Solubility of Toluene in Aqueous Solutions of Various Benzenecarboxylates with or without 1-Butanol

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Miscibility relationships in systems containing short alkyl-side-chain sodium benzenecarboxylates, toluene, and water without (three-component systems) or with (four-component systems) 1-butanol were studied at 55 and 25 °C, respectively. The results are compared with corresponding sulfonates. The benzenecarboxylates included those of benzene, 2,4-dimethylbenzene, 2,4,6-trimethylbenzene, and *tert*-butylbenzene. The solubility of toluene in aqueous solutions of the carboxylates increases with the number of alkyl carbons "N_{AC}" attached to the benzene ring and generally with carboxylate concentration (up to ca. 3 mol/kg of H_2O); it is somewhat higher in the carboxylate solutions than in the corresponding sulfonate solutions. Four-component systems were treated as pseudoternary systems by maintaining a constant carboxylate to water ratio (2 mol/kg of water). Boundaries between one and two phases are fairly symmetrical. The amount of 1-butanol (cosolvent) required to produce miscibility decreases with increasing number of alkyl carbons on the carboxylate. These systems required somewhat less 1-butanol to produce miscibility than the corresponding sulfonate systems.

Introduction

In previous papers (*1*, *2*) we reported the solubility of toluene in aqueous solutions of benzenesulfonates substituted with alkyl groups and the miscibility of aqueous sulfonate–hydrocarbon systems in the presence of a cosolvent. Here we report the solubility of toluene in aqueous solutions of four alkyl-substituted benzenecarboxylates and phase boundary curves for systems containing aqueous solutions of these carboxylates with toluene in the presence of 1-butanol. As before, the four-component systems will be treated as pseudo-three-component systems by fixing the ratio of moles of carboxylate to kilograms of water (molality, *m*). Here the aqueous solution is 2.0 *m* in carboxylate systems. Phase boundaries of 2.0 *m* aqueous solutions of corresponding sulfonates–toluene–1-butanol were also measured for comparison; reported values (*2*) for the sulfonates were at 2.5 *m*.

An important motivation for our studies of these systems is the hope that the behavior of these relatively simple systems helps to clarify some of the interactions occurring in complex micellar floods used for enhanced oil recovery. Compositions in floods are chemically related to those studied. The systems in this and the related studies (*1*, *2*) are simpler in that they are composed of pure components and in that the alkyl chains of surfactant surrogates are believed to be too short to result in formation of micelles. Present measurements are additionally simplified by the absence of inorganic salts, important components of practical systems. Interest in other parts of the program at this laboratory in carboxylate surfactants (*3*) led us to carry out this comparison between carboxylates and sulfonates.

Experimental Section

Toluene and 1-butanol were certified ACS grade from Fisher Scientific Co. The sodium benzoate was from Mallinckrodt. The compounds, 2,4-dimethylbenzoic acid (99%), 2,4,6-trimethylbenzoic acid (98%), and *tert*-butylbenzoic acid (99%) were from Aldrich and were converted to sodium salts by titration to pH 7 with 10% NaOH. After the titrations the solutions were filtered and washed three times with $CHCl_3$ to remove the excess acid and the salts crystallized after volume reduction (40 °C, under vacuum).

Sodium *p*-*tert*-butylbenzenesulfonate was synthesized by sulfonation of *tert*-butylbenzene followed by neutralization and crystallization of the sodium salt, essentially as described previously for similar compounds (*1*). Proton NMR confirmed that the compound contained one sulfonate group para to the *tert*-butyl group.

The solubility of toluene in the aqueous solutions of the above carboxylates was determined by a gas chromatographic method similar to that used previously (*1*). Duplicates agreed to within about 5%, as expected from the innate precision of the method. In order to do the measurements over a wide range of benzoate concentrations and to be able to compare with systems containing corresponding sulfonates which we reported before (*1*), a temperature of 55 °C was chosen for the equilibration.

A Perkin-Elmer Model Sigma 3 gas chromatograph, equipped with flame ionization detector, was used for all GC analyses. The column used in the chromatograph was a 2 ft × $^1/_8$ in. o.d. stainless steel column packed with 60/80 mesh Tenax GC (Applied Science Laboratory). The instrument parameters were column-temperature programmed from 80 °C (2-min hold) to 200 °C with an increase of 10°/min. Inlet and detector temperatures were set at 250 °C; the helium carrier gas was used with inlet pressure set to 30 psig. The column was baked out overnight at 250 °C and gave a constant, low-level baseline at the most sensitive setting. The instrument was calibrated by using standard solutions of toluene in acetone. The stock solutions were prepared by volume and converted to weight percentage with the known densities (*4*).

For computation of toluene activity coefficients in three-component systems, the water contents in the toluene-rich phases were determined by Karl Fischer titrations and the solubility of the various carboxylates by residue analyses. Water contents were less than 0.1 wt %. Carboxylate concentrations were less than 0.06 wt %.

The phase boundary curves for the four-component systems were determined by the weight titration procedure described before (*2*). The titrations were carried out at 25 ± 0.1 °C. The titrant (1-butanol) was added from a syringe into an 8-mL test tube, with screw-on, Teflon-lined caps, containing 0.5–4.0 mL of mixtures of the hydrocarbons and aqueous solutions. The end point was indicated by the disappearance of the second liquid phase. The pseudoternary diagrams are plotted on triangular graphs, with the aqueous component taken to be 2.0

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Table I. Solubility of Toluene in Aqueous Sodium Alkylbenzenecarboxylate Solutions (55 °C)

aqueous solution of	carboxylate concn, mol/kg of H_2O	solubility, mol of toluene/kg of H_2O
sodium benzenecarboxylate	0.49	0.014
	1.09	0.016
	1.50	0.020
	1.78	0.022
	3.27	0.073
sodium 2,4-dimethylbenzene-carboxylate	0.77	0.022
	1.24	0.036
	1.48	0.043
	2.52	0.250
sodium 2,4,6-trimethylbenzene-carboxylate	0.84	0.035
	1.02	0.040
	1.60	0.079
	2.17	0.163
sodium *p-tert*-butylbenzene-carboxylate	0.50	0.059
	0.96	0.203
	1.59	0.609
	2.17	1.20

m substituted benzenecarboxylates or benzenesulfonates.

Results

1. Solubilities of Toluene in Aqueous Sodium Benzenecarboxylates. The solubilities of toluene at 55 °C (mol of toluene/kg of H_2O) in aqueous solutions of alkyl-substituted sodium benzenecarboxylates are summarized in Table I.

From the solubilities, the activity coefficients $\gamma_{T(aq)}$ of toluene in the aqueous solutions were computed by the method discussed in ref 1 which uses the relationship $\gamma_{T(aq)} = m_T^\circ \gamma_T^\circ / m_{T(aq)}$ where m_T° and γ_T° are the solubility and activity coefficient of toluene in water and $m_{T(aq)}$ is the solubility in various electrolyte solutions. We have used $\gamma_T^\circ = 1$, its assigned value at infinite dilution, since the toluene concentration in water is very low. The relationship further assumes that the composition of the toluene-rich phase is essentially independent of the composition of the water-rich phase in equilibrium with it. We confirmed this experimentally by measuring the water content and electrolyte concentrations of the toluene-rich phases; they were less than 0.1 and 0.06 wt %, respectively, in all cases or less than a total mole fraction of 0.0054. The results of the computations are given in Figure 1. It can be seen from Table I that the solubility of toluene usually increases with concentration of carboxylates. With sodium benzoate, the solubility of toluene first decreases with increasing carboxylate concentration, to below 0.5 *m*, and then increases in a manner similar to sodium benzenesulfonate (*1*). The more highly substituted benzenecarboxylates show pronounced increases in solubility with carboxylate concentration and no minima.

Toluene solubility increases (activity coefficients of toluene decrease) with the number of alkyl carbons "N_{AC}" on the benzene ring of the benzenecarboxylates. The trend in the increase of solubility is parallel to that observed in the corresponding systems containing aqueous solution of alkyl-substituted benzenesulfonates (*1*).

2. Miscibility of Four-Component Systems. (a) With Alkylbenzene Carboxylates. Compositions at boundaries between one- and two-liquid phases for four-component systems containing toluene, 1-butanol, and 2.0 *m* solutions of alkyl-substituted benzenecarboxylates are summarized in Table II and graphically presented in Figure 2. The phase diagram for the ternary system toluene–1-butanol–water at 25 °C (*5*, *6*) is included for comparison. In four-component systems with benzenecarboxylates, the shapes of phase boundary curves are fairly symmetrical despite difference among the carboxylates

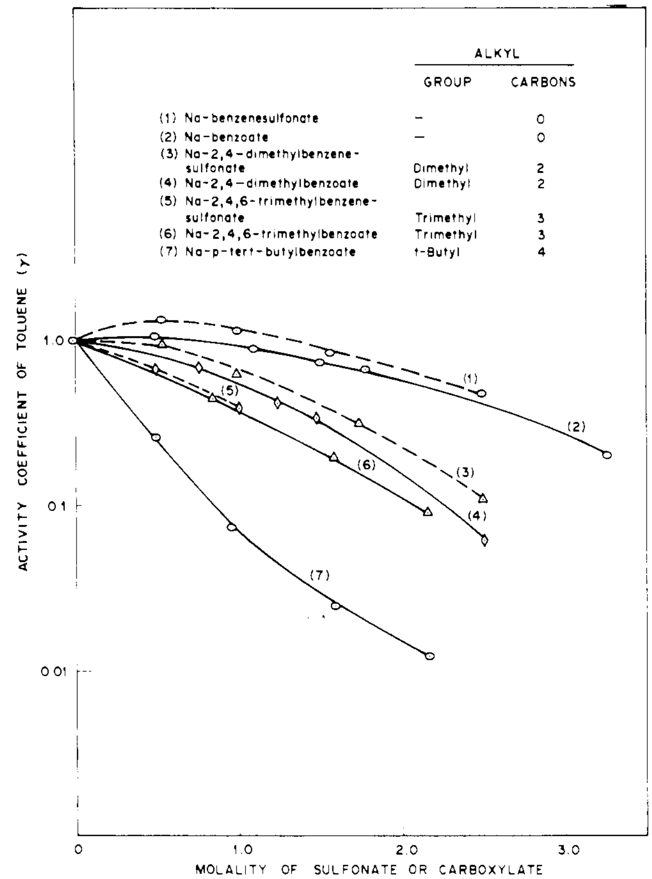

Figure 1. Comparison of activity coefficients of toluene in substituted sodium benzenesulfonate or carboxylate solutions at 55 °C.

Table II. Composition of 1-Butanol–Toluene–2.0 M Aqueous Alkylbenzenecarboxylate Systems at Boundaries between One- and Two-Liquid Phases (25 °C)

	wt %		
sodium carboxylate of	toluene	1-butanol	solution
benzene	2.5	11.0	86.5
	6.6	18.4	75.0
	14.7	29.4	55.9
	22.1	37.0	40.9
	28.4	42.9	28.7
	35.4	45.5	19.1
	48.2	41.6	10.2
	65.3	30.5	4.2
2,4-dimethylbenzene	2.2	6.1	91.7
	7.4	13.3	79.3
	16.9	21.1	62.0
	27.4	25.7	46.8
	37.3	28.2	34.5
	46.7	29.7	23.6
	59.0	29.8	11.2
	71.3	24.4	4.3
2,4,6-trimethylbenzene	7.2	12.9	79.9
	17.2	19.7	63.1
	27.2	23.8	49.0
	37.3	26.0	36.7
	48.0	26.9	25.1
	56.7	26.6	16.7
	60.3	27.0	12.7
	63.8	26.3	9.9
	78.1	19.2	2.7
p-tert-butylbenzene	2.4	1.2	96.4
	7.4	7.2	85.4
	19.0	14.9	66.1
	31.0	20.3	48.7
	51.1	22.3	26.6
	64.9	21.7	13.4
	80.9	16.3	2.8

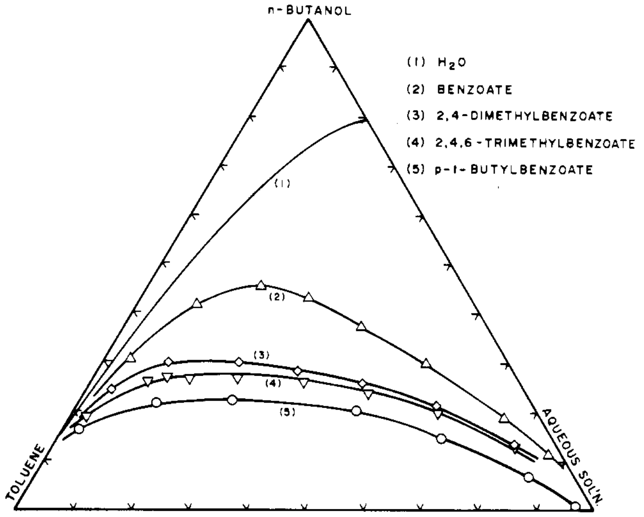

Figure 2. Effect of substituents on phase relations in the toluene–1-butanol–aqueous carboxylate systems (2.0 *m* substituted sodium benzoate, 25 °C).

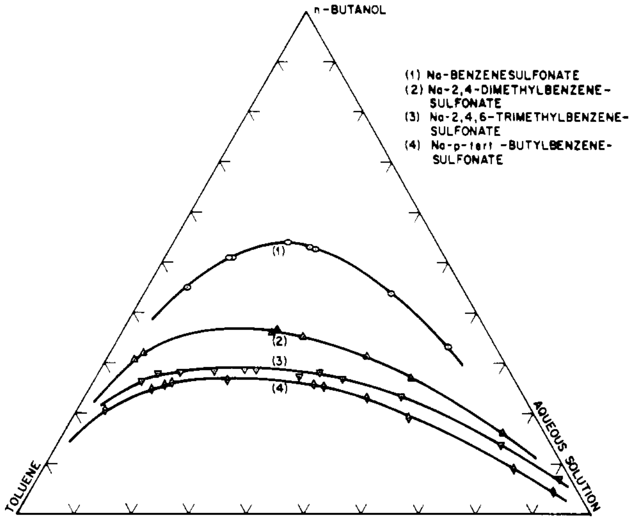

Figure 3. Effect of substituents on phase relations in the toluene–1-butanol–aqueous sulfonate systems (2.0 *m* substituted sodium benzenesulfonate, 25 °C).

in size and location of the substituent groups. The minimum amount of 1-butanol (cosolvent) required to produce miscibility decreases with the increase of N_{AC}.

(*b*) *With Alkylbenzene Sulfonates*. The phase boundary curves of systems toluene–1-butanol–2.0 *m* aqueous solution of sulfonates (the concentration of measurements with carboxylates) with corresponding N_{AC} are presented in Table III and Figure 3.

Discussion

The trends of miscibility of toluene-containing systems in the presence of sodium alkylbenzenecarboxylates are similar to those in the presence of alkylbenzenesulfonates (*1*, *2*). Miscibilities usually increase with increasing number of alkyl carbons on the sulfonate and carboxylate.

In Figure 1 are reproduced from ref 1 activity coefficients of toluene in three-component systems containing benzenesulfonates of the same alkyl substitution as of carboxylates reported here. It can be seen that behavior is similar. For zero and two alkyl carbons, activity coefficients are slightly higher (toluene solubilities are lower) in the presence of sulfonate than in the presence of carboxylate. For three alkyl carbons, values are essentially identical, a little lower in the presence of the carboxylate, if anything.

Table III. Composition of 1-Butanol-Toluene-2.0 M Aqueous Alkylbenzenesulfonate Systems at Boundaries between One- and Two-Liquid Phases (25 °C)

sodium sulfonate of	wt % toluene	wt % 1-butanol	wt % solution
benzene	8.7	33.2	58.1
	13.0	44.1	42.9
	22.0	52.7	25.3
	22.8	53.1	24.1
	26.0	54.0	20.0
	37.6	50.7	11.7
	37.7	50.9	11.4
	48.2	44.9	6.9
2,4-dimethylbenzene	7.3	16.3	76.4
	18.1	27.0	54.9
	23.4	31.6	45.0
	32.6	35.5	31.9
	36.4	37.0	26.6
	37.2	37.4	25.4
	37.7	36.2	26.1
	62.2	32.1	5.7
	64.6	30.8	4.6
2,4,6-trimethylbenzene	1.4	7.4	91.2
	8.6	13.7	77.7
	21.3	23.5	55.2
	29.7	27.1	43.2
	33.0	27.4	39.6
	37.2	27.4	35.4
	44.0	29.1	26.9
	46.4	28.5	25.1
	51.6	28.3	20.1
	57.8	27.6	14.6
	61.5	29.2	9.3
	65.2	26.6	8.2
p-tert-butylbenzene	4.1	4.6	91.3
	8.6	9.2	82.2
	22.1	19.0	58.9
	25.0	20.4	54.6
	33.7	25.8	40.5
	50.3	26.4	23.3
	60.0	26.4	13.6
	61.8	25.3	12.9
	64.3	24.7	11.0
	74.5	20.8	4.7

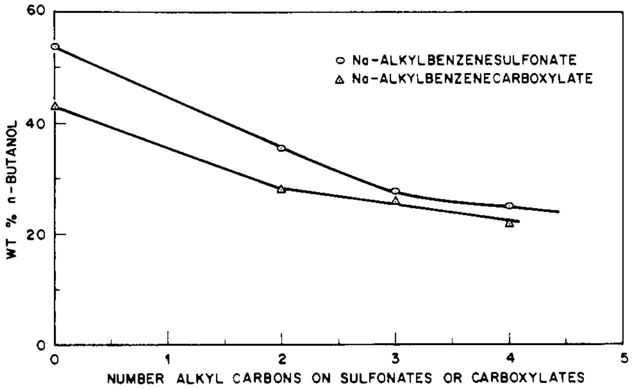

Figure 4. Comparison of minimum amount of 1-butanol required to produce miscibility in a system containing 2.0 *m* substituted sodium benzenesulfonates or carboxylates and toluene (1:1 wt ratio of toluene to sulfonate or carboxylate, 25 °C).

Parallel trends are observed in the four-component system, in terms of the amount of 1-butanol required to attain a single-phase system from various ratios of toluene to aqueous alkyl benzenecarboxylate and sulfonate systems. Less 1-butanol is required in the 2 *m* systems reported here and in the 2.5 *m* sulfonate systems reported earlier as the number of alkyl carbons substituted on the ring increases. The curves in both Figures 2 and 3 are fairly symmetrical. The relative effect of carboxylate and sulfonate may be compared in Figure 4, a plot of the amount of alcohol required for miscibility of a toluene:

aqueous weight ratio of 1:1 as a function of N_{AC}. Substantially less is needed for the carboxylate at zero and at two alkyl carbons and a little less for $N_{AC} = 3$ or 4.

In summary, the results presented here indicate no major differences between the miscibility of aqueous–hydrocarbon systems containing alkylbenzenesulfonates and alkylbenzenecarboxylates, under otherwise comparable conditions. At low degrees of alkyl substitution, carboxylates appear somewhat more effective in attaining miscibility than sulfonates.

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Excess Volumes of Mixing of Binary Mixtures of Arsenic Tribromide with Benzene, Cyclohexane, and Carbon Tetrachloride at 303.15, 308.15, and 313.15 K

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Excess volumes, V^E, of binary mixtures of arsenic tribromide with benzene, cyclohexane, and carbon tetrachloride have been calculated from experimental density data at 303.15, 308.15, and 313.15 K over the entire composition range. The V^E for solutions of arsenic tribromide with benzene are negative indicating the strong intermolecular interactions between the components resulting in the formation of a 1:1 charge-transfer type complex. For the other two binary mixtures V^E is positive. V^E decreases with an increase of temperature for the binary mixtures studied.

Introduction

In this laboratory, we have been interested in the determination of thermochemical and thermodynamic properties of halides and their solutions with organic solvents (*1*). As a part of our investigation, excess volumes of mixing for the binary mixtures of arsenic tribromide with benzene, cyclohexane, and carbon tetrachloride have been determined at 303.15, 308.15, and 313.15 K over the entire composition range and reported in this paper.

Experimental Section

Preparation of Arsenic Tribromide. Arsenic tribromide was synthesized by refluxing a slight excess of the arsenic metal (A.R. Grade) with bromine in carbon tetrachloride solution till the solution was no longer brown. The solution was filtered hot, the solvent was distilled off, and the compound was finally distilled over the metal under vacuum.

Purification of Solvents. The organic solvents, viz., benzene, cyclohexane, and carbon tetrachloride were purified according to standard procedures (*2*). Some measured physical properties of these liquids have been compared with the literature values (*2–4*) in Table I.

Density Measurements. The excess volumes of mixing have been calculated from experimental density data. We preferred this method for estimation of V^E over the direct dilatometric measurements because of the chemically agressive nature of arsenic tribromide toward the blocking fluid mercury.

A single stem capillary pycnometer of $\sim$20-cm^3 capacity was used for all our measurements. The stem consisted of a 1 mm i.d. precision bore capillary, having a reference mark lightly etched all around. The pycnometer was filled with a hypodermic syringe fitted with a specially long needle, care being taken to avoid trapping of fine air bubbles. Corrections for buoyancy and vapor space were applied. The temperature equilibrium was achieved by keeping the pycnometer in a thermostat controlled to ±0.01 °C for 6–8 h. The temperature fluctuations were observed with a 5° Beckmann thermometer graduated in 0.01 °C and absolute temperature was measured by calibrated thermometer to ±0.05 °C. The liquid meniscus in the capillary stem was read by a traveling microscope to ±0.01 mm.

The solutions for the measurement of density were prepared by weight in well-stoppered Pyrex glass bottles. The bromide being less volatile was weighed first. After the addition of organic solvent the contents of the stoppered bottles were thoroughly mixed. The use of male joints on the mixing bottles minimized the possibility of wetting glass joints which were used ungreased. Precautions were taken to reduce vapor losses during the preparation of the solutions and their transfer to the pycnometers. Corrections to the composition changes resulting from vapor losses were made whenever unavoidable losses occurred. Internal checks on the validity of these corrections to the composition were made by preparing a number of solutions in situ in a single-stem pycnometer. Duplicate densities agreed within 2×10^{-5} g cm^{-3}. The maximum uncertainty in excess volumes is expected to be around 0.005 cm^3 mol^{-1}.

Results and Discussion

The excess volumes of mixing V^E for the binary mixtures at 303.15, 308.15, and 313.15 K are recorded in Table II and are

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