

TABLE 1 — HEATS OF FORMATION OF SOME ORGANIC COMPOUNDS

Compounds	Bond energy (eV)	$\Delta H_f$ (eV)	
		Cal.	Exptl
Cycl[3.2.2]azine	27.01	103.72	—
Cycl[3.3.3]azine	7.49	100.44	—
Cycl[4.4.3]azine	61.99	171.17	—
Pyridine	9.29	52.04	52.00
Aniline	18.74	65.99	65.94
Pteridine	20.03	72.06	—
Thiophene	5.58	39.90	38.53
1,4-Dithiazine	4.66	41.21	—
Benzoic acid	11.99	75.44	75.70
Fluorobenzene	6.73	56.70	57.80
Chlorobenzene	6.96	54.72	—

Where  $q_r$  is the electronic charge at an atom  $r$ ,  $p_{rs}$  is the bond-order between atoms  $r$  and  $s$  and  $\omega$  is an empirical parameter. In literature the proposed value of the parameter  $\omega$  ranges from 0.33 to 1.8. The empirically adjusted parameter  $\beta$  has been assigned a value of 1.5. The  $\sigma$ -bond energy ( $E_{\sigma b}$ ) may be evaluated using Eq. 3.

$$E_{\sigma b} = N_C E_C + N_H E_H + N_X E_X \quad \dots(3)$$

where  $N_C$ ,  $N_H$  and  $N_X$  are the number of C-C, C-H and C-X bonds respectively in the given compound, and X represents the heteromolecule.  $E_H$ ,  $E_C$  and  $E_X$  are the respective bond energies of C-H, C-C and C-X bonds. Bond energy values of  $E_H = 4.43$ ,  $E_N = 2.9$ ,  $E_S = 3.29$ ,  $E_{Cl} = 3.41$ ,  $E_F = 5.62$  and  $E_O = 7.7$  eV are well established<sup>7</sup>. The value of  $E_C = 3.7$  eV has been empirically adjusted which is very close to the value 3.80 used by Dewar<sup>8</sup>.

Although the experimental values of heats of formation of cycl[3.2.2]azine, cycl[3.3.3]azine and cycl[4.4.3]azine are not available, the values calculated in the present study seem to be correct as the calculated heats of formation of pyridine, aniline, thiophene, benzoic acid and fluorobenzene, for which the experimental data are available, are in fairly good agreement (Table 1). The experimental values of heats of formation have been obtained from corresponding heats of combustion using the Born-Haber cycle.

The electronic charge and bond-order data of all the compounds have been taken from the literature<sup>9-14</sup>. The results obtained clearly indicate that the simplified form of IOC- $\omega$ -technique is quite satisfactory for calculating the heats of formation of organic compounds.

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### Viscosities of Binary Liquid Mixtures of 1-Propanol, 1-Butanol, 1-Pentanol & 1-Hexanol with Methylcyclohexane, Cyclopentanone & Cyclohexanone

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Viscosities of twelve binary liquid mixtures of 1-propanol, 1-butanol, 1-pentanol and 1-hexanol with methylcyclohexane, cyclopentanone and cyclohexanone, have been determined at 30° and data analysed on the basis of viscosity-composition relations formulated by Grunberg and Nissan and Katti and Chaudhri. The analysis showed that the two equations are not applicable to the mixtures studied.

IN continuation of earlier work<sup>1</sup>, on viscosities of binary liquid mixtures, made up of one associated component and another non-associated component, we report in this note viscosities of twelve binary liquid mixtures at 30° ± 0.1°. 1-Propanol, 1-butanol, 1-pentanol and 1-hexanol constituted the associated components while methylcyclohexane, cyclopentanone and cyclohexanone formed the non-associated components. The results have been analysed on the basis of the relations developed for non-ideal liquid mixtures by Grunberg and Nissan<sup>2</sup> relation (1).

$$\eta = X_1 \eta_1 + X_2 \eta_2 + X_1 X_2 d \quad \dots(1)$$

and by Katti and Chaudhri<sup>3</sup> using Reed and Taylor equation for ideal solutions<sup>4</sup> relation (2).

$$\ln \eta_s V_s = X_1 \ln \eta_1 V_1 + X_2 \ln \eta_2 V_2 + \frac{W_{\text{visc}}}{RT} \quad \dots(2)$$

The liquids were purified by the methods described earlier<sup>5-7</sup>. Viscosities of pure liquids and of mixtures at 30° ± 0.01° were determined by the relative method of Ostwald. The values are accurate to ±0.5% and include kinetic correction. The densities required to compute viscosities and molar volumes were determined with the aid of a double stem pycnometer described by Rao<sup>8</sup>. The density values are accurate to 2 parts in 10<sup>5</sup>.

The viscosity data and molar volumes, computed from densities, and the values of  $d$  and  $W_{\text{visc}}$ , the interaction energy between the components, for the twelve mixtures are given in Tables 1-3. The

TABLE 1 — VISCOSITY AND MOLAR VOLUME DATA FOR VARIOUS MIXTURES AT 30°

Mole fraction of methylcyclohexane	$\rho$ (g cm <sup>-3</sup> )	$V$ (cm mole <sup>-1</sup> )	$\eta$ centipoise	$d$ Eq. (1)	$W_{\text{visc}}$ (cal. mole <sup>-1</sup> ) Eq. (2)
METHYLCYCLOHEXANE + 1-PROPANOL					
0.0000	0.79596	75.499	1.711	—	—
0.0998	0.78929	80.954	1.420	-0.980	-479.7
0.2182	0.78308	87.351	1.188	-0.874	-424.9
0.4212	0.77424	98.338	9.918	-0.846	-415.1
0.5760	0.76911	106.660	0.777	-0.903	-454.4
0.7398	0.76455	115.455	0.677	-1.021	-528.5
0.9000	0.76156	123.919	0.637	-1.089	-572.3
1.0000	0.76033	129.130	0.637	—	—
METHYLCYCLOHEXANE + 1-BUTANOL					
0.0000	0.80195	92.425	2.240	—	—
0.1000	0.79585	96.155	1.825	-0.882	-490.6
0.2604	0.78718	102.118	1.383	-0.804	-444.6
0.4200	0.77940	108.066	1.072	-0.857	-477.1
0.5788	0.77275	113.939	0.854	-0.974	-547.3
0.7414	0.76689	119.911	0.719	-1.065	-602.4
0.9013	0.76221	125.697	0.643	-1.300	-741.3
1.0000	0.76033	129.130	0.637	—	—
METHYLCYCLOHEXANE + 1-PENTANOL					
0.0000	0.80760	109.151	3.012	—	—
0.0947	0.80186	111.117	2.283	-1.547	-901.3
0.2614	0.79259	114.525	1.737	-0.748	-430.4
0.4200	0.78434	117.759	1.289	-0.806	-472.3
0.5783	0.77568	120.993	0.968	-0.973	-571.6
0.7422	0.76950	124.230	0.777	-1.055	-620.6
0.9027	0.76331	127.347	0.663	-1.274	-748.1
1.0000	0.76033	129.130	0.637	—	—
METHYLCYCLOHEXANE + 1-HEXANOL					
0.0000	0.81195	125.796	3.818	—	—
0.1015	0.80609	126.212	3.051	-0.465	-275.4
0.2596	0.79750	126.787	2.193	-0.466	-277.3
0.4197	0.78884	127.078	1.536	-0.642	-361.6
0.5820	0.78024	127.956	1.110	-0.793	-473.4
0.7447	0.77195	128.496	0.852	-0.872	-519.7
0.8989	0.76450	128.950	0.693	-1.057	-628.9
1.0000	0.76033	129.130	0.637	—	—

TABLE 2 — VISCOSITY AND MOLAR VOLUME DATA FOR VARIOUS MIXTURES AT 30°

Mole fraction of cyclopentanone	$\rho$ (g cm <sup>-3</sup> )	$V$ (cm mole <sup>-1</sup> )	$\eta$ centipoise	$d$ Eq. (1)	$W_{\text{visc}}$ (cal. mole <sup>-1</sup> ) Eq. (2)
CYCLOPENTANONE + 1-PROPANOL					
0.0000	0.79596	75.499	1.711	—	—
0.1001	0.81269	76.903	1.333	-2.162	-1294.3
0.2566	0.83738	79.127	1.091	-1.620	-966.9
0.4203	0.86196	81.432	0.974	-1.368	-815.8
0.5821	0.88484	83.721	0.922	-1.229	-732.7
0.7382	0.90571	85.934	0.915	-1.145	-682.3
0.8967	0.92608	88.154	0.935	-1.209	-724.2
1.0000	0.93896	89.589	0.989	—	—
CYCLOPENTANONE + 1-BUTANOL					
0.0000	0.80195	92.425	2.240	—	—
0.1010	0.81591	92.081	1.725	-1.968	-1189.7
0.2614	0.83719	91.656	1.339	-1.556	-939.0
0.4183	0.85823	91.238	1.143	-1.358	-819.1
0.5813	0.88047	90.785	1.026	-1.255	-757.1
0.7417	0.90245	90.350	0.974	-1.182	-712.6
0.8990	0.92471	89.877	0.959	-1.245	-755.8
1.0000	0.93896	89.589	0.989	—	—

NOTES

TABLE 2 — VISCOSITY AND MOLAR VOLUME DATA FOR VARIOUS MIXTURES AT 30° — *contd*

Mole fraction of cyclopentanone	$\rho$ (g cm <sup>-3</sup> )	$V$ (cm mole <sup>-1</sup> )	$\eta$ centipoise	$d$ Eq. (1)	$W^{\text{visc}}$ (cal. mole <sup>-1</sup> ) Eq. (2)
CYCLOPENTANONE + 1-PENTANOL					
0.0000	0.80760	109.151	3.012	—	—
0.0989	0.81830	107.236	2.258	-1.995	-1190.0
0.2598	0.83654	104.123	1.682	-1.493	-888.5
0.4202	0.85561	101.047	1.353	-1.363	-807.7
0.5803	0.87604	97.954	1.179	-1.198	-707.2
0.7374	0.89834	94.482	1.057	-1.165	-699.6
0.9009	0.92303	91.567	0.980	-1.328	-791.0
1.0000	0.93896	89.589	0.989	—	—
CYCLOPENTANONE + 1-HEXANOL					
0.0000	0.81195	125.796	3.818	—	—
0.0985	0.82040	122.336	2.896	-1.611	-933.1
0.2605	0.83616	116.539	2.093	-1.292	-742.3
0.4224	0.85383	110.712	1.641	-1.122	-638.1
0.5807	0.87333	104.973	1.333	-1.100	-624.0
0.7406	0.89519	99.191	1.132	-1.119	-633.5
0.9025	0.92155	93.188	1.016	-1.185	-676.1
1.0000	0.93896	89.589	0.989	—	—

TABLE 3 — VISCOSITY AND MOLAR VOLUME DATA FOR VARIOUS MIXTURES AT 30°

Mole fraction of cyclohexanone	$\rho$ (g cm <sup>-3</sup> )	$V$ (cm mole <sup>-1</sup> )	$\eta$ centipoise	$d$ Eq. (1)	$W^{\text{visc}}$ (cal. mole <sup>-1</sup> ) Eq. (2)
CYCLOHEXANONE + 1-PROPANOL					
0.0000	0.79596	75.499	1.711	—	—
0.1012	0.81536	78.425	1.452	-1.851	-1081.4
0.2601	0.84326	83.001	1.283	-1.546	-901.2
0.4199	0.86745	87.695	1.243	-1.378	-799.1
0.5794	0.88967	92.325	1.300	-1.218	-702.9
0.7393	0.90928	97.025	1.392	-1.219	-705.0
0.8997	0.92721	101.730	1.576	-1.301	-752.5
1.0000	0.93759	104.672	1.778	—	—
CYCLOHEXANONE + 1-BUTANOL					
0.0000	0.80195	92.425	2.240	—	—
0.1001	0.81741	93.620	1.855	-1.838	-1103.9
0.2591	0.84101	95.532	1.662	-1.243	-746.0
0.4202	0.86372	97.502	1.556	-1.098	-658.1
0.5804	0.88539	99.461	1.517	-1.050	-629.8
0.7265	0.90431	101.261	1.534	-1.061	-636.6
0.8935	0.92490	103.343	1.622	-1.224	-734.2
1.0000	0.93759	104.672	1.778	—	—
CYCLOHEXANONE + 1-PENTANOL					
0.0000	0.80760	109.151	3.012	—	—
0.1012	0.82008	108.723	2.388	-1.968	-1184.1
0.2586	0.84089	107.902	1.983	-1.469	-886.8
0.4201	0.86160	107.181	1.737	-1.350	-814.8
0.5809	0.88243	106.471	1.622	-1.287	-776.0
0.7407	0.90269	105.850	1.565	-1.376	-827.7
0.9001	0.92372	105.164	1.635	-1.517	-910.6
1.0000	0.93759	104.672	1.778	—	—
CYCLOHEXANONE + 1-HEXANOL					
0.0000	0.81195	125.796	3.818	—	—
0.1001	0.82192	123.783	3.014	-1.776	-1054.6
0.2599	0.83977	120.390	2.391	-1.399	-830.8
0.4199	0.85856	117.010	2.008	-1.322	-784.1
0.5798	0.88008	113.422	1.861	-1.132	-674.2
0.7404	0.90085	110.094	1.738	-1.150	-683.9
0.8990	0.92311	106.697	1.707	-1.299	-781.7
1.0000	0.93759	104.672	1.778	—	—

values of  $d$  and  $W_{\text{visc}}$  were calculated for each composition from Eqs. (1) and (2) respectively using the observed viscosity values of pure liquids and of mixtures.

An examination of the data in Tables 1-3 reveals that  $d$  and  $W_{\text{visc}}$  vary with composition. Hence it is concluded that Eqs. (1) and (2) are not applicable to these mixtures, which therefore cannot be classified as quadratic mixtures as defined by Rowlinson.<sup>9</sup>

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### Fe(II)-induced Oxidation of Phosphite by Peroxydiphosphate in Acid Medium

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The induction factor in Fe(II)-induced oxidation of phosphite comes out to be unity, as has been observed in Fe(II)-induced oxidation of hypophosphite.

RECENTLY we reported<sup>1</sup> Fe(II)-induced oxidation of hypophosphite by peroxydiphosphate in acid medium with a limiting value of unity for the induction factor. We have now found that phosphite behaves similarly.

Stock solutions of  $K_4P_2O_8$ ,  $Na_2HPO_3$ , Ce(IV) sulphate and diammonium iron(II) bis-sulphate were prepared as described earlier<sup>1</sup>. Phosphite was standardized cerimetrically<sup>2</sup>.

Fe(II) solutions (10 and 20 ml) were titrated in the acid medium against Ce(IV) using *n*-phenylanthranilic acid as an indicator. Mixtures containing Fe(II) solution (10 ml) and  $K_4P_2O_8$  (5 ml) (Set-I) and Fe(II) (20 ml) and  $K_4P_2O_8$  (10 ml) (Set-II) were then titrated<sup>3</sup> in the same way. Varying amounts of 0.1M phosphite were then added to equinormal solutions of these mixtures [ $Fe(II)+K_4P_2O_8$ ] and titrated against Ce(IV) in acid medium. The amount of Ce(IV) required for titration increases with an increase of  $H_3PO_3$  and reaches a limiting value which is half the amount of peroxydiphosphate. The results are given in Table 1 and Fig. 1. The limiting value of the induction factor is unity.

The induced reaction suggests an intermediate species derived from peroxydiphosphate, possibly a free radical  $HPO_4^-$  as shown in Eqs. (1)-(3).

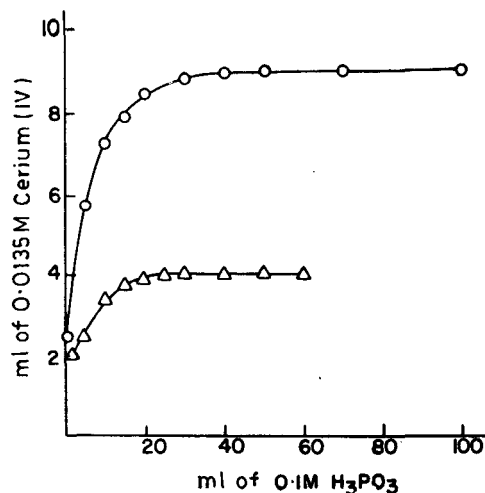
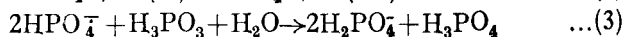
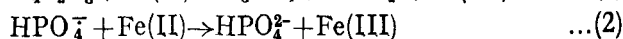
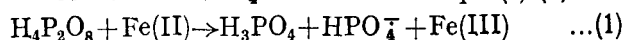


Fig. 1 — Fe(II)-induced oxidation of phosphite [Curve 1, 20 ml Fe(II) and 10 ml  $K_4P_2O_8$  and curve 2, 10 ml Fe(II) and 5 ml  $K_4P_2O_8$ ]

TABLE 1 — RESULTS OF CERIMETRIC TITRATION OF VARIOUS SOLUTIONS

{[Fe(II)] = 0.01M; [ $K_4P_2O_8$ ] = 0.01M; [ $Na_2HPO_3$ ] or [ $H_3PO_3$ ] = 0.1M; [ $H_2SO_4$ ]  $\approx$  2.0M; [Ce(IV)] = 0.0135M}

10 ml Fe(II) (A)	ml of Ce(IV) for			Oxidation of $H_3PO_3$ (A-C)	Induction factor [ $H_3PO_3$ ] oxidized / [Fe(II)] oxidized
	A+5 ml $K_4P_2O_8$ (B)	B+excess $H_3PO_3$ (C)	$K_4P_2O_8$ (A-B)		
SET-I					
7.4	0.75	4.05	6.65	3.35	$\frac{3.35}{3.30} = 1.0$
SET-II					
15.65	2.50	9.05	13.15	6.60	$\frac{6.60}{6.55} = 1.0$