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Liquid-Liquid Equilibria for Alcohol-Sodium Hydroxide-Water Systems

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Solubility data have been published for sodium hydroxide in aqueous ethyl alcohol (2) and in aqueous isobutyl alcohol (*1*), but no data were available for aqueous isopropyl alcohol (I.P.A.). Information on the solubility of strong caustic soda solutions in isopropyl alcohol and in industrial methylated spirit (I.M.S.) was required for pilot plant neutralization experiments. Industrial methylated spirit is the commercial form of ethyl alcohol available in the United Kingdom.

On refining petroleum, particularly on processing for highly refined white oils by sulfonation, it is necessary to extract oil-soluble sulfonic acids from the sulfonated oil and to neutralize to the corresponding sodium salts. The quality and especially the color of the by-product sodium petroleum sulfonates are influenced by the residence time of the sulfonic acid-oil reaction product, particularly if the equipment is mild steel. For the two systems of processing which may be applied—centrifuge or batch—it is essential that, for the centrifuge process, neutralization and extraction proceed simultaneously, whereas for batch processing it is preferred that the two stages should take place concurrently. For either processing system, it is a distinct advantage if a homogeneous neutralizing-extracting solution is used.

Preliminary experiments indicated that industrial methylated spirit and ethyl alcohol behave differently and it was decided therefore to investigate the systems for industrial methylated spirit and isopropyl alcohol at 25° and 60°C.

MATERIALS

As it was expected that information resulting from this project might be applied to plant scale processing, no attempt was made to purify materials which were of technical quality and had the following properties.

	Specific Gravity at 20°C.	Strength, Weight %
Aqueous caustic soda	1.4590	43.0
I.M.S.	0.8064	94.2
I.P.A.	0.7852	100.0

Table I. Solubility Data for Isopropyl Alcohol-Sodium Hydroxide-Water System (Per Cent by Weight at 25° and 60°C. Figures 1 and 4)

I.P.A.	NaOH	H_2O	I.P.A.	NaOH	H_2O
		Data at 25°C.			
97.2	1.2	1.6	30.9	4.3	64.8
87.1	0.4	12.5	21.8	5.8	72.4
75.1	0.4	24.5	13.4	7.8	78.8
63.1	1.0	35.9	5.8	11.7	82.5
51.5	2.0	46.5	2.3	18.2	79.5
41.1	2.7	56.2	0.0	50.0	50.0 (*1*)
Tie Lines, Water Layer			Tie Lines, Solvent Layer		
0.6	31.5	67.9	97.4	0.6	2.0
1.5	23.7	74.8	97.2	0.6	2.2
		Data at 60°C.			
96.3	1.6	2.1	31.2	3.2	65.6
74.3	0.6	25.1	21.9	4.8	73.3
62.5	1.0	36.5	13.5	6.7	79.8
51.7	1.4	46.9	5.9	10.6	83.5
40.9	2.4	56.7	1.5	16.6	81.9
36.0	2.8	61.2	0.0	63.5	36.5 (*3*)
Tie Lines, Water Layer			Tie Lines, Solvent Layer		
0.7	30.5	68.8	98.8	0.2	1.0
1.3	23.4	75.3	97.0	0.6	2.4

Table II. Solubility Data for Industrial Methylated Spirit-Sodium Hydroxide-Water System (Per Cent by Weight at 25° and 60°C. Figures 1 and 3)

I.M.S.	NaOH	H_2O	I.M.S.	NaOH	H_2O
		Data at 25°C.			
51.0	21.1	27.9	17.1	22.0	60.9
49.2	18.9	31.9	11.8	23.1	65.1
43.7	18.4	37.9	7.1	24.6	68.3
37.1	18.6	44.3	2.9	27.6	69.5
29.6	19.7	50.7	1.2	30.2	68.6
23.0	20.8	56.2	0.0	50.0	50.0 (*1*)
Tie Lines, Water Layer			Tie Lines, Solvent Layer		
1.9	29.0	69.1	50.5	20.4	29.1
0.8	34.4	64.8	50.7	21.0	28.3
		Data at 60°C.			
60.7	16.9	22.4	27.1	16.4	56.5
60.3	13.4	26.3	19.8	18.2	62.0
54.3	12.2	33.5	13.6	19.8	66.6
45.3	12.9	41.8	7.8	22.5	69.7
35.6	14.7	49.7	3.1	26.2	70.7
30.0	15.8	54.2	0.0	63.5	36.5 (*3*)
Tie Lines, Water Layer			Tie Lines, Solvent Layer		
1.2	31.1	67.7	60.1	13.5	26.4
0.5	36.1	63.4	60.8	16.6	22.6

Table III. Solubility Data for Isobutyl Alcohol-Sodium Hydroxide-Water System (*7*) (Per Cent by Weight at 25°C. Figure 2)

Isobutyl Alcohol	NaOH	H_2O	Isobutyl Alcohol	NaOH	H_2O
93.0	1.1	5.9	3.1	6.7	90.2
6.2	1.3	92.5	0.9	14.5	84.6
5.2	2.8	92.0	0.4	21.7	77.9
4.5	3.9	91.6	0.1	32.1	67.8
3.5	5.8	90.7	0.0	50.0	50.0
Tie Lines, Water Layer			Tie Lines, Solvent Layer		
0.1	35.0	64.9	99.5	0.3	0.2
0.4	24.8	74.8	99.5	0.3	0.2

PROCEDURE

The ternary diagrams for sodium hydroxide and water with industrial methylated spirit and isopropyl alcohol were constructed at 25° and 60°C.; the cloud point method was used to determine the boundary of the two-layer region. Tie lines were constructed by preparing mixtures of known composition, shaking them thoroughly, and separating them after equilibrium was established. The separated layers were analyzed for sodium hydroxide content by titration with standard acid and for alcohol content by oxidation with standard potassium dichromate and iodometric determination of the excess reagent with potassium iodide and sodium thiosulfate. Water contents were determined by difference. All data were recalculated to solid sodium hydroxide content, so that they would be clearer and more precise in meaning.

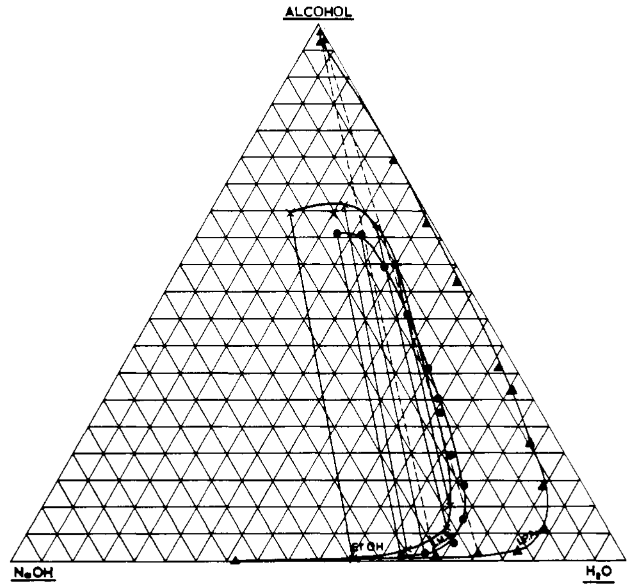

Figure 1. Ternary diagrams for industrial methylated spirit (94.2% ethyl alcohol) isopropyl alcohol, and ethyl alcohol-sodium hydroxide-water systems
Per cent by weight at 60°C.
- - - Tie lines for isopropyl alcohol
● I.M.S., this work
▲ I.P.A., this work
X Ethyl alcohol (2)

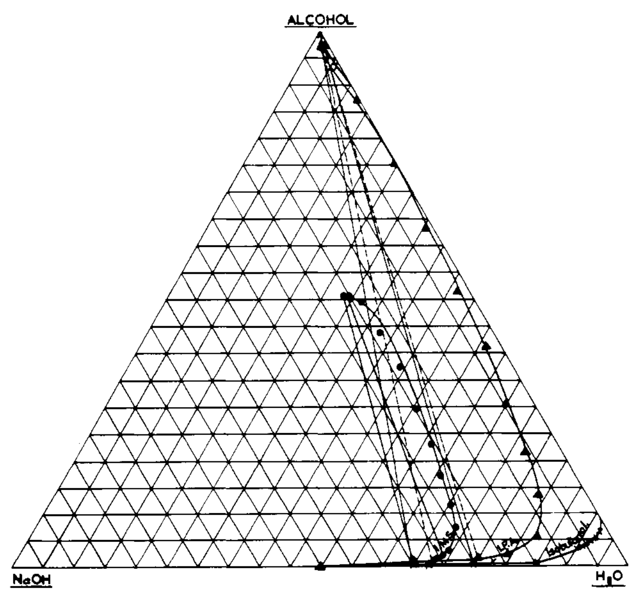

Figure 2. Ternary diagrams for industrial methylated spirit, isopropyl alcohol, and isobutyl alcohol-sodium hydroxide-water systems
Per cent by weight at 25°C.
- - - Tie lines for isopropyl alcohol
● I.M.S., this work
▲ I.P.A., this work
X Isobutyl alcohol (7)

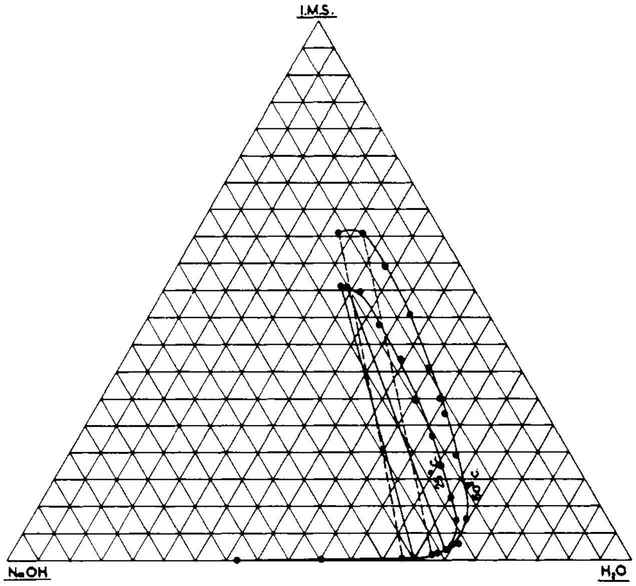

Figure 3. Ternary diagrams for industrial methylated spirit-sodium hydroxide-water system Per cent by weight at 25 °and 60 °C. - - - Tie lines at 60 °C.

RESULTS

The data for the four systems are given in Tables I to IV. Data for ethyl alcohol, industrial methylated spirit, and isopropyl alcohol at 60 °C. are shown on triangular coordinates in Figure 1; data for isobutyl alcohol, industrial methylated spirit, and isopropyl alcohol at 25 °C. are shown in Figure 2. Figures 3 and 4 compare data at 25 ° and 60 °C. for industrial methylated spirit and isopropyl alcohol, respectively.

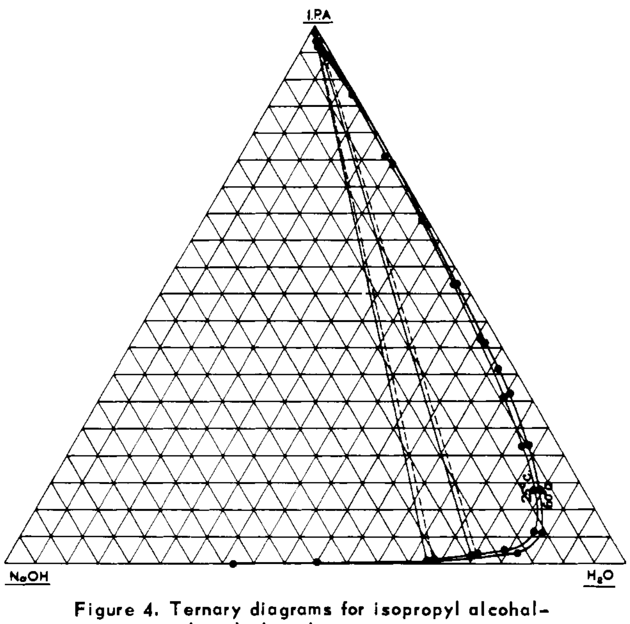

Figure 4. Ternary diagrams for isopropyl alcohol-sodium hydroxide-water system Per cent by weight at 25 ° and 60 °C. - - - Tie lines at 60 °C.

Table IV. Solubility Data for Ethyl Alcohol-Sodium Hydroxide-Water System (2) (Per Cent by Weight at 60°C. Figure 1)

EtOH	NaOH	H_2O	EtOH	NaOH	H_2O
64.1	15.4	20.5[a]	0.0	63.5	36.5 (*3*)
Tie Lines, Water Layer			Tie Lines, Solvent Layer		
0.0	44.5	55.5	64.2	22.4	13.4
1.8	34.8	63.4	65.2	13.7	21.1
5.2	26.4	68.4	62.5	9.5	28.0
10.0	23.3	66.7	54.1	10.2	35.7

[a] This work.

DISCUSSION

Sodium hydroxide is considerably less soluble in isopropyl and isobutyl alcohols than in ethyl alcohol, the zones of immiscibility increasing with increasing molecular weight of alcohol. It would be interesting to compare these results with those obtained for *n*-propyl and *n*-butyl alcohols. The zones of immiscibility increase for both industrial methylated spirit and isopropyl alcohol with increasing temperature, confirming the findings of Peyronel (2) who observed similar behavior with ethyl alcohol, and suggested that rupture of the ethyl alcohol-sodium hydroxide association is greatly affected by temperature. The phenomenon is not so apparent with isopropyl alcohol and would probably be even less so with isobutyl alcohol. The concavity on the water-isobutyl alcohol side of the triangular graph, observed by Fritzsche and Stockton (*1*) was found with isopropyl alcohol.

Sodium hydroxide is more soluble in industrial methylated spirit than ethyl alcohol at high alcohol concentrations but at concentrations below 48% (by weight) of alcohol the solubility is reversed, probably again because of different molecular associations.

The graphs and data may be advantageously used where neutralizing blends of sodium hydroxide in alcohol are required, particularly in the petroleum industry where simultaneous neutralization and extraction of sulfonic acids may be effected. Blend proportions and concentrations to provide completely miscible neutralizing solutions may be deduced and are particularly important in centrifugal separations.

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