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KRAFFT-CLEAR POINT DIAGRAMS FOR SOME SODIUM 1,4 Di-n-ALKYLBENZENE SULPHONATES

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The sodium salts of 1,4-di-n-butylbenzene-, 1,4-di-n-pentylbenzene-, 1,4-di-n-hexylbenzene- and 1,4-di-n-octylbenzene sulphonates were prepared and evaluated, on a laboratory scale, for enhanced oil recovery (EOR) formulation systems. Krafft-Clear Point Diagrams, for the aqueous solutions of these sulphonates, in presence of added electrolyte and/or alcohols, were drawn. The study revealed that the most distinctive property of 1,4-di-n-alkylbenzene sulphonates which sets them apart from the corresponding 1-phenyl-n-alkane sulphonates having the same molecular weight, is their low Krafft points in presence of the same electrolyte and/or alcohol concentrations.

Introduction

The adsorption of surfactants onto reservoir rock has been one of the major difficulties and the key factor which governed the economics of surfactants flooding process [1]. This adsorption can hamper the surfactant's ability to give the lowest possible interfacial tension [2], which is the backbone of this process. Adsorption onto rock surfaces and poor solubility at high salinity, are the main drawbacks of monoalkylated benzene sulphonates employed for this purpose [3].

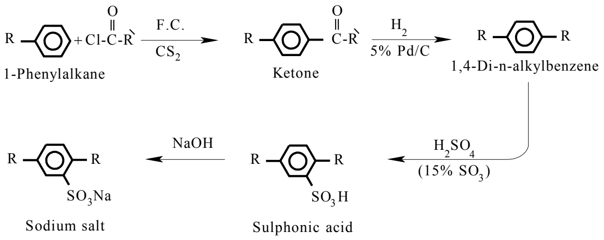
The importance of the Krafft-clear point diagrams is that the boundaries are defined where clear and cloudy solutions can exist. The Krafft-clear point diagram separates the various surfactant phases and defines the boundaries where adsorption can be avoided. Based on these diagrams, a laboratory evaluation of any given class of surfactant, for enhanced oil recovery (EOR) applications, has to be conducted at a temperature above the Krafft point.

In some previous investigations [4,5], several equation models have been developed to evaluate the effect of alkyl chain length; added alcohols and/or electrolyte on the Krafft points of linear 1-phenylalkane sodium sulphonates. The present study deals with the Krafft and clear point diagrams of some sodium 1,4-di-n-alkylbenzene sulphonates and applies the previously established equations [4] to this group of anionic surfactants.

Experimental

Surfactants

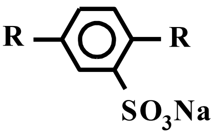
The sodium salts of isomerically pure 1,4-di-n-butylbenzene-, 1,4-di-n-pentylbenzene-, 1,4-di-n-hexylbenzene-, 1,4-di-n-heptylbenzene- and 1,4-di-n-octylbenzene sulphonates were prepared according to the synthesis scheme shown in *Fig.1*. Details including synthesis steps, mass spectroscopy, NMR and IR that confirmed the structure of the intermediate and the final products, have been reported [6,7]. The critical micelle concentrations (cmc), surface properties and thermodynamic parameters have also been reported [8].



where R = C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, and C_8H_{17}
R’ = C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, and C_7H_{15}
(R and R’) are linear chains)

Fig.1 Synthesis Scheme of Monoisomeric 1,4-Di-n-alkylbenzene Sodium Sulphonates

Table 1 Physical Properties of 1,4-Di-n-alkylbenzene Sodium Sulphonates

General Structure	R	Abbreviation	Mol. wt.	Colour of Powder	CMC (μmoles per litre) 28 °C	38 °C	48 °C	58 °C
	C_4H_9	1,4-di-n-C_4-BS	292	white	6348	7432	9502	14341
	C_5H_{11}	1,4-di-n-C_5-BS	320	white	2366	3219	3484	4549
	C_6H_{13}	1,4-di-n-C_6-BS	384	white	906	1091	1521	2114
	C_7H_{15}	1,4-di-n-C_7-BS	376	lightly tan	300	373	527	660
	C_8H_{17}	1,4-di-n-C_8-BS	404	lightly tan	—	198	301	616

Krafft and Clear Point Determination

Krafft point of sulphonate aqueous solution was obtained by observing the temperature at which a solid precipitate disappeared [6,9]. A sulphonate solution of approximately 5000 μmole per litre was prepared. If no precipitate appeared at room temperature, the solution was cooled in an acetone-dry ice bath until a precipitate was observed. The sulphonate solution was then heated slowly (1 to 2 °C min^{-1}) while being stirred by a magnetic stirrer. The temperature at which the precipitate suddenly disappeared was taken as the Krafft point [6,10]. The same procedure was used for the determination of clear point. The temperature at which the solution went from turbid to completely clear was taken as the clear point.

Results and Discussion

Very little work has appeared in literature concerning the utilisation of dialkylated benzene sulphonates for tertiary oil recovery formulation systems [11]. No one has published any results of a systematic study dealing with the structure-performance of these components. In this concern, alkyl ortho-xylene sulphonates are the only trialkyl benzenes which have received a considerable attention [12-14].

The present study deals therefore, with a laboratory-scale evaluation of a homologous series of 1,4-di-n-alkylbenzene sulphonates for tertiary oil recovery formulation systems.

The sodium salts of 1,4-di-n-butylbenzene-, 1,4-di-n-pentylbenzene-, 1,4-di-n-hexylbenzene-, 1,4-di-n-heptylbenzene and 1,4-di-n-octylbenzene sulphonates were prepared. The physical properties of the prepared sulphonates and their critical micelle concentrations (cmc) in aqueous solutions are given in *Table 1*. The determined Krafft and clear points, in the presence of added electrolyte and/or alcohols, are shown in *Tables 2* and *3*.

Table 2 Experimental Values of Krafft and Clear Points in Presence of Added Sodium Chloride (A: 1,4-di-n-C_4-BS, B: 1,4-di-n-C_5-BS, C: 1,4-di-n-C_6-BS, D: 1,4-di-n-C_7-BS, E: 1,4-di-n-C_8-BS; Additive =NaCl)

Additive wt.%	A	B	C	D	E
	Krafft Point , °C				
-	≤ 5	≤ 5	≤ 5	8	$31^{(t)}$
0.50%	≤ 5	≤ 5	≤ 5	8	$31^{(t)}$
1.00%	≤ 5	≤ 5	7	12	$33^{(t)}$
1.25%	≤ 5	7	10	$18^{(st)}$	$37^{(t)}$
1.50%	8	12	$23^{(st)}$	$31^{(t)}$	$40^{(t)}$
1.75%	$15^{(st)}$	$21^{(st)}$	$28^{(t)}$	$39^{(t)}$	$*^{(bt)}$
2.00%	$18^{(st)}$	$24^{(st)}$	$32^{(t)}$	$*^{(bt)}$	
2.50%	$28^{(t)}$	$63^{(t)}$	$*^{(bt)}$		
3.00%	$78^{(t)}$	$*^{(bt)}$			
3.25%	$*^{(bt)}$				
	Clear Point , °C				
-	≤ 25	≤ 25	30	34	38
0.50%	≤ 25	≤ 25	32	36	51
1.00%	≤ 25	≤ 25	35	41	72
1.25%	≤ 25	≤ 25	39	58	90
1.50%	≤ 25	≤ 25	45	86	96
1.75%	48	52	58	> 100	> 100
2.00%	56	71	83		
2.25%	63	79	> 100		
2.50%	70	92			
3.00%	87	> 100			
3.25%	> 100				

(st) = Slightly turbid solution , (t) = turbid solution, (bt) = Badly turbid solution and it is difficult to define its solubility

It is apparent from data in *Table 2* that for the lower molecular weight members of the investigated sulphonates, the Krafft points can be easily determined even at higher electrolyte concentrations. For instance, up to 1.5 wt.% added NaCl, the Krafft point of 1,4-di-n-C_4-BS remains at 5 °C or lower. At 1.75, 2.0 and 2.5 wt.% NaCl, slightly turbid (st) solutions are obtained and solid sulphonate crystals disappear at their Krafft points : 15, 18 and 28 °C, respectively. These slightly turbid solutions turn clear upon heating to their clear points at 48, 56 and 70 °C , respectively.

At 3.0 wt.% NaCl, the Krafft point of 1,4-di-n-C_4-BS aqueous solution, is found to be 78 °C. It gives a turbid (t) solution in spite of the fact that it contains no solid precipitate, since upon heating to its clear point (87 °C) it turns clear. At 3.25 wt.% NaCl, a badly turbid (bt) solution is obtained. Consequently, it is difficult to distinguish between a true solution and a fine suspension. At this electrolyte content, the solution does not render clear by increasing temperature since it has a clear point above the boiling point of the solution.

The problem seems to be in the Krafft point determination of the higher molecular weight 1,4-di-n-C_8-BS. This sulphonate gives a turbid solution even in absence of an added electrolyte. The turbidity remains up to 1.5 wt.% NaCl. At 1.75 wt.% NaCl, the sulphonate solution is found to be so badly turbid that it does not permit visual observation to define the

Table 3 Experimental Values of Krafft and Clear Points in Presence of Added NaCl and Alcohols (B: 1,4-di-n-C_5-BS, C: 1,4-di-n-C_6-BS, D: 1,4-di-n-C_7-BS, E: 1,4-di-n-C_8-BS; Additive =NaCl, Alcohol)

Additive wt.%	B	C	D	E
	Krafft Point , °C			
2.0% NaCl, 1.0% IPA	19	26	35	47
2.0% NaCl, 2.0% IPA	15	22	29	41
2.0% NaCl, 3.0% IPA	11	18	24	36
2.0% NaCl, 4.0% IPA	7	15	20	29
2.0% NaCl, 5.0% IPA	6	10	16	23
1.5% NaCl, 3.0% IBA	≤ 5	6	11	19
2.0% NaCl, 1.0% IBA	9	10	13	23
2.0% NaCl, 2.0% IBA	7	11	12	20
2.0% NaCl, 3.0% IBA	6	8	12	18
1.5% NaCl, 1.0% IAA	≤ 5	9	17	24
2.0% NaCl, 1.0% IAA	6	11	20	27
2.0% NaCl, 2.0% IAA	≤ 5	8	15	22
2.0% NaCl, 3.0% IAA	≤ 5	6	10	14
	Clear Point , °C			
1.0% NaCl, 3.0% IPA	≤ 25	≤ 25	31	45
1.5% NaCl, 4.0% IPA	≤ 25	≤ 25	42	48
1.0% NaCl, 2.0% IBA	≤ 25	≤ 25	30	46
1.5% NaCl, 3.0% IBA	≤ 25	28	48	52
1.0% NaCl, 1.0% IAA	≤ 25	≤ 25	≤ 25	32
1.5% NaCl, 1.0% IAA	≤ 25	27	46	51

solubility of the sulphonate crystals. It becomes difficult to determine the Krafft point exactly because many surfactants give cloudy solutions which do not sediment.

SALAGER [15] has determined the size of light scattering particles causing the turbidity of sulphonate solutions. It has been suggested that the turbidity is caused by the formation of liquid crystals or swollen micelles. The clear point represents the transition temperature at which these liquid crystals or swollen micelles disperse, perhaps to form smaller micelle structures, which are too small to scatter light.

Data presented in *Table 2* indicate that up to 1.5 wt.% NaCl addition, the clear points of 1,4-di-n-C_4-BS and 1,4-di-n-C_5-BS do not exceed 25 °C, i.e. they have clear aqueous solutions at room temperature. However, this is not the case of 1,4-di-n-C_6-BS, 1,4-di-n-C_7-BS and 1,4-di-n-C_8-BS solutions which have clear points at 45, 86 and 96 °C, respectively. At 1.75 wt.% NaCl, 1,4-di-n-C_7-BS and 1,4-di-n-C_8-BS have clear points above the boiling points of their solutions.

It is also obvious from data in *Table 2* that the addition of an electrolyte to the surfactant solution has resulted in an increase in their Krafft and clear points due to the reduced solubility of surfactants in salt solutions [16,17].

It may be also pointed out that the sulphonates with longer hydrocarbon chains have higher Krafft and clear points. This may be attributed to the decrease in the sulphonate solubility as the hydrocarbon chains are increased [18].

It may be interesting, to compare the reported Krafft point values of linear 1-phenylalkane sodium sulphonate [4] with the obtained Krafft points of the corresponding 1,4-di-n-alkylbenzene sulphonates. For example, at 1.0 wt.% of added NaCl, the Krafft points of linear 1-phenyldecane-, 1-phenyldodecane-, 1-phenyltetradecane- and 1-phenylhexadecane sulphonates have been found to be 58, 67, 73 and 82 °C, respectively. Whereas, the determined Krafft points of 1,4-di-n-C_5-BS, 1,4-di-n-C_6-BS, 1,4-di-n-C_7-BS and 1,4-di-n-C_8-BS have been found to be 5, 7, 12 and 33 °C, respectively, at the same electrolyte concentration.

Based on this comparison, it may be concluded that the most distinctive property of 1,4-di-n-alkylbenzene sulphonates, and one which sets them apart from the corresponding linear 1-phenylalkane sulphonates having the same molecular weight, is their lower Krafft points in presence of the same electrolyte concentrations.

Aqueous surfactant formulation systems, for EOR applications, contain a co-surfactant which is usually an alcohol (or alcohols). This added alcohol affects not only the solubility but also the performance of the surfactant in these systems. Moreover a considerable reduction in Krafft and clear points, of aqueous sulphonate solutions, is caused by the alcohol addition in the presence or absence of added electrolytes [4,17,18]. The determined values of the Krafft and clear points, of 1,4-di-n-alkylbenzene sulphonates in presence of added alcohol and electrolyte, are given in *Table 3*.

The effect of added isopropyl alcohol (IPA) on the Krafft points of this class of surfactants is presented graphically in *Fig.2*. A regular decrease in Krafft point is seen in presence of 2 wt.% NaCl. At the same salinity, the effect of alcohol molecular weight, on Krafft point, is illustrated in *Fig.3*. It is obvious that 3.0 wt.% of isoamylalcohol (IAA) or iso-butyl alcohol (IBA) is sufficient for reducing the Krafft points of the investigated sulphonates below 20 °C. Addition of the same amount of IPA is found to be insufficient to cause such a reduction in the Krafft points of 1,4-di-n-C_7-BS and 1,4-di-n-C_8-BS. *Fig.3* illustrates also that the higher molecular weight IAA is more efficient, for reducing Krafft point, than IBA.

The effect of added alcohol structure on the Krafft and clear points of 1,4-di-n-alkylbenzene sulphonates, was studied. Four butanol isomers, namely; n-butyl-, sec-butyl-, iso-butyl- and tert-butyl alcohols (NBA, SBA, IBA and TBA), were investigated. The Krafft and clear points were determined at 3.0 wt.% of butanol isomer in presence of 2.0 wt.% NaCl. The data obtained are presented graphically in *Figs.4* and *5*.

Fig.4 illustrates that the efficiency in the Krafft point reduction is in the following order : NBA > IBA > SBA > TBA. This sequence may lead to the conclusion that this efficiency is linked, in someway, with the miscibility of these alcohols with water. For example, the least miscible n-butyl alcohol (NBA) is the most efficient while the completely miscible tertiary butyl alcohol (TBA) is the least efficient for reducing the Krafft point. The miscibility of NBA, IBA and SBA with water is 9, 10 and 12.5 g pro 100 g H_2O, respectively [19].

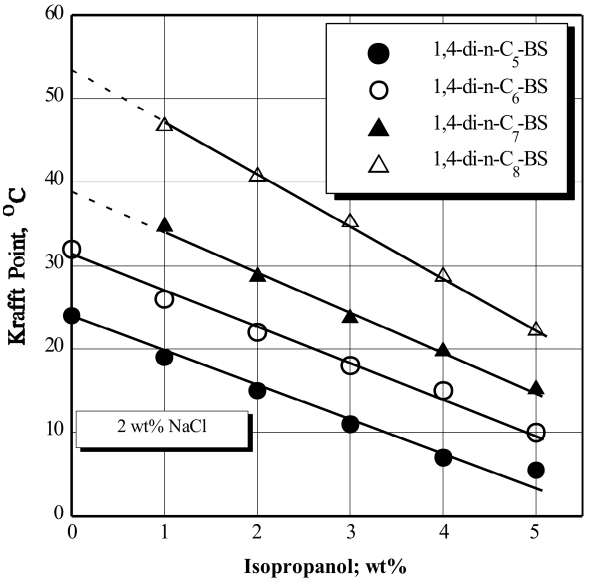


Fig.2 Effect of Added Isopropanol on Krafft Point of 1,4-Di-n-Alkylbenzene Sodium Sulphonates

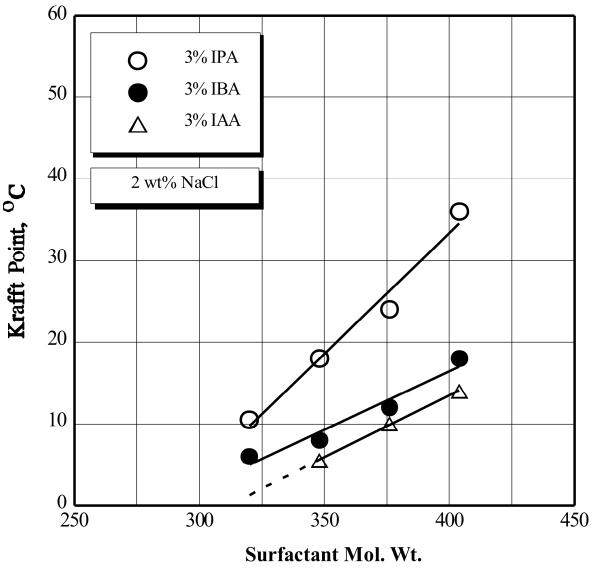


Fig.3 Effect of Alcohol Mol. Wt. on Krafft Point of 1,4-Di-n-Alkylbenzene Sodium Sulphonates

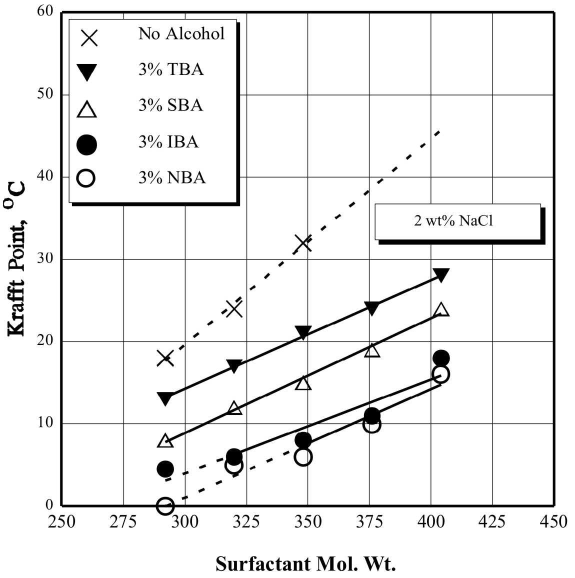


Fig.4 Effect of Alcohol Structure on Krafft Point of 1,4-Di-n-Alkylbenzene Sodium Sulphonates

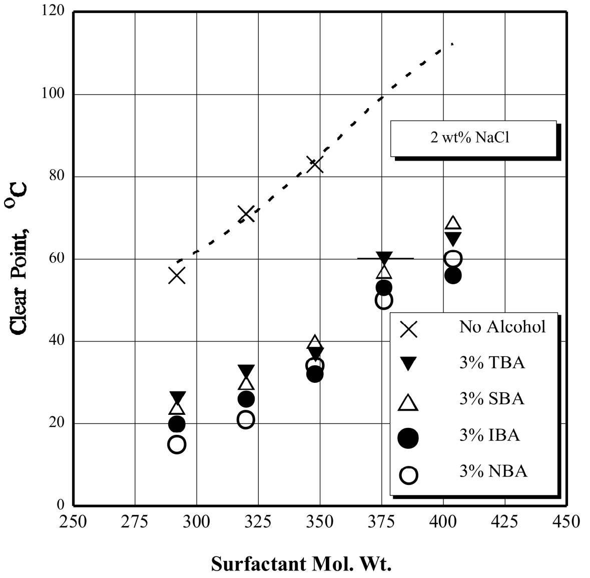


Fig.5 Effect of Alcohol Structure on Clear Point of 1,4-Di-n-Alkylbenzene Sodium Sulphonates

Fig.5 shows a general trend in clear point reduction, by the addition of any butanol isomer. However, an undefined sequence and an insignificant difference in the efficiencies of the four butanol isomers, are observed. Based on these results, it seems also reasonable to conclude that water miscibility of the investigated butanol isomers has nothing to do with their efficiencies in clear point reduction.

Krafft - Clear Point Diagrams

Krafft-clear point diagrams for 1,4-di-n-alkylbenezne sulphonates at 1.25 and 1.5 wt.% NaCl are shown in *Fig.6*. At 1.25 wt.% NaCl, all the investigated members of this homologous sulphonate series have Krafft points below room temperature except 1,4-di-n-C_8-BS. At 1.5 wt.% NaCl; both 1,4-di-n-C_7-BS and 1,4 -di-n-C_8-BS have Krafft points above room temperature.

On the other hand, at these electrolyte concentrations, only 1 ,4-di-n-C_4-BS and 1,4-di-n-C_5-BS give clear aqueous solutions. Sulphonates having a Krafft point above room temperature, can not be used for surfactant flooding at room temperature because precipitation occurs. Adsorption of a cloudy or turbid sulphonate solution has been found to be highly due to physical entrapment by porous media [20]. Addition of small amounts of alcohol depresses the Krafft and clear points [15,21].

Krafft-clear point diagrams for 1,4-di-n-alkylbenzene sulphonates at 1.5 wt.% NaCl after the addition of 3.0 wt.% isobutanol and 1.0 wt.% isopentanol are shown in *Fig.7*. It is apparent from these diagrams that both the Krafft and clear point curves are lowered. This is expected because alcohols tend to increase the solubility of the surfactants.

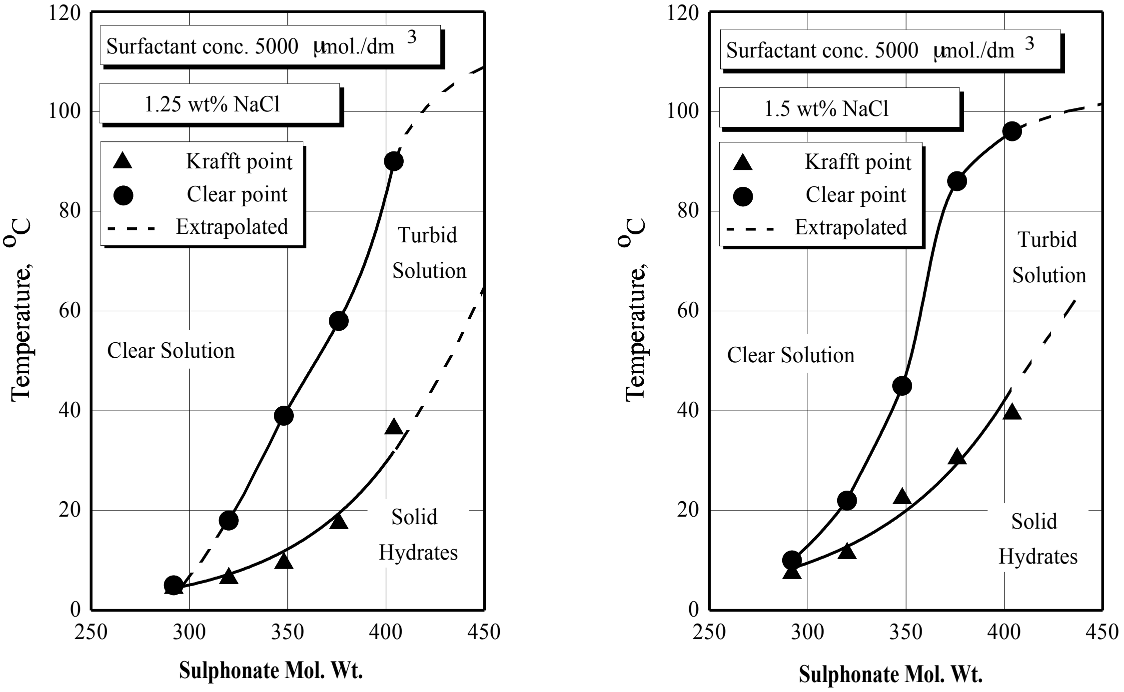


Fig.6 Krafft - Clear Point Diagrams of 1,4-Di-n-alkylbenzene Sulphonates at 1.25 and 1.5 wt.%

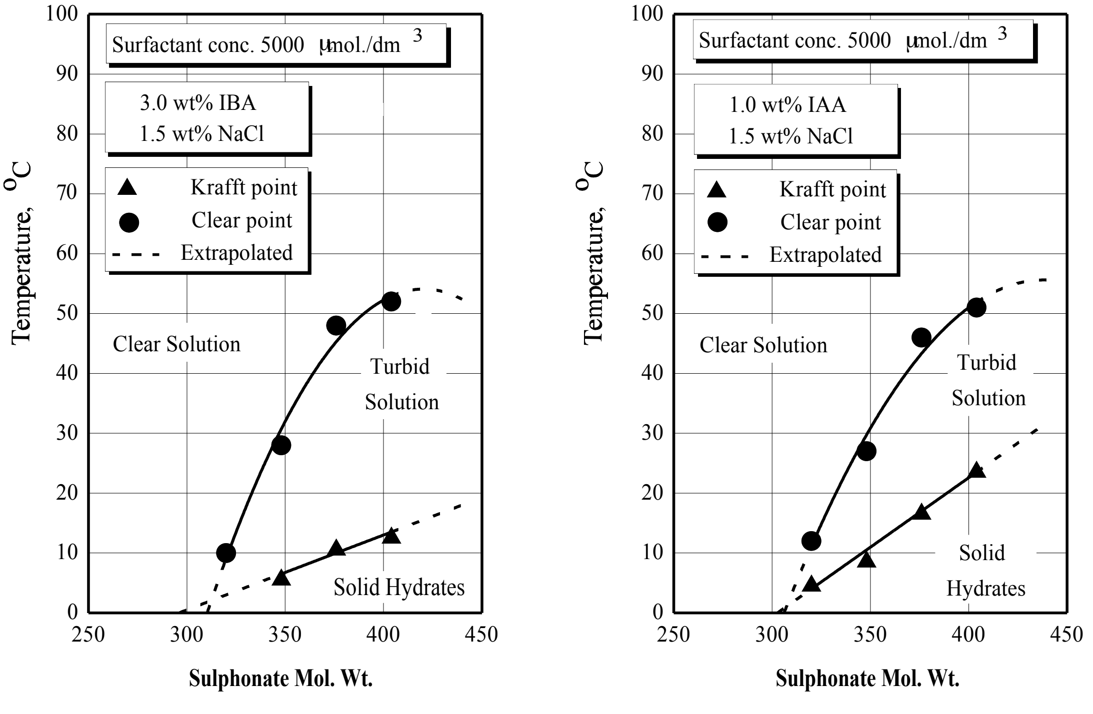


Fig.7 Krafft - Clear Point Diagrams of 1,4-Di-n-alkylbenzene Sulphonates at 3.0 wt.% IBA and 1.0 wt.% IAA

The qualitative appearance of the diagrams obtained is not altered by the molecular weight of the added alcohols. For example, 1.0 wt.% isopentanol addition is found to be more or less effective as the addition of 3.0 wt.% isobutanol in reducing the Krafft and clear points of the investigated sulphonates. 1,4-di-n-C_4-BS has a Krafft point below 0 °C after the addition of the alcohol.

Fig.7 shows that the clear points of 1,4-di-n-C7-BS and 1,4-di-n-C8-BS remain in the vicinity of 50 °C after the alcohol addition. Some investigators have reported [12,22] that between 18 and 50 °C, the highly turbid aqueous solutions of alkyl ortho-xylene sulphonate gave the same interfacial behaviour. This means that, within this range of temperature, turbidity does not alter the sulphonate performance. Taking these results into consideration and provided that the oil field temperatures are from 50 °C upwards [12], it may be predicted that, with these amounts of added alcohols, negligible physical entrapment may take place if any of the investigated sulphonates are run through porous media (reservoir rocks).

Conclusion

Krafft and clear points of 1,4-di-n-alkylbenzene sulphonates are lower than those of isomeric sulphonates in which the benzene ring is attached to a mid-chain alkyl carbon or to a terminal chain alkyl carbon.

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