.423	3.267	5 860	5004	1125	
0.443	3.229	6 137	4578	1048	4.528
0.456	3.208	6.317	4522	1000	
0.473	3.181	6.553	4179	938	
0.485	3.157	6.719	3990	898	
Acetic acid					
0.510	2.965	7.065	2716	1237	
0.526	2.928	7.287	2510	1155	2.185
0.543	2.897	7.522	2350	1079	
0.560	2.860	7.758	2172	1002	
0.577	2.836	7.993	2061	929	
0.611	2.764	8.464	1756	790	
Propionic acid					
0.495	3.070	6.857	3364	1596	
0.511	3.040	7.079	3165	1498	
0.528	3.007	7.315	2959	1400	2.118
0.544	2.975	7.536	2770	1309	
0.560	2.945	7.758	2600	1223	
0.593	2.872	8.215	2228	1052	
<i>n</i> -Butyric acid					
0.482	3.126	6.677	3757	1963	
0.498	3.091	6.899	3508	1844	
0.514	3.069	7.121	3358	1738	
0.530	3.033	7.3	3119	1628	1.936
0.546	3.006	7.564	2953	1525	
0.578	2.927	8.007	2504	1326	
<i>n</i> -Valeric acid					
0.464	3.186	6.428	4216	2321	
0.480	3.158	6.650	4000	2183	1.839
0.496	3.128	6.871	3767	2052	
0.510	3.091	7.065	3508	1932	
0.526	3.071	7.287	3368	1815	
0.542	3.029	7.509	3098	1692	
0.557	2.988	7.716	2849	1584	
Caprylic acid					
0.447	3.222	6.192	4552	3529	
0.461	3.197	6.386	4312	3355	1.294
0.476	3.172	6.594	4106	3178	
0.491	3.144	6.802	3890	3002	
0.506	3.117	7.010	3691	2835	
0.521	3.082	7.218	3441	2668	
Pelargonic acid					
0.441	3.233	6.109	4107	3933	
0.456	3.209	6.317	4412	3724	1.163
0.471	3.171	6.525	4100	3530	
0.485	3.150	6.719	3934	3347	
0.500	3.129	6.927	3780	3163	
0.514	3.085	7.121	3464	2986	
0.529	3.060	7.301	3298	2817	
Capric acid					
0.439	3.234	6.082	4628	4301	
0.449	3.220	6.220	4505	4150	
0.463	3.191	6.414	4266	3951	1.081
0.477	3.165	6.608	4050	3745	
0.491	3.144	6.802	3890	3562	
0.506	3.103	7.010	3591	3359	
0.521	3.077	7.218	3408	3165	

Table 1 (Contd.)

1	2	3	4	5	6
Benzene					
0.486	2.957	6.736	2670	3088	
0.504	2.924	6.980	2492	2761	1.0
0.522	2.891	7.236	2323	2490	
0.539	2.855	7.471	2150	2261	
0.557	2.819	7.721	1987	2101	
0.575	2.783	7.970	1835	1950	

$$1. T/T_c; \quad 2. V_c/V; \quad 3. \frac{5 RT}{3 T_c}$$

$$4. \frac{R}{(v-\mu)} \left[ \mu \left( \frac{V_c}{V} \right)^v - v \left( \frac{V_c}{V} \right)^\mu \right]; \quad 5. \frac{MC^2}{T_c};$$

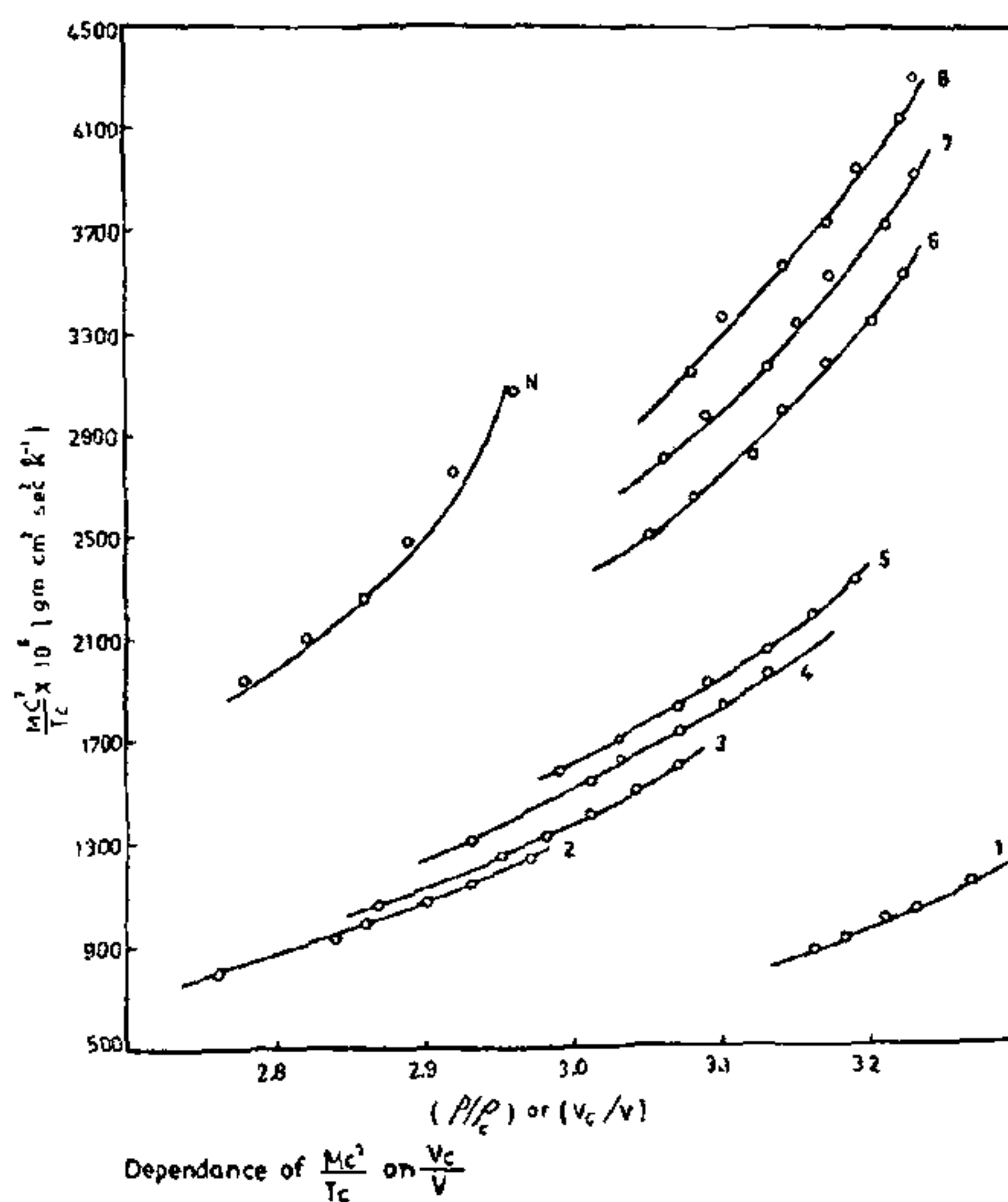
6.  $x$ .

Figure 1. Dependence of  $MC^2/T_c$  on  $V_c/V$ . [1. Formic acid; 2. Acetic acid; 3. Propionic acid; 4. *n*-butyric acid; 5. *n*-valeric acid; 6. Caprylic acid; 7. Pelargonic acid; 8. Capric acid; 9. Benzene].

ported by Millikan and Pitzer<sup>11</sup> from his spectroscopic studies. The gradual decrease in the value of  $x$  with molecular weight of the higher members of the fatty acids may be attributed to the gradual weakening of the hydrogen bond with increased length of

the molecular chain. The association factors evaluated here are in general agreement with those reported earlier.

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## SYNTHESIS OF 5,6-DIHYDROXY-7,4'-DIMETHOXYFLAVONE BY TRANSACYLATION METHOD

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In continuation of our work on the synthesis of partial methyl ethers of flavones<sup>1</sup> by transacylation method, we now report here the synthesis of 5,6-dihydroxy-7,4'-dimethoxyflavone (I) from the readily accessible scutellarein (5,6,7,4'-tetrahydroxyflavone) (II) by transacylation method<sup>2</sup>. The flavone, I, had earlier been synthesised<sup>3</sup> by Allan-Robinson method and known to occur in *Nepeta hindustana*<sup>4</sup>, *Galeopsis ladanum*<sup>5</sup> and as 6-glucoside in the seeds of

*Catalpa ovata*<sup>6</sup> and in the leaves of *Angelonia grandiflora*<sup>7</sup>.

Scutellarein<sup>8</sup> (II) was fully benzoylated and the tetrabenzoylscutellarein (III) on reaction with two mols of dry phenol in the presence of silver carbonate and pyridine yielded 5,6-dibenzoyloxy-7,4'-dihydroxyflavone (IV). Methylation of IV with an ethereal solution of diazomethane afforded 5,6-dibenzoyloxy-7,4'-dimethoxyflavone (V), which on saponification yielded I. The synthetic product was identical with natural I (melting point, colour reactions and spectral data<sup>7</sup>) and the identity confirmed by direct comparison (co-PC) with an authentic sample from *Angelonia grandiflora*<sup>7</sup>.

### 5,6-Dibenzoyloxy-7,4'-dihydroxyflavone (IV)

5,6,7,4'-Tetrabenzoxyflavone (tetrabenzoylscutellarein) (III) (3 g), silver carbonate (1 g), phenol (0.75 ml) and dry pyridine (15 ml) were stirred for 3 h with exclusion of light and moisture at room temperature. The reaction mixture was treated with perchloric acid (20%, 100 ml) and the product IV crystallised from acetone-methanol, (1.8 g), m.p. 256–57°. It gave no ferric colour; UV (MeOH): 275, 333, 374 sh nm; + NaOAc: 277, 370 nm; + NaOMe: 275, 390 nm; + AlCl<sub>3</sub>: 287, 333, 374 sh nm; IR (KBr): 3320 (br), 1730, 1650, 1600, 1370, 1260, 1220, 1100, 1080, 1060, 820 and 700 cm<sup>-1</sup>.

### 5,6-Dibenzoyloxy-7,4'-dimethoxyflavone (V)

To an ether solution of compound IV (1.5 g), an excess of ethereal solution of diazomethane was added and 5,6-dibenzoyloxy-7,4'-dimethoxyflavone (V) crystallised from methanol as pale brown powder (1 g), m.p. 238–39° (d), IR (KBr): 3010, 2900, 1730, 1650, 1600, 1490, 1440, 1350, 1290, 1190, 1110, 1060, 1010 and 830 cm<sup>-1</sup>.

### 5,6-Dihydroxy-7,4'-dimethoxyflavone (I)

Saponification of V with sodium methoxide afforded I, which crystallised from methanol-acetone as pale yellow needles, (0.1 g), m.p. 213–14° (lit<sup>7</sup>, 214–15°). It gave a positive ferric colour, green colour with sodium hydroxide, and was purple under UV and UV/NH<sub>3</sub>; UV (MeOH): 270, 330 nm; + NaOAc: 270, 332 nm; + NaOMe: 275, 330 nm; + AlCl<sub>3</sub>: 277, 304, 370 nm; IR (KBr): 3220, 2910,