adsorbed state can be supported by the conductivity data in Figure 5, since the π_g orbitals of molecular O_2 accept the conduction electrons trapped at $V_{\ddot{O}}$. On the other hand, the kinetic data should not agree with $O^{2-}_{2(ads)}$, since the rate law, *i.e.*, the half-order with respect to oxygen, satisfies with atomic oxygen species. The conductivity and kinetic data support that $O^-_{(ads)}$ is a reasonable species at investigated temperatures, indicating the reaction(2) is an elementary reaction included in the oxidation process of CO.

The kinetic data in Tables 1 and 2 and the conductivity data of Figures 5 and 6 support that the following elementary reaction should be included in the overall reaction. From the

$$O^-_{iads} + CO^-_{2ads} \xrightarrow{k'} O^{2-}_{lath} + CO_2 (g) \qquad (4)$$
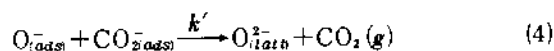
kinetic data in Figures 2 and 4, and the conductivity data in Figures. 5 and 6, the adsorption *rate* of CO on lattice oxygen (equilibrium(3)) is lower than that of O_2 on an $V_{\ddot{O}}$ (equilibrium(2)) at constant temperature, P_{O_2} and catalyst. Therefore, the equilibrium(3) must be the rate-determining step.

The experimental rate law, $r = kP_{CO} \cdot P_{O_2}^{1/2}$ should be derived from the above mechanism, if the elementary reactions (2)-(4) are true in the oxidation process of CO. In equilibrium (2) $(O^-) = K_1^{1/2}P_{O_2}^{1/2}(e^-)$, and $(CO_2^-) = K_2P_{CO}(O^{2-})/(e^-)$ in equilibrium(3) with omissions of the obvious subscripts. The rate of elementary reaction(4) which produces CO_2 is $dP_{CO_2}/dt = k'(CO_2^-) (O^-)$. Substituting $(O^-) = K_1^{1/2}P_{O_2}^{1/2}(e^-)$ and $(CO_2^-) = K_2P_{CO}(O^{2-})/(e^-)$ into this rate law, the overall rate is consistent with the experimentally observed rate law, indicating $k = k' \cdot K_2K_1^{1/2}$ and $(O^{2-}_{latt}) \simeq$ constant. The elementary reactions (2), (3), and (4) are possibly suggested as the reaction mechanism, since the observed rate law can be derived from above elementary reactions.

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Solvolysis of 2-Phenylethyl Benzenesulfonates in Methanol-Water Mixtures

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Solvolyses of 2-phenylethyl benzenesulfonates have been studied in methanol-water mixtures. Cross interaction constants, ρ_{YZ}, between substituents Y in the substrate and Z in the leaving group indicated somewhat closer distance between the two substituents than expected for the reaction system, which supported the involvment of phenyl group assisted pathway in the solvolysis. A smaller magnitude of ρ_{YZ} for MeOH was interpreted as the enhencement of solvent assisted pathway since MeOH is more nucleophilic than H_2O. Other selectivity parameters, Winstein coefficient m, Hammett's ρ_Y^+ and ρ_Z, as well as activation parameters supported the participation of aryl assisted and aryl unassisted pathways in the S_N2 process of the solvolysis reaction.

Introduction

2-Phenylethyl derivatives have attracted considerable attention of physical organic chemists ever since phenonium

ions (I) were first proposed as solvolysis intermediates in solvolyses of 2-arylalkyl systems.[1] It has since been well established that solvolyses of 2-arylalkyl systems proceed through discrete aryl assisted(k_Δ) and/or aryl unassisted(k_s)
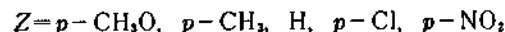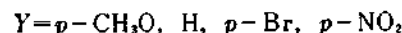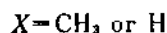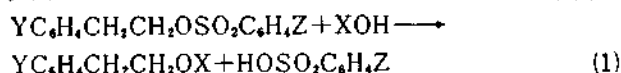
pathways[1c] (scheme 1).
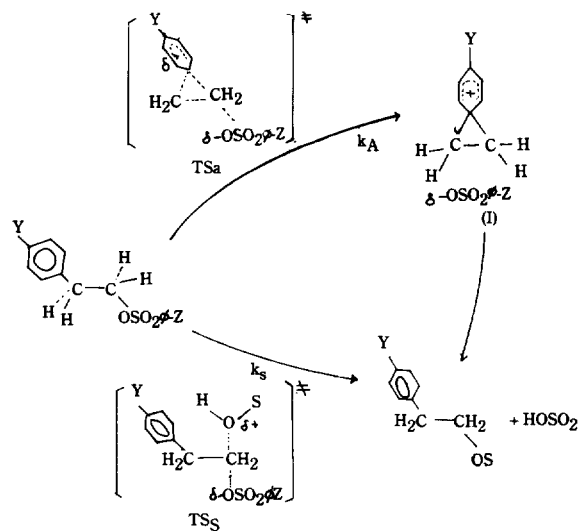
Scheme 1

Aryl participation was used to account for dominant retention of product stereochemistry and rate enhancements observed with activated phenyl groups in solvolyses of the 2-arylalkyl systems. Schleyer et al.[1c] have shown that increased solvent ionizing power changes little the degree of aryl participation in transition state (TS) leading to the phenonium intermediate, but nucleophilic solvent assistance plays a dominant role in the k_s pathway.

In this work, we report on the solvolyses of 2-(Y)-phenylethyl(Z)-benzenesulfonates in methanol-water mixtures, (1).

$$YC_6H_4CH_2CH_2OSO_2C_6H_4Z + XOH \longrightarrow$$
$$YC_6H_4CH_2CH_2OX + HOSO_2C_6H_4Z \qquad (1)$$

$X = CH_3$ or H

$Y = p\text{-}CH_3O, \quad H, \quad p\text{-}Br, \quad p\text{-}NO_2$

$Z = p\text{-}CH_3O, \quad p\text{-}CH_3, \quad H, \quad p\text{-}Cl, \quad p\text{-}NO_2$

The degree of bond cleavage in the TS was assessed using the magnitude of cross interaction constants[2] ρ_{YZ}, (2).

$$\log(k_{YZ}/k_{HH}) = \rho_Y\sigma_Y^+ + \rho_Z\sigma_Z + \rho_{YZ}\sigma_Y^+\sigma_Z \qquad (2)$$

Results and Discussion

Rate constants, k_1, are summarized in Table 1. The rate is seen to increase with a more electron withdrawing substituent (EWS) in the leaving group ($Z = p\text{-}NO_2$) and with a more electron donating substituent (EDS) in the substrate ($Y = p\text{-}CH_3O$). The rate ratio R, $[k(Z = p\text{-}NO_2)/k(Z = p\text{-}CH_3O)]$, becomes greater with a more EDS in the substrate and with an increase in the water content of the solvent, as shown in Table 2.

A greater rate increase with a more EDS in the substrate ($Y = p\text{-}CH_3O$) is indicative of the participation of the phenyl assisted pathway, $k\Delta$, in scheme 1. since the EDS stabilizes the phenonium ion, (I), and hence the TSΔ.

Table 1. Pseudo first order rate constants ($k_1 \times 10^6$ sec^{-1}) for the Solvolysis of $YC_6H_4CH_2CH_2OSO_2C_6H_4Z$ in MeOH-H$_2$O solvents

MeOH V/V%	p-Z p-Y Temp	NO$_2$ 45°C	NO$_2$ 55°C	Cl 45°C	Cl 55°C	H 45°C	H 55°C	CH$_3$ 45°C	CH$_3$ 55°C	CH$_3$O 45°C	CH$_3$O 55°C
100	CH$_3$O	19.0	61.0	4.36	14.7	2.36	8.12	1.43	5.01	1.13	3.98
	H	9.15	26.9	2.29	7.08	1.32	4.17	0.776	2.50	0.596	1.95
	Br	5.56	15.8	1.43	4.27	0.800	2.45	0.510	1.58	0.408	1.29
	NO$_2$	3.90	11.0	1.02	3.02	0.568	1.74	0.370	1.15	0.306	0.995
90	CH$_3$O	38.5	121	8.75	28.8	4.48	15.1	2.85	9.77	1.99	6.92
	H	14.8	42.7	3.62	11.0	1.88	5.88	1.17	3.71	0.851	2.75
	Br	8.78	24.5	2.10	6.17	1.12	3.39	0.710	2.19	0.556	1.74
	NO$_2$	5.32	14.8	1.47	4.27	0.808	2.40	0.520	1.58	0.407	1.26
80	CH$_3$O	63.7	197	13.8	44.6	6.90	22.9	4.17	14.1	2.85	9.77
	H	21.2	60.3	5.02	15.1	2.52	7.76	1.51	4.78	1.13	3.63
	Br	12.0	33.1	2.87	8.32	1.53	4.57	0.990	3.02	0.739	2.29
	NO$_2$	7.45	20.4	1.91	5.50	1.05	3.09	0.670	2.00	0.504	1.55
70	CH$_3$O	105	317	22.8	72.4	11.9	38.9	7.22	24.0	4.59	15.5
	H	31.0	87.1	6.73	20.0	3.55	10.8	2.02	6.31	1.48	4.68
	Br	16.4	44.7	3.80	10.9	2.03	6.03	1.29	3.89	0.982	3.01
	NO$_2$	9.92	26.9	2.42	6.92	1.34	3.89	0.840	2.51	0.626	1.91
60	CH$_3$O	172	514	34.3	107	16.3	52.5	10.1	33.1	7.02	23.4
	H	40.1	111	8.16	24.0	4.29	12.9	2.56	7.94	1.83	5.75
	Br	22.9	61.7	4.88	13.8	2.59	7.59	1.56	4.68	1.19	3.63
	NO$_2$	12.6	33.9	3.01	8.51	1.65	4.78	1.02	3.02	0.756	2.29
50	CH$_3$O	252	735	45.5	140	22.3	70.8	13.4	43.7	9.36	30.9
	H	51.5	141	11.1	32.4	5.43	16.2	3.11	9.55	2.21	6.91
	Br	29.8	79.4	6.33	17.8	3.13	9.12	1.98	5.89	1.48	4.46
	NO$_2$	16.9	44.7	3.93	11.0	2.00	5.75	1.23	3.63	0.874	2.63

Table 2. The rate ratio, R = [k(Z = p-NO₂) / k(Z = p-CH₃O)], at 55.0°C for reaction(1)

% MeOH	Y = p-CH₃O	H	p-NO₂
100	15.3	13.6	11.5
80	20.2	16.6	13.2
50	23.8	20.4	17.0

Table 3. Hammett $\rho_Y^{\ddagger}$ Values for solvolysis of YC₆H₄CH₂CH₂ OSO₂C₆H₄Z in MeOH-H₂O at 55°C

V/V% MeOH ＼ p-Z	NO₂	Cl	H	CH₃	CH₃O
100	−0.48	−0.45	−0.44	0.42	−0.41
90	−0.59	−0.54	−0.53	−0.52	−0.49
80	−0.64	−0.60	−0.57	−0.56	−0.52
70	−0.70	−0.67	−0.65	−0.64	−0.59
60	−0.77	−0.72	−0.68	−0.68	−0.66
50	−0.79	−0.73	−0.71	−0.71	−0.70

Table 4. Hammett ρ_Z Values for solvolysis of YC₆H₄CH₂CH₂ OSO₂C₆H₄Z in MeOH-H₂O at 55°C

V/V% MeOH ＼ p-Y	CH₃O	H	Br	NO₂
100	1.12	1.07	1.03	1.01
90	1.16	1.12	1.09	1.01
80	1.21	1.15	1.09	1.05
70	1.21	1.19	1.10	1.08
60	1.26	1.20	1.16	1.10
50	1.28	1.23	1.18	1.15

r >0.997 ± 0.003

$$
\begin{array}{c}
\overset{OCH_3}{\underset{\downarrow}{}} \\
\textcircled{+} \quad {}^-OSO_2\emptyset Z \\
H_2C\!-\!\!-\!CH_2
\end{array}
$$

(I)
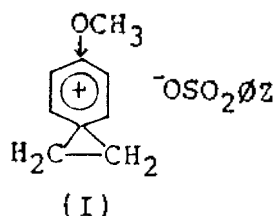
The greater *R* values in the water-rich solvent in Table 2 indicate that (i) the intermediate (I) is more stabilized, and hence contribution of aryl assisted pathway, *k*Δ, increases, by the stronger ionizing power of the solvent, and (ii) the solvent assisted pathway, *k_s*, decreases with a decrease in the nucleophilicity of the solvent since MeOH has greater nucleophilicity than H₂O.

Simple Hammett plots of the rate constants with respect to variations in substituents in the substrate gave curvatures with σ, but linearities improved when σ⁺ values are used in the plots.[3] The $\rho_Y^{\ddagger}$ values obtained with σ⁺ are summarized in Table 3.

The magnitude of $\rho_Y^{\ddagger}$ value increases again with a more EWS in the leaving group and in the water-rich solvents, indicating increases in contribution of aryl assisted pathway.

The Hammett plots for substituent variations in the leaving group (σ_Z) gave good linearities (r >0.997) with relatively large, positive ρ_Z values as shown in Table 4. The trends in the change of the ρ_Z values are the same as those found for

Table 5. The $\rho_Y^{\ddagger}$, ρ_Z and ρ_{YZ} Values for solvolysis of YC₆H₄CH₂ CH₂OSO₂C₆H₄Z in MeOH-H₂O at 55°C
(C.C = multiple correlation coefficient).

V/V% MeOH	$\rho_Y^{\ddagger}$	ρ_Z	ρ_{YZ}	r(C.C)
100	−0.43	1.07	−0.07	0.993
90	−0.52	1.10	−0.09	0.990
80	−0.56	1.14	−0.11	0.990
70	−0.64	1.15	−0.09	0.989
60	−0.69	1.19	−0.10	0.989
50	−0.72	1.22	−0.09	0.988

Table 6. Winstein-Grunwald m values for solvolysis of YC₆H₄ CH₂CH₂OSO₂C₆H₄Z in MeOH-H₂O at 55°C

p-Y ＼ p-Z	Yt-BuCl				
	NO₂	Cl	H	CH₃	CH₃O
CH₃O	0.35	0.32	0.31	0.31	0.29
H	0.24	0.21	0.19	0.19	0.18
Br	0.23	0.20	0.19	0.19	0.18
NO₂	0.20	0.18	0.17	0.16	0.14

r >0.997 ± 0.003.

the rate constant, k_1; a greater ρ_Z value is consistent with an increasing contribution of the aryl assisted pathway, resulting in a greater degree of bond cleavage, for a more EDS in the substrate as well as for a water-rich solvent.

Twelve rate constants for each solvent mixture were subjected to multiple linear regression analysis[4] using eq (2), and the cross interaction constants ρ_{YZ} were obtained as summarized in Table 5. Inspection of Table 5 reveals that $\rho_Y^{\ddagger}$ and ρ_Z values agree well with those from the simple Hammett correlations in Tables 3 (for Z = H) and 4 (for Y = H). Since

$$\rho_{YZ} = \left(\frac{\partial^2 \log k_{YZ}}{\partial \sigma_Y^+ \partial \sigma_Z}\right) = \frac{\partial \rho_Z}{\partial \sigma_Y^+} < 0 \tag{3}$$

eq (2) shows that the negative ρ_{YZ} values imply a greater degree of bond cleavage ($\rho_Z > 0$) with a more EDS ($\sigma_Y^+ < 0$) in the substrate. The magnitude of ρ_{YZ} is comparable to that found for the reactions of benzyl benzenesulfonates with anilines,[2a,5] ($|\rho_{YZ}| \approx 0.11$ for X = H). This is, however, surprising since the 2-phenylethyl system has an extra CH₂ group in between the substituent Y and the reaction center, β-carbon atom; an extra CH₂ group will increase the distance and hence is expected to decrease the $|\rho_{YZ}|$ value in comparison with the benzyl system. Since we expect both benzyl and 2-phenylethyl systems to react by the S_N2 mechanism, a comparable magnitude of ρ_{YZ} would indicate that in the latter system the participation of aryl assisted pathway reduces the distance between the two substituents. The distance between the two substituents, Y and Z, are indeed nearer in the TS structure for the aryl assisted pathway, TSΔ, compared with that for the solvent assisted one, TS_S; the C_α carbon is also partially attached to the ring carbon in TSΔ, whereas no such bond formation is possible in TS_S. The $|\rho_{YZ}|$ value is the smallest for MeOH and increases to a greater value until 80% MeOH, then it levels off to a near constant value. This can be due to the greater nucleophilicity of MeOH contributing more initially and reducing the contribution of kΔpath relative to that of k_s; the size of ρ_{YZ} in the methanol-rich solvent decreases since the solvent assisted pathway, k_s, is ex-

Table 7. Activation Parameters, ΔH^* (kcal / mol) and ΔS^* (e.u.), for Solvolysis of $YC_6H_4CH_2CH_2OSO_2C_6H_4Z$ in $MeOH\text{-}H_2O$ solvents

MeOH V/V%		Z = p-NO₂ ΔH^*	$-\Delta S^*$	p-Cl ΔH^*	$-\Delta S^*$	H ΔH^*	$-\Delta S^*$	p-CH₃ ΔH^*	$-\Delta S^*$	p-CH₃O ΔH^*	$-\Delta S^*$
100	Y = p-CH₃O	23.6	6.2	24.6	6.0	25.0	5.9	25.3	5.7	25.6	5.4
	H	21.7	13.4	22.8	12.9	23.2	12.6	23.6	12.4	23.9	11.9
	p-Br	21.0	16.7	22.0	16.3	22.6	15.7	23.0	15.2	23.2	14.9
	p-NO₂	20.9	17.8	21.8	17.6	22.2	17.4	22.6	16.9	23.0	16.3
90	p-CH₃O	23.1	6.3	24.1	6.2	24.6	5.9	24.9	5.8	25.2	5.6
	H	21.4	13.6	22.4	13.1	23.0	12.7	23.4	12.4	23.7	12.0
	p-Br	20.6	16.9	21.7	16.6	22.3	15.8	22.8	15.3	23.0	14.9
	p-NO₂	20.6	18.1	21.5	17.7	21.9	17.6	22.4	17.0	22.8	16.3
80	p-CH₃O	22.7	6.3	23.7	6.3	24.3	6.1	24.6	5.8	24.9	5.7
	H	21.1	13.8	22.2	13.1	20.7	12.9	23.2	12.4	23.5	12.0
	p-Br	20.3	17.2	21.4	16.8	22.1	15.9	22.5	15.4	22.8	15.0
	p-NO₂	20.3	18.4	21.3	17.9	21.7	17.7	22.2	17.1	22.7	16.3
70	p-CH₃O	22.2	7.0	23.3	6.7	23.8	6.2	24.3	5.9	24.6	5.7
	H	20.8	13.9	21.9	13.4	22.4	13.1	23.0	12.4	23.3	12.1
	p-Br	20.1	17.3	21.2	16.8	21.9	16.0	22.3	15.5	22.6	15.1
	p-NO₂	20.0	18.6	21.2	17.9	21.5	17.9	22.0	17.2	22.5	16.4
60	p-CH₃O	21.9	7.1	23.0	6.3	23.6	6.3	24.0	6.0	24.3	5.8
	H	20.5	14.4	21.7	13.6	22.2	13.4	22.8	12.5	23.2	12.1
	p-Br	19.9	17.4	20.9	17.1	21.7	16.2	22.2	15.5	22.5	15.2
	p-NO₂	19.8	18.8	20.9	18.1	21.4	17.9	21.9	17.3	22.4	16.4
50	p-CH₃O	21.5	7.5	22.7	7.2	23.4	6.5	23.8	6.1	24.1	5.8
	H	20.3	14.6	21.4	13.9	22.0	13.6	22.6	12.7	23.0	12.2
	p-Br	19.7	17.6	20.8	17.1	21.5	16.2	22.0	15.6	22.3	15.3
	p-NO₂	19.6	19.0	20.7	18.3	21.2	18.0	2L7	17.4	22.3	16.6

pected to contribute more in a methanol-rich solvent and hence the distance is kept farther apart between the two substituents Y and Z.

The Grunwald-Winstein plots,[6] (4), yielded good linearities in general with m values shown in Table 6. The m values are small, supporting that the reaction proceeds via a typical

$$\log (k/k_o) = mY \tag{4}$$

S_N2 process.[6] The size, however, increases with a better nucleofuge and with a more EDS in the substrate, indicating again a greater contribution of the ionizing power of solvent in favor of the aryl assisted pathway, $k\Delta$.

Activation parameters calculated at two temperatures are summarized in Table 7. A striking anomaly in the magnitude of activation parameters is shown to be an exceptionally low negative entropy of activation for the p-MeO substituted substrate ($Y = p$-MeO). If we compare entropy changes involved in the TS formation for the two pathways, $k\Delta$ and k_s, we can see why the negative ΔS^* value for $Y = p$-MeO is so small: since p-MeO substituent in the substrate is very efficient in stabilizing the $TS\Delta$, the contribution of the $TS\Delta$ increases relative to that of TS_s, which in turn will contribute to increase the entropy. It is obvious that the $TS\Delta$ itself is a higher entropy state than the reactant since the TS is formed unimolecularly, while the TS_s is formed bimolecularly and a decrease in entropy is expected. Disregarding an approximately equal contribution of electrostriction entropy decrease for both pathways, an increase in the contribution of $k\Delta$ will result in an increase in (positive) entropy. This is supported

Table 8. Isokinetic Temperature β(K) for Solvolysis of YC_6H_4 $CH_2CH_2OSO_2C_6H_4Z$ in $MeOH\text{-}H_2O$ (Texp = 328.15 K).

MeOH V/V %	p-Z NO₂	Cl	H	CH₃	CH₃O	Correl. Coeft.
100	238	245	241	241	244	
80	207	211	224	214	214	r>0.913
50	170	185	192	187	181	

MeOH V/V %	p-Y CH₃O	H	Br	NO₂	Correl. Coeft.
100	2420	1480	1150	1219	
80	2491	1353	1041	1083	r>0.995
50	1382	1081	1043	1067	

by the entropy controlled[7] nature of the reaction exhibited by a low isokinetic temperature β, eq 5, for variations in the substituent Y in the substrate.

$$\delta \Delta H^* = \beta \delta \Delta S^* \tag{5}$$

Reference to Table 8 reveals that due to the involvement of aryl assisted pathway, the variations in the substituent Y in the substrate cause wider range variations in ΔS^* as compared with the variations accompanying with substituent Z in the leaving group.

We conclude that all available evidence, especially the magnitude of the cross interation constants, supports the interpretation that 2-phenylethyl benzenesulfonates sovolyze by competing aryl assisted and solvent assisted pathways.

Experimental

Materials. G. R. grade methanol from Merck was used without further purification. Water was passed through an ion exchange column and distilled three times over KMnO₄, which gave conductivity of less than 20 μmho. 2-Phenylethyl benzenesulfonates were prepared, adopting Tipson's method,[8] by reacting phenylethyl alcohols with benzenesulfonyl chlorides in pyridine, and recrystallized form n-hexane and ether more than twice. Melting points and spectral data for compounds synthesized are as follows:

$C_6H_5CH_2CH_2OSO_2C_6H_4NO_2$; m.p, 99-100° (lit. 101.5-102),[9] 1615cm⁻¹ ($\nu C=C$), 1370cm⁻¹ ($\nu as\ SO_2$), 1190cm⁻¹ (νSO_2), 1050cm⁻¹ ($\nu S-O$), 2.9 (β, 2H, t), 4.2 (α, 2H, t), 7.0 (phenyl, 9H, m).

$C_6H_5CH_2CH_2OSO_2C_6H_4Cl$; m.p, 48-51° (lit. 51°),[10] 1590cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1185cm⁻¹ ($\nu S-O$), 1050cm⁻¹ ($\nu S-O$), 3.0 (β, 2H, t), 4.4 (α, 2H, t), 7.3 (phenyl, 9H, m).

$C_6H_5CH_2CH_2OSO_2C_6H_5$; m.p, oil (lit. 14-15°),[9] 1605cm⁻¹ ($\nu C=C$), 1365 cm⁻¹ ($\nu as\ SO_2$), 1190cm⁻¹(νSO_2), 1030cm⁻¹ ($\nu S-O$), 2.8 (β, 2H, t). 4.0 (α, 2H, t), 6.9 (phenyl, 10H, m).

$C_6H_5CH_2CH_2OSO_2C_6H_4CH_3$; m.p, 38-39° (lit. 36-37°),[9] 1600 cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1175cm⁻¹ (νSO_2), 1050cm⁻¹ ($\nu S-O$), 2.4 (CH₃, 3H, s), 2.9 (β, 2H, t), 4.2 (α, 2H, t), 7.2 (phenyl, 9H, m).

$C_6H_5CH_2CH_2OSO_2C_6H_4OCH_3$; m.p, 27° (lit. 26°),[10] 1600cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1170cm⁻¹ (νSO_2), 1025cm⁻¹ ($\nu S-O$), 2.9 (α, 2H, t), 3.8 (CH₃O, 3H, s) 4.0 (α, 2H, t) 7.0 (phenyl, 9H, m). $CH_3OC_6H_4CH_2OSO_2C_6H_4NO_2$; m.p, 96-97° (lit. 98°),[9] 1615 cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1185cm⁻¹ (νSO_2), 1040cm⁻¹ ($\nu S-O$), 2.8 (β, 2H, t), 3.7 (CH₃O, 3H, s), 4.1 (α, 2H, t), 6.7 (phenyl, 8H, m). $CH_3OC_6H_4CH_2CH_2OSO_2C_6H_4Cl$; m.p, 41-42°, 1615cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1180 cm⁻¹ (νSO_2), 1030cm⁻¹ ($\nu S-O$), 2.8 (β, 2H, t), 3.7 (CH₃O, 3H, s), 4.0 (α, 2H, t), 6.6 (phenyl, 8H, m). $CH_3OC_6H_4CH_2CH_2OSO_2C_6H_5$; m.p, 69-70° (lit. 72-73°),[9] 1615cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1185 cm⁻¹ (νSO_2), 1035cm⁻¹ ($\nu S-O$). 2.8 (β, 2H, t), 3.7 (CH₃O, 3H, s), 4.1 (α, 2H, t), 6.7 (phenyl, 9H, m). $CH_3OC_6H_4CH_2CH_2OSO_2C_6H_4CH_3$; m.p, 54-55° (lit. 57-58°),[9] 1620 cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1180cm⁻¹ (νSO_2), 1040cm⁻¹ ($\nu S-O$), 2.4 (CH₃, 3H, s), 2.8 (β, 2H, t), 3.7 (CH₃O, 2H, s), 4.0 (α, 2H, t), 6.6 (phenyl, 8H, m). $CH_3OC_6H_4CH_2CH_2OSO_2C_6H_4OCH_3$; m.p, 55-56°, 1600cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1170cm⁻¹ (νSO_2), 1030cm⁻¹ ($\nu S-O$), 2.7 (β, 2H, t), 3.6 (CH₃O, 6H, s), 4.0 (α, 2H, t), 6.6 (phenyl, 8H, m). $BrC_6H_4CH_2CH_2OSO_2C_6H_4NO_2$· m.p, 150° 1610 cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1180cm⁻¹ ($\nu SO_2$), 1020 cm⁻¹ ($\nu S-O$), 2.8 ($\beta$, 2H, t). 4.2 ($\alpha$, 2H, t), 6.8 (phenyl, 8H, m). $BrC_6H_4CH_2CH_2OSO_2C_6H_4Cl$; m.p, 73-75°, 1595cm⁻¹ ($\nu C=C$), 1365cm⁻¹ ($\nu as\ SO_2$), 1180cm⁻¹ (νSO_2), 1020cm⁻¹ ($\nu S-O$), 2.8 (β, 2H, t), 4.1 (α, 2H, t), 6.8 (phenyl, 8H, m).

$BrC_6H_4CH_2CH_2OSO_2C_6H_5$; m.p, 56-57°, 1590cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1180cm⁻¹ (νSO_2), 1020cm⁻¹ ($\nu S-O$), 2.8 (β, 2H, t), 4.1 (α, 2H, t), 6.9 (phenyl, 9H, m). $BrC_6H_4CH_2CH_2OSO_2C_6H_4CH_3$; m.p, 84-85° (lit. 82-83°),[10] 1600 cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1175cm⁻¹ (νSO_2), 1025 cm⁻¹ ($\nu S-O$), 2.3 (CH₃, 3H, s), 2.8 (β, 2H, t), 4.0 (α, 2H, t), 7.0 (phenyl, 8H, m). $BrC_6H_4CH_2CH_2OSO_2C_6H_4OCH_3$; m.p, 71-72°, 1600cm⁻¹ ($\nu C=C$), 1360cm⁻¹ ($\nu as\ SO_2$), 1170 cm⁻¹ (νSO_2), 1020cm⁻¹ ($\nu S-O$), 2.8 (β, 2H, t), 3.8 (CH₃O, 3H, s), 4.0 (α, 2H, t), 6.8 (phenyl, 8H, m). $NO_2C_6H_4CH_2CH_2OSO_2C_6H_4Cl$; m.p, 137-139°, 1610cm⁻¹ ($\nu C=C$), 1365cm⁻¹ ($\nu as\ SO_2$),
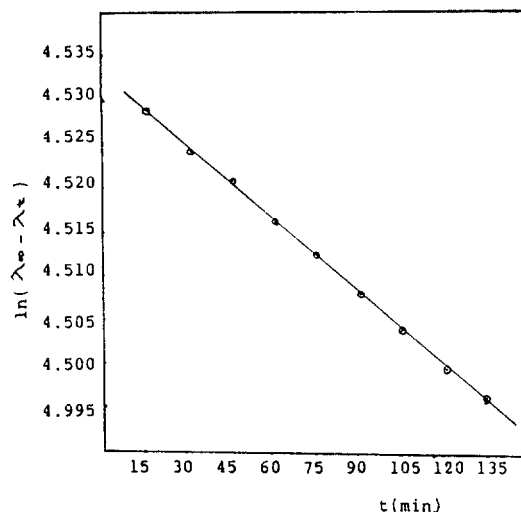
Figure 1. The plot of $\ln(\lambda_\infty - \lambda_t)$ vs. t for solvolysis of $C_6H_5CH_2CH_2$ $OSO_2C_6H_5$ in MeOH-H₂O at 55°C (MeOH V/V%; 100%).

1180cm⁻¹ (νSO_2), 1020cm⁻¹ ($\nu S-O$), 3.1 (β, 2H, t), 4.4 (α, 2H, t), 7.5 (phenyl, 8H, m). $NO_2C_6H_4CH_2CH_2OSO_2C_6H_5$; m.p, 75-76°, 1605cm⁻¹ ($\nu C=C$), 1350cm⁻¹ ($\nu as\ SO_2$), 1180cm⁻¹ (νSO_2), 1020cm⁻¹ ($\nu S-O$), 2.9 (β, 2H, t), 4.1 (α, 2H, t), 6.9 (phenyl, 9H, m). $NO_2C_6H_4CH_2CH_2OSO_2C_6H_4CH_3$; m.p, 117-119° (lit. 117-118°)[10], 1605cm⁻¹ ($\nu C=C$), 1350cm⁻¹ ($\nu as\ SO_2$), 1180cm⁻¹(νSO_2), 1025cm⁻¹($\nu S-O$), 2.5 (CH₃, 3H, s), 3.0 (β, 2H, t), 4.3 (α, 2H, t), 7.3 (phenyl, 8H, m). $NO_2C_6H_4CH_2CH_2OSO_2C_6H_4OCH_3$; m.p, 76°, 1595cm⁻¹ ($\nu C=C$), 1380cm⁻¹ ($\nu as\ SO_2$), 1180cm⁻¹ ($\nu SO_2$), 1050cm⁻¹ ($\nu S-O$), 3.1 ($\beta$, 2H, t), 3.9 (CH₃O, 3H, s), 4.3 (α, 2H, t), 6.9 (phenyl, 8H, m). NO_2 $C_6H_4CH_2CH_2OSO_2C_6H_4NO_2$; m.p, 118-120°, 1608cm⁻¹ ($\nu C=C$), 1375cm⁻¹ ($\nu as\ SO_2$), 1190cm⁻¹ (νSO_2), 1020cm⁻¹ ($\nu S-O$), 3.0 (β, 2H, t), 4.2 (α, 2H, t), 7.0 (phenyl, 8H, m).

Rate constants. Rates were monitored conductometrically using Toa Electronic CM-20E type conductivity bridge with a cell of cell constant 1.695cm. Substrate concentrations were ~10⁻³M and temperature was kept to ±0.05°C at 45.0 and 55.0°C. Pseudo-first order rate constants, k_1, for solvolyses were obtained from the Guggenheim plots,[11] eq (6).

$$\ln (\lambda_\infty - \lambda_t) + k_1 t = \text{const} \tag{6}$$

Rate constants, k_1, were reproducible to ±5%. An example of the Guggenheim plot in shown in Figure 1.

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Polymer Adsorption at the Oil-Water Interface

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A general theory of polymer adsorption at a semi-permeable oil-water interface of the biphasic solution is presented. The configurational factor of the solution in the presence of the semi-open boundary at the interface is evaluated by the quasi-crystalline lattice model. The present theory gives the feature of the bulk concentration equilibria between oil-water subsystems and the surface excesses of Γ^{α} and Γ^{β} of the polymer segments as a function of the degree of polymerization r, the Flory-Huggins parameter in β-phase x_p^β, the differential adsorption energy parameter in β-phase x_s^β, the differential interaction energy parameter Δx_p and the bulk concentration of the polymer in β-phase $\varphi_2^{\beta'*}$. From our numerical results, the characteristics of Γ^{α} are shown to be significantly different from those of Γ^{β} in the case of high polymers, and this would be the most apparent feature of the adsorption behavior of the polymer at a semi-permeable oil-water interface, which is sensitively dependent on Δx_p and r.

Introduction

The adsorption behavior of the polymer at an interface from its solution is of great importance in theoretical and practical aspects, and it plays an essential role in colloid science, such as adhesion, flocculation, stablization and destabilization of colloid particles by polymeric additives. But, there have been comparatively little researches concerned with the adsorption of polymer molecules at a "*semipermeable*" liquid-liquid interface which only the solute molecules can penetrate. Most of researches[1-7] in adsorption phenomena of the polymer have been confined to the adsorption behavior at the impermeable interface from binary polymer solution. Recently, Halperin and Pincus[8] have developed a theory of adsorption behavior at a liquid-liquid interface based on the van der Waals-Cahn-de Gennes theory.[9-12] This theory, though presenting the semi-quantitative descriptions of the adsorption behavior, comprehensively made the theoretical demonstration of the polymer adsorption behavior at a liquid-liquid interface.

In the case of a ternary mixture consisting of the polymer and the biphasic solvents, the adsorption behavior of the polymer at a semi-permeable liquid-liquid interface may be quite different from the corresponding case of impermeable interface and significantly pertaining to wetting behavior, stabilization of emulsion and colloidal dispersion by polymeric additives, etc. Each walk of a polymer chain near or at the interface is considerably influenced by its solubility factors determined by the biphasic solvents. Therefore, unlike the feature of an impermeable interface, at only one side of which the polymer adsorption takes place, the possible segmental walk of a polymer chain at the semi-permeable liquid-liquid interface under consideration may be allowed for passing through the interface from one phase into another. From the results of our numerical calculation, the adsorption amount of the polymer in poor phase is considerably recognizable even when its solubility in poor solvent is extremely small, and its adsorption behavior in poor phase is significantly different from that in good phase.

In this paper, we present a general theory of polymer adsorption from its biphasic solutions at a semi-permeable liquid-liquid interface. Our theory is based on a quasi-crystalline lattice model consisting of lattice layers parallel to the interface. The expression for the configurational term of present system is derived by a lattice statistics closely similar to the one used by Flory[13,14] in his works of Flory-Huggins lattice model of ideal polymer solution. The lattice model in our theory has a semi-open boundary at the interface. Therefore, at first we derive a general expression for the configurational term of the arbitrary lattice and apply this general expression to the present system. This procedure is closely similar to the one used in comprehensive lattice model of the polymer adsorption at an impermeable interface by Roe,[4] but the reference state of each phase in our system corresponds to its bulk polymer solution instead of the amorphous polymer state as assumed in ealier lattice theories.[4,6]