CONF-780305--16

Symposium on Chemistry of Oil Recovery

Presented Before The Division of Petroleum Chemistry, Inc.

American Chemical Society

Anaheim Meeting, March 1978

COLLOIDAL PROPERTIES OF SODIUM CARBOXYLATES

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Tall oils are obtained in large quantity from the pulping of soft woods to make paper. Hoyt and Goheen (1) state that in 1964 the yield of fatty and rosin acids exceeded 400,000 tons. Tall oil contains about 94% total acids and 6% alcohols. The fatty acid fraction contains oleic - 24%, linoleic - 19% and conjugated linoleic acid - 4% of the Tall oil. The rosin acid fraction contains abietic acid - 14% and related acids 53% of the total (2).

Knowledge of the ready supply of acids from Tall oils and the well-known colloidal properties of fatty acid soaps was sufficient encouragement to warrant a comparison of the colloidal properties of carboxylates with sulfonates in aqueous mixtures with petroleum hydrocarbons. A great body of literature already exists that treats their colloidal properties ref. (3) and (4). However recent advances in the measurement of interfacial tensions by the spinning drop technique have made it easier to investigate multiphase systems. Cayias, Schechter and Wade (5) reported the measurement of low interfacial tensions at variable speeds. Gash and Parish (6) described a spinning drop tensiometer that is capable of handling several samples, simultaneously, at a constant velocity. For the work described here, sodium oleate was selected as the model for intensive study of several variables and other carboxylate structures have been included for comparison.

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Experimental

The acids: 95 and 99% oleic, 95% linoleic, 99% linolenic, 99% elaidic and cholic acids were obtained from chemical supply houses. Mixed rosin acids were a commercial product, acintol R type S (2). Sodium salts of fatty acids were formed by electrometric libration of an aqueous-ethanol solution with sodium hydroxide, evaporated to dryness to remove ethanol and stored dry or as an aqueous stock solution. A sample of mixed rosin acids was assayed electrometrically with potassium hydroxide in benzene-ethanol. A stock solution was then prepared in water from a weighed quantity of acintol R and the amount of sodium hydroxide calculated from the assay. Other materials were reagent grade chemicals.

Interfacial tension measurements were made on one or both of the devices mentioned (5,6). Spinning of the samples was continued until successive readings were constant, usually 24 hours was sufficient.

Precision of Measurements - Aliquots from a stock solution of 0.1 M sodium oleate (five months old) were used to prepare aqueous test solutions that were 0.01 M sodium oleate, 0.1 sodium chloride pH 9.5. Interfacial tensions were measured against n-undecane without pre-equilibration. The second solution was made and measured one week after the first and the third solution two weeks after the first. The results in Table I show the measurements to be reliable to one significant figure.

Table I

Precision of Interfacial Tension Measurements

0.01 M Sodium Oleate, 0.1 M Sodium Chloride pH 9.5

vs n-Undecane

	Run I	Run II	Run III
Multi-drop constant velocity	0.065	0.140	0.062
	0.058	0.070	0.054(a)
	0.085	0.068	0.062
	0.062	0.068	0.080(a)
	0.070	0.077	0.068
Av.	0.068 ± 0.009	0.085 ± 0.022	0.064 ± 0.008
Single-drop variable velocity	0.098	0.094	0.080
		av. 0.091 ±	0.067

(a) Air bubbles appeared. Results discarded

Sodium Oleate Concentration - The observed interfacial tension was high at low sodium oleate concentration but above 0.001 M the interfacial tension increase as the sodium oleate concentration was increased.

Table 2

Interfacial Tension as a Function of Sodium Oleate Concentration

0.1 M Sodium Chloride, pH 9.5 vs n-Undecane

Sodium Oleate (M./ℓ.)	Interfacial Tension (dynes/cm)
0.0001	> 10
0.001	0.05
0.01	0.2, 0.07
0.1	0.3, 0.07
0.3	0.3

Sodium Chloride Concentration - Sodium chloride concentration had a negligible effect on interfacial tensions (see Table 3).

Table 3

Interfacial Tension as a Function of Sodium Chloride

0.1 M Sodium Oleate, pH 9.5 vs n-Undecane

Sodium Chloride (M/ℓ)	Interfacial Tension (dynes/cm)
0.01	0.3
0.1	0.3, 0.07
0.2	0.2

Effect of pH - A dramatic effect of pH was observed at the lower (0.01 M) sodium oleate tested. Less effect was found at 0.1 M sodium oleate (see Table 4).

Table 4

Interfacial Tension as a Function of pH

0.1 M Sodium Chloride vs Undecane

pH 0.01 M Sodium Oleate	Interfacial Tension (dynes/cm)
9.5	0.07 ± 0.003
	0.09 ± 0.007
	0.2 ± 0.01
10.1	0.1
11.1	1.0
12.1	1.9
0.1 M Sodium Oleate	
9.5	0.3
10.4	0.3
11.4	0.4
12.4	0.5

A test of the acid side was made by using a mixture of sodium oleate and oleic acid. The observed interfacial tensions varied inversely with the amount of oleic acid added. However, it is not clear to what extent the total oleate concentration has affected the results.

We plan to repeat this experiment at constant oleate concentration and measure the distribution of oleate between the two phases. This test (Table 5) was run with 5% isobutyl alcohol in the aqueous phase and the two phases were equilibrated before measurement was made.

Table 5

Interfacial Tension as a Function of Added Oleic Acid

0.01 M Sodium Oleate, 0.1 M Sodium Chloride, 5% Isobutyl
Alcohol Pre-equilibrated with 0.25 Volume of
n-Undecane

Oleic Acid Added (m./l. aqueous)	Interfacial Tension (dynes/cm)
0	0.6
0.001	0.5
0.002	0.4
0.005	0.5
0.008	0.3
0.01	0.2

Effect of Added Alcohols - The addition of alcohols has had relatively little effect on the measured interfacial tension.

Table 6

Effect of Added Alcohols

Sodium Oleate, 0.1 M Sodium Chloride, pH 10.4
vs n-Undecane

Sodium Oleate (m/ℓ)	Co-Solvent % Aqueous	Interfacial Tension (dynes/cm)
0.01	None	0.2
	5-isobutyl alcohol	0.6
0.1	None	0.3
	1-isopropyl alcohol	0.3
	1-hexanol-2	0.2

Interfacial Tension with Various Alkanes - Minimum interfacial tensions were found with different hydrocarbons (see Table 7). The minima observed with carboxylates were not so dramatic as those that have been reported for sulfonates and did shift with the structure. The absolute values of interfacial tensions varied with structure; linoleate, linolenate, and elaidate were higher than oleate.

Table 7

Interfacial Tension of Carboxylates vs Alkanes

Sodium Carboxylate 0.1 M Sodium Chloride pH 9.5

vs Alkane

n-Alkane	Interfacial Tension (dynes/cm)				
	Oleate		Linoleate	Linolenate	Elaidate
	0.01 M/ℓ	0.1 M/ℓ	0.01 M/ℓ	0.01 M/ℓ	0.01 M/ℓ
Hexane					0.4
Heptane					0.4
Octane		0.3			0.5
Nonane					0.5
Decane	0.11	0.10	1.4		0.5
Undecane	0.07	0.07	1.2	0.7	0.7
Dodecane	0.14	0.08	0.6	0.3	0.7
Tridecane		0.14	0.6	0.3	
Tetradecane			1.5	0.4	
Pentadecane				1.1	

Rosinate and Cholate - These carboxylates were included because of their different (from fatty acid) structure, rosin acids compose about half of the tall oil acids and cholic acid is a representative bile acid that is important in the animal metabolism of fats. Salts of these acids had interfacial tensions that were significantly higher than oleate; no minima were found.

Table 8

Rosinate and Cholate

Sodium Carboxylate, 0.1 M Sodium Chloride, pH 9.6

n-Alkane	Interfacial Tension (dynes/cm)		
	Rosinate	Cholate	
	0.01 M/ℓ	0.01 M/ℓ	0.1 M/ℓ
Hexane			10
Heptane			10
Octane			10
Nonane	1.4		9
Decane	1.4	7	10
Undecane	1.2	8	
Dodecane	1.2	8	
Tridecane		9	

Discussion

The sources of error in the measurement of interfacial tensions by the spinning drop method remain a problem. A test was made (see Table 1) to control as many variables as possible to estimate the reproducibility of the measurement. The results obtained do not justify reporting more than one significant figure.

Among the variables studied so far, the pH of the dilute aqueous sodium oleate produced the most dramatic effect on interfacial tension, (see Table 4). In mixtures containing significant quantities of free oleic acid (see Table 5) the interfacial tensions were uniformly ~~high~~. low

Among our critics are those who are disappointed that these carboxylates do not give so low interfacial tensions as the sulfonates. One obvious answer is that oleate is not so highly branched as the sulfonates with which it has been compared. Other unsaturated 18-carbon acids are compared with sodium oleate (see Table 7). While minimum alkane numbers were observed, sodium oleate solutions gave lower interfacial tensions than the isomer and the analogs.

Two other carboxylates (rosinate and cholate that are cyclic in nature) were tested (see Table 8) and found to have higher interfacial tensions than sodium oleate.

It must be pointed out at this time that the approach to equilibrium in these mixtures can be quite slow (ref. 3, p. 142, ref. 4, p. 181). Obviously, slow equilibration can be important to laboratory measurements and to actual practice in the field. Studies are being continued on this problem.

Literature Cited

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