higher concentrations of sodium salts in molten KNO_3 due to the formation of $NaNO_3$-KNO_3 solid solutions.

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Viscosities of Binary Liquid Mixtures of Carbon Tetrachloride with Toluene & Xylenes

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Viscosities and densities of the binary mixtures of carbon tetrachloride with toluene, *o*-xylene, *m*-xylene and *p*-xylene have been measured at 298.15 K. Grunberg and Nissan relations and Bloomfield and Dewan theory have been used to study the molecular interactions. The results indicate that the molecular interactions are unsymmetrical in the four mixtures.

VISCOSITIES of four binary liquid mixtures, viz. carbon tetrachloride + toluene, + *o*-xylene, + *m*-xylene and + *p*-xylene, measured at 298.15K, are reported in this note. The results have been analysed on the basis of viscosity relation developed for non-ideal liquid mixtures by Grunberg and Nissan[1] to study the molecular interactions. The recent theory proposed by Bloomfield and Dewan[2] has also been used to predict the excess viscosity data.

Carbon tetrachloride (BDH), toluene (BDH) and isomeric xylenes (Riedel) were purified by the methods described in the literature[3] and their purity checked by comparing the measured density and boiling point data with those reported in the literature[4].

Viscosities of liquids and liquid mixtures were measured using an Ostwald viscometer with water as reference liquid. The viscosity values were accurate within 0.5%. These included kinetic corrections. Densities used in the calculation of viscosities were measured using bicapillary pycnometer described by Rao and Naidu[5]. The density values were accurate to 5 parts in 10^5.

According to Grunberg and Nissan[1] viscosity of a non-ideal mixture is given by the relation

$$\ln \eta_{exp} = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d \qquad .. (1)$$

The last term takes into account the additional interactions that arise mainly due to the differences in free energy and free volume of the molecules in liquids and liquid mixtures[6]. Grunberg[7] pointed out that the parameter, d, is proportional to the term W/RT in two-suffix Margules equation. Therefore, the parameter depends on the molecular complexity of the solution and it is constant for mixtures in which molecular interactions are symmetrical with respect to composition[8].

Equation (1) can be written as

$$\triangle \ln \eta_{exp} = x_1 x_2 d \qquad .. (2)$$

where $\triangle \ln \eta_{exp}$ is the experimental excess viscosity. Viscosity data for mixtures, the values of parameter d and the excess viscosity are given in Table 1.

According to Bloomfield and Dewan[2] the excess viscosity is given by

$$\triangle \ln \eta_{the} = -\frac{\triangle G^R}{RT} + \frac{1}{\bar{v} - 1} - \left(\frac{x_1}{\bar{v}_1 - 1} + \frac{x_2}{\bar{v} - 1} \right) \qquad .. (3)$$

This can also be written as

$$\triangle \ln \eta_{the} = \ln \eta_H + \ln \eta_s + \ln \eta_v \qquad .. (4)$$

where $\ln \eta_H$, $\ln \eta_s$ and $\ln \eta_v$ are the enthalpy, entropy and free volume contributions to the excess viscosity. Enthalpy contribution is calculated from experimental excess enthalpy data reported in the literature[9,10]. Entropy and free volume contributions are related to the residual entropy of mixing $\triangle S^R$, and reduced volume $\bar{v}$. The values of $\triangle S^R$ and $\bar{v}$ are calculated using Flory's[11] equations :

$$\triangle S^R = -3x_1 \frac{P_1^* V_1^*}{T_1^*} \ln \frac{\bar{v}_1^{1/3} - 1}{\bar{v}^{1/3} - 1}$$
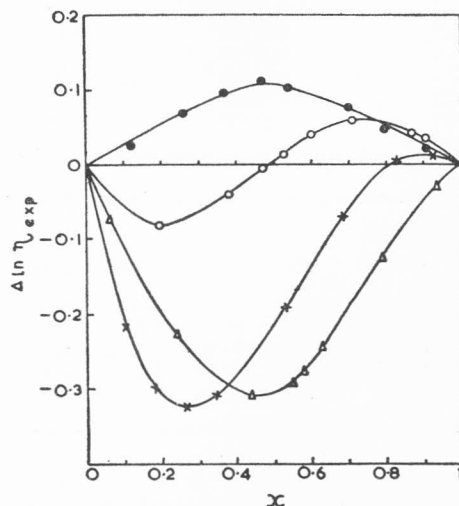$$-3x_2 \frac{P_2^* V_2^*}{T_2^*} \ln \frac{\bar{v}_2^{1/3} - 1}{\bar{v}^{1/3} - 1} \qquad .. (5)$$

and

Fig. 1 — Viscosity versus mole fraction curves for carbon tetrachloride + toluene($\times$), + *o*-xylene ($\triangle$), + *m*-xylene ($\bigcirc$), and + *p*-xylene ($\bullet$) at 298.15K

TABLE 1 — MOLE FRACTION OF THE FIRST COMPONENT, DENSITY, VISCOSITY, VALUES OF d AND EXCESS VISCOSITY FOR THE BINARY MIXTURES AT 298.15 K

x	ρ (g cm^{-3})	η (cp)	$\ln\eta$	d	$\triangle\ln\eta_{exp}$	$\triangle\ln\eta_{the}$
		CARBON	TETRACHLORIDE	+ TOLUENE		
0.0000	0.86238	0.556	—0.587			
0.1009	0.92933	0.469	—0.757	—2.414	—0.219	—0.004
0.1855	0.98641	0.451	—0.796	—1.985	—0.300	—0.007
0.2612	0.03823	0.456	—0.785	—1.685	—0.325	—0.007
0.3536	1.10249	0.484	—0.725	—1.357	—0.310	—0.008
0.5363	1.23291	0.593	—0.523	—0.764	—0.190	—0.012
0.6882	1.34466	0.726	—0.320	—0.321	—0.069	—0.009
0.8272	1.44981	0.837	—0.178	—0.035	0.005	—0.005
0.9246	1.52456	0.884	—0.123	0.186	0.013	—0.003
1.0000	1.58436	0.906	—0.099			
		CARBON	TETRACHLORIDE	+ o-XYLENE		
0.0000	0.87596	0.765	—0.268			
0.0656	0.91364	0.722	—0.326	—1.125		
0.2424	1.02034	0.636	—0.452	—1.225	—0.069	—0.001
0.4464	1.15393	0.606	—0.500	—1.242	—0.225	—0.005
0.5536	1.22904	0.628	—0.465	—1.174	—0.307	—0.014
0.5803	1.24832	0.639	—0.448	—1.142	—0.290	—0.018
0.6341	1.28784	0.666	—0.406	—1.056	—0.278	—0.019
0.7930	1.41044	0.772	—0.258	—0.756	—0.245	—0.018
0.9312	1.52463	0 872	—0.137	—0.406	—0.124	—0.017
1.0000	1.58436	0.906	—0.099		—0.026	—0.007
		CARBON	TETRACHLORIDE	+ m-XYLENE		
0.0000	0.85990	0.588	—0.531			
0.1974	0.97691	0.509	—0.529	—0.524	—0.083	—0.003
0.3803	1.09484	0.665	—0.407	—0.170	—0.040	—0.003
0.4687	1.15662	0.716	—0.334	—0.024	—0.006	—0.002
0.5267	1.19691	0.751	—0.286	—0.068	0.017	—0·002
0.5964	1.24817	0.792	—0.233	0.166	0.040	—0.002
0.7155	1.34001	0.851	—0.161	0.300	0.061	—0.002
0.8693	1.46741	0.894	—0.112	0.378	0.043	—0.002
0.9105	1.50339	0.902	—0.103	0.429	0.035	—0.002
1.0000	1.58436	0.906	—0.099			
		CARBON	TETRACHLORIDE	+ p-XYLENE		
0.0000	0.85661	0.615	—0.486			
0.1248	0.92959	0.662	—0.412	0.238	0.026	0.009
0.2635	1.01571	0.729	—0.316	0.350	0.068	0.018
0.3695	1.08534	0.781	—0.247	0.412	0.096	0.024
0.4691	1.15399	0.826	—0.191	0.454	0.113	0.026
0.5467	1.21103	0.844	—0.169	0.424	0.105	0.024
0.7054	1.33104	0.872	—0.137	0.366	0.076	0.020
0.7959	1.40469	0.882	—0.126	0.320	0.052	0.015
0.9130	1.50539	0.894	—0.112	0.264	0.021	0.007
1.0000	1.58437	0.906	—0.099			

TABLE 2 — PARAMETERS FOR THE PURE COMPONENTS AT 298.15K

Component	$\alpha \times 10^3$ (deg^{-1})	$\bar{v}$	v^* (cm^3 mol^{-1})	P^* (J cm^{-3})	T^* (deg)	K_T (TPa^{-1})
CCl$_4$	1.229	1.2927	75.10	566.72	4699.7	1079.9
Toluene	1.067	1.2612	84.71	546.11	5051.6	926.5
o-Xylene	0.952	1.2377	99.92	536.20	5378.8	810.5
m-Xylene	0.981	1.2436	99.27	524.01	5290.1	862.1
p-Xylene	0.956	1.2385	100.06	509.00	5366.3	858.8

TABLE 3 — LEAST SQUARE PARAMETERS AND THE STANDARD DEVIATION OF $\triangle\ln\eta_{exp}$

CCl$_4$+	a_0	a_1	a_2	σ
Toluene	—0.852	1.588	—0.417	0.004
o-Xylene	—1.209	0.407	0.603	0.003
m-Xylene	0.030	0.732	—0.315	0.002
p-Xylene	0.430	0.022	—0.299	0.004

$$\bar{v} = V/(x_1 V_1^* + x_2 V_2^*) \qquad .. (6)$$

The parameters in Eqs (5) and (6) have the same significance as described by Flory and the values are given in Table 2. The values of $\triangle\ln\eta_{the}$ predicted using Eq. (4) are also included in Table 1.

The plots of excess viscosity with mole fraction, presented in Fig. 1, are described by an equation of the form

$$\triangle\ln\eta_{exp} = x_1 x_2 [a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \qquad .. (7)$$

The constants a_0, a_1 and a_2 are obtained by the method of least squares and are given in Table 3 along with the standard deviations $\sigma(\triangle \ln \eta_{exp})$.

The variation of d with composition (Table 1) shows that the molecular interactions are unsymmetrical in the four mixtures. Hence, Grunberg and Nissan relation, which is applicable to quadraratic mixtures defined by Rowlinson[12] is not applicable to the four mixtures studied presently. Further, a comparison of the values of $\triangle \ln\eta$ and $\triangle \ln\eta_{the}$ (Table 1) indicates that the theory due to Bloomfield and Dewan is capable of predicting the sign of excess viscosity correctly in mixtures of carbon tetrachloride with toluene, o-xylene and p-xylene. However, the quantitative agreement between predicted and experimental excess viscosity is poor in the three systems. The theory fails to predict even the sign of excess viscosity over certain range of mole fractions in the system carbon tetrachloride + m-xylene.

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Kinetics & Mechanism of Oxidation of Diaryl Sulphoxides by Cr(VI)

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The kinetics of oxidation of a few diaryl sulphoxides by Cr(VI) in 75% aqueous acetic acid has been studied. The reaction follows second-order kinetics, first-order each in sulphoxide and Cr(VI). A mechanism analogous to the one proposed for the oxidation of aryl methyl sulphoxides [*Indian J. Chem.*, 16A (1978), 966] has been suggested.

DURING our investigations on the kinetics of oxidation of organic sulphur compounds we observed certain interesting features: (i) the oxidation of aryl methyl sulphides by peroxydisulphate[1,2] and peroxydiphosphate[3] ions is second order (first order in each reactant), but in contrast the oxidation of diphenyl sulphide by these peroxyanions[4,5] is first order in the peroxy anion and zero order in diphenyl sulphide; and (ii) while the oxidation of methyl phenyl sulphoxide by peroxydiphosphate[6] is first order in each reactant, the oxidation of diphenyl sulphoxide (DPSO) by peroxydiphosphate[7] is definitely different, i.e. zero order in DPSO and first order in the oxidant. The recent publication of Baliah and Satyanarayana[8] on the oxidation of aryl methyl sulphoxides by Cr (VI) and the intrinsically exceptional behaviour of diphenyl sulphide and diphenyl sulphoxide with the isoelectronic and isostructural peroxyanions, prompted us to study in particular the kinetics of oxidation of a few diaryl sulphoxides by Cr(VI). The results are reported in this note.

All the diaryl sulphoxides were prepared and purified by standard methods. Acetic acid was purified by the method of Orton and Bradfield[9]. All the other chemicals employed were AR/GR grade. The kinetic studies were carried out in 75% (v/v) aqueous acetic acid under pseudo-first order conditions. The titrimetric procedure of Wiberg and Mill[10] was followed for the estimation of the unreacted Cr(VI). The pseudo-first order rate constant, (k_1) for each run was evaluated from the slope of the linear plot of log $(a-x)$ versus time by the method of least squares[3] using a Micro 2200 diskette recorder (Hindustan Computers Limited). For each run the correlation coefficient, $r > 0.995$. The second order rate constants were obtained from the relation, $k_2 = k_1/[\text{sulphoxide}]$. The activation parameters were computed from the Arrhenius and Eyring plots. TLC of the reaction mixture of an actual kinetic run showed that DPSO was oxidised to diphenyl sulphone. Stoichiometric studies indicated that the reaction could be written as :

$$3\ Ph_2SO + 2HCrO_3^+ + 4H^+ \longrightarrow 3Ph_2SO_2 + 2Cr^{3+} + 3H_2O$$
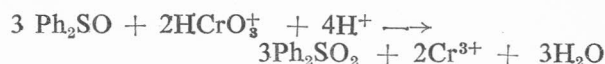
Effect of [Cr(VI)] and [DPSO] — There is a clean first order dependence on [Cr(VI)] (Table 1). The constancy of second order rate constants at different [DPSO] shows that the reaction is first order in DPSO (Table 1). Further a plot of k_1 versus [DPSO] is linear passing through the origin indicating that the reaction follows second order kinetics.

The oxidation is practically negligible in the absence of perchloric acid and the data in Table 2 reveal that the rate increases with increase in [perchloric acid] at constant ionic strength. The rate also increases slightly with increase in ionic strength (Table 2). The oxidation rate increases with increase in the acetic acid content in the solvent mixture (cf. Table 2). The decrease in rate with increase in water content of the solvent may be due to a greater solvation of the sulphoxide group and its consequent decreased nucleophilicity.

The rate constants and the activation parameters for a few 4,4'-disubstituted diphenyl sulphoxides are given in Table 3. The rate of the oxidation is accelerated by electron-releasing and retarded by electron-withdrawing substituents indicating a rate-determining electrophilic attack by the oxidant at the reaction site, sulphur. A good correlation is found to exist when $\Sigma\sigma^+$ values are plotted against