Isopropyl Alcohol-Sodium Sulfate-Water System Liquid-Liquid Equilibria

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During the sulfonation of petroleum distillates for highly refined white oils, oil-soluble mahogany sulfonic acids are obtained as a by-product in the sour oil. This oil may be considered a heterogeneous system, as it contains some of the spent sulfuric acid not separated with the acid sludge phase and traces of sulfur dioxide formed by redox side reactions. The corresponding sodium soap may be obtained as a crude product by neutralization with sodium hydroxide and extraction from the refined oil with aqueous alcoholic solutions. The crude extract, referred to as raw soap, is essentially an aqueous alcoholic solution of mahogany sulfonates and oil, sodium sulfate, and traces of sodium sulfite.

In the course of several experiments, it was observed that when aqueous ethyl alcohol was used as the extracting solvent, the raw soap could be separated from the refined neutral oil as a homogeneous solution, whereas with isopropyl alcohol the raw soap further separated into two individual layers. Analyses have shown that in such instances the lower soap phase was mainly an aqueous solution of sodium sulfate, while the upper soap phase was an alcoholic solution containing most of the available sodium sulfonates.

Solubility data for sodium sulfate in aqueous solutions of ethyl and isopropyl alcohols were required to permit a thorough examination of the possible application of alcohol for the removal of inorganic salts (mainly sodium sulfate) from the raw soap by either precipitation or solution in water. By this means and after solvent evaporation, a salt-free solution of sodium sulfonates in oil may be obtained. Solubility data for the ternary system ethyl alcohol-sodium sulfate-water have been reported by Seidell (*3*) and have been extensively studied by Vener and Thompson (*5*). The latter authors studied the system at temperatures between 25° and 70°C. and found only one liquid phase over the range of conditions examined. They were able to demonstrate, however, that two liquid phases were obtained, over most of the solvent composition range, when acetone or isopropyl alcohol was the organic component. The saturated density data recorded was used by Tursi and Thompson (*4*) to study the effect of sodium sulfate on the vapor-liquid equilibrium of ethyl alcohol and water. de Bruyn (*1*) has reported liquid-liquid equilibria for the system ethyl alcohol-sodium sulfate-water between certain concentrations of alcohol and these data are copied by Seidell. Schreinemakers and de Baat (*2*) later noted that de Bruyn's data were metastable equilibria.

Evidence to suggest a close relationship between the phenomenon of two-phase formation in raw sodium sulfonate solutions and in solutions of sodium sulfate in aqueous isopropyl alcohol was obtained from preliminary experiments. Phase separation occurred when both aqueous isopropyl alcohol and desalted (sodium sulfate-free) raw soap solutions in isopropyl alcohol were saturated with sodium sulfate at 60°C.

The isopropyl alcohol-sodium sulfate-water system was found to behave similarly to the ethyl alcohol system at temperatures below 25°C.—where the solid phase was sodium sulfate decahydrate—in that only one liquid phase was formed. The system was fully investigated at 40° and 60°C. where two-phase formation occurred.

MATERIALS

Isopropyl alcohol was dried over anhydrous sodium sulfate and redistilled before use. Sodium sulfate, anhydrous analytical reagent grade, was not further purified. Water was freshly distilled and freed of carbon dioxide.

PROCEDURE

The ternary diagrams for isopropyl alcohol-sodium sulfate-water were constructed at 40° and 60°C. using the cloud point method to determine the boundaries of the two-layer regions. Tie lines were constructed by preparing mixtures of known composition, shaking thoroughly, and analyzing both layers after equilibrium was established. Sodium sulfate was determined using ethylenediamine tetraacetate (*6*), whereas isopropyl alcohol was estimated by oxidation with standard potassium dichromate and iodometric determination of the excess reagent. Water contents were found by difference.

Since only one liquid phase was formed at 25°C., the effect of cooling the two liquid phases obtained at higher temperatures was studied. Identical mixtures of the three components within the immiscible area—namely, 25% (by weight) of isopropyl alcohol, 15% of sodium sulfate, and 60% of water—were allowed to reach equilibrium at several temperatures. The mixtures were then gradually cooled to room temperature (23°C.) for visual comparison.

RESULTS

Data for the system at 40° and 60°C. are given in Table I and are compared on triangular coordinates in Figure 1. The solid phase at each temperature was anhydrous sodium sulfate.

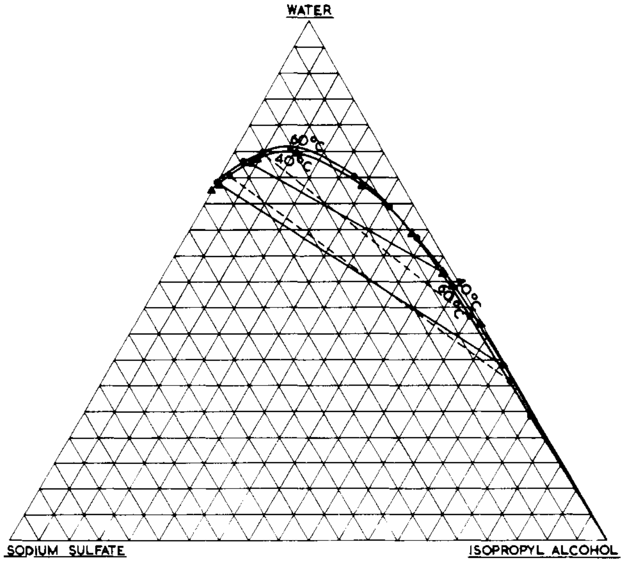

Figure 1. Ternary diagrams for isopropyl alcohol-sodium sulfate-water system in per cent by weight at 40° and 60° C.
Tie lines at 60° C. in broken lines
● 60° C.
▲ 40° C.

Table I. Solubility Data for Isopropyl Alcohol-Sodium Sulfate-Water System

Isopropyl Alcohol	Sodium Sulfate	Water	Isopropyl Alcohol	Sodium Sulfate	Water
In Per Cent by Weight at 40 °C.					
57.6	0.5	41.9	10.3	14.9	74.8
49.7	1.2	49.1	4.6	22.0	73.4
37.5	3.0	59.5	0.5	30.4	69.1
24.8	6.8	68.4	0.0	32.8	67.2 (*3*)
Tie Lines, Water Layer			Tie Lines, Solvent Layer		
0.6	30.8	68.6	65.3	0.5	34.2
3.9	23.4	72.7	46.2	1.8	52.0
In Per Cent by Weight at 60 °C.					
75.0	0.2	24.8	9.0	15.2	75.8
38.7	2.9	58.4	2.4	24.4	73.2
31.0	4.3	64.7	1.6	27.7	70.7
22.4	7.4	70.2	0.0	31.2	68.8 (*3*)
Tie Lines, Water Layer			Tie Lines, Solvent Layer		
1.2	28.3	70.5	68.8	0.6	30.6
5.0	20.3	74.7	55.4	1.4	43.2

Observations on the appearances of the phases after cooling to 23 °C. from higher temperatures are recorded in Table II. The system of two liquid phases obtained at 60 °C. was maintained at 23° ±2 °C. for 3 months; even periodic gentle agitation failed to induce precipitation and reversion. Similar stability was found with the systems obtained at 40° and 50 °C., but to a lesser extent, in that reversion to single liquid phases and precipitation of sodium sulfate occurred after 2 and 5 hours, respectively, at 23 °C. Seeding with sodium sulfate caused instant precipitation and reversion to one liquid phase in all instances.

Table II. Stability of Complementary Phases at Several Temperatures

	Appearance of Phases	
Initial temp., °C.	At initial temp.	After 5 hours cooling to room temp.
Room (23 °C.)	Solid plus 1 liquid	Solid plus 1 liquid
30	Solid plus 1 liquid	Solid plus 1 liquid
40	Two liquid	Solid plus 1 liquid
50	Two liquid	Solid plus 1 liquid
60	Two liquid	Two liquid

DISCUSSION

At 30 °C. and lower temperatures, the solubility of sodium sulfate in aqueous isopropyl alcohol is normal, in that a single liquid phase is formed. At temperatures of 40 °C. and above, two liquid phases are formed, confirming the findings of Vener and Thompson (*5*).

Although the total areas of immiscibility are practically equal at 40° and 60 °C., the tie lines are of different slope, with the result that the curve is displaced as illustrated in Figure 1. Thus at high concentrations of alcohol, the maximum solubility of sodium sulfate increases with increasing temperature; at low concentrations the reverse is true. For a particular distribution of components within the immiscible region, the concentration of sodium sulfate in the lower aqueous layer is least at 60 °C. This phase is therefore less supersaturated, after cooling, than one obtained at a lower temperature confirming the observations in Table II. Reversion to a solid and one liquid phase occurs more readily, after cooling, when the two liquid phases are obtained at lower temperatures. For practical purposes it would therefore be better to maintain a temperature of 60 °C., until such layers were separated.

A similar phenomenon of two-phase formation was observed with raw sodium sulfonate solutions in aqueous isopropyl alcohol but not in aqueous ethyl alcohol. Thus if the sour oils after sulfonation of petroleum distillates are neutralized with sodium hydroxide and extracted at 60 °C. with the correct proportion of aqueous isopropyl alcohol to sodium sulfate (which may be adjusted by addition during neutralization) three phases are obtained: refined oil, middle raw soap layer, and lower aqueous sodium sulfate layer. On extraction with ethyl alcohol, however, the raw soap appears as a single phase.

Further experiments using raw soaps indicated that at concentrations of sodium sulfonates less than 25% (by weight) the distribution of sodium sulfate, isopropyl alcohol, and water between the two phases follows the curve for the pure components fairly closely. The boundary between the miscible and immiscible regions is actually lowered, particularly near the water-sodium sulfate side of the triangle, and the tie lines are of different slope. By separating the lower aqueous phase the concentration of sodium sulfate in the raw soap is considerably reduced. In one pilot experiment the sodium sulfonate-sodium sulfate ratio was increased from 5 to 1 to 60 to 1 by this means.

Practical application of this method of desalting sodium sulfonates is limited to operations where fairly low concentrations of inorganic salt may be tolerated in the final product. Complete desalting cannot be obtained by this means, as the boundary between the miscible and immiscible regions of the graph is lowered by the presence of sodium sulfonates and oil.

Thus the upper alcoholic soap phase contains a higher concentration of sodium sulfate with increasing concentration of sodium sulfonates. Furthermore, the proportion of sodium sulfate to aqueous alcohol is critical and relies on the accurate control and rapid determination of the inorganic acidity of the sour oils in the presence of organic sulfonic acids.

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