Catalyses of Polymer Complexes. 4. Polysoap-Catalyzed Decarboxylation of 6-Nitrobenzisoxazole-3-carboxylate Anion. Importance of the Hydrophobic Environment in Activation of the Anion

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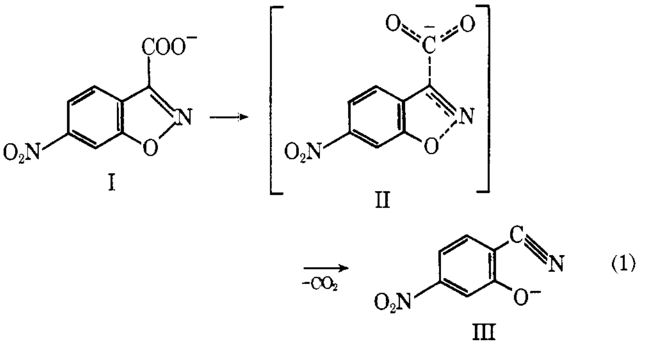
The unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion is markedly catalyzed by cationic polysoaps: partially laurylated poly(4-vinylpyridine) and poly(2-ethyl-1-vinylimidazole). The polymers which acted as efficient catalysts invariably caused the hypsochromic shift of the absorption maximum of methyl orange, and increased dissociation of dichlorophenolindophenol and the fluorescent emission of 1-anilinonaphthalene-8-sulfonate. The linear correlation observed between the logarithm of the rate constant and the wavenumber of the absorption maximum of methyl orange indicates the importance of the hydrophobic environment of polymer micelles in the rate enhancement. The decarboxylation reaction in aprotic solvents, which was performed in connection with the environmental effect of polysoaps, is relatively insusceptible to small amounts of water. The polysoap catalysis can be further enhanced by adding hydrophobic anions and organic solvents (methanol, *tert*-butyl alcohol, acetone). The catalytic efficiency of the polysoap is related to the formation of the hydrophobic domain and the desolvation of the anion is of less importance than in other micelle-catalyzed bimolecular reactions involving oxy anionic nucleophiles.

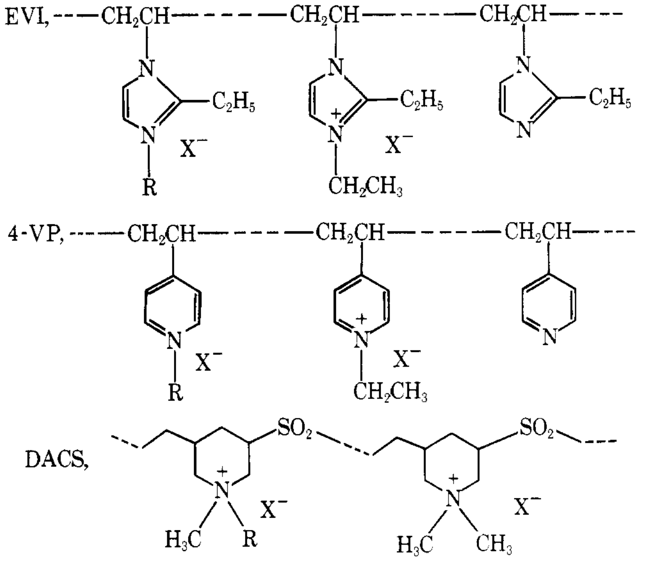
Electrostatic and hydrophobic interactions are major driving forces for the binding of small molecules to enzymes and cause activation of adsorbed substrates.[1,2] The use of micelles and polyelectrolytes which serve as efficient catalysts for many organic reactions would be among the most expeditious methods to employ these interactions in model enzyme systems.[3,4] Charged polysoaps (polymer micelles) such as poly(vinylpyridines) quaternized by long alkyl chains combine within a molecule structural characteristics of the conventional micelles and polyelectrolytes, and supposedly adopt globular conformations in aqueous media with the hydrophobic region inside and the charged group outside as in some water-soluble proteins.[5,6] The hydrophobicity of polysoap is readily adjustable by changing the content of the long alkyl group. Thus, the charged polysoap would be one of the best model enzyme systems.

The study of the catalytic behavior of polysoaps has been very limited.[7–10] Recently, we found that cationic polysoaps unusually enhanced the nucleophilic reactivity of the bound hydroxamate and thiolate anions toward *p*-nitrophenyl acetate.[10–12] This unusual rate acceleration is largely derived from formation of "*hydrophobic ion pairs*" between anionic nucleophiles and cationic surfactant molecules.[13–15] Unimolecular reactions would be better probes of the environmental effect on the anionic reactivity than bimolecular reactions, since one need not take the proximity term into account. The decarboxylation of carboxylic acids would meet this requirement, since it is unimolecular, almost free from acid and base catalysis, and the rate constants are extremely solvent dependent.[16]

In this paper, we wish to report the polysoap-catalyzed decarboxylation of 6-nitrobenzisoxazole-3-carboxylate anion (I) and to discuss the influence of the electrostatic and hydrophobic environments on the reaction rate. The polymers employed are derivatives of poly(2- and 4-vinylpyridines) (2-VP and 4-VP), poly(2-ethyl-1-vinylimidazole) (EVI), and a copolymer of diallylammonium chloride and SO_2 (DACS). As for example, the polymer abbreviated as EVI-L-9 contains 9 mol % of the lauryl group (for details see Table I).



Polymers:



Experimental Section

Materials. 6-Nitrobenzisoxazole-3-carboxylic acid was prepared according to the method of Borche,[17] and recrystallized from methanol, mp 167–169 °C [lit.[17] 167–169 °C (monohydrate)]. Hexadecyltrimethylammonium bromide (CTAB) and hexadecyltrimethylammonium chloride (CTAC) were purchased from Wako Pure Chemical Industries, and recrystallized from ethanol before use. Proton sponge [1,8-bis(dimethylamino)naphthalene] was the product of Aldrich, and used without further purification.

Preparations of polysoaps from 4-VP, 2-VP, and EVI have been described.[9–11] DACS was kindly supplied by the Nitto-Boseki Co. Research Laboratories for Chemical Fibers.

Purification of Solvents. Acetonitrile and benzonitrile were distilled from phosphorus pentoxide. Benzene was distilled from sodium metal. All the solvents were stored over molecular sieve 5A, and used within 1 week from the day of preparation.

Spectroscopic Measurements. Absorption spectra of methyl orange in the presence of polysoaps were measured on a Hitachi 124

Table I. Composition of Polymers and Several Aqueous Properties

Registry no.	Polymer	Lauryl group content, mol %	Ethyl group content, mol %	$[\eta]$,[a] dl g^{-1}	λ_{max} of methyl orange,[b] nm	K_{DCPI}, M^{-1}
60595-46-2	EVI-L-41	41	49	0.048	433	379
	EVI-L-29	29	67	0.037	417	1207
	EVI-L-9	9	83	0.496	463	~10
59950-02-6	2-VP-L-30	30	~70		427	
59950-03-7	4-VP-L-33	33	48		421	1020
	4-VP-L-22	22	42		440	479
	4-VP-L-12	12	65		449	~30
	4-VP-L-3	3	96		456	
57033-24-6	4-VP-Et-85	0	85		465	
60595-47-3	4-VP-Hx-65	65[c]	0		465	
60595-48-4	4-VP-Bzl-95	95[c]	0		472	
60607-13-8	DACS-LB-22	22[c]	0		437	
	None				465	

[a] 30 °C, μ = 0.02 with KBr; cited from ref 9. [b] 30 °C, pH 9.0, [methyl orange] = 2.50×10^{-5} M, [polymer] = $(1\text{–}3) \times 10^{-2}$ M; partially cited from ref 12. [c] Hx (hexyl group), Bzl (benzyl group), LB (*p*-laurylbenzyl group).

UV-visible spectrophotometer at 30 °C in aqueous solutions adjusted to pH 9.0 with 0.02 M borate buffer. Absorption spectra of dichlorophenolindophenol (DCPI) were obtained at 30 °C in aqueous 0.1 M acetate buffer (pH 3.4). Fluorescence spectra of 1-anilinonaphthalene-8-sulfonate were measured at room temperature by Dr. K. Kano.

Kinetics in Aqueous Systems. The stock solution of I for kinetic measurements in aqueous systems was prepared in ethanol on the day of use. The reaction was initiated by mixing of an aqueous polysoap solution buffered at pH 9.0 with 0.02 M borate with an ethanol solution of I. The progress of the reaction was followed spectrophotometrically at 410 nm (λ_{max} of 2-cyano-5-nitrophenolate, III) using a Hitachi 124 spectrophotometer with a thermostated cell holder. All the kinetic experiments were performed at a calculated ionic strength of 0.01 with KCl unless otherwise stated. The first-order rate constants (k_d) for decarboxylation were determined for up to 4 half-lives (correlation coefficient >0.998).

Kinetics in Organic Solvents. The reaction in organic solvents was initiated by neutralizing the carboxylic function of I by excess proton sponge (ca. three times).

In a rubber-sealed cuvette purged with nitrogen was placed a benzene solution of I and the solution was equilibrated to 30 °C. Then a benzene solution of proton sponge was rapidly added from a syringe, and the reaction was followed spectrophotometrically at 410 nm. The reaction in acetonitrile and benzonitrile was too fast to follow by the conventional spectrophotometer. A stopped-flow apparatus (Union Giken RA-1300), the mixing cell of which is covered with a nitrogen globe, was used for the kinetic measurements. *p*-Toluenesulfonic acid (10 mol % of I) was added to the substrate solution in order to suppress the spontaneous decay of I.

The water content in organic solvents was measured immediately after the reaction with a Hiranuma Aquacounter AQ-1. Several determinations was averaged and the relative error was 5% for benzene and ca. 10% for acetonitrile and benzonitrile.

Surface Tension. Surface tension of aqueous polysoap solutions was measured at room temperature by using a Kyowa Kagaku SR-IV apparatus.

Results

Characterization of Polysoaps. Prior to the kinetic study, several properties of the aqueous polysoap were evaluated. The composition of polysoaps was estimated by both elemental analysis and NMR spectroscopy[9-12] and recorded in Table I. Table I also gives viscosities of the quaternized polymers and absorption spectra of methyl orange measured in the presence of these polymers.

It has been noticed that the intrinsic viscosity of EVI-L-9 is more than ten times larger than those of EVI-L-29 and EVI-L-41.[9] Supposedly, the EVI-L-9 polymer adopts an expanded conformation owing to the electrostatic repulsion like some polyelectrolytes. On the other hand, EVI-L-29 and EVI-L-41 seem to assume compact conformations owing to the hydrophobic aggregation of lauryl groups in spite of the electrostatic repulsion.

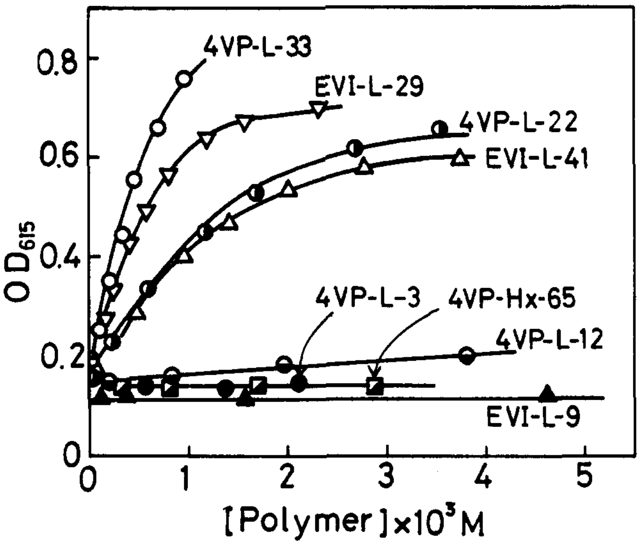


Figure 1. Absorbance of dissociated dichlorophenolindophenol (λ_{max} 615 nm) plotted against the polymer concentration (calculated based on the total concentration of the monomer unit). [DCPI] = $(0.96\text{–}1.36) \times 10^{-4}$ M, pH 3.4 with 0.1 M acetate.

Visible spectra of methyl orange are frequently employed in order to detect the hydrophobic region present in aqueous media,[18-20] since λ_{max} near 465 nm shifts to shorter wavelengths owing to the hydrophobic environment surrounding the methyl orange molecule. Table I shows that the aqueous solutions of EVI-L-9, 4-VP-L-3, 4-VP-Et-85, 4-VP-Hx-65, and 4-VP-Bzl-95 hardly affected the visible spectra of methyl orange. In contrast, appreciable hypsochromic shifts occurred in the presence of EVI-L-29, EVI-L-41, 2-VP-L-30, 4-VP-L-22, 4-VP-L-33, and DACS-LB-22. The largest hypsochromic shift was observed for EVI-L-29 (417 nm), which is comparable to that in ethanol (418 nm).[21] The polymer which contains more than 10 mol % of the lauryl group appears to form sufficiently hydrophobic domains and causes the spectral shift of adsorbed methyl orange.

2,6-Dichlorophenolindophenol (DCPI) in aqueous acidic solutions is an excellent probe for the micelle formation, the critical micelle concentration (cmc) being detectable based on the color change from light red (undissociated phenol: 517 nm) to blue (phenolate anion: 606 nm).[22] As shown in Figure 1, the polymers with no or small lauryl group contents (less than 12 mol %) little affected the absorption spectrum of DCPI. On the other hand, the absorption band at 615 nm increased with increasing concentrations of EVI-L-41, EVI-

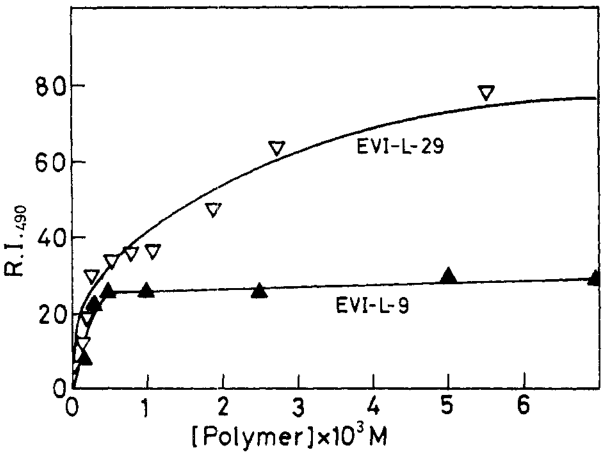


Figure 2. Relative intensity of fluorescent emission of 1-anilinonaphthalene-8-sulfonate (490 nm) plotted against the polymer concentration. [1-Anilinonaphthalene-8-sulfonate] = 1.0 × 10^{-4} M, room temperature.

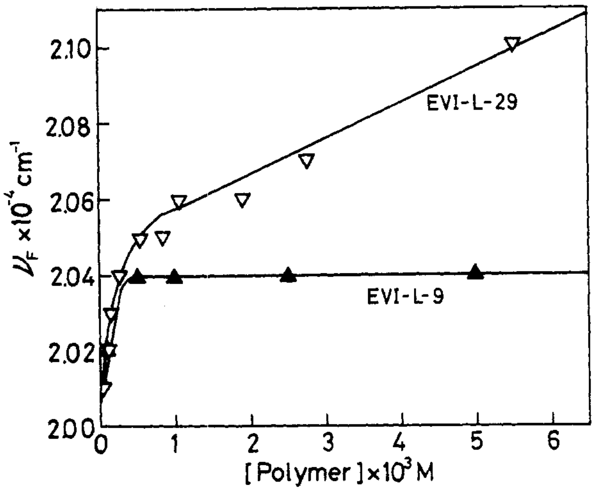


Figure 3. Wavenumber of maximum fluorescence of 1-anilinonaphthalene-8-sulfonate plotted against the polymer concentration. [1-Anilinonaphthalene-8-sulfonate] = 1.0 × 10^{-4} M, room temperature.

L-29, 4-VP-L-33, and 4-VP-L-22, and gradually reached saturation. Thus, these polymers can bind DCPI in the hydrophobic domain, causing the dissociation of DCPI. The binding constants (K_{DCPI}) evaluated based on the Benesi–Hildebrand equation[23] (correlation coefficient >0.99) are recorded in Table I.

Another useful method to monitor the formation of the hydrophobic region is the fluorescent emission. In Figure 2, the normalized relative intensity (R.I.) of 1-anilinonaphthalene-8-sulfonate (490 nm) is plotted as a function of the polymer concentration. The plots for EVI-L-9 rapidly saturated at [EVI-L-9] = ca. 5 × 10^{-4} M to give a plateau below R.I. 30. On the other hand, those for EVI-L-29 gradually increased up to R.I. 85 with increasing polysoap concentrations, indicating that the hydrophobicity is strengthened by the increased polysoap concentration. We also estimated the value for the conventional cationic micelle of hexadecyltrimethylammonium chloride (CTAC: 1.0 × 10^{-2} M) to be 32 under a similar condition.

Turner and Brand[24] have correlated the fluorescent emission maximum with the Kosower's Z value (a measure of the medium polarity[25])—the higher the wavenumber of maximum fluorescence (ν_F) of the adsorbed probe, the smaller the Z value. Figure 3 shows that the ν_F value reaches a constant value at a small concentration of EVI-L-9, whereas EVI-L-29 causes a significant shift to higher frequencies. The highest value (ν_F = 2.12 × 10^4 cm^{-1}) is close to those observed in ethanol (2.083 × 10^4 cm^{-1}) or in dioxane (2.118 × 10^4 cm^{-1}).[24]

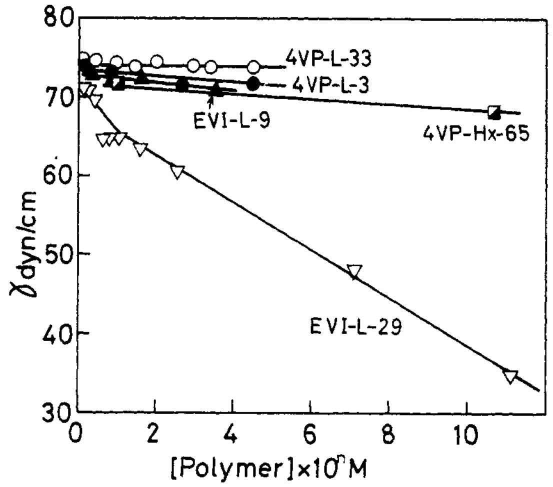


Figure 4. Surface tension at room temperature plotted against the polymer concentration: n = 4 for 4VP-L-33; n = 3 for other polymers.

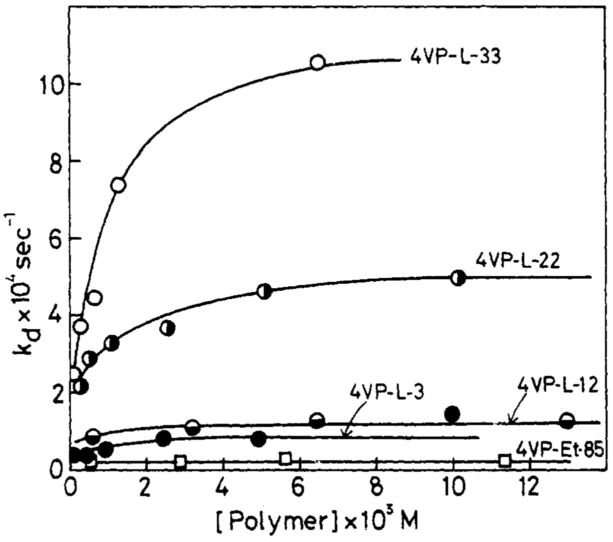


Figure 5. Decarboxylation rate plotted against the concentration of 4-VP-polymers: [I] = 1.35 × 10^{-4} M, pH 9.0 with 0.01 M borate, μ (KCl) = 0.013.

Surface tension has been also utilized to demonstrate the aggregative behavior of surfactants. Polysoaps have been believed to be surface inactive, since they form the intramolecular micelle at very low concentrations.[5] As anticipated, EVI-L-9, 4-VP-L-33, 4-VP-L-3, and 4-VP-Hx-65 did not reduce the surface tension (γ) (Figure 4). The EVI-L-29 polymer, on the other hand, was surface active. The γ value plotted as a function of the polymer concentration gradually decreased, and was 36 dyn cm^{-1} at [EVI-L-29] = 1.1 × 10^{-2} M. This value is comparable to that of the micellar hexadecyltrimethylammonium bromide (CTAB).

Polysoap-Catalyzed Decarboxylation. The catalysis of decarboxylation of I by conventional cationic micelles features the sigmoidal dependence on the surfactant concentration[26,27]—the rate constant (k_d) is almost independent of the surfactant concentration below the cmc, while it rapidly rises with increasing concentration of surfactants above the cmc, and finally a plateau is obtained for surfactant concentrations well above the cmc. The catalysis by polysoaps with high lauryl group content showed a rapid increase in the rate constant at

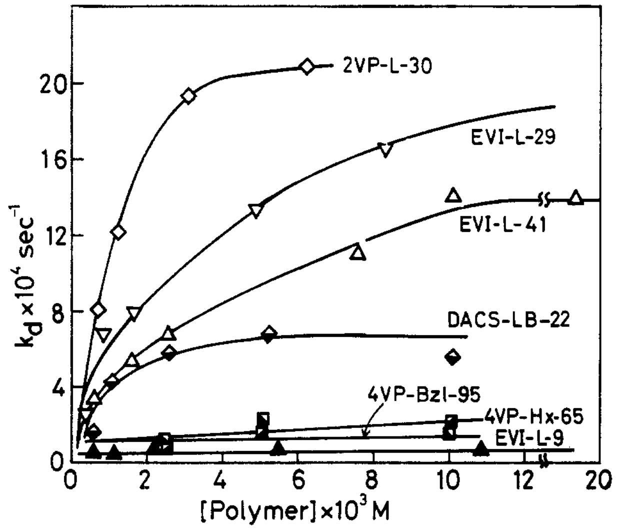


Figure 6. Decarboxylation rate plotted against the concentration of EVI and other polymers: [I] = 1.35 × 10^{-4} M, pH 9.0 with 0.01 M borate, μ (KCl) = 0.013.

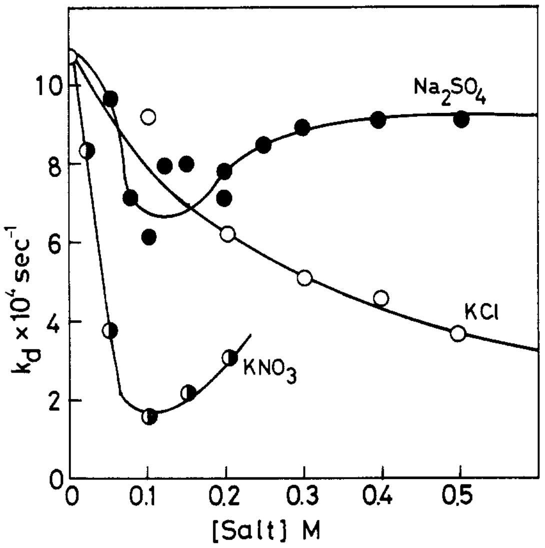


Figure 7. Effect of inorganic salts on the EVI-L-29 catalyzed decarboxylation: [I] = 1.35 × 10^{-4} M, pH 9.0 with 0.01 M borate, [EVI-L-29] = 8.4 × 10^{-3} M.

very low concentrations of the polysoap, followed by gradual rate saturation (Figures 5 and 6). As anticipated from the spectral data, EVI-L-29 showed the maximal catalytic efficiency for the decarboxylation (k_d = 2.10 × 10^{-3} s^{-1} at μ = 0.004), which amounts to the rate augmentation of 350-fold compared with that in the nonmicellar system (6.0 × 10^{-6} s^{-1}). The catalytic efficiency of EVI-L-29 exceeds that of the CTAB micelle (k_d = 3.10 × 10^{-4} s^{-1} at [CTAB] = 3 × 10^{-3} M). Figures 5 and 6 indicate that 4-VP-L-33, 4-VP-L-30, DACS-LB-22, and EVI-L-41 also serve as efficient catalysts for the decarboxylation. It is worth emphasizing that these polysoaps all caused appreciable hypsochromic shifts for methyl orange and enhanced dissociation of DCPI. In contrast, less hydrophobic polysoaps such as 4-VP-L-3, 4-VP-Et-85, 4-VP-Bzl-95, and EVI-L-9, which hardly affected the spectra of methyl orange and DCPI, did not display significant catalysis. It is evident, therefore, that the decarboxylation is only accelerated by those polysoaps with hydrophobic regions as detected by the spectral shift studies.

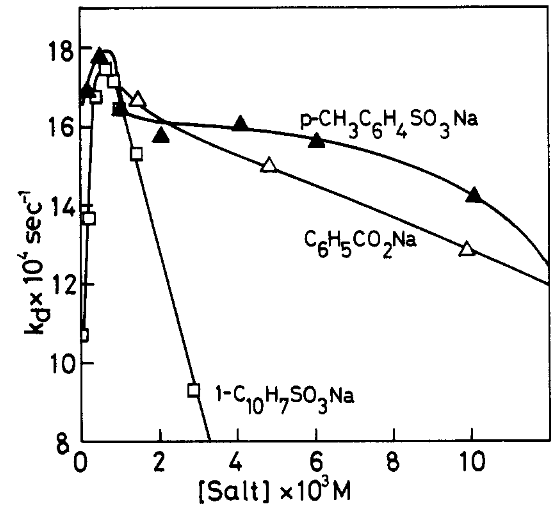


Figure 8. Effect of organic salts on the EVI-L-29 catalyzed decarboxylation: [I] = 1.35 × 10^{-4} M, pH 9.0 with 0.01 M borate, [EVI-L-29] = 8.4 × 10^{-3} M.

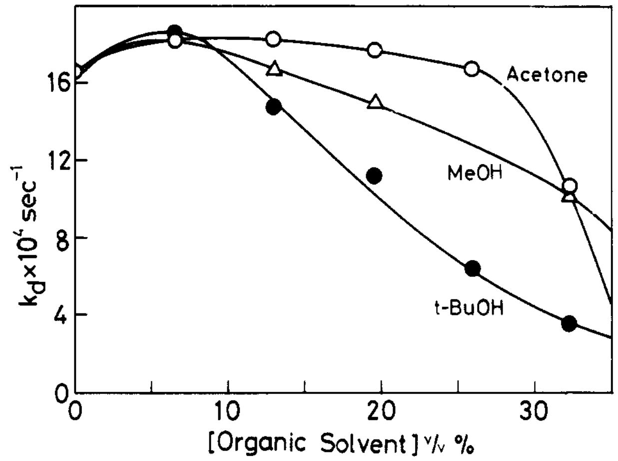


Figure 9. Effect of organic solvents on the EVI-L-29 catalyzed decarboxylation: [I] = 1.35 × 10^{-4} M, pH 9.0 with 0.01 M borate, [EVI-L-29] = 8.4 × 10^{-3} M.

Further studies of the polysoap-catalyzed decarboxylation was conducted with EVI-L-29, the most efficient catalyst among polysoaps tested herein. Figures 7 and 8 give the influence of added salts on the EVI-L-29 catalysis. The kinetic salt effect observed is complex, as in the case of the conventional cationic micelles.[26,27] Addition of inorganic, hydrophilic salts (KCl, KNO_3, Na_2SO_4) first retarded the reaction, but the rate increased at higher concentrations except for KCl. k_d might be also raised at the KCl concentration well above the concentration recorded in Figure 7. However, the EVI-L-29 solution became turbid at much higher KCl concentrations. Interestingly, low concentrations of organic salts (sulfonate and benzoate) appreciably enhanced the reaction rate, and rate maxima were observed. The maxima appeared where the concentration of the aromatic anions is close to that of the laurylated EVI unit.

Addition of organic solvents also affected the decarboxylation rate (Figure 9). In general, the reaction accelerated by hydrophobic environments is suppressed by addition of organic solvents. For decarboxylation of I this is not the case, however. Three solvents tested provided slight rate maxima at 5–10 vol/vol % of the solvent added. The influence was small below 20 vol/vol %, but the larger rate decreases were found above 20 vol/vol %.

Decarboxylation in Organic Solvents. The reaction in organic solvents was initiated by neutralizing the carboxylic acid with excess proton sponge [1,8-bis(dimethylamino)-naphthalene]. The water content was determined immediately after the reaction. The increase in the water concentration in

Table II. Decarboxylation Rates Adsorbed to the Polymer and the Association Constants[a]

Polymer	$k_d'' \times 10^3$, s^{-1}	K, M^{-1}	r
EVI-L-41	1.62	301	0.988
EVI-L-29	2.63	231	0.999
EVI-L-29[b]	2.86	991	0.994
EVI-L-29[c]	2.24	555	0.992
EVI-L-9	(0.04)		
2-VP-L-30	2.63	671	0.998
4-VP-L-33	1.01	2370	0.997
4-VP-L-22	0.460	3270	0.979
4-VP-L-12	(0.120)		
4-VP-L-3	(0.083)		
4-VP-Et-85	(0.021)		
4-VP-Hx-65	(0.210)		
4-VP-Bzl-95	(0.110)		
DACS-LB-22	0.643	1740	0.898
None	(0.006)		

[a] 30 °C, pH 9.0 with 0.01 M borate, μ (KCl) = 0.013, [EVI-L-29] = 5.0×10^{-3} M. [b] μ (KCl) = 0.004. [c] [p-Toluenesulfonate] = 5.0×10^{-4} M. Parenthesized data mean the decarboxylation rates at the highest polymer concentrations.

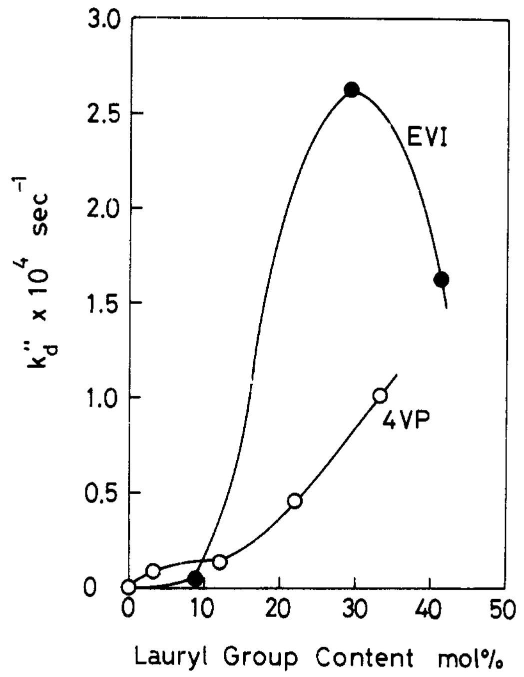


Figure 10. Decarboxylation rate of I adsorbed to the polymer plotted against the lauryl group content.

benzonitrile from 3 to 83 mM caused the rate decrease from 2.1 to 1.6 s^{-1}. The rate changes in benzene (H_2O: 6–20 mM) and in acetonitrile (H_2O: 16–125 mM) were smaller. Therefore, the decarboxylation rate is much less susceptible to minute amounts of water than the rate of bimolecular reactions involving oxyanionic nucleophiles.[14,15]

Discussion

The polysoap is generally believed not to possess the cmc unlike conventional micelles.[5] Instead, the transition from polyelectrolyte to polymer micelle is observed at 10–13 mol % of the lauryl-group content, where drastic reduction in viscosity and increase in solubilization ability occur.[5,6,9] The spectral studies also indicated this transition: polymers with more than 12 mol % of the lauryl group caused the micellelike spectral changes, while polymers with less lauryl groups hardly affected the spectrum of the adsorbed dye. Thus, the former polymers would be classified as polymer micelles and the latter as typical polyelectrolytes. The decarboxylation of I was catalyzed only by polymer micelles.

The absorption spectrum of methyl orange and the fluorescent emission of 1-anilinonaphthalene-8-sulfonate indicate that the hydrophobic environment of some polymer micelles is comparable to that of ethanol. In particular, aqueous EVI-L-29 showed the highest hydrophobic nature, despite its lower lauryl-group content than that of EVI-L-41. It is said that incorporation of excess lauryl groups stiffens the polymer chain and an expanded conformation results.[5] Table I shows that the smaller the intrinsic viscosity, the larger are the shifts of methyl orange and the K_{DCPI} value (EVI-L-29 > EVI-L-41 ≫ EVI-L-9). Therefore, the hydrophobicity of the polymer micelle is closely related to the conformational compactness of the polymer chain.

Plots of the rate constant against the polymer concentration (Figures 5 and 6) resemble those for spectral data (Figures 1–3), except that R.I. of the fluorescent emission increases at high polymer concentrations (Figure 3). Concentration–rate profiles in Figures 5 and 6 can be rationalized by the necessity of micellelike hydrophobic environments for the catalysis and by adsorption of a progressively greater fraction of the substrate into the polymer phase. The kinetic situation is expressed by Scheme I, where K is the equilibrium constant for

Scheme I

$$\begin{tikzcd}
\text{I} + \text{polysoap} \arrow[r, shift left, "K"] \arrow[d, "k_d'"] & \text{I-polysoap} \arrow[l, shift left] \arrow[d, "k_d''"] \\
\text{products} & \text{products}
\end{tikzcd}$$

the association of substrate with polymer (= [I adsorbed]/[I][polymer]), k_d' is the decarboxylation rate constant in the nonpolymeric system, and k_d'' is that for the polymer-bound species. The following equation has been derived for [polymer] ≫ [I][28]

$$\frac{k_d'}{k_d - k_d'} = \frac{1}{qK\,[\text{polymer}]} + \frac{1}{q} \qquad (2)$$

where k_d is the rate constant obtained at a given polymer concentration and $q = (k_d''/k_d') - 1$. Excellent correlations (r = 0.98–0.99 except for DACS-LB-22; Table II) were found for this treatment. The decarboxylation rates of the polymer-bound substrate (k_d'', Table II) are parallel to the hydrophobicity evaluated by spectral studies (EVI-L-29 > EVI-L-41 ≫ EVI-L-9).

In Figure 10, k_d'' was plotted against lauryl-group contents of 4-VP and EVI polymers. Equation 2 could not be applied to polymers of low lauryl contents and, in these cases, rate constants observed at highest polymer concentrations were employed. Marked rate enhancements are found at ca. 15 mol % of the lauryl group content, which undoubtedly indicates the transition from polyelectrolyte to polymer micelle.

The correlation recognized between the decarboxylation rate and spectral data suggests that this reaction may serve as a kinetic probe to assess the hydrophobic environments of polysoaps. Figure 11 shows plots of log k_d'' against the wavenumber of the absorption maximum of methyl orange (ν_{MO}). For most polysoaps, log k_d'' is linearly correlated with ν_{MO} by eq 3 (solid line in Figure 11).

$$\log k_d'' = 1.03 \times 10^{-3}\, \nu_{MO} - 26.8 \qquad (3)$$

Plots for 4-VP-Hx-65 and 4-VP-Bzl-95 deviate to the upper side. These polysoaps would be able to provide the hydrophobic domain for the catalysis, but it is not sufficient for the spectral shift. On the other hand, polysoaps with large hy-

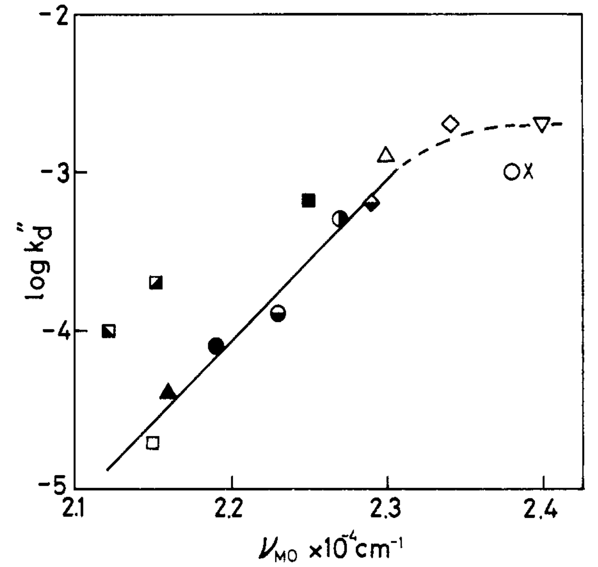


Figure 11. Correlation between log k_d'' and the frequency of absorption maximum of methyl orange: (△) EVI-L-41; (▽) EVI-L-29; (▲) EVI-L-9; (◇) 2-VP-L-30; (○) 4-VP-L-33; (◑) 4-VP-L-22; (⊖) 4-VP-L-12; (●) 4-VP-L-3; (□) 4-VP-Et-85; (◪) 4-VP-Hx-65; (◙) 4-VP-Bzl-95; (◆) DACS-LB-22; (X) ethanol; (■) formamide.

drophobicity such as EVI-L-29 and 4VP-L-33 give plots deviated to the lower area. The polysoap catalysis may have an upper limit, though no saturation is observed for the methyl orange shift. The plots for ethanol (ν_{MO} = 2.39 × 10^4 cm^{-1}) and formamide (ν_{MO} = 2.25 × 10^4 cm^{-1}) were placed close to those for polysoaps.

Bovine serum albumin, a carrier protein, efficiently binds methyl orange and causes a hypsochromic shift.[18-20] Therefore, we expected that albumin also serves as catalyst for the decarboxylation. However, addition of bovine serum albumin (4 × 10^{-4} M) did not increase the decarboxylation rate.[29]

Now we discuss the origin of the rate enhancement. We previously pointed out that anionic nucleophiles are unusually activated by cationic micelles and that this is mainly caused by the formation of hydrophobic, desolvated ion pairs.[13-15] Very recently, Kemp and co-workers, who had reported for the first time (1970) decarboxylation of I to be remarkably solvent dependent,[30] claimed that the decarboxylation rate was influenced by hydrogen bonding of the carboxylate ion with protic solvents (inhibition), and the stabilization of the transition state in dipolar aprotic solvents (acceleration).[31,32] They argued that these factors are the essential conditions for the construction of practical enzymelike catalysts. Bunton and co-workers[25-27] claimed that the micellar catalysis of the decarboxylation of I is due to the action of the positive charge of the micelles for stabilizing the anionic transition state (II). On the other hand, Berezin and co-workers[33] emphasized the importance of dehydration of the carboxylate anion by the hydrophobic environment of micelles, and proposed that the micellar charges are utilized only for binding the reactant to the micelles.

The solvent effect on the decarboxylation of the carboxylate anion possesses contrasting behavior with the bimolecular nucleophilic reaction of some oxy anions: (1) the rate of the decarboxylation in benzene (4.8 × 10^{-3} s^{-1}) is not much different from that in formamide (7.4 × 10^{-4} s^{-1}),[31] whereas the nucleophilic attack of the hydroxamate anion toward *p*-nitrophenyl acetate is more than 10^6 times faster in benzene than in formamide;[15] (2) the decarboxylation is almost independent of the small variation of the water content in aprotic solvents, whereas the nucleophilic reaction involving oxy anionic nucleophiles is suppressed by extremely minute amounts of water.[14,15,32] Thus, it is implied that the decarboxylation involving an extensively delocalized transition state (II) is relatively insusceptible to desolvation (dehydration) as compared with the nucleophilic process. The transition state stabilization seems to play a heavier role in the decarboxylation.

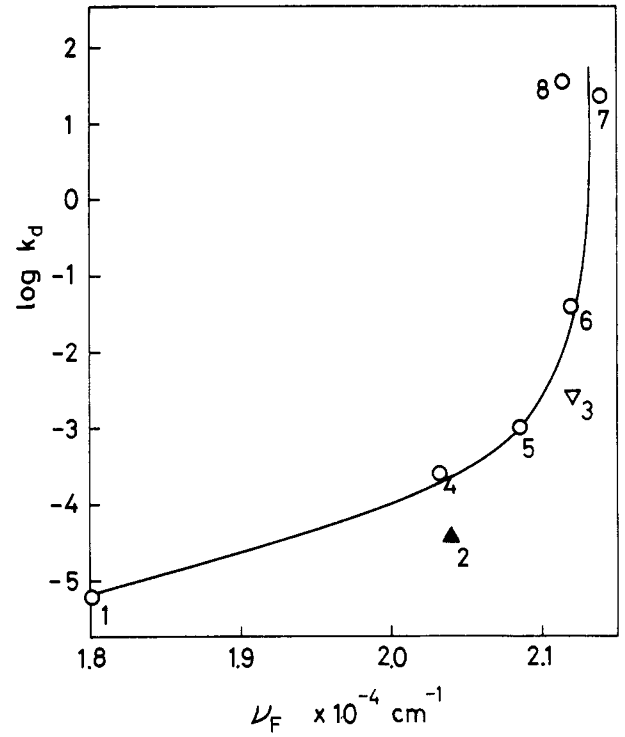


Figure 12. Correlation between log k_d and the frequency of fluorescent emission maximum of 1-anilinonaphthalene-8-sulfonate: (1) H_2O; (2) EVI-L-9; (3) EVI-L-29; (4) methanol; (5) ethanol; (6) dioxane; (7) acetone; (8) dimethylformamide. Plots for 4–8 are cited from ref 24 and 31.

The logarithm of the rate constant was plotted against the ν_F value, a measure of the medium polarity.[24] Figure 12 shows that plots for the polysoap-catalyzed reaction are placed close to those for methanol and ethanol, dipolar protic solvents. On the other hand, dipolar aprotic solvents such as acetone and dimethylformamide further accelerate the decarboxylation rate in spite of the similar ν_F values. This difference may be attributable to desolvation of the carboxylate anion.

Kinetic salt effects observed in the presence of EVI-L-29 are complicated. Generally, addition of electrolytes inhibits micellar catalyses. This inhibition was rationalized by assuming that a counterion competes with an ionic reactant for a site on the ionic micelle. However, Bunton and co-workers[26,27] noticed that the CTAB micelle-catalyzed decarboxylation of I is unexpectedly enhanced by some salts: small, hydrophilic anions enhance the rate at concentrations of 0–0.8 M, while hydrophobic anions such as aryl sulfonates, phosphates, and carboxylates increase the rate, giving maxima characteristic of each anion. They attributed their peculiar finding to the change in the micellar structure. In the polysoap system, the salt effect found for hydrophobic anions is similar to that found in the conventional micelle system (Figure 8), but addition of hydrophilic anions retarded the rate, and gave rate minima with KNO_3 and Na_2SO_4. These effects probably reflect the conformational change of polymer micelles. However, no simple explanation is apparent at present.

In conclusion, cationic polysoaps are found to serve as efficient catalysts for decarboxylation of I compared with the conventional cationic micelles. At the same time, the importance of the hydrophobic environment is substantiated through the correlation between the spectral and kinetic data.

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The Molecular Structure of Athabasca Asphaltene. Cleavage of the Carbon–Sulfur Bonds by Radical Ion Electron Transfer Reactions

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The molecular structure of Athabasca asphaltene from northeastern Alberta has been investigated. The large asphaltene molecules of mol wt 5920 were reduced by electron transfer from naphthalene radical anions produced in situ by treatment of naphthalene with potassium in tetrahydrofuran solution. The asphaltene anions were stabilized by octylation or protonation. From the number of octyl groups and potassium atoms consumed and the number average molecular weight of the treated asphaltene it was determined that the molecular weight on an octyl-free basis decreased tenfold during reduction. The extent of hydrogen bonding in the molecule was determined from the reduction in molecular weight upon silylation and diazomethane treatment to be one bond per molecule. It was also established that at least two-thirds of the oxygen is present in hydroxyl groups and some in carbonyl groups. The average aromatic carbon and aromatic hydrogen contents were determined to be 42 and 8%, respectively, by NMR spectroscopy. From the above results and those obtained in an auxiliary study of naphthalene anion reduction of simple model sulfur compounds, it is concluded that the Athabasca asphaltene has a sulfur polymeric framework in which the average carbon moieties, consisting of an alicyclic diaromatic structure with some alkyl substituents, are held together by sulfide linkages. It is shown experimentally that at least 65% of the sulfur is present in sulfide bonds, but other considerations suggest that the true figure is at least 90%. A solvent extraction scheme allowed some fractionation of the whole asphaltene. The 15% alcohol and acetone soluble fraction contains 40% of the oxygen present in the asphaltene molecule.

Asphaltene, the ubiquitous high molecular weight pentane insoluble fraction of petroleum, is a complex mixture of polycyclic aromatic molecules. In general, petroleum asphaltene is characterized by its high heteroatom content which in the case of the northeastern Alberta Athabasca asphaltene is in the range of sulfur 8–9%, oxygen 2–3%, and nitrogen ~1%. The chemical composition and molecular weight distribution show considerable variation with the source reservoir and depth, and the concentration may also vary from a few tenths of 1% in light crude oils to 25% in the Athabasca bitumen.

The molecular structure of asphaltene poses a challenge to the structural chemist and in spite of the numerous studies addressed to the problem the crucial question of whether asphaltene is a carbon polymer or a polymer in which the smaller carbon monomers are joined together by heteroatom linkages still remains unresolved. According to currently accepted notions the heteroatoms present in asphaltene are built into the ring systems of the molecules, which view, if correct, would favor a carbon polymer skeleton. A knowledge of the molecular structure would have practical and theoretical ramifications. It could have potential significance on the refining and upgrading processes of heavy crudes and bitumens, the production of bitumen from oil sands, and the possible commercial utilization of asphaltene and could also shed light on the mode of the formation of asphaltene and the diagenetic history of the source reservoir.

Most of the earlier studies reported in the literature on the molecular structure of asphaltene employed physical methods and the few chemical investigations which appeared were rather limited in scope. The most informative study is probably that published by Sawatzky and Montgomery[1] in which the molecular weight of Mildred Lake (northeastern Alberta) asphaltene was decreased from 6110 to 3547 by a single step reduction with lithium aluminum hydride and also by three successive reductions in ethylenediamine with a large excess of lithium. The decrease in molecular weight was attributed to cleavage of sulfide or ether bonds. More recently reduction