Solubility of Toluene in Aqueous Solutions of Sodium Butyl MonoGlycol Sulfate in the Presence of Various Alcohols

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The miscibilities of toluene in systems containing aqueous solutions of sodium butyl monoglycol sulfate (NaBMGS) and various alcohols have been determined at 30 °C. The solubility of toluene depends on the similarities in the structures of the alcohols and NaBMGS and consequently increases when they are almost identical.

Introduction

Hydrotropes are highly water soluble organic salts which at sufficiently high concentrations can enhance the solubility of sparingly soluble or practically insoluble organic compounds in aqueous solutions. This phenomenon of increased solubility was first reported by Neuberg (*1*) in 1916. The conventional hydrotropes include calcium, potassium, and sodium salts of arenesulfonic and benzoic acids. Linear nonaromatic compounds such as the diacid (5-(or 6-)carboxy-4-hexyl-2-cyclo-hexen-1-yl)octanoic acid and sodium salt of butyl monoglycol sulfate (NaBMGS) are the most recently studied hydrotropes. (*2*).

It has been observed that not all organic compounds are readily solubilized by hydrotropes. For example, sodium *p*-toluenesulfonate is unable to enhance sufficiently the solubility of aromatics like toluene and xylene and aliphatics like hexane and heptane. However, the presence of a cosolvent such as an alcohol can substantially increase the solubility of hydrocarbons in aqueous hydrotrope solutions. Previous researchers (*3*–*6*) have studied the enhancements in solubility of a number of hydrocarbons in aqueous solutions of alkyl benzenesulfonates in the presence and absence of 1-butanol. The studies indicate that, as the number of substituents on the aryl ring of the hydrotrope increases, the amount of alcohol required to solubilize a fixed amount of toluene decreases. Also as the alkyl chain length on the hydrotrope increases, the amount of 1-butanol required to produce miscibility with toluene decreases.

We report on the solubility of toluene in the presence of a linear hydrotrope, NaBMGS, and alcohols of varying structures. An explanation of the effect of the alcohols on the solubility enhancement is given.

Materials and Experimental Section

All the chemicals were obtained from S.D. Fine Chemicals, Bombay. The purities of the organic solvents were checked by gas–liquid chromatography. Toluene, butoxyethanol, and 1-butanol were found to have purities of 99.99% and more while cyclohexanol and 2-methyl-2-propanol were of purity greater than 99.90%. NaBMGS was obtained as a clear yellow solution by appearance with a concentration of 3.737 mol·kg^{-1} of water from Hüls, Germany, and used as such. Experiments were carried out by a titrimetric technique on the phase boundary curves at 30 °C as discussed below. All the concentrations are expressed in terms of per kilogram of water.

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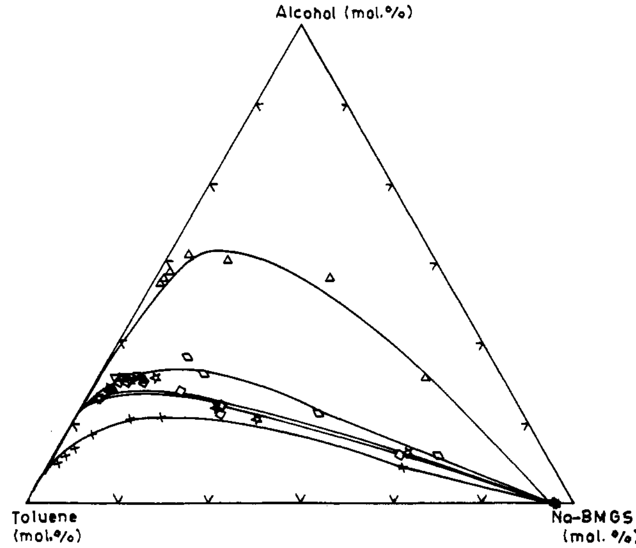

Figure 1. Ternary plot for the solubility of toluene in an aqueous solution of NaBMGS (3.737 mol·kg^{-1} of water) in the presence of (+) butoxyethanol, (□) 2-methylpropanol, (◇) cyclohexanol, (☆) 1-butanol, and (△) 2-methyl-2-propanol.

Part A. Toluene was added from a buret accurate to 0.1 cm^3 to a mixture of known concentrations of hydrotrope and an alcohol. The end point was indicated by the appearance of turbidity. The turbidity remained the same even after 24 h without any phase separation.

Part B. From experiments conducted in part A, butoxyethanol behaved as a better cosolvent. Hence, a study was conducted wherein the concentration of hydrotrope was varied from 0.109 to 1.89 mol·kg^{-1} and a similar procedure as in part A was used. All the experiments were conducted in duplicates and in some cases triplicates. The maximum error in the reproducibility was less than 7% at the lower alcohol and hydrotrope concentrations while at the higher concentrations the error was less than 1%.

Results and Discusssion

The *pseudo*ternary phase diagrams are plotted in Figure 1 as mole percent on triangular graphs, with the aqueous compound being the hydrotrope (3.737 mol·kg^{-1}) solution. The solubility values of toluene in aqueous solutions of NaBMGS with respect to the alcohols are given in Table 1, and a comparison of these results shows the enhanced solubility of toluene in the presence of the alcohols in the

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Table 1. Solubility of Toluene in NaBMGS in the Presence of Alcohols[a]

alcohol	amount of alcohol (mol·kg^{-1} of water)	toluene solubilized (mol·kg^{-1} of water)	alcohol	amount of alcohol (mol·kg^{-1} of water)	toluene solubilized (mol·kg^{-1} of water)
1-butanol	0.61	1.45	2-methylpropanol	0.75	2.90
	1.96	5.47		2.67	7.90
	3.05	8.42		2.99	8.04
	9.16	22.16		5.34	13.70
	15.20	40.63		10.68	27.90
	21.30	56.99		16.02	43.70
	27.49	83.90		21.36	59.60
butoxyethanol	0.43	1.58		26.70	82.30
	6.42	26.38	cyclohexanol	0.53	1.05
	10.69	60.15		1.59	3.16
	12.83	96.03		2.69	5.78
	14.97	134.02		5.38	10.76
	17.11	186.79		8.07	14.65
2-methyl-2-propanol	5.44	2.45		10.76	27.78
	16.32	12.21		13.45	33.61
	27.97	18.56		16.14	41.67
	48.95	42.10		18.84	49.08
	62.94	59.70		21.53	56.34
	76.93	79.20		24.22	73.39
	90.92	100.00		29.60	80.00
	97.91	112.67	2-ethylbutanol	3.53	0.72
			1,1-dimethylhexanol	2.66	0.45
				(no more alcohol taken up by the solution)	
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[a] Hydrotrope: NaBMGS (3.737 mol·kg^{-1} of water).

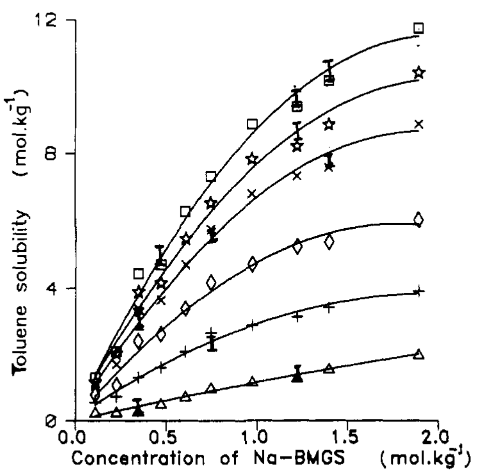

Figure 2. Variation in the solubility of toluene with varying concentrations of NaBMGS and butoxyethanol: (△) 3.21 mol of alcohol/kg of water, (+) 5.34 mol of alcohol/kg of water, (◇) 7.48 mol of alcohol/kg of water, (×) 8.55 mol of alcohol/kg of water, (☆) 10.69 mol of alcohol/kg of water, (□) 11.76 mol of alcohol/kg of water, (I) deviation wherever obtained.

hydrotrope solutions. The solubility of toluene in water is 0.008 mol·kg^{-1}, and in aqueous NaBMGS solution (3.737 mol·kg^{-1}) it is 0.13 mol·kg.$^{-1}$

Hydrotropes are surface-active amphiphiles with a strong ionized group and a smaller hydrophobic group as compared to conventional surfactants. Hydrotropes form aggregates in aqueous solutions that are reminiscent of surfactant micelles, and the formation of such associated structures is necessary for the hydrotropic effect (2). Earlier Saleh and his co-workers (*7, 8*) proposed the necessity of a planar structure for association and thus for the hydrotropic effect. NaBMGS is a short-chain hydrotrope and structurally different from aromatic hydrotropes because of the absence of a planar benzene ring, but it is an excellent hydrotrope (*3*). NaBMGS alone is unable to enhance the solubility of toluene beyond 0.13 mol·kg.$^{-1}$ This may be because the aggregated assembly does not provide a suitable environment for toluene. Alcohols of suitable chain length are known to form swollen micelles/microemulsions with conventional surfactants by the process of coaggregation (*9, 10*). Because of the similarity of NaBMGS with the surfactant molecules and its known aggregational behavior in aqueous solutions (similar to micelles), we expected that NaBMGS might form a similar coaggregative structure with alcohols. The solubilization in the presence of butoxyethanol is most favored because of the identical chain lengths of NaBMGS and the alcohol. Such aggregates can provide more of the hydrophobic microdomains like in microemulsions for solubilization of hydrocarbons.

It is known that addition of a cosurfactant such as an alcohol to surfactant solutions decreases the critical micellar concentration of the surfactant (*9*). A similar behavior is expected in the case of hydrotropes which show a similarity with surfactants in many properties (*2*). Figure 2 shows the solubility of toluene as a function of the hydrotrope concentration in the presence of butoxyethanol. The vertical bars indicate the spread of the observed values which are within the experimental error because of the buret used for the titration. The enhancement in solubility occurs at a concentration much below the MHC which has been defined as the minimum hydrotrope concentration required for hydrotropic solubilization in the aqueous phase. (The MHC of NaBMGS is 1.22 mol·kg^{-1}) (*2*). The decrease depends on the amount and nature of the alcohol present in the aqueous solution. This is probably possible because of enhanced hydrophobic interactions in the presence of the alcohols.

Conclusion

The solubility of toluene in an aqueous solution of NaBMGS increases in the presence of alcohols. Butoxyethanol is the best cosolvent to solubilize toluene which also reduces the minimum hydrotrope concentration. The effect has been attributed to coaggregation of the hydrotrope and the alcohol which is influenced by similarities in their structures.

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