Interaction of a Polymeric Detergent with Surfactant Micelles in Hydrocarbon Media

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ABSTRACT: The capacity of a bis(alkenylsuccinimide) of triethylenetetramine to solubilize pyruvic acid in hydrocarbon solvents was found to increase in the presence of a detergent copolymer of alkyl methacrylate and vinylpyrrolidone. Viscometric study of the system indicates that interaction occurs between the polymer and the micelle when the latter contains solubilized acid. A nondetergent, monophyletic poly(alkyl methacrylate) does not exhibit these effects. The greater activity of the detergent copolymer over that of the nondetergent polymer toward interaction with the solute is also observed in the absence of the surfactant and has been demonstrated spectrophotometrically.

Interaction in aqueous medium of neutral polymers with ionic surfactants was first described by Saito.[1] An interesting property of such complexes, for example, of poly(vinylpyrrolidone)[2] or of bovine serum albumin[3] with sodium dodecyl sulfate, is the synergistic effect of the polymer on the capacity of the surfactant to solubilize an oil-soluble dye. The oleophilic interior is apparently retained in the polymer–micelle complex. Such an arrangement is feasible since the polymer can interact with the outer shell of the surfactant micelle. In aqueous medium the micellar surface consists of the polar (ionic) portions of the surfactant molecules. The micelles formed from oil-soluble surfactants, however, are inverted with the polar ends in the interior.[4] Thus, the nonpolar exterior of such a micelle might be expected to inhibit interaction with polar segments of an oil-soluble polymer.

It will be shown here, however, that polymer–surfactant micellar complexing can occur in a hydrocarbon medium when the surfactant micelle is sufficiently swollen with solubilized polar solute. The concurrent polymer requirements of polar segments for interaction and nonpolar segments for solubility apparently limit the phenomenon to detergent polymers. The latter are nonionic copolymers containing a relatively small proportion of highly polar segments and are capable of efficiently peptizing solids in hydrocarbon media.[5] This latter ability arises from the selective adsorption of the more highly polar segments.[6]

Experimental Section

Materials. The preparation, fractionation, and characterization of the polymers used are described in a previous publication.[7] The polymer fraction designated PAM was a poly(lauryl methacrylate) of ~560,000 molecular weight. The two polymer fractions designated PAM·VP-1 and -2 were copolymers of stearyl methacrylate and N-vinyl-2-pyrrolidone with about 5:1 monomer ratio and of molecular weights ~410,000 and ~280,000, respectively.

TABLE I

SOLVENT PROPERTIES, 25°

Solvent	d^{25}_{4}	Viscosity, η_0, cP	Pyruvic acid solubility, mmol/kg
n-Octane	0.6988	0.5022	19
n-Dodecane	0.7457	1.352	13
n-Hexadecane	0.7706	3.015	9
cis-Decalin	0.8929	2.978	12

The surfactant designated PB·TETA was a bispolyisobutenylsuccinimide of triethylenetetramine (*cf.* U. S. Patent 3,219,666). Nonpolar impurities were removed by dialysis through a rubber membrane in a hexane–acetone solvent and low molecular weight polar impurities by acetone extraction. The final product was freed from solvent *in vacuo* at 84°. The molecular weight based on N analysis was 2250.

Pyruvic acid was Matheson "99%," used as received. Titration to the first inflection at pH ~5.7 in water gave an apparent equivalent weight of 98.0 (89.9% as pyruvic acid). A second inflection at pH ~8.8 indicates the presence of 7.6 mol % of weaker acid impurities (probably a pyruvic acid condensation product), and Karl Fischer titration reveals 2 wt % water.

The *n*-hydrocarbon solvents were 99% grade. The *cis*-decalin was obtained by fractionation of Du Pont decalin. All were percolated through silica gel and stored under nitrogen. Table I gives measured solvent physical properties pertinent to the present studies as well as the measured solubility of pyruvic acid.

Measurements. The solubilization experiments were carried out by mixing pyruvic acid and the appropriate solution in sealed vials in a thermostated rocker (25 ± 0.5°) for 24–48 hr. This time interval had no appreciable effect within the experimental accuracy of 2–3%. The mixtures were then centrifuged for 15 min at 7000 rpm (nominal 6000 G) in a Sorvall RC-2 centrifuge thermostated at ~25°. About 85% of the clear supernatant solution was then removed and a weighed aliquot of this was taken for analysis.

Pyruvic acid in the latter solutions was determined by electrometric titration with 0.1 *N* ethanolic KOH in a 47:47:6 vol % ethanol–ether–water solvent using glass and calomel electrodes with a Sargent recording titrator, Model D. Sharp inflections were obtained. All solubilization results given are corrected for the small solubility of pyruvic acid in the pure solvents (Table I).

Viscosity measurements at 25.00° were made in Zeitfuchs

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(1) S. Saito, *Kolloid Z.*, **133**, 12 (1953).

(2) S. Saito, *ibid.*, **158**, 120 (1958).

(3) I. Blei, *J. Colloid Sci.*, **15**, 370 (1960).

(4) C. R. Singleterry, *J. Amer. Oil Chemists' Soc.*, **32**, 446 (1955).

(5) A. L. Lyman and F. W. Kavanagh, *Proc. Amer. Petrol. Inst., Sect. III*, **39**, 296 (1959).

(6) B. J. Fontana, *J. Phys. Chem.*, **67**, 2360 (1963).

(7) B. J. Fontana and J. R. Thomas, *ibid.*, **65**, 480 (1961).

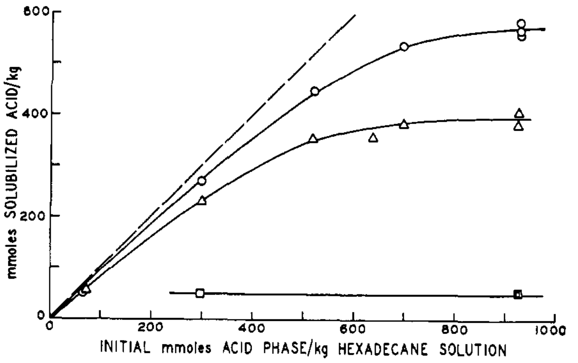

Figure 1. Solubilization of pyruvic acid in *n*-hexadecane solutions at 25°: □, 3.00 wt % PAM·VP-2; △, 2.00 wt % PB·TETA; ○, 3.00 wt % PAM·VP-2 plus 2.00 wt % PB·TETA.

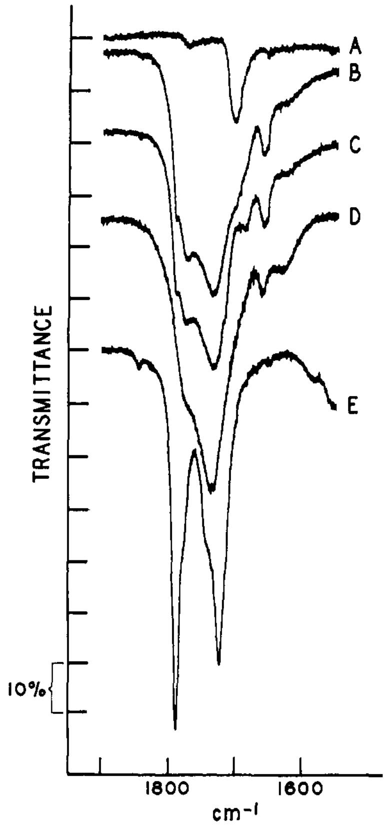

Figure 2. Infrared spectra of different physical states of pyruvic acid: A, 0.5 wt % PB·TETA in *n*-hexadecane (*vs.* *n*-hexadecane); B, A with solubilized pyruvic acid, 87 mmol/kg (or 67 mmol/l.); C, B *vs.* 0.5 wt % PB·TETA in *n*-hexadecane; D, bulk pyruvic acid film (between Irtran plates, *vs.* air); E, saturated pyruvic acid in CCl_4, 64 mmol/l. (*vs.* CCl_4).

cross-arm viscometers.[8] The absolute viscosities were calculated using measured densities of the original solutions in each case and interpolated values for subsequent dilutions.

Infrared measurements were made with a Model 257 Perkin-Elmer spectrophotometer (slow scan, normal slit). All of the spectra, except that for bulk pyruvic acid, were run in a pair of matched, 0.2-mm path length, NaCl cells from Barnes Engineering Co. In all of the figures of spectra to be shown, the transmission ordinates have been shifted for pictorial convenience. In every case the initial transmission at 1900 cm^{-1} was about 90%.

Solubilization Results

The surfactant PB·TETA solubilizes pyruvic acid efficiently. At 2 wt % PB·TETA in *n*-hexadecane, corresponding theoretically to 18 mmol of amine nitrogen/kg, up to 395 mmol of pyruvic acid/kg can be solubilized at 25°. The detergent polymer PAM·VP solubilizes pyruvic acid only weakly; however, the combination of surfactant and detergent polymer solubilizes the acid to an appreciably greater extent than the simple sum of the two effects. These results are illustrated in Figure 1 as a function of the initial amount of pyruvic acid. Normal behavior would require an initial slope of unity (dashed line) before leveling off at the saturation values. The observed deviations are probably due to fractionation effects on the impure pyruvic acid.

The solutions of solubilized pyruvic acid appear optically clear by transmitted light but show a Tyndall effect by reflected light. Evidence that the acid is solubilized as a colloidal dispersion rather than as a molecular solution is apparent from the infrared spectra shown in Figure 2. Dilute solutions of pyruvic acid (E) show two distinct, sharp carbonyl absorption peaks at about 1788 and 1723 cm^{-1}. Hydrogen bonding effects (*e.g.*, dimerization) in bulk liquid acid (D) cause these peaks to merge into one broad asymmetric absorption with a peak at 1732 cm^{-1}. It is apparent that the spectrum of the solubilized solution (C) at about the same stoichiometric concentration as in E resembles that of bulk pyruvic acid. Minor additional features in spectrum C are due to the small amount of acid soluble in the solvent.

The solubilization data summarized in Table II were all obtained with sufficient initial pyruvic acid to yield saturation values (*cf.* plateaus of Figure 1). Solubilization by PB·TETA alone is approximately linear with surfactant concentration and, in the *n*-hydrocarbon solvents, is independent of a sixfold factor in solvent viscosities (see Table I). This latter observation suggests a sharply defined particle-size distribution (at the high end, at least), as is usually the case for micellar particles.[4] On the basis of the sedimentation conditions used, a very rough upper limit to the micelle size is estimated to be 200 Å.

The synergistic effect (%) = [100(observed solubilization/sum of the solubilizations for polymer and surfactant acting alone) − 100]. It is apparent that the nondetergent polymer PAM shows little or no synergism. In the *n*-paraffin solvents, the detergent polymer PAM·VP shows 30 ± 2% synergistic effect independent of a fourfold change in concentration at 3/2 weight ratio of polymer to surfactant. Change in the polymer/surfactant weight ratio from 0.375/1 to 6/1 results in an increase in the synergistic ratio from 21% to a maximum value of about 35%. In the manner typical of polymers, PAM·VP attains equilibrium adsorption on silica at very low concentrations (see Figure 1 of ref 7). Thus, the concentration and ratio effects noted above are compatible with the view that polymer sorption onto the surfactant micelle is occurring.

Viscometry, Results, and Discussion

Reduced Specific Viscosities. Viscosity studies were made in the manner usual for polymeric materials by

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[8] J. R. Johnson, R. L. LeTourneau, and R. Matteson, *Anal. Chem.*, **24**, 1505 (1952).

TABLE II
SOLUBILIZATION DATA

Solvent	Polymer		PB·TETA, wt %	Solubilized pyruvic acid,[a] mmol/kg	Synergistic effect,[b] %
	Fraction	Wt %			
n-Hexadecane	...	...	2.00	396	...
	...	...	1.00	191	...
			0.50	89	...
	PAM	3.00	...	13	...
		2.00	...	7	...
		3.00	2.00	430	5
	PAM·VP-2	3.00	...	52	...
		2.00	...	35	...
		3.00	2.00	572	28
		1.50	1.00	280	29
		0.75	0.50	135	32
		3.00	1.00	327	35
		3.00	0.50	189	34
		1.50	2.00	527	25
		0.75	2.00	494	21
n-Dodecane	...	...	2.00	403	...
n-Octane	...	...	2.00	401	...
	PAM	3.00	...	4	...
	PAM·VP-2	3.00	...	41	...
	PAM	3.00	2.00	404	0
	PAM·VP-2	3.00	2.00	580	31
cis-Decalin	...	...	1.74	240	...
	PAM·VP-1	2.60	...	36	...
	PAM·VP-1	2.60	1.74	307	11

[a] Corrected for solubility in pure solvent (Table I). [b] Assuming maximum possible solubilization by polymer.

measurement of the viscosity of successive dilutions with pure solvent. Of particular interest here are the solutions containing polymer plus surfactant and solubilized acid. For comparison in each case, measurements were made on three additional systems: polymer alone, polymer plus surfactant, and polymer plus pyruvic acid. More than one solute is present in most of the systems above; however, in every case the specific viscosity is reduced by and plotted against the concentration, C_2, of polymer alone. The specific viscosity in every case is the ratio of the measured viscosity to the viscosity of pure solvent, less unity. In addition, the viscosity behavior of solutions of the surfactant alone, with and without solubilized acid, was studied.

In Figures 3, 4, and 5, the viscosity data for solutions containing 3/2 weight ratio of polymer to surfactant plus solubilized pyruvic acid at saturation are shown and compared with the pertinent systems noted above. It is apparent in Figure 3 that solubilization of pyruvic acid by the surfactant has little additional effect on the viscosity behavior of the nondetergent polymer PAM. Under analogous conditions, however, the detergent polymer PAM · VP shows (Figure 4) a marked increase in the reduced specific viscosity. The intrinsic viscosities of the polymers PAM and PAM · VP-2 differ by about a factor of 2. Thus, it appeared pertinent to compare also the behavior of PAM with a suitable detergent polymer fraction PAM · VP-1 in a sufficiently better solvent, decalin, such that the intrinsic viscosities were approximately the same. The marked rise in viscosity (Figure 5) and the synergistic effect (Table II) are still readily apparent under these latter circumstances. Thus, these effects appear to be characteristic of the detergent polymer and not of the nondetergent polymer.

The sharp rise in viscosity indicates the onset of strong interactions. The discussion by Gillespie[9] of the effect of aggregation on the viscosity of dilute suspensions is applicable here. There appears to be a paucity of data in the literature that illustrate the effects of strong interactions, however. The data of Morawetz[10] for mixtures of two distinct but strongly interacting polymers (copolymers of methyl methacrylate with an acidic and a basic comonomer) show a striking increase in viscosity. The latter is reflected in an increased value of the apparent Huggins constant, k', for the mixture. In the aqueous systems[1,2] noted in the beginning of this article, Saito also observed[11] that the synergistic effect of the polymers on dye solubilization by surfactant was always associated with an increase in viscosity. The limiting behavior as $C_2 \rightarrow 0$ of the data of Figures 3, 4, and 5 is used below to determine the apparent changes for the polymer of the intrinsic viscosity and Huggins constant. The Huggins equation as applied to the case of two solutes is used with suitable assumptions for the systems: polymer plus surfactant or polymer plus surfactant and solubilized acid.

Huggins Equation for Two Solutes. The Huggins equations for the two solutes taken separately are eq 1

$$\frac{\eta_1 - \eta_0}{\eta_0 C_1} = [\eta]_1 + k_1'[\eta]_1^2 C_1 \qquad (1)$$

for the surfactant at concentration C_1 (with or without

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(9) T. Gillespie, *J. Colloid Sci.*, **18**, 32 (1963).

(10) H. Morawetz, "Macromolecules in Solution," Interscience Publishers, Inc., New York, N. Y., 1965, p 309.

(11) S. Saito, *Kolloid Z.*, **154**, 19 (1957).

Table III
Viscometric Behavior of the Surfactant and of Solubilized Acid

Solvent	PB·TETA, wt %, C_1	Solubilized acid, wt %, C_s	$[\eta]_{C_1}{}^a$	$k_{C_1}{}'^a$	$[\eta]_{C_s}{}^b$	$[\eta]_s{}^c$
n-Hexadecane	2.00	...	8.1[d]	~0.0	...	...
	2.00	0.54	8.8	~0.5	32.6	2.6
	2.00	3.97	12.6	~0.8	6.4	2.2
cis-Decalin	1.74	2.35	12.4	~1.3	9.2	3.1
						2.6 av

[a] Derived from η_{sp}/C_1 *vs.* C_1 (Figure 3). [b] Derived from η_{sp}/C_s *vs.* C_s (plot not shown). [c] Corrected for contribution of $[\eta]_1$ with equation 8 in variables C_s and C_1. [d] This is the true value $[\eta]_1$ for PB·TETA alone.

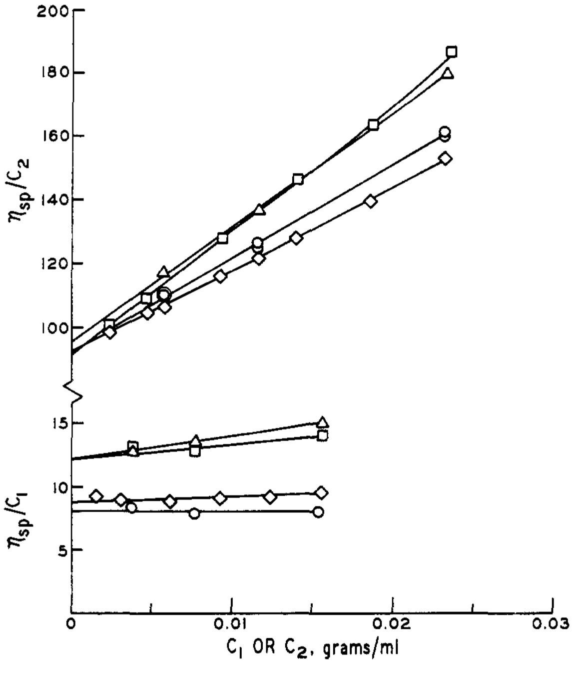

Figure 3. Reduced specific viscosity at 25°; polymer PAM (C_2), 3.00 wt % in *n*-hexadecane: ○, PAM alone; ◇, with 0.11 wt % pyruvic acid; △, with 2.00 wt % PB·TETA; □, with 2.00 wt % PB·TETA and 4.19 wt % pyruvic acid. Surfactant PB·TETA (C_1), 2.00 wt % in *n*-hexadecane: ○, PB·TETA alone; ◇, with 0.54 wt % pyruvic acid; □, with 3.97 wt % pyruvic acid; and 1.74 wt % in *cis*-decalin: △, with 2.35 wt % pyruvic acid.

solubilized acid) and eq 2 for the polymer at concentration C_2.

$$\frac{\eta_2 - \eta_0}{\eta_0 C_2} = [\eta]_2 + k_2'[\eta]_2{}^2 C_2 \tag{2}$$

In the absence of any interactions these two equations may be combined as follows. The measured viscosity η for the combination of the two solutes at concentrations C_1 and C_2, respectively, is eq 3 and the

$$\eta = \eta_1 + \eta_2 - \eta_0 \tag{3}$$

specific viscosity, η_{sp}, plotted in Figures 3, 4, and 5 is, from eq 3

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{(\eta_1 + \eta_2 - \eta_0) - \eta_0}{\eta_0} \tag{4}$$

and when plotted with respect to, say, the polymer concentration, C_2

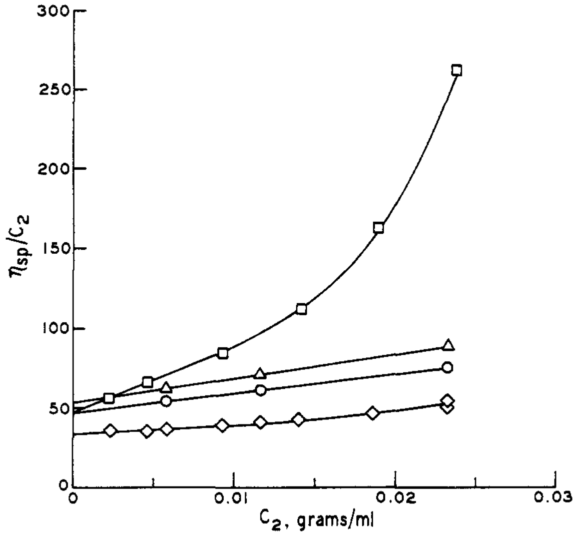

Figure 4. Reduced specific viscosity at 25°; detergent polymer PAM·VP-2, 3.00 wt % in *n*-hexadecane: ○, PAM·VP-2 alone; ◇, with 0.48 wt % pyruvic acid; △, with 2.00 wt % PB·TETA; □, with 2.00 wt % PB·TETA and 5.71 wt % pyruvic acid.

$$\eta_{sp}/C_2 = \frac{\eta_2 - \eta_0}{\eta_0 C_2} + \frac{\eta_1 - \eta_0}{\eta_0 C_2} \tag{5}$$

When the dilutions are made with pure solvent, then C_1/C_2 = constant = a, and

$$\eta_{sp}/C_2 = \frac{\eta_2 - \eta_0}{\eta_0 C_2} + a\left(\frac{\eta_1 - \eta_0}{\eta_0 C_1}\right) \tag{6}$$

Substituting eq 1 and 2 into eq 6

$$\eta_{sp}/C_2 = \{[\eta]_2 + k_2'[\eta]_2{}^2 C_2\} + a\{[\eta]_1 + k_1'[\eta]_1{}^2 C_1\} \tag{7}$$

and substituting $C_1 = aC_2$ and rearranging gives

$$\eta_{sp}/C_2 = \{[\eta]_2 + a[\eta]_1\} + \{k_2'[\eta]_2{}^2 + a^2 k_1'[\eta]_1{}^2\}C_2 \tag{8}$$

Now it is apparent that the intercept on the ordinate of the η_{sp}/C_2 *vs.* C_2 plot is the value of the first term in brackets of eq 8, and the limiting slope, as $C_2 \rightarrow 0$, is given by the second term in brackets.

Application of eq 8 to interacting solutes is admissible if the effective hydrodynamic volume of one of the solutes remains unchanged. The surfactant micelle, then, is assumed always to behave as a relatively incompressible sphere. This assumption implies that, over the concentration range of concern (C_1, $C_2 \rightarrow 0$), the $a^2k_1'[\eta]_1^2$ term of equation 8 is negligible. This implication is qualitatively apparent in Figure 3 from the slight slopes of η_{sp}/C_1 *vs.* C_1 for surfactant alone and for surfactant plus solubilized acid. The effects of interaction with polymer then should appear in the values of $[\eta]_2$ and k_2' for the polymer.

In the discussion below, effective values of $[\eta]$ and k' obtained by application of eq 8 with the pertinent variables will be designated by the subscripts 1, 2, or s, corresponding to surfactant, polymer, or solubilized acid, respectively. Apparent values obtained directly from η_{sp}/C *vs.* C plots and the usual Huggins equation for a single solute will be given corresponding subscripts C_1, C_2, or C_s, depending upon the particular concentration dependence used. Of course, in this latter case, if the data are for a system containing only one solute, the values obtained are true values with no ambiguity.

It should also be noted that the values of the concentrations C_1 and C_2 plotted and tabulated throughout are initial concentrations before solubilization of any acid, while C_s is the measured final concentration. Hence, all of the tabulated values of $[\eta]$ and k' have been corrected where necessary for the small contribution of solubilized acid to the final weight of the solutions.

Surfactant and Solubilized Acid. The values of $[\eta]_{C_1}$ and k_{C_1}' obtained from data plotted in Figure 3 are given in Table III. The value $[\eta]_{C_1} = 8.1 = [\eta]_1$, the true value for PB·TETA. The values for the systems containing solubilized acid may be considered as true values for surfactant and solubilized acid considered as a single solute, as indeed the micelle is, but expressed in terms of concentration C_1 alone. These values will be used later in conjunction with eq 8 to obtain the effective values for the polymers.

If the viscosity data are plotted instead *vs.* the concentration C_s of solubilized pyruvic acid, the values of $[\eta]_{C_s}$ given in Table III are obtained. Now using eq 8 with C_s in place of C_2, and C_1 representing the surfactant component only, we may obtain effective values $[\eta]_s$ for the solubilized acid component alone of the micelle: $[\eta]_s = [\eta]_{C_s} - 8.1C_1/C_s$. It is expected that the droplets of bulk acid in the interior of the solubilizing surfactant micelle behave as incompressible, spherical particles. In accord with this, the $[\eta]_s$ values are seen to be reasonably close to the Einstein intrinsic viscosity for rigid spheres (= 2.0, corrected for the density of pyruvic acid, $d^{25}{}_4 = 1.280$). The agreement may be taken as additional evidence of the micellar state of the solubilized acid. Calculation of k' for these particles is not warranted because of the uncertainty in the very small η_{sp}/C_1 *vs.* C_1 slopes.

Polymers with Solubilized Acid. The values of the apparent and effective intrinsic viscosities and Huggins constants obtained as discussed above for all of the systems involving the polymers PAM and PAM·VP are collected in Table IV. In the discussion to follow only the effective or true values of $[\eta]$ and k' (columns 8 and 9) are considered. The values in parentheses are for the cases with essentially only one solute (polymer); thus, the apparent and true value are the same. As noted above, in every case the contribution of the $a^2k_1'[\eta]_1^2$ term in eq 8 is negligible, never amounting to more than 3% of the value of k_2'. Thus, the corrections to the k_{C_2}' values are primarily due to the correction in intrinsic viscosity $[\eta]_2$.

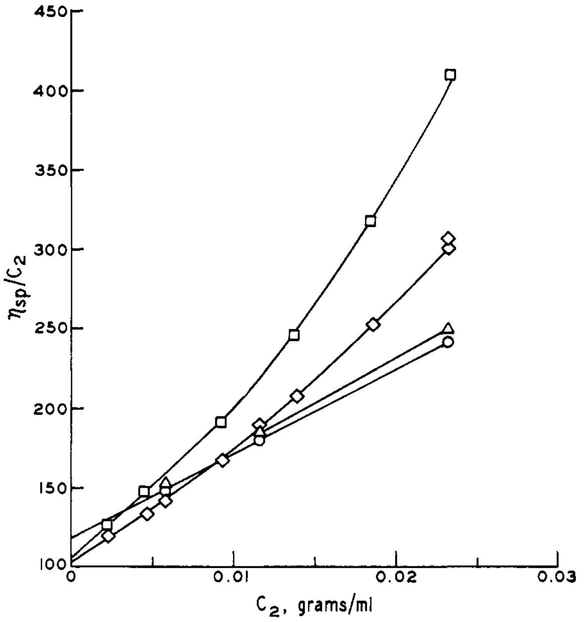

Figure 5. Reduced specific viscosity at 25°; detergent polymer PAM · VP-1, 2.60 wt % in *cis*-decalin: ○, PAM · VP-1 alone; ◇, with 0.35 wt % pyruvic acid; △, with 1.74 wt % PB·TETA; □, with 1.74 wt % PB·TETA and 3.01 wt % pyruvic acid.

The effects of pyruvic acid alone and the surfactant PB·TETA alone on the polymer constants are first considered. Generally the effects are relatively minor. Only a small decrease in k_2' occurs for PAM or PAM·VP-2 in *n*-hexadecane solution saturated with pyruvic acid. An appreciable decrease in $[\eta]_2$ occurs for the PAM·VP-2 which, judging from the solubilization data (Table II), interacts appreciably more than PAM with pyruvic acid. Additional evidence for this increased interaction will be presented in the next section. It is pertinent at this point to note that examination of the data of Alfrey, *et al.*,[12] shows that unexplained deviations occur from the expectation that $[\eta]$ and k' change inversely for a given polymer in different solvents.

The higher molecular weight fraction PAM·VP-1 in the better solvent decalin also shows a small decrease in $[\eta]_2$ on saturating with the acid, but in this case an appreciable increase in k_2' also occurs. This is perhaps more normal behavior as the result of the initially more extended state of the polymer in this case.

The effect of PB·TETA alone on the polymer solutions is also slight. Little or no decrease in $[\eta]_2$ and small increases in k_2' occur, suggesting a feeble decrease in solvency. This could be caused by the highly polar amine groups of the surfactant. Molecular weight determinations on the surfactant indicate that it is dissociated in solution and apparently associates to form micelles only upon the inception of solubilization.

With the polymer–surfactant–solubilized acid combination, a small (6%) decrease in $[\eta]_2$ and 1.6 times in-

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[12] T. Alfrey, Jr., A. I. Goldberg, and J. A. Price, *J. Colloid Sci.*, **5**, 251 (1950).

Table IV
Viscometric Behavior of the Polymers

Solvent	Polymer Fraction	Polymer Wt %, C_2	PB·TETA, wt %, C_1	Solubilized acid, wt %, C_s	$[\eta]_{C_2}{}^a$	$k_{C_2}{}'^{a}$	$[\eta]_2{}^b$	$k_2{}'^{b}$
n-Hexadecane	PAM	3.00	...	...	93	0.35	(93)	(0.35)
		3.00	...	0.11	93	0.29	(93)	(0.29)
		3.00	2.00	...	96	0.39	90	0.44
		3.00	2.00	4.19	96	0.46	87	0.55
n-Hexadecane	PAM·VP-2	3.00	...	...	47	0.56	(47)	(0.56)
		3.00	...	0.48	34	0.50	(34)	(0.50)
		3.00	2.00	...	54	0.53	48	0.65
		3.00	2.00	5.71	50	1.78	42	2.52
		0.75	0.50	1.32	50	0.95	42	1.33
		3.00	2.00	0.49	44	0.72	39	0.94
		3.00	0.50	1.83	38	1.03	36	1.15
cis-Decalin	PAM·VP-1	2.60	...	...	118	0.38	(118)	(0.38)
		2.60	...	0.35	103	0.62	(103)	(0.62)
		2.60	1.74	...	118	0.40	113	0.45
		2.60	1.74	3.01	108	0.85	100	0.99

[a] Derived from η_{sp}/C_2 *vs.* C_2 (Figures 3, 4, and 5). [b] Corrected with eq 8 for contribution of PB·TETA or PB·TETA plus solubilized acid.

crease in k_2' for polymer PAM is noted. Thus, there appears to be only a relatively weak interaction. However, with the detergent polymer PAM·VP-2 under analogous conditions, a somewhat larger decrease (11%) in $[\eta]_2$ is observed, with very marked (4.5 times) increase in k_2'. At the same polymer–surfactant ratio and weight–volume concentration in decalin, fraction PAM·VP-1 shows a 15% decrease in $[\eta]_2$ and 2.6 times increase in k_2'. Large increases in this effective Huggins constant for the detergent polymer PAM·VP-2 are still apparent (Table IV) in experiments at reduced (one-fourth) initial concentrations, in solutions containing solubilized pyruvic acid at approximately one-tenth of the saturation value, or with the polymer–surfactant ratio increased fourfold. In the latter two cases $[\eta]_2$ approaches the value of 34 observed for the polymer alone with pyruvic acid. This must be due to the existence of more "free" polymer, not interacted with *solubilized* acid, under these conditions.

According to the treatment of Gillespie,[13] increasing values of k' may be taken as evidence of decreasing molecular entanglement. Ordinarily the latter is due to the increased compactness of the polymer molecule resulting from solution in a poorer solvent, and a corresponding decrease in the intrinsic viscosity occurs. In the present case, very large increases in k_2' appear coincident with rather small decreases in $[\eta]_2$. Thus, it appears that the interaction of polymer molecules with surfactant micelles may result in an effective polymer "cross-linking" that inhibits polymer–polymer interpenetration. The latter effect might be expected to be less efficient with more voluminous polymer molecules, for example, as observed with PAM·VP-1 in decalin.

The above view requires that the detergent polymer molecules interact with the micelle without a large decrease in voluminosity. Rowland and Eirich[14] have shown in adsorption studies that when the polymer–surface interactions are not too strong the adsorbed film thicknesses are of the order of magnitude of the free coil diameters in solution and are directly proportional to the intrinsic viscosity of the polymer. In the present case, the nature of the detergent polymer dictates that primarily only the less abundant vinylpyrrolidone segments will attach to the micelle, resulting in long unadsorbed loops.[6]

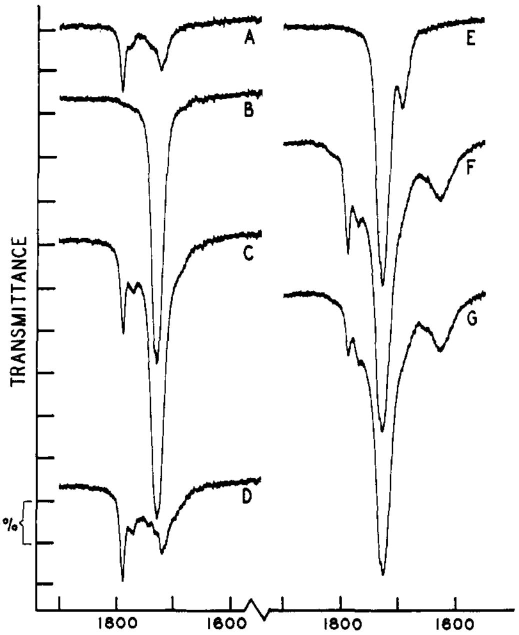

Figure 6. Infrared spectra of polymers and pyruvic acid in *n*-hexadecane (*vs.* *n*-hexadecane unless otherwise noted): A, pyruvic acid (9 mmol/kg); B, 2.00 wt % PAM; C, B with pyruvic acid (16 mmol/kg); D, C *vs.* 2.00 wt % PAM; E, 2.00 wt % PAM·VP-2; F, E with pyruvic acid (44 mmol/kg); G, F *vs.* pyruvic acid (9 mmol/kg).

Polymer–Pyruvic Acid Interaction. The data presented above indicate that the polymer ester segments do not, and vinylpyrrolidone segments do, interact with pyruvic acid. This is apparent either with surfactant-solubilized acid or in solutions saturated with acid alone. Direct evidence of this was obtained in the

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(13) T. Gillespie, *J. Polym. Sci.*, 3, 31 (1963).

(14) F. W. Rowland and F. R. Eirich, *ibid.*, 4, 2401 (1966).

latter systems by the infrared spectroscopic study depicted in Figure 6. There is a complete absence of hydrogen bonding of PAM ester carbonyl to pyruvic acid, as evidenced by the lack of any shift of the normal carbonyl vibration frequency at 1729 cm^{-1}. Note especially (D) where use of PAM solution in the reference beam reproduces only the spectrum due to pyruvic acid. The ester segments of PAM·VP also show no evidence of hydrogen bonding. However, the small absorption peak at 1694 cm^{-1} (E) due to vinylpyrrolidone carbonyl is observed to shift virtually completely to 1628 cm^{-1} (F) in the presence of pyruvic acid. The value here of $\Delta\nu/\nu = 0.039$ is very similar to the value of 0.040 found[15] for N,N-diethyldodecanamide adsorbed on silica. In the latter studies, dodecyl esters adsorbed on silica gave smaller values of $\Delta\nu/\nu$ of around 0.02 in accord with the relative polarity of esters and amides. It is surprising that in the present studies the ester segments show such complete inactivity; the reason for this is not apparent. Unfortunately, it is not feasible to compare the behavior of PAM and PAM·VP with solubilized pyruvic acid in a study such as that of Figure 6 because the acid C=O absorptions are then large enough to jam the spectral region of interest.

A spectrophotometric examination of mixtures of the polymers with the surfactant PB·TETA showed no evidence of interactions. This is to be expected since no donor–acceptor relationship exists in this case.

Nature of the Synergism. The evidence presented here suggest that the more highly polar vinylpyrrolidone segments of the detergent copolymer interact with the acid solute in the interior of the surfactant micelle. This interaction must be *via* hydrogen bonding of pyrrolidone carbonyl oxygen to the carboxylic hydrogen. It is interesting to note that even in aqueous systems[1,2] Saito found[16] that the synergizing polymer causes a shift in the spectrum of the solubilized dye.

The amine surfactant PB·TETA must obviously interact with the acid solute to form a salt. Thus, the active micellar species is actually the ionic salt, PB·TETA pyruvate. Certain mixtures of ionic with nonionic surface-active agents demonstrate an increased efficiency of formation of microemulsions.[17] Goodrich[18] suggests that the binding forces between the ionic and nonionic surfactants reside in the van der Waals attraction between the paraffin chains and that, in addition, the repulsive forces between the charged ionic head groups are reduced by the screening effect of the intervening polar, nonionic groups. It is possible then that the synergistic effect of the detergent copolymer PAM·VP on the solubilization of pyruvic acid by the surfactant PB·TETA is the result of analogous interplay between the ionic amine–salt head of the surfactant and the nonionic pyrrolidone groups of the copolymer.

Acknowledgment. The author wishes to thank Mr. G. L. Matthias for carrying out the experimental measurements in this work.

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Heterogeneous Nucleation of Polymer Melts on High-Energy Surfaces. II. Effect of Substrate on Morphology and Wettability[1]

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Received December 1, 1967

ABSTRACT: Heterogeneous nucleation and crystallization of polymer melts against high-energy surfaces (*e.g.*, metals, metal oxides, and alkali halide crystals) have been found to result in marked changes in both the surface region morphology and wettability of these polymers even though the chemical constitution of the polymer is unchanged. The critical surface tensions (γ_C) of a variety of polymers nucleated against gold are considerably in excess of the commonly accepted values. Employing a modified Fowkes-Young equation can account for these sizable differences if the surface layer of these crystallizable polymers generated against high-energy surfaces is essentially crystalline.

Although considerable effort has been expended in determining the relationship between the contact angle of a liquid on a polymer surface and the chemical constitution of that surface, little attention has been paid to the detailed physical properties (*e.g.*, molecular weight distribution, density, crystallization behavior, etc.) of the polymer and, more important, the detailed procedure for preparing the polymer surface for wettability studies.[2a] In general, there is rather widespread agreement in the acceptable values for the critical surface tensions of wetting for a variety of polymeric

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