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MASTER

The Effect of Hydrotropic Salts on Phase Relationships
Involving Hydrocarbons, Water, and Alcohols*

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ABSTRACT

Hydrotropic salts, which can increase the solubility of organic materials in aqueous solutions, are of interest in a variety of industries including those related to tertiary oil recovery. We have examined effects on solubility of hydrocarbons in water (with and without alcohols) through addition of inorganic hydrotropic salts, such as perchlorates, thiocyanates, and iodides - high in the usual Hofmeister series - and of organic salts such as short chain alkyl benzene sulfonates and other salts based on substituted benzene derivatives. Although the inorganic salts are relatively ineffective in increasing solubility of hydrocarbons in water, many of the organic salts are excellent hydrotropic agents for hydrocarbons.

We have examined the phase relationships for several series of aromatic salts such as sulfonates, carboxylates and hydroxycarboxylates, as a function of alkyl-carbon substitution in three-component (hydrocarbon, salt, water) and in four-component (hydrocarbon, salt, alcohol, water) systems. We have also examined miscibility relationships for a given hydrotropic salt as the chain length of alkanes and alkyl benzenes is systematically varied.

While miscibilities decrease with increase in chain length of the hydrocarbon, the hydrotropic properties in these systems increase rapidly with the number of alkyl carbons on the benzene ring of the salts and they are relatively insensitive to the type of charged group (sulfonate vs. carboxylate) attached to the benzene ring. However, there were significant increases in hydrotropy as one goes from equally substituted sulfonates or carboxylates to salicylates. A number of salts have been identified which have much greater hydrotropic properties for hydrocarbons than such well-known hydrotropic materials as toluene and xylene sulfonates.

References and illustrations at end of paper.

INTRODUCTION

Hydrotropic materials are compounds which in aqueous solutions tend to increase the solubility of materials normally slightly soluble in water. This phenomenon is also commonly referred to as salting-in. Salting-in was noted by Hofmeister¹ in 1888; Neuberg² introduced the term "hydrotropic" in 1916. Hydrotropic salts may be organic or inorganic. Typical of organic materials are alkali metal or alkaline earth salts of sulfonic acids, carboxylic acids, and salicylic acids; and of inorganic salts, alkali metal or alkaline earth perchlorates, ammonium thiocyanate, and iodides. Such materials have been proposed for use in many industries,³⁻⁶ including pulp and paper, soap and detergent, leather, dye and textile, and cosmetics.

In the past two years we have published several papers on the effect of organic hydrotropic salts on solubility of hydrocarbons in either water or aqueous-alcohol systems.⁷⁻¹¹ Much of the work was with low-molecular-weight alkyl benzene sulfonates. These are chemically similar to components of practical surfactants used in enhanced oil recovery, except that their alkyl chains are shorter than usually thought necessary for formation of micelles and other aggregates. A series of alkyl benzoates and of alkyl salicylates were also investigated. We believe that the miscibilities of systems containing these classes of compounds, which we refer to as "protosurfactants," will prove helpful in understanding the much more complicated hydrocarbon/water/inorganic salt/surfactant/cosurfactant systems of micellar flooding. These simpler systems can be regarded as limiting cases of practical micellar-flood chemistry, and may help establish rules for mutual hydrocarbon-water solubility. Studies of phase behavior of simple systems comprised of hydrocarbon-alcohol-water-salt have been carried out at the University of Minnesota, apparently from similar motivations.¹² In addition, low-molecular-weight organic salts are probably components of practical oil-recovery surfactants, or may be advantageously added, as they frequently are in conventional detergent formulations.

In this paper, we present extensions of earlier measurements and review the status in light of these results. We also present some results with inorganic hydrotropic agents, i.e., perchlorate, thiocyanate, and iodide salts.¹³

EXPERIMENTAL

Materials. The sources of the hydrocarbons, alcohols, substituted benzenesulfonates, and benzoates used in this paper can be found in references 7 to 11. Butylcellosolve (2-butoxyethanol, 99%, Aldrich), butylcarbitol (diethylene glycol monobutyl ether, reagent grade, Fisher Scientific), and 1-propanol (Matheson Coleman & Bell) were used as received without further purification. Sodium salicylate was obtained from Fisher Scientific Co. 3-Methylsalicylic acid (99%, Aldrich), 3,5-butyl-5-methylsalicylic acid (99%, Pfaltz & Bauer), and 3,5-diisopropylsalicylic acid (Purum, Fluka AG) were converted to the sodium salt by titration to pH 7 with 10% NaOH. After the titration the solutions were filtered and washed three times with CHCl_3 to remove excess acid and the salts crystallized after volume reduction (40°C, under vacuum). Microanalysis of each salt was done by Galbraith Laboratories, Inc., Knoxville, Tennessee, and the results are as follows: Na-3-methylsalicylate: Calcd: C 55.17, H 4.05. Found: C 55.08, H 4.09. Na-3-tert-butyl-5-methylsalicylate: Calcd: C 62.58, H 6.57. Found: C 62.48, H 6.69. Na-3,5-diisopropylsalicylate: Calcd: C 63.90, H 7.02. Found: C 63.91, H 7.15. LiClO_4 , (Anhydrous, G. Frederick Smith), NaClO_4 (Certified, Fisher Scientific), $\text{Mg}(\text{ClO}_4)_2$ (Anhydrous, Reagent Grade, Fisher Scientific), and $\text{Ca}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (99%, Alfa Product) were used as received without further purification.

The aqueous hydrotropic salt solutions were prepared with distilled water and concentrations are expressed in terms of molality, m (moles/kg H_2O).

Methods. The solubility of toluene in the aqueous solutions was determined by a gas chromatographic method similar to that used previously.^{7,8} Duplicates agreed to within about 5%, as expected from the innate precision of the method. In order to compare with systems containing corresponding sulfonates and benzoates which were reported before, a temperature of 55°C was chosen for equilibration of the toluene-aqueous salicylate mixtures.

A Perkin-Elmer Model Sigma 3 gas chromatograph, equipped with flame ionization detector, was used for all GC analyses. The (glass) column used in the chromatograph was a 12 ft $\times$ 1/4 in o.d. packed with 60/80 mesh Tenax CC (Applied Science Laboratory) and coupled to the chromatograph by swagelok fittings with graphite ferrules. Column temperature was programmed from 120°C (2 min. hold) to 280°C (2 min. hold) with an increase of 20°C/min. Inlet and detector temperatures were set at 280°C; helium carrier gas was used with inlet pressure at 75 psig. The column was baked out overnight at 270°C and gave a constant, low-level baseline at the most sensitive setting. The instrument was calibrated using standard solutions of the hydrocarbons in acetone. These were prepared by volume and converted to weight percentages with the known densities.¹⁴

The phase boundary curves (miscibility curves) for the four-component systems were determined by the titration procedure described before. The titrations

were carried out at $25 \pm 0.1^\circ\text{C}$. All quantities were determined by weight. The phase boundary curves are plotted as weight percentages on triangular coordinates, a simplification possible because the ratio of water to hydrotropic material is kept constant.

RESULTS AND DISCUSSION

Inorganic Hydrotropic Materials. Some years ago, Raridon and Kraus¹⁵ investigated organic-water mixtures modelling some aspects of casting solutions for cellulose acetate membranes. They examined the effect of some salts of the conventional Hofmeister series¹ on the miscibility gap of the glycerol triacetate (GTA) - water system. They found that the addition of perchlorates, thiocyanates, iodides, bromides, salicylates, and zinc chloride increased greatly the mutual solubility of GTA and water, frequently to such an extent that the miscibility gap disappeared at moderate salt concentration. When we began this study of the solubility of hydrocarbons in water, the first hydrotropic materials investigated included some of these salts (LiClO_4 , NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$, NH_4SCN , and NaI) along with the sodium salts of benzene and toluene sulfonic acids and sodium salicylate, which is high in the various Hofmeister series.¹³ We also examined alkali metal and alkaline earth chlorides, which are low in the series. The systems investigated at that time contained four components (alcohol, hydrocarbon, water, salt). We found that in these systems, with some though not all cosolvents, perchlorates can be about as effective as Na-benzenesulfonate in promoting miscibility. Figure 1 presents miscibility curves (phase boundary curves) of systems containing toluene, butylcellosolve ($\text{C}_4\text{H}_9\text{O}(\text{CH}_2)_2\text{OH}$), and aqueous solutions of LiClO_4 , NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Ca}(\text{ClO}_4)_2$, and the sodium salt of benzenesulfonate. The concentration of all salts in molality (moles/kg water) is such that the anion concentration is in all cases 2 m . In Figure 1 (as well as all other phase boundary curves of this paper), the region above the curves, adjacent to the butylcellosolve apex, represents compositions at which a single phase is present. Below the curves, there is more than one phase. All of these salts have a significant and approximately equal salting-in effect. From the similarity of the various perchlorate salts, one might infer that the anion is dominant in solubilization in this system as was the case in the glycol acetate systems.¹⁵ In other systems studied, salts of the same cations but other anions, NaCl , for example, have a salting-out effect,¹⁵ in agreement with the usual Hofmeister series.

Organic Hydrotropic Materials. We shall first discuss systems containing organic hydrotropic materials in three- and four-component systems. Then we summarize results which emphasize in turn the effect of various hydrocarbons and of various cosolvents on miscibility.

1. Hydrotropic Materials. (a) Three-Component Systems. Three series of organic hydrotropic salts were studied: short chain alkyl-substituted sodium sulfonates,⁷ benzoates,⁸ and salicylates. There were nine sulfonates ranging in alkyl substitution from benzene (no alkyl carbon, $S_{AC} = 0$) to 2,5-diisopropylbenzene ($S_{AC} = 6$); four benzoates, from sodium benzoate ($S_{AC} = 0$) to sodium *p*-*t*-butylbenzoate ($S_{AC} = 4$); and four salicylates from sodium salicylate ($S_{AC} = 0$) to 3,5-diisopropylsalicylate ($S_{AC} = 6$). The solubilities of these salts in water are rather high even at 25°C; solubilities generally increase with temperature.⁷

We previously reported that in the three-component systems of toluene, water, and the sodium alkyl benzene sulfonates,⁷ or benzoates,⁸ the solubility of the hydrocarbon in the aqueous phase increases sharply as the number of alkyl carbons substituted on the benzene ring of the organic salt increases and as the aqueous concentration of the organic salt increases.

Figure 2 presents the solubility (55°C) of toluene in aqueous solutions of various alkyl substituted sodium salicylates vs. molality of the salicylates. It can be seen that with the salicylates, as with the benzoates and sulfonates, solubility of toluene in water increases with salt concentration and with the number of alkyl carbons on the benzene ring. However, the salicylates show much more pronounced increases in solubility than the analogous sulfonates or benzoates. Figure 3 compares these three series of compounds at a concentration of 2.5 moles/kg H₂O and the effect of alkyl substitution on the solubility of toluene in water. The solubility values of toluene in 2.5 m salicylates with $S_{AC} = 5$ and 6 are extrapolated from Figure 2. The logarithm of the solubility of toluene increases almost linearly with the number of alkyl carbons.

Figures 4 a-c compare the solubility of toluene as a function of molality of aqueous salt solutions for three groups of compounds with corresponding alkyl substitution. At a given aqueous concentration, say 1.0 m, with no alkyl carbons (Figure 4 a), the solubility of toluene in aqueous salicylate is about four times larger than in aqueous benzenesulfonate and three times larger than in aqueous benzoate. With 5 and 6 alkyl carbons (Figures 4 b and 4 c), the solubility of toluene in 1.0 m aqueous salicylates is about 9 and 6 times larger than in the corresponding sulfonates. From these results, it appears that not only the alkyl groups affect the solubility but that other substituents are important: the charged groups, -SO₃Na and -COONa to a modest extent, and the unionized ortho-hydroxy group to a surprisingly large extent.

(b) **Four Component Systems.** In the presence of cosolvents (usually alcohols) and a given hydrocarbon we have reported^{8,9} for sulfonates and benzoates that the amount of cosolvent required to obtain a single phase decreases in general with increasing alkyl substitution on the protosurfactants and that the phase boundary curves depend to a small extent on the type of charged group present. This study has now been extended to salicylates. Figure 5 gives phase boundary curve (25°C) of systems containing toluene, 1-butanol, and solutions containing 2 moles/kg water of four alkyl-substituted salicylates. (As in Figure 1, the results are plotted on triangular coordinates by taking advantage of the fact that the ratio of protosurfactant to water is constant.^{16,17} As with sulfonates and benzoates, the single-phase region next to the alcohol apex increases with the number of alkyl carbons on the benzene ring of the salicylates. There is little difference between sodium 3-*t*-butyl-5-methyl-salicylate and sodium 3,5-diisopropylsalicylate.

Figure 6 presents the weight percent butanol required to achieve miscibility at toluene to aqueous solution weight ratios of 1:1 for various 2 m benzene sulfonate,⁸ benzoate⁸ and salicylate solutions. Sulfonates seem to require the largest amount of alcohol for miscibility and salicylates the least amount, consistent with the results in the corresponding three-component system.

We have examined the solubilizing effects of single protosurfactants and of mixtures by determining the amount of butanol required to achieve miscibility at 1:1 weight ratios of hydrocarbon to aqueous 2.5 m sulfonate solution at 25°C. The results are given in Figure 7 for decane and for toluene as the hydrocarbon. The fact that more alcohol is required to produce a single phase with decane than with toluene is consistent with the effect of alkyl chain length on miscibility discussed in reference 11 and again later in this paper. The solubilizing effect of the protosurfactant seems principally dependent on the average equivalent weight of the materials and mixtures. This is similar to the averaging rules regarding effect of mixtures of surfactants on interfacial tensions developed by Wade and coworkers¹⁸ and also discussed by Puerto and Gale.¹⁹

We frequently compare miscibilities in various systems at 1:1 weight ratio of hydrocarbon to aqueous protosurfactant solution. This procedure seems adequate where the phase boundary curves are reasonably symmetrical. This is usually the case when the protosurfactant concentration is high, e.g. larger than 2 m. However, in some systems this symmetry disappears at lower protosurfactant concentrations.¹³ This behavior is illustrated in Figure 8 which gives the phase boundary curves for systems containing toluene, butylcellosolve, and aqueous sodium *t*-butylbenzoate solutions from zero to 2.5 moles/kg water. Dramatic asymmetries develop in this system in spite of the fact that at this temperature (25°C) butylcellosolve is miscible with both water and toluene. The amount of cosolvent required to produce a single phase is larger in the toluene-rich region than in the aqueous-rich region. Below the phase boundary curves three liquid phases frequently occur.

We have earlier attempted to correlate solubilities of toluene in a series of three-component systems with the amount of cosolvent required to achieve miscibility in the corresponding four-component systems.⁹ We now attempt a similar correlation in Figure 9 for a number of sulfonates, benzoates and salicylates. Unfortunately, presently available information is sufficient only for comparison of solubilities at 55°C with miscibilities obtained at 25°C. While solubilities are almost surely strongly dependent on temperature, this is probably not the case for the four-component miscibilities (phase boundary curves) and the results presented should be reasonably applicable to 55°C. The compounds A to I, with S_{AC} from zero to 6, are identified in the figure. For some compounds several aqueous concentrations of protosurfactants are included. In general, as the solubility of toluene in the aqueous phase increases, the amount of butanol required for miscibility (at 1:1 weight ratio of toluene to aqueous solution) decreases. At the higher solubilities the relationship between the logarithm of solubility and percentage alcohol is approximately linear. Results for the benzoates and sulfonates are similar and internally consistent. The salicylates, on the other hand, are very different, reflecting the surprisingly high solubilization properties discussed earlier. A perhaps obvious point should be mentioned here: the relationships between solubility in three-component systems and miscibilities almost surely will be strongly influenced by the cosolvent, as we shall discuss later, as well as by the shape of the 4-component phase boundary curves.

2. Hydrocarbons. We have discussed so far largely the effect of systematically varying the hydro-tropic agents on toluene solubilities and miscibilities. We shall now briefly discuss some of our results in which the hydrotropic agent remains the same but where the hydrocarbons are systematically varied.

Our results on hydrocarbon solubilities in aqueous solutions (3-component systems) are only fragmentary at present. However, for alkane solubilities shown in Figure 10, the systematics is at least qualitatively as expected. The figure shows for 2.5 *m* sodium *p*-cymene-sulfonate solutions an essentially linear decrease of the logarithm of solubilities with number of alkyl carbons in the hydrocarbon (N_{AC}) in the range from 10 to 16. The relationship is approximately $\log s = 0.301 - 0.135 N_{AC}$. It should be noted that the solubilities in this hydrotropic medium are in the range 0.01 to 0.1 moles/kg H₂O, i.e., probably orders of magnitude larger than they would be in water in the absence of the hydrotropic agent.

Regarding four-component systems, we have reported earlier¹¹ phase boundary relationships for a large number of alkanes and alkylbenzenes using Na-*p*-cymene sulfonate (2.5 *m*) as the hydrotropic agent and 1-butanol as cosolvent. We have now completed a similar study with Na-2,5-diisopropylbenzenesulfonate as hydrotropic agent, retaining 1-butanol as cosolvent. Some of the results are presented in Figure 11, which gives the percent butanol required to achieve miscibility at a 1:1 weight ratio of hydrocarbon to 2.4 *m* aqueous diisopropylbenzenesulfonate solution. The hydrocarbons studied include alkanes with N_{AC} from 6 to 15 and alkylbenzenes with N_{AC} from 0 to 10. Figure 11 also includes the results of our earlier measurements with cymenesulfonate. The fact that the measurements were carried out at somewhat different temperatures probably does not affect the trends of primary interest here.

While the diisopropylbenzenesulfonate is clearly a much better hydrotropic agent than cymenesulfonate (requiring less butanol to achieve miscibility), the dependence of miscibility on N_{AC} is very similar for the two compounds. In both series the alkylbenzenes required more butanol to achieve miscibility than the normal alkanes. Further, the amount of butanol required for miscibility increases almost linearly with N_{AC} for the higher values of N_{AC} . Also, with both agents the amount of butanol required for miscibility is significantly lower for cyclohexane than for the *n*-alkanes.

Because oil contains many components, rules for mixtures of hydrocarbons are of interest. Results published in reference 11 for four systems containing mixtures of hexane-pentadecane, hexane-1-phenyltridecane, toluene-pentadecane, toluene-1-phenyltridecane, showed that the amount of 1-butanol required in the central portion of the phase boundary curve varied approximately linearly with the weight fraction of one hydrocarbon in the hydrocarbon mixture. The relatively simple dependence on EACN (equivalent alkyl carbon number) whose applicability the Texas group demonstrated for hydrocarbon mixtures in interfacial tension measurements does not seem to apply to these miscibility relationships.

3. Cosolvent. Importance of type of cosolvent (alcohol) to the chemistry of aqueous surfactant-hydrocarbon systems involved in micellar flood is well

known (see, for example, references 20 and 21). In an earlier paper¹⁰ we reported a striking effect of varying the cosolvent in a protosurfactant system. With sodium salicylate the relative miscibilities of *n*-alkanes and alkylbenzenes are different for 1-butanol and butylcarbitol. This effect seems general. In Figure 12 we present results for a number of hydrocarbons with *p*-*t*-butylbenzoate as protosurfactant and 1-butanol and butylcarbitol as cosolvents. For the aliphatic hydrocarbons changing from alcohol to carbitol causes a large increase in percent cosolvent required for miscibility. For the alkylbenzenes the effect is much smaller, though in the same direction as for the alkanes. The net effect is a reversal of relative miscibilities of alkanes and alkylbenzenes.

The effect of the cosolvent on miscibility is not independent of the protosurfactant used, at least for any given hydrocarbon. We demonstrate this in Figure 13 with toluene as hydrocarbon, a series of six substituted benzene sulfonates as protosurfactants (with S_{AC} from zero to 6) and 1-propanol and 1-butanol as cosolvents. The figure gives the amount of alcohol required for miscibility at a 1:1 weight ratio of toluene to aqueous 1 *m* sulfonate solution. The results essentially follow two straight lines with different slopes for the two alcohols. These lines cross at $S_{AC} = 4$ (cymenesulfonate) so that at this weight ratio of hydrocarbon to aqueous solution more butanol is required for miscibility than propanol for $S_{AC} < 4$, but the reverse is the case for $S_{AC} > 4$.

NOMENCLATURE

S_{AC} = number alkyl carbons on benzene ring of protosurfactants
 N_{AC} = number alkyl carbons of hydrocarbons
m = moles protosurfactant per kg of water

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Fig. 1. EFFECT OF HYDROTROPIC SALTS ON PHASE RELATIONS IN TOLUENE-BUTYLCELLOSOLVE-AQUEOUS SALT SOLUTION SYSTEMS (25°C).

Fig. 2. SOLUBILITY OF TOLUENE IN AQUEOUS SOLUTIONS OF VARIOUS SODIUM SALICYLATES (55°C).

Fig. 3. SOLUBILITY OF TOLUENE IN AQUEOUS SOLUTIONS OF VARIOUS SODIUM BENZENE SULFONATES, BENZOATES, AND SALICYLATES (55°C); EFFECT OF ALKYL SUBSTITUENTS ON AROMATIC SALTS.

Fig. 4. COMPARISON OF SOLUBILITY OF TOLUENE IN AQUEOUS SOLUTIONS OF SUBSTITUTED SODIUM BENZENESULFONATES, BENZOATES, AND SALICYLATES (55°C).

Fig. 5. EFFECT OF SUBSTITUENTS ON PHASE RELATIONS IN THE TOLUENE-1-BUTANOL-AQUEOUS SALICYLATE SYSTEMS 2.0 MOLES OF SUBSTITUTED Na-SALICYLATE/KG H_2O , 25°C).

Fig. 6. MINIMUM AMOUNT OF 1-BUTANOL REQUIRED TO PRODUCE MISCIBILITY IN SYSTEMS CONTAINING TOLUENE AND 2.0 MOLES OF SUBSTITUTED SODIUM BENZENESULFONATES, BENZOATES, OR SALICYLATES PER KG WATER (1:1 WT. RATIO OF TOLUENE TO AQUEOUS SOLUTION, 25°C).

Fig. 7. MINIMUM AMOUNT 1-BUTANOL REQUIRED TO PRODUCE MISCIBILITY AT 1:1 WT. RATIO TOLUENE/AQUEOUS SOLUTION (2.5 MOLES SULFONATES/KG WATER; 25°C).

FIGURE 8. MISCIBILITY OF TOLUENE/BUTYLCELLOSOLVE/AQUEOUS SODIUM *p-tert*-BUTYLBENZOATE SYSTEMS. NUMBERS ON CURVES INDICATE MOLES OF ORGANIC SALT PER KG OF WATER. 25° C.

Fig. 9. RELATIONSHIP BETWEEN WEIGHT PERCENT OF 1-BUTANOL NECESSARY TO PRODUCE A SINGLE PHASE IN 1:1 WEIGHT RATIO OF TOLUENE TO AQUEOUS SOLUTIONS OF VARIOUS ORGANIC SALTS (25°C) AND SOLUBILITY OF TOLUENE IN AQUEOUS SOLUTIONS OF THE ORGANIC SALTS (55°C). (m INDICATES ORGANIC SALT CONCENTRATION IN MOLES/KG WATER.)

Fig. 10. SOLUBILITY OF ALKANES IN 2.5 m Na-p-CYMENESULFONATE AT 25°C.

Fig. 11. MINIMUM AMOUNT OF 1-BUTANOL REQUIRED TO PRODUCE MISCIBILITY AT 1:1 WT. RATIO ALKANE (ALKYLBENZENE)/AQUEOUS 2.5 m Na-p-CYMEMESULFONATE (25°C) OR 2.4 m Na-2,5-DIISOPROPYLBENZENESULFONATE (40°C).

MINIMUM AMOUNT OF COSOLVENT REQUIRED TO PRODUCE MISCIBILITY
 AT 1:1 WT % HYDROCARBON/ 2.5 MOLAL AQUEOUS SODIUM p-tert-
 BUTYLBENZOATE (25 °C)

Fig 12

Fig. 13 RELATIONSHIP BETWEEN AMOUNT OF ALCOHOL REQUIRED TO EFFECT MISCIBILITY OF 1:1 WT. RATIO TOLUENE TO AQUEOUS SODIUM BENZENE SULFONATES (1 MOLE/KG H₂O), 25°C AND SOLUBILITY OF TOLUENE IN AQUEOUS SOLUTION OF SAME SULFONATE, AND MOLALITY 55°C.