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Miscibility Relationships in Systems Containing Various Hydrocarbons, *n*-Butylcarbitol, and Aqueous Solutions of Sodium Salicylate[†]

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A study has been made of miscibility relationships in systems containing an aqueous solution of sodium salicylate, *n*-butylcarbitol, and various hydrocarbons, including both *n*-alkanes and alkylbenzenes. At any fixed concentration of sodium salicylate, the minimum amount of *n*-butylcarbitol required to produce miscibility at 1:1 weight percent hydrocarbon–water mixtures increases nearly linearly with the number of alkyl carbon atoms in the hydrocarbon. In all cases a considerably higher weight fraction of *n*-butylcarbitol is required to produce miscibility in the systems containing the alkanes than in those containing alkylbenzenes with the same alkyl carbon number. When the *n*-butylcarbitol is replaced by 1-butanol as the cosolvent, this order is reversed and the miscibility relationships are similar to those observed in the hydrocarbon–1-butanol–aqueous sodium *p*-cymenesulfonate systems, where a higher weight fraction of cosolvent is usually needed to produce miscibility with the alkylbenzenes than with the alkanes.

Ho and Kraus[1,2] have investigated miscibility relationships in a series of systems containing a hydrocarbon, a cosolvent, and an aqueous solution of a substituted sodium benzenesulfonate; while Ho and Ogden[3] have studied the solubility of toluene in aqueous solutions of various benzenecarboxylates both with and without 1-butanol as the cosolvent. In these studies the side chains on the benzenesulfonates or benzenecarboxylates have been kept shorter than those usually thought to result in micelle formation. The hope is that the study of these well-defined, simpler systems may help elucidate the more complex systems containing alkyl benzenesulfonate surfactants used in the micellar-flood method of enhanced oil recovery by uncoupling those aspects of behavior arising from solubility effects from behavior resulting from micelle formation.

The present paper deals with miscibility relationships in systems containing an aqueous solution of sodium salicylate, *n*-butylcarbitol, and a series of hydrocarbons, including both *n*-alkanes and alkylbenzenes. The sodium salicylate was chosen as the protosurfactant because of its high solubility in water, permitting the studies to be made over a wide range of salt concentration. Also, miscibility studies previously made in this laboratory by Moisio[4] on systems containing toluene, 1-butanol, and aqueous solutions of sodium salicylate had indicated that further studies using sodium salicylate as the protosurfactant might help shed light on the complex behavior observed in organic–aqueous mixtures. The cosolvent chosen for the studies in this paper, *n*-butylcarbitol (diethyleneglycol monobutyl ether), is a widely used commercial solvent.

Our previous work on systems employing benzenesulfonates[1,2] or benzenecarboxylates[3] as the protosurfactant was made by using 1-butanol as the cosolvent. In order to make possible a comparison of the phase boundary relationships observed in those systems with that observed in corresponding systems containing sodium salicylate as the protosurfactant, we investigated a few of the systems reported in this paper both with *n*-butylcarbitol and with 1-butanol as the cosolvent.

Experimental Section

All chemicals were used without further purification or drying. The benzene and *n*-heptane were reagent grade from Mallinckrodt, while the toluene and *n*-butylcarbitol were certified ACS grade from Fisher Scientific Co. The 1-phenylhexane, 1-phenylheptane, 1-phenyloctane, 1-phenylnonane, 1-phenyldecane, *n*-nonane, *n*-undecane, *n*-tridecane, *n*-pentadecane, and *n*-hexadecane were all from Aldrich and varied from 96 to 99+% purity. The 1-phenylethane, *p*-xylene, 1-phenylbutane, cyclohexane, and sodium salicylate were from Matheson Coleman and Bell. The aqueous sodium salicylate solutions were prepared from distilled water and concentrations are expressed in terms of molality, m (mol/kg of H_2O).

The phase-boundary curves were constructed by titrating mixtures of hydrocarbon and aqueous sodium salicylate solution containing various weight ratios of hydrocarbon to aqueous sodium salicylate solution to a clear end point with the *n*-butylcarbitol. In carrying out the titrations, samples of the hydrocarbon and aqueous sodium salicylate solution were weighed into small tubes that had specially designed caps.[1] Each cap contained a silicone septum through which the *n*-butylcarbitol could be injected. The tubes containing the hydrocarbon and the aqueous solution were thermostated at 25 °C for 30 min in a constant-temperature water bath. At this point two distinct liquid phases were present. After 30 min, *n*-butylcarbitol was added through the septum from a syringe until a clear one-phase solution resulted. Mixing during the titration was accomplished by using a "vortex mixer". All quantities were determined by weight.

Results and Discussion

As in previous papers in this series[1-3] the four-component systems hydrocarbon, *n*-butylcarbitol, sodium salicylate, and water have been treated as pseudo-three-component systems by considering the aqueous solution of sodium salicylate (at a fixed concentration) as one component. The miscibility data obtained in this study are shown in Tables I–IV. All values shown in the tables are in weight percent. Table I shows the compositions of the *n*-butylcarbitol, hydrocarbon, water (no sodium salicylate) systems at the boundaries between one and two liquid phases, while the remaining tables show the compositions of the *n*-butylcarbitol, hydrocarbon systems containing 1.0, 2.5, and 6.0 m aqueous sodium salicylate solutions. All measurements were made at 25 °C.

Miscibility data for systems containing 2.5 mol of sodium salicylate/kg of water are shown plotted as phase boundary

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Table I. Compositions of *n*-Butylcarbitol, Hydrocarbon, Water Systems at Boundaries between One and Two Liquid Phases (25 °C)[a, b]

n-BC	H	H_2O	*n*-BC	H	H_2O	*n*-BC	H	H_2O
H = benzene			H = toluene			H = 1-phenylethane		
18.7	80.5	0.8	13.7	85.8	0.5	19.2	80.3	0.5
21.7	77.4	0.9	35.7	60.9	3.4	37.0	59.0	4.1
37.9	58.9	3.2	51.6	35.6	12.8	45.8	44.1	10.1
51.2	40.1	8.7	53.3	25.5	21.2	48.7	35.3	15.9
55.1	32.0	12.9	51.6	19.5	28.9	48.7	21.9	29.5
55.7	21.5	22.8	47.7	15.1	37.2	42.7	11.6	45.7
47.9	11.6	40.5	43.7	11.1	45.2	29.5	3.6	66.9
31.1	4.0	64.9	37.6	7.5	54.9	17.7	0.6	81.7
15.6	0.8	83.6	32.5	5.3	62.2			
			16.7	0.8	82.5			
H = *p*-xylene			H = 1-phenylbutane			H = 1-phenylhexane		
17.3	82.0	0.7	15.2	84.4	0.4	12.7	87.0	0.3
21.0	78.0	1.0	29.1	67.2	3.7	26.4	69.8	3.8
34.8	61.6	3.6	38.7	51.0	10.3	39.9	50.2	10.0
45.7	44.1	10.2	45.3	32.9	21.8	50.3	29.4	20.3
49.3	28.6	22.0	45.5	19.6	34.8	53.0	17.5	29.5
46.8	18.8	34.4	41.7	12.1	46.2	51.1	9.7	39.2
42.8	11.8	45.4	31.5	3.9	64.7	42.3	3.4	54.3
28.8	3.8	67.4	23.1	0.7	76.2	29.2	0.6	70.2
18.2	0.7	81.1						
H = 1-phenylhaptane			H = 1-phenyloctane			H = 1-phenylnonane		
13.0	86.4	0.6	13.8	85.5	0.7	12.8	86.7	0.5
25.5	70.8	3.6	29.5	66.8	3.7	29.6	67.0	3.5
47.2	38.9	13.9	46.2	43.6	10.2	48.3	42.7	9.0
54.4	24.0	21.6	53.6	31.8	14.6	56.4	30.7	12.8
56.3	16.3	27.4	60.0	19.0	21.1	64.8	15.1	20.1
56.1	11.9	32.0	59.5	7.8	32.7	62.2	6.2	31.7
54.0	8.0	38.0	50.3	2.9	46.8	55.0	2.6	42.4
50.8	5.5	43.7	34.9	0.5	64.6	39.2	0.6	60.2
44.3	2.7	52.9						
35.4	1.1	63.5						
H = 1-phenyldecane			H = cyclohexane			H = *n*-heptane		
13.3	86.0	0.6	9.4	90.2	0.4	12.5	87.0	0.6
30.2	66.3	3.4	17.2	80.6	2.3	40.0	56.1	3.9
43.1	50.7	6.2	22.3	73.6	4.1	65.8	23.0	11.2
59.0	29.7	11.3	40.4	48.6	10.9	68.2	14.6	17.2
65.3	18.3	16.4	48.5	35.1	16.4	66.4	10.5	22.9
67.2	12.5	20.3	53.0	21.9	25.1	65.0	8.1	26.9
67.0	9.2	23.8	48.9	10.3	40.9	61.3	5.7	33.0
65.8	6.5	27.7	35.4	3.7	61.0	45.9	2.6	51.5
55.1	2.2	42.7	20.7	0.6	78.7	29.0	0.5	70.5
40.7	0.5	58.7						
H = *n*-nonane			H = *n*-undecane			H = *n*-tridecane		
12.0	87.6	0.5	17.3	82.1	0.5	11.9	87.8	0.3
47.1	49.2	3.7	40.8	57.2	2.0	60.7	37.1	2.2
68.9	23.6	7.5	58.3	38.6	3.1	76.1	19.2	4.5
73.8	11.9	14.3	73.3	20.6	6.2	81.5	6.0	12.5
55.1	1.8	43.1	77.3	14.3	8.4	78.7	3.6	17.7
35.6	0.4	64.0	78.4	9.4	12.2	70.8	1.5	27.6
			62.3	1.6	36.2	53.9	0.4	45.7
			35.1	0.4	64.5			
			32.5	0.1	67.4			
H = *n*-pentadecane			H = *n*-hexadecane					
17.9	81.8	0.4	42.3	57.1	0.6			
61.3	37.1	1.6	71.2	27.2	1.6			
79.6	16.6	3.8	82.0	14.7	3.4			
83.8	10.0	6.2	85.9	8.1	6.0			
84.7	6.8	8.5	86.0	4.8	9.3			
83.0	3.8	13.3	84.0	2.9	13.1			
75.9	1.6	22.6	76.9	1.2	21.9			
60.0	0.4	39.7	64.0	0.3	35.7			

[a] *n*-BC = *n*-butylcarbitol. H = hydrocarbon. [b] Compositions are in weight percent.

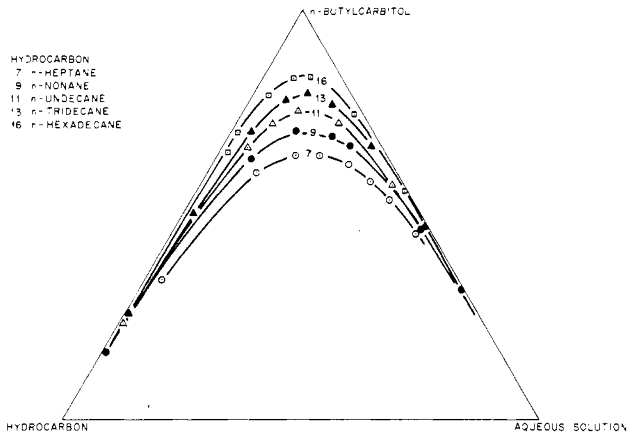

Figure 1. Phase-boundary relationships in several *n*-alkane–*n*-butylcarbitol–2.5 *m* aqueous sodium salicylate systems at 25 °C.

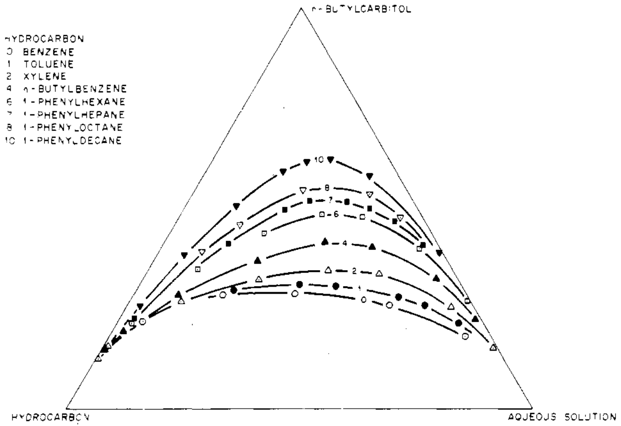

Figure 2. Phase-boundary relationships in several *n*-alkylbenzene–*n*-butylcarbitol–2.5 *m* aqueous sodium salicylate systems at 25 °C.

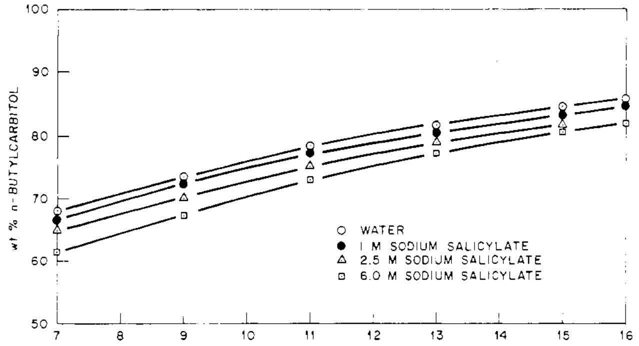

Figure 3. Minimum weight percents of *n*-butylcarbitol necessary to produce miscibility in 1:1 weight percent mixtures of a series of *n*-alkanes and 1.0, 2.5, and 6.0 *m* aqueous sodium salicylate solutions.

curves in Figures 1 and 2. The area above each curve (adjacent to the *n*-butylcarbitol apex) is the single liquid-phase region; two liquid phases occur below the boundary curves. The phase-boundary diagrams for the systems containing either 1.0 or 6.0 mol of sodium salicylate/kg of water are similar in shape (but displaced) to those shown in Figures 1 and 2 for the systems containing 2.5 *m* sodium salicylate.

Values of the minimum weight fraction of *n*-butylcarbitol necessary to produce miscibility in 1:1 weight percent mixtures of hydrocarbon and water and of hydrocarbon and 1.0, 2.5, and 6.0 *m* aqueous sodium salicylate solution, as read from the full phase boundary curves, are shown plotted vs. the alkyl carbon number N_{AC} of the hydrocarbon for the alkanes in Figure 3 and for the alkylbenzenes in Figure 4. Except with benzene and with 1.0 *m* sodium salicylate solution the amount of *n*-butyl-

Table II. Compositions of *n*-Butylcarbitol, Hydrocarbon, 1.0 *m* Aqueous Sodium Salicylate Systems at Boundaries between One and Two Liquid Phases (25 °C)[a, b]

n-BC	H	1.0 *m* Na salic	*n*-BC	H	1.0 *m* Na salic	*n*-BC	H	1.0 *m* Na salic
H = benzene			H = toluene			H = 1-phenylethane		
10.1	89.7	0.2	31.1	62.9	6.1	25.8	71.0	3.3
34.0	62.7	3.3	33.9	50.5	15.6	33.9	55.7	10.4
37.8	50.8	11.4	32.8	21.3	46.0	38.0	36.5	25.5
38.8	36.7	24.5	29.8	15.6	54.7	33.8	14.2	51.9
33.3	25.1	41.7	25.7	8.7	65.5	27.9	5.0	67.1
25.5	13.8	60.7	25.9	7.4	66.7	17.6	0.9	81.5
18.9	5.0	76.2	19.9	2.8	77.4			
10.8	0.9	88.3						
H = *p*-xylene			H = 1-phenylbutane			H = 1-phenylhexane		
12.8	86.9	0.3	11.6	88.2	0.3	10.8	88.9	0.3
26.2	69.8	4.0	24.1	72.7	3.2	24.3	72.1	3.6
35.4	53.2	11.4	34.5	55.8	9.7	38.0	52.1	9.9
39.0	36.72	24.3	42.1	36.0	22.0	46.0	35.5	18.5
35.8	22.73	41.5	44.0	22.1	34.0	51.5	18.3	30.2
33.9	14.01	52.1	42.4	12.2	45.4	49.7	10.7	39.6
24.9	4.02	71.1	34.1	4.2	61.7	40.7	3.7	55.6
17.0	0.8	82.2	22.8	0.8	76.4	28.2	0.7	71.1
H = 1-phenylheptane			H = 1-phenyloctane			H = 1-phenylnonane		
4.7	95.2	0.2	5.0	94.8	0.2	6.9	93.0	0.2
23.6	72.7	3.7	24.7	72.0	3.2	27.8	69.1	3.0
31.7	61.2	7.1	36.5	56.2	7.4	43.6	48.3	8.1
44.3	41.7	14.0	40.5	50.9	8.6	52.0	36.5	11.5
52.0	26.2	21.8	49.5	37.2	13.3	61.7	19.2	19.1
54.2	18.1	27.7	51.3	33.6	15.1	60.7	7.7	31.6
54.1	13.2	32.7	56.4	8.6	35.0	53.7	3.5	42.8
52.4	9.4	38.2	49.1	3.6	47.3	39.0	0.9	60.1
42.3	3.0	54.8	34.8	0.7	64.6			
29.0	0.7	70.4						
H = 1-phenyldecane			H = cyclohexane			H = *n*-heptane		
5.4	94.5	0.1	8.9	90.9	0.3	8.3	91.6	0.2
28.7	67.9	3.4	25.3	70.3	4.4	39.7	56.9	3.4
54.5	34.3	11.1	39.5	49.1	11.4	63.0	26.2	10.8
63.1	20.0	16.9	50.3	28.3	21.4	66.9	16.2	16.9
64.0	8.3	27.7	51.9	17.5	30.6	63.7	9.0	27.3
39.5	0.7	59.8	47.3	9.6	43.1	66.4	11.8	21.8
			36.0	3.0	60.0	60.0	6.2	33.8
			20.1	0.6	79.3	55.3	4.4	40.3
						48.5	2.8	48.7
						25.3	0.5	74.2
H = *n*-nonane			H = *n*-undecane			H = *n*-tridecane		
7.9	92.0	0.1	8.2	91.7	0.1	18.9	80.7	0.4
43.1	53.6	3.3	47.3	50.1	2.6	53.5	44.7	1.8
63.3	30.1	6.6	68.6	26.3	5.1	72.0	24.0	3.9
72.1	15.8	12.1	76.5	14.0	9.5	79.5	13.5	7.0
71.6	9.0	19.4	77.2	8.6	14.3	77.4	5.6	17.0
68.4	6.1	25.5	73.9	5.4	20.6	70.6	2.2	27.2
55.8	2.5	41.8	61.1	2.1	36.8	52.7	0.6	46.8
34.2	0.5	65.3	42.6	0.5	56.9			
H = *n*-pentadecane			H = *n*-hexadecane					
7.2	92.8	0.1	39.9	59.5	0.6			
59.3	39.0	1.7	68.8	29.7	1.6			
76.1	20.4	3.5	80.9	15.7	3.4			
8 0	11.9	6.1	85.0	8.8	6.2			
83.3	7.3	9.5	85.0	5.3	9.7			
82.3	4.5	13.2	82.9	3.4	13.7			
74.9	1.9	23.2	74.8	1.4	23.8			
71.5	1.4	27.1	66.0	0.6	33.4			
61.8	0.7	37.5						

[a] *n*-BC = *n*-butylcarbitol. H = hydrocarbon. [b] Compositions are in weight percent.

Table III. Compositions of *n*-Butylcarbitol, Hydrocarbon, 2.5 *m* Aqueous Sodium Salicylate Systems at Boundaries between One and Two Liquid Phases (25 °C)[a, b]

n-BC	H	2.5 *m* Na salic	*n*-BC	H	2.5 *m* Na salic	*n*-BC	H	2.5 *m* Na salic
H = benzene			H = toluene			H = 1-phenylethane		
8.5	91.1	0.3	7.5	92.2	0.3	11.8	87.9	0.4
17.1	82.1	0.8	26.2	66.7	7.1	19.1	77.3	3.7
21.7	75.1	3.3	28.5	50.2	21.3	24.0	62.8	12.2
26.3	62.1	11.6	31.0	34.5	34.5	30.4	49.6	20.0
28.2	52.5	19.3	30.8	26.9	42.2	34.0	31.5	34.5
28.6	36.6	34.7	27.9	14.8	57.4	32.7	15.6	51.7
25.9	17.8	56.3	26.0	10.1	63.9	25.5	5.1	69.5
18.2	5.4	76.4	21.5	5.2	73.3	15.2	0.8	83.9
8.1	0.9	91.0	12.7	1.2	86.1			
H = *p*-xylene			H = 1-phenylbutane			H = 1-phenylhexane		
14.8	84.4	0.7	14.1	85.2	0.7	12.4	87.1	0.5
21.5	72.8	5.8	19.2	78.0	2.8	20.7	75.8	3.5
26.4	62.1	11.5	28.1	62.2	9.8	34.6	54.7	10.7
32.3	42.7	25.1	36.9	40.9	22.2	43.7	36.0	20.3
34.4	26.9	38.7	41.8	23.7	34.6	48.4	21.5	30.1
33.7	16.4	49.9	40.6	14.3	45.1	47.8	12.8	39.4
25.3	4.8	69.9	32.5	4.6	63.0	39.7	4.5	55.9
15.1	0.8	84.1	22.3	1.1	76.6	26.6	0.8	72.6
H = 1-phenylheptane			H = 1-phenyloctane			H = 1-phenylnonane		
22.3	74.1	3.6	3.3	96.7	0.1	7.3	92.5	0.2
40.8	45.0	14.3	21.6	75.2	3.2	27.2	69.8	3.0
49.4	28.6	22.0	39.0	51.5	9.5	42.3	49.1	8.7
52.4	19.6	28.0	45.4	40.5	14.1	48.9	39.8	11.3
51.7	14.5	33.9	54.5	22.0	23.5	59.1	20.3	20.7
50.0	10.5	39.5	53.3	8.8	38.0	58.8	8.0	33.2
46.8	6.4	46.8	47.8	4.7	47.5	49.9	3.4	46.7
40.9	3.4	55.7	31.0	0.7	68.3	36.3	0.7	63.1
33.3	1.4	65.3						
H = 1-phenyldecane			H = cyclohexane			H = *n*-heptane		
6.2	93.7	0.1	8.5	91.2	0.4	7.9	91.9	0.2
25.3	71.7	3.0	12.7	85.9	1.4	34.0	62.1	3.8
38.2	56.1	5.8	21.3	74.2	4.5	60.2	28.7	11.2
50.3	38.6	11.1	38.0	50.1	11.9	64.6	18.8	16.6
59.0	24.2	16.8	44.8	37.9	17.3	64.6	13.8	21.6
61.9	17.8	20.4	48.6	23.9	27.5	62.1	9.2	28.8
62.1	12.7	25.3	45.5	10.0	43.5	57.9	6.9	35.3
58.1	6.2	35.8	33.5	3.7	62.8	53.5	4.8	41.7
38.9	0.8	60.2	14.7	0.6	84.7	45.4	3.0	51.6
						25.4	0.6	74.0
H = *n*-nonane			H = *n*-undecane			H = *n*-tridecane		
16.4	83.0	0.6	23.2	76.1	0.7	25.7	73.6	0.7
63.6	28.7	7.7	66.0	28.3	5.8	50.4	47.7	2.0
70.4	16.2	13.4	72.0	20.1	7.9	70.2	25.7	4.1
69.3	9.1	21.6	75.3	12.8	11.9	78.2	14.4	7.4
65.9	6.2	27.9	72.4	5.9	21.8	79.6	9.0	11.5
52.2	2.2	45.6	56.9	2.5	40.6	77.1	5.2	17.7
31.7	0.4	67.9	34.4	0.5	65.1	66.7	2.2	31.1
						46.7	0.6	52.7
H = *n*-pentadecane			H = *n*-hexadecane					
10.1	89.8	0.1	28.5	71.1	0.5			
57.8	40.4	1.7	65.4	33.1	1.5			
72.3	23.7	4.0	79.4	17.3	3.4			
78.8	13.7	7.5	83.8	10.0	6.3			
81.2	7.6	11.2	83.9	6.2	9.9			
79.7	4.8	15.5	82.0	3.9	14.1			
71.1	2.0	26.9	74.8	1.9	23.2			
52.2	0.5	47.3	55.6	0.5	44.0			

[a] *n*-BC = *n*-butylcarbitol, H = hydrocarbon. [b] Compositions are in weight percent.

carbitol necessary to produce miscibility of the hydrocarbon and the aqueous solution increases nearly linearly as the number of alkyl carbon atoms in the hydrocarbon N_{AC} increases. However, in all cases a considerably higher weight fraction of *n*-butylcarbitol is required to produce miscibility in the systems containing the alkanes than in the systems containing alkylbenzenes with the same alkyl carbon number. This behavior

Table IV. Compositions of *n*-Butylcarbitol, Hydrocarbon, 6.0 m Aqueous Sodium Salicylate Systems at Boundaries between One and Two Liquid Phases (25 °C)[a, b]

n-BC	H	6.0 m Na salic	*n*-BC	H	6.0 m Na salic	*n*-BC	H	6.0 m Na salic
H = benzene			H = toluene			H = 1-phenylethane		
5.3	94.5	0.2	6.4	93.4	0.2	4.6	95.2	0.2
11.6	84.3	4.1	11.9	84.1	4.0	12.6	83.6	3.8
16.5	70.4	13.1	20.9	60.2	18.9	18.9	68.6	12.5
20.0	59.0	21.0	26.1	41.9	32.0	23.9	55.6	20.5
24.0	40.8	35.2	27.4	31.8	40.8	30.1	35.1	34.8
23.0	19.3	57.7	27.1	22.5	50.4	30.2	16.8	53.0
15.2	5.7	79.1	25.5	15.6	58.9	22.6	5.5	71.9
8.7	1.0	90.3	24.0	12.1	63.9	11.5	1.0	87.5
			17.4	5.1	77.5			
			8.0	1.4	90.6			
			7.2	0.9	91.9			
H = *p*-xylene			H = 1-phenylbutane			H = 1-phenylhexane		
8.8	90.7	0.5	6.4	93.4	0.2	10.2	89.6	0.2
12.7	83.9	3.4	9.0	90.7	0.3	18.5	78.2	3.3
19.7	68.3	0	12.5	85.0	2.5	32.5	54.4	13.1
27.9	45.5	26.6	23.2	65.2	11.6	39.6	38.7	21.7
31.5	27.7	40.8	32.5	43.6	23.9	44.4	22.7	32.9
31.1	16.1	52.8	37.4	25.3	37.3	43.7	12.8	43.5
24.2	5.8	0	36.7	13.9	49.4	35.9	4.7	59.4
11.0	0.9	88.1	28.8	4.6	66.6	22.3	1.0	76.7
			17.7	1.0	81.3			
H = 1-phenylheptane			H = 1-phenyloctane			H = 1-phenylnonane		
6.5	93.2	0.3	3.8	96.1	0.1	7.3	92.6	0.1
14.5	85.2	0.3	13.6	84.8	1.6	20.8	76.3	2.9
14.1	82.5	3.4	30.9	59.5	9.6	35.4	56.1	8.5
24.4	66.4	9.2	36.1	50.8	13.1	44.0	42.8	13.2
33.9	50.8	15.3	49.2	25.7	25.1	53.3	23.7	23.0
42.2	35.6	22.2	49.4	10.5	40.1	53.3	10.1	36.6
44.4	32.5	23.1	42.7	4.6	52.7	46.3	4.4	49.3
47.1	22.9	30.0	27.8	0.9	71.3	30.5	0.8	68.7
47.1	16.9	36.0						
46.3	11.7	42.0						
43.0	7.7	49.3						
37.3	3.8	58.9						
29.5	1.7	68.8						

n-BC	H	6.0 m Na salic	*n*-BC	H	6.0 m Na salic	*n*-BC	H	6.0 m Na salic
H = 1-phenyldecane			H = cyclohexane			H = *n*-heptane		
8.5	91.2	0.3	6.3	93.5	0.2	7.9	91.9	0.2
21.5	75.3	3.2	10.6	88.0	1.4	35.8	59.4	4.8
30.2	63.8	6.0	16.6	79.4	4.0	58.4	28.2	13.4
43.5	45.0	11.5	31.5	56.9	11.6	61.6	17.7	20.7
54.0	27.4	18.6	39.7	43.1	17.2	60.9	13.7	25.4
57.1	19.6	23.3	45.9	27.7	26.4	58.6	10.1	31.3
57.3	13.7	29.0	43.8	12.8	43.4	55.0	7.6	37.4
56.2	9.8	0	31.6	4.2	64.2	47.9	4.7	47.4
46.9	3.4	49.7	13.1	0.8	86.1	40.7	2.7	56.6
33.2	0.9	65.9				27.0	0.0	72.0
H = *n*-nonane			H = *n*-undecane			H = *n*-tridecane		
6.6	93.2	0.2	6.9	92.9	0.2	19.8	79.6	0.6
35.8	60.5	3.7	27.3	71.1	1.6	41.7	56.6	1.7
58.0	33.8	8.2	42.4	54.5	3.1	68.0	27.3	4.7
67.0	18.6	14.4	64.2	29.1	6.7	75.7	16.0	8.3
66.7	11.0	22.3	70.5	19.9	9.6	77.4	10.2	12.4
62.8	7.1	30.1	72.9	14.0	13.1	75.6	6.8	17.6
49.4	2.7	47.9	69.0	6.2	24.8	65.7	2.9	31.4
31.9	0.5	67.6	56.1	2.3	41.6	46.4	0.6	53.0
			38.1	0.6	61.3			
			30.6	0.3	69.1			
H = *n*-pentadecane			H = *n*-hexadecane					
26.7	72.6	0.7	7.8	92.1	0.1			
53.1	45.0	1.9	44.8	54.3	0.9			
72.7	23.3	4.0	61.9	36.4	1.7			
79.1	14.2	6.7	72.2	23.6	4.2			
80.5	8.8	10.7	82.0	11.3	6.7			
78.8	5.7	15.5	82.3	7.3	10.4			
70.2	2.5	27.3	80.0	4.5	15.5			
50.3	0.7	49.0	70.5	1.9	27.6			
			50.6	0.5	48.9			

[a] *n*-BC = *n*-butylcarbitol, H = hydrocarbon. [b] Compositions are in weight percent.

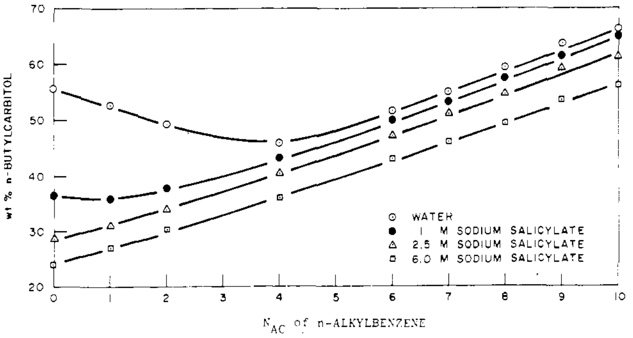

Figure 4. Minimum weight percents of *n*-butylcarbitol necessary to produce miscibility in 1:1 weight percent mixtures of a series of *n*-alkylbenzenes and 1.0, 2.5, and 6.0 m aqueous sodium salicylate solutions.

contrasts with that observed in aqueous-hydrocarbon systems containing 1-butanol as the cosolvent and aqueous solutions of sodium *p*-cymenesulfonate.[2] In this latter system a higher weight fraction of cosolvent was needed to produce miscibility with the alkylbenzenes than with the alkanes.

To determine whether the cosolvent *n*-butylcarbitol used in the present study was responsible for this reversal, we determined phase-boundary curves for systems containing 1-butanol, 2.5 m aqueous sodium salicylate solution, and a series of hydrocarbons, including four alkanes and the corresponding alkylbenzenes. The minimum weight percent of either *n*-butylcarbitol or 1-butanol necessary to produce miscibility in 1:1 weight percent mixtures of hydrocarbon and 2.5 m aqueous sodium salicylate solution is shown in Table V. As can be seen, it requires a higher weight percent of *n*-butylcarbitol to produce miscibility with the alkanes than with the corresponding alkylbenzenes, while the opposite is true when 1-butanol is the cosolvent. Hence, it appears it is more important that the nature of the cosolvent determines the relative miscibilities in these aqueous-hydrocarbon systems than whether the protosurfactant is a benzenesulfonate or a benzenecarboxylate.

Table V. Minimum Weight Percent Cosolvent Necessary to Produce Miscibility in 1:1 Weight Percent Mixtures of Hydrocarbon and 2.5 m Aqueous Sodium Salicylate Solution

hydrocarbon	cosolvent: *n*-butylcarbitol	cosolvent: 1-butanol
hexane		39.6
1-phenylhexane	47.2	41.0
octane	67.5	43.0
1-phenyloctane	54.5	46.0
decane	72.6	48.0
1-phenyldecane	61.3	53.0
tridecane	79.0	57.6
1-phenyltridecane		62.5

In Table VI is shown a comparison of the minimum amounts of either *n*-butylcarbitol or 1-butanol required to produce miscibility in mixtures containing 1:1 weight fractions of toluene and

Table VI. Minimum Weight Percent Cosolvent Necessary to Produce Miscibility in 1:1 Weight Percent Mixtures of Toluene and 2.0 *m* Aqueous Solutions of Sodium Salicylate, Sodium Benzoate, or Sodium Benzenesulfonate

aqueous solution	cosolvent	wt % cosolvent
sodium salicylate (2.0 *m*)	*n*-butylcarbitol	31.8
sodium benzoate (2.0 *m*)	*n*-butylcarbitol	35.1
sodium benzenesulfonate (2.0 *m*)	*n*-butylcarbitol	36.0
sodium salicylate (2.0 *m*)	1-butanol	37.5
sodium benzoate (2.0 *m*)	1-butanol	43.0
sodium benzenesulfonate (2.0 *m*)	1-butanol	53.7

2.0 *m* aqueous solutions of sodium salicylate, sodium benzoate, or sodium benzenesulfonate. These values were either determined in the present study or are taken from ref 2 and 3.

Thus it is apparent that with either *n*-butylcarbitol or 1-butanol a smaller weight percent of cosolvent is required to produce miscibility of toluene and the aqueous solution when sodium salicylate is the protosurfactant than when either sodium benzoate or sodium benzenesulfonate is used. Moreover, with any of the three protosurfactants *n*-butylcarbitol is a more efficient cosolvent in promoting miscibility in 1:1 weight percent mixtures of toluene and aqueous solution.

Hence, the cosolvent plays an important role in determining miscibility relationships in systems containing an aqueous solution of a protosurfactant and a hydrocarbon. Not only is the minimum amount of cosolvent necessary for miscibility affected but so are the relative miscibilities of alkanes and the corresponding alkylbenzenes.

The role of the cosolvent in interfacial tension studies involving hyrocarbon–cosolvent–aqueous surfactant systems has been examined by many (see, e.g., ref 5). In such systems sharp minima in interfacial tension occur as a function of the number of alkyl carbon atoms (ACN) in the hydrocarbon. Cosolvents of low molecular weight, such as 2-propanol, may shift the value of the ACN of lowest interfacial tension, $n_{\min}$, downward to lower values (compared to $n_{\min}$ with no cosolvent present), while cosolvents of higher molecular weight, such as 3-methyl-1-butanol, may have a large upward effect on $n_{\min}$. In the interfacial tension studies the presence of a benzene ring in the hydrocarbon does not affect the value of $n_{\min}$. Only the alkyl carbon atoms are involved. Thus a system exhibiting a minimum interfacial tension with decane also shows a minimum with phenyldecane.[6] Nearly analogous behavior was observed in our studies of miscibility in aqueous–hydrocarbon systems containing 1-butanol as the cosolvent and a sodium benzenesulfonate as the protosurfactant. In those systems almost the same amount of 1-butanol was required to produce miscibility of the aqueous benzenesulfonate solution and either hexane or phenylhexane. Such behavior is, however, not observed in the miscibility studies reported here. Comparison of the plots in Figures 3 and 4 reveals that in all cases considerably more *n*-butylcarbitol is required to produce miscibility in 1:1 weight percent mixtures of aqueous sodium salicylate solution and the series of alkanes than with the corresponding series of alkylbenzenes. Hence, whereas the presence of a benzene ring does not contribute to the effective carbon number for minima in interfacial tension, its presence has an influence on miscibility in the systems studied here, the extent depending on the cosolvent used.

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Solubility of Carbon Dioxide in Molten Salts

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The solubilities of carbon dioxide in molten $ZnCl_2$, $ZnBr_2$, $SnCl_2$, and $NaNO_3$ were determined at 1 atm and temperatures from 270 to 475 °C. By the simplified elution method used in this work, solubilities of carbon dioxide were able to be measured with the use of small amounts of molten salts. The solubilities of carbon dioxide slightly decreased with increasing temperature in this temperature range.

Molten salts have recently been used as solvents, catalysts, and/or reactants in organic and inorganic reactions such as the chlorination of hydrocarbons and the desulfurization of waste gas. For the investigation of the kinetics of these reactions, physical properties of gases in molten salts, such as the solubility and the diffusivity, are essential. However, there have been few data of gas solubilities in molten salts (*2*, *3*, *6*, *7*). Especially, the solubility data of triatomic gases, such as CO_2 and SO_2, are very scarce.

In the present work, solubilities of carbon dioxide in molten salts were determined with a simplified elution method at 1 atm and temperatures from 270 to 475 °C. In this temperature range there is no reaction between carbon dioxide and molten halides and nitrates. The molten salts used were the halides which showed some degree of association above the melting point, such as $ZnCl_2$, $ZnBr_2$, and $SnCl_2$, and the ionic nitrate, i.e., $NaNO_3$.

Experimental Section

The experimental apparatus is shown in Figure 1. A stainless steel crucible, used as an absorption and elution chamber, was

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