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Research Paper :

Anionic-anionic mixed aqueous micellar systems-A study to explore synergistic effects on micellisation

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ABSTRACT

The present study has been initiated with a view to explore synergistic effects on micellar behaviour of anionic – anionic mixed aqueous micellar systems. The conductometric technique has been used to measure the specific conductivity of the aqueous surfactant systems involving alkali metal dodecylsulphates (abbreviated as LiDS, NaDS, KDS) in presence of microquantity (1.0 x 10^{-4} mol. dm^{-3}) of various anionic surfactant additives *viz.* caprate, laurate, myristate, and dodecylsulphates of Li, Na, K metals. The comparative assessment of the data reported in Table I and Table II suggest that micellisation is facilitated in presence of the above cited additives *i.e.*, cmc is lowered with additives.

Key words : Anionic surfactants, Synergism, Conductance, Alkali metals and Wanionic surfactant additives

Researchers and academicians alike (Aicart *et al.*, 2006; Atwood and Flovenie, 1983; Avakawa and Brain, 1980; Barry and Russel, 1972 and Bufe and Wolff, 2006) have already shown a keen interest for various surface active agents, also termed as surfactants. They have been enthusiastic about their various facets *viz.* the physicochemical characterization, shape/size determination of micellar aggregates. W.J. Leigh and coworkers (Bunajdad and Eastore, 2004; Cook *et al.*, 2001 and Hartl *et al.,* 2007) have, of late, shown how significant organometallics are to the wide domain of surfactants. Several national/ international publications (Jacobs *et al.,* 2006; Jaliceour and Philip, 1975; Kim *et al.,* Kumar, 1994 and Leigh and Li, 2002) have appeared in literature just to prove the merit of various physical properties of surfactants. Techniques such as viscometry and electrical conductivity have proved handy to study neutral polymer micelle interactions (Lelong *et al.,* 1951). Bumajdad and Eastoe (Malik *et al.,* 1984) employed conductivity to study water in oil microemulsions stabilized by mixed surfactants. Tania *et al.* (Mc. Brain, 1939) have resorted to spectroscopy and conductomretry to probe interaction between water soluble poly {1,4- phenylene – [9, 9 – bis (4- phenoxy butyl- sulfonate)] fluorene -2, 7 diyl} copolymer and ionic surfactants. Aicart and co-workers (Mehta *et al.,* 1979) examined electrochemical, microscopic and spectroscopic characterization of vesicles and prevesicle nanostructures of mixed cationic surfactant systems.

In the recent past, researchers (Mehrota *et al.,* 1970) have undertaken a study on electrically conductive bacterial cellulose by incorporation of carbon nanotubes. Kim and co-workers (Modaressi *et al.*, 2007) have, however, carried out a similar looking study using dielectrophoresis of surface conductance modulated single-walled carbon nanotubes with cationic surfactants. Hartl *et al.* (Niisson *et al.,* 2006) have investigated into ion sensitivity of surface conductive single crystalline diamond. Jacobs *et al.* (Niisson *et al.,* 2006) have dealt with aspects on dynamics of alkyl ammonium intercalants with in organically modified montmorillonite: Dielectrical relaxation and ionic conductivity. Rajamani *et al.* (Robins *et al.,* 2003) have performed a study on carbon nanotube based transparent conductive thin films. NMR diffusometry and electric conductometric techniques have been employed to study interactions between gemine surfactants, 12-s-12, and beta cyclodextrin (Sarah *et al.*, 2006). Bufe and Wolff (Sibel and Osman, 2007) have recently undertaken a study on switching electrical conductivity in an AOT – isooctane –water microemulsion through photodimerization of solubilized N-methyl-2-quinoline, conductometric measurements have been found extremely handy to look into CTAB aggregation in aqueous solutions of ammonium based ionic liquids (Sharma *et al.,* 1986). Conductometric method (Shun-Cheng *et al.,* 2004) has also been a worthy tool to investigate interaction between some anionic dyes and cationic surfactants. Sarah *et al.* (Tania *et al.,* 2005) have carried out work on conductometry and fluorometry on using mixed micellar systems of cationic surfactants in aqueous media.

The present investigation has been initiated with a view to explore synergistic effects on micellar behaviour of anionic – anionic mixed aqueous micellar systems. The microquantity (1.0 x 10^{-4} mol.dm^{-3}) of different anionic surfactant additives *viz.* caprate, laurate, myristate etc. has been introduced to the aqueous solutions of dodecylsulphates of alkali metals *viz.* lithium, sodium, potassium. The change in micellar behaviour (with and without the presence of additives) of the surfactant system, under study has been inferred by employing conductometric technique.

MATERIALS AND METHODS

The dodecylsulphates of Lithum and Potassium are not commercially available, these were therefore prepared in our laboratory. However, GR quality NaDS from E. Merck, having a very high stated purity, was used as received. Warm aqueous solutions of respective carbonates of Li and K were treated with warm aqueous sodium dodecylsulphate with constant stirring. The white coloured products obtained as precipitated after metathesis were recovered from their respective mother liquors. The products were washed/vacuum dried and recrystallised to ensure good quality. The m.p. of pure compounds as 189 and 225^{0}C for Li, K dodecylsulphates, respectively, were recorded. Results of CHNS (elemental analysis) were found to be in close agreement with the theoretical data suggesting proper syntheses of these compounds.

A digital conductivity meter (Elico Pvt. Ltd. Hyderabad, India, Type 032, No. 1455) and a dipping type conductivity cell with platinised electrodes were used for measuring the conductance of the aqueous solutions of alkali metal dodecylsulphates. All the measurements were made at a constant temperature in a thermostat (+0.01^{0}C).

RESULTS AND DISCUSSION

Fig. 1 is a representative illustration of the conductance behaviour of alkali metal dodecylsulthates in water at different temperatures (25 - 45^{0}C). The data reported in Table 1 has been obtained from these κ-C plots (Fig.1). Significantly, the micellisation in the present case is facilitated (*i.e.* cmc is lowered) as temperature increases. Increasing surfactant concentration leads to an increase in the specific conductantance of these micellar solutions.

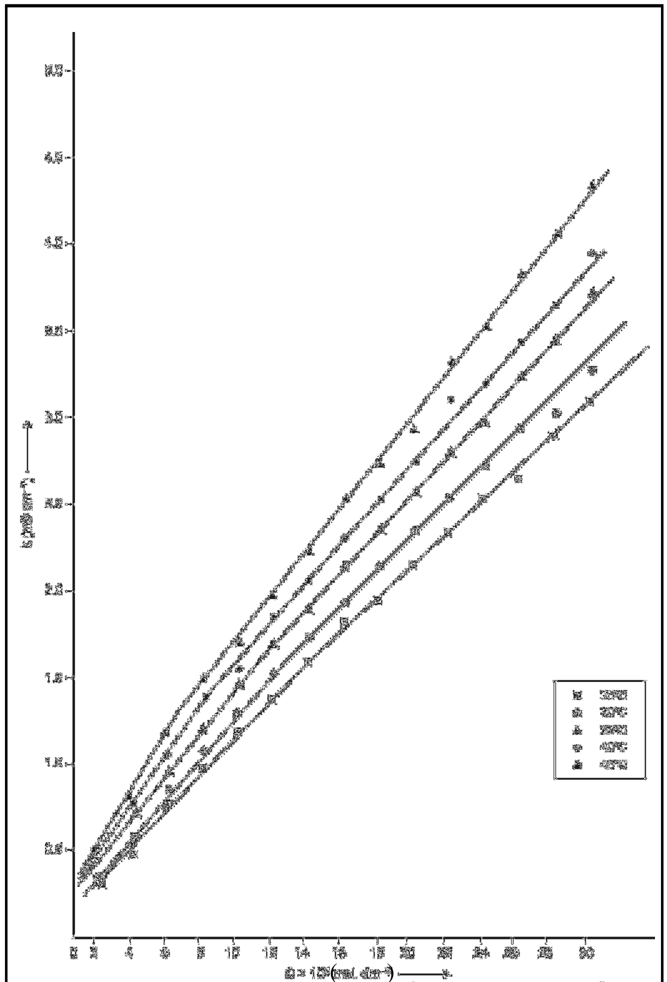

Fig. 1 : Plots of specific conductance, k (mS cm^{-1}) vs. concentration, C (mol. dm^{-3}) forLiDS (aq) with no additive at different temperatures (25-45^{0}C)

Table 1 : cmc (mol. dm^{-3}) data for aqueous alkali metal dodecylsulphates at different temperatures (25^0– 45^0 C)

Surfactant	cmc x10^2 Temperature				
	25^{0}C	30^{0}C	35^{0}C	40^{0}C	45^{0}C
NaDS	20	18	16	14	13
LiDS	1.4	1.2	1.0	0.8	0.7
KDS	0.24	0.22	0.18	0.16	0.12

Since the present investigation is an attempt to explore synergism in anionic-anionic mixed aqueous micellar systems, the dodecylsulphates of lithium, sodium, potassium in water are chosen as main micellar systems whereas the microquantity (1.0 x 10^{-4}mol. dm^{-3}) of caprates, laurates, myristates etc. have been used as additives to study their combined effects *i.e.* synergism. Table 2 explicitly mention different combinations of mixed micellar systems. For instance, Li caprate – LiDS; K laurate – KDS; Na myristate-NaDS systems involve Li caprate, K laurate and Na myristate (Fig. 2, 3 and 4) as additives where as LiDS, KDS and NaDS refer to main surfactant systems. Likewise, for systems such as NaDS – LiDS; LiDS – NaDS; LiDS– KDS (Fig. 5, 6 and 7) the former species refer to an additive whereas latter species

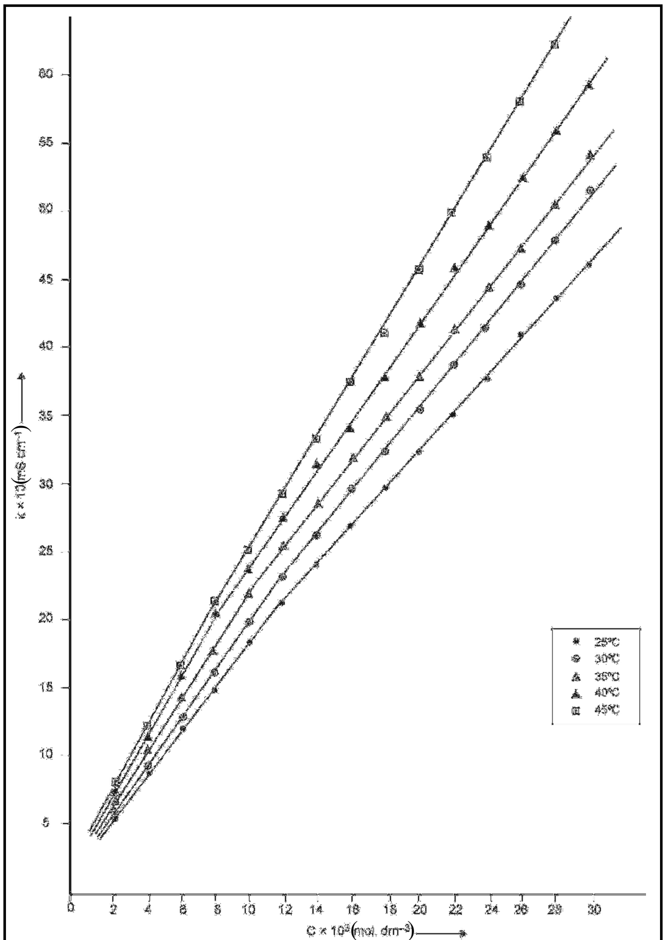

Fig. 2 : Plots of specific conductance, k (mS cm^{-1}) vs. concentration, C (mol. dm^{-3}) for Lithium caprate-Lithium dodecylsulphate (Li caprate-LiDS) mixed aqueous micellar systems at different temperatures (25-45⁰C)

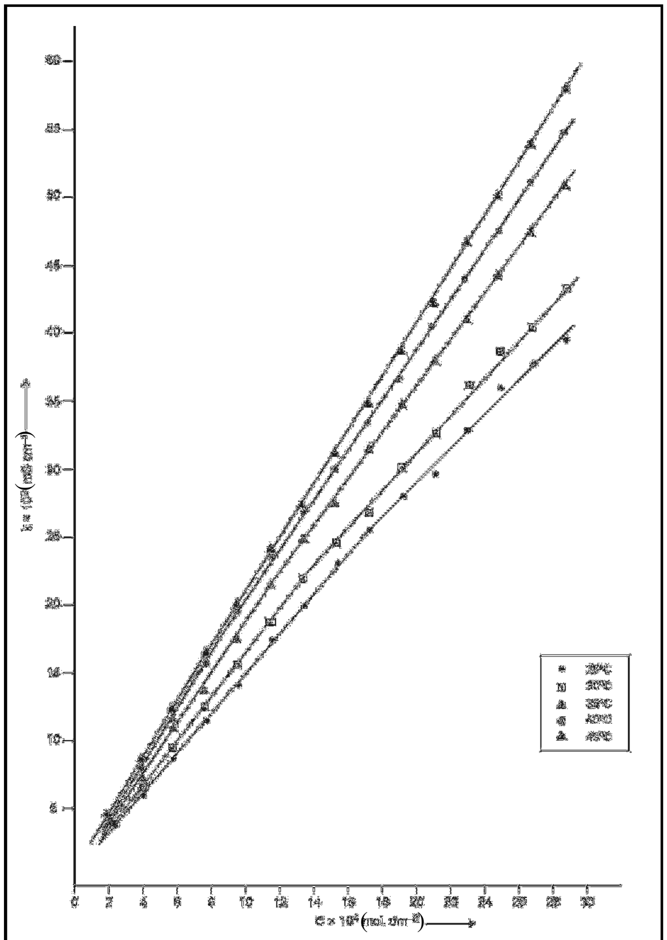

Fig. 3 : Plots of specific conductance, k (mS cm^{-1}) vs. concentration, C (mol. dm^{-3}) of Potassium laurate-Potassium dodecylsulphate (K laurate-KDS) mixed aqueous micellar systems at different temperatures (25-45⁰C)

Table 2 : Critical micelle concentration, cmc for different anionic–anionic mixed aqueous micellar systems at different temperatures

Mixed micellar systems	25^0C	30^0C	35^0C	40°C	45°C
Li caprate–LiDS	11.0X10^{-3}	10.2X10^{-3}	9.0X10^{-3}	7.8X10^{-3}	6.6X10^{-3}
Li laurate–LiDS	9.6X10^{-3}	9.0X10^{-3}	8.6X10^{-3}	7.0X10^{-3}	6.0X10^{-3}
Li myristate–LiDS	8.8X10^{-3}	8.0X10^{-3}	7.6X10^{-3}	6.6X10^{-3}	5.0X10^{-3}
K caprate–KDS	21.4X10^{-4}	19.8X10^{-4}	17.0X10^{-4}	14.0X10^{-4}	11.0X10^{-4}
K laurate– KDS	18.0X10^{-4}	14.4X10^{-4}	12.0X10^{-4}	9.0X10^{-4}	7.6X10^{-4}
K myristate– KDS	11.6X10^{-4}	11.0X10^{-4}	10.0X10^{-4}	7.0X10^{-4}	5.0X10^{-4}
Na caprate–NaDS	20.0X10^{-2}	17.8X10^{-2}	15.8X10^{-2}	14.0X10^{-2}	13.4X10^{-2}
Na laurate– NaDS	17.0X10^{-2}	15.6X10^{-2}	15.0X10^{-2}	13.8X10^{-2}	13.0X10^{-2}
Na myristate– NaDS	14.0X10^{-2}	13.0X10^{-2}	12.0X10^{-2}	11.4X10^{-2}	10.0X10^{-2}
NaDS–LiDS	13.6X10^{-3}	12.0X10^{-3}	11.0X10^{-3}	9.0X10^{-3}	8.0X10^{-3}
KDS–LiDS	11.0X10^{-3}	10.0X10^{-3}	9.0X10^{-3}	7.8X10^{-3}	7.0X10^{-3}
LiDS–NaDS	14.0X10^{-2}	12.6X10^{-2}	11.0X10^{-2}	10.0X10^{-2}	8.0X10^{-2}
KDS–NaDS	11.8X10^{-2}	10.6X10^{-2}	10.0X10^{-2}	8.0X10^{-2}	6.0X10^{-2}
LiDS–KDS	14.0X10^{-4}	12.0X10^{-4}	10.0X10^{-4}	8.0X10^{-4}	6.0X10^{-4}
NaDS –KDS	12.0X10^{-4}	10.0X10^{-4}	8.0X10^{-4}	6.0X10^{-4}	4.0X10^{-4}

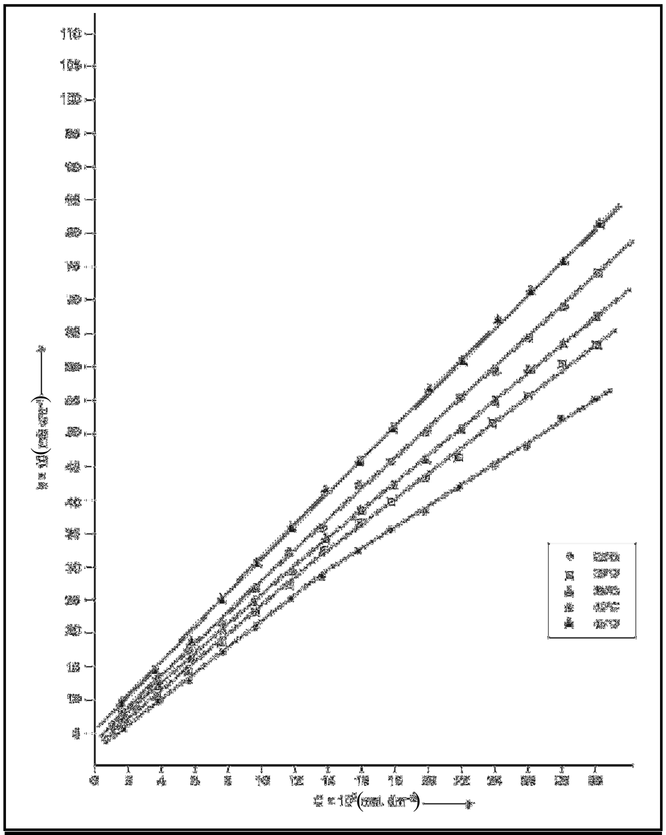

Fig. 4 : Plots of specific conductance, k (mS cm^{-1}) vs. concentration, C (mol. dm^{-3}) of Sodium Myristate-Sodium dodecylsulphate (Na Myristatee-NaDS) mixed aqueous micellar systems at different temperatures (25-45^{0}C)

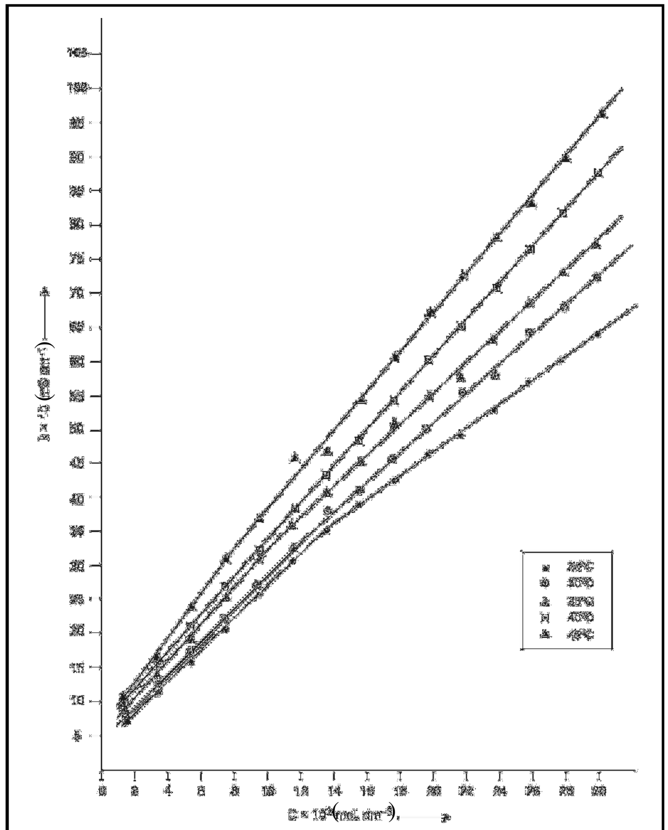

Fig. 6 : Plots of specific conductance of k (mS cm^{-1}) vs. concentration, C (mol. dm^{-3}) of Lithium dodecylsulphate- Sodium dodecylsulphate (LiDS-NaDS) mixed aqueous micellar systems at different temperatures (25-45^{0}C)

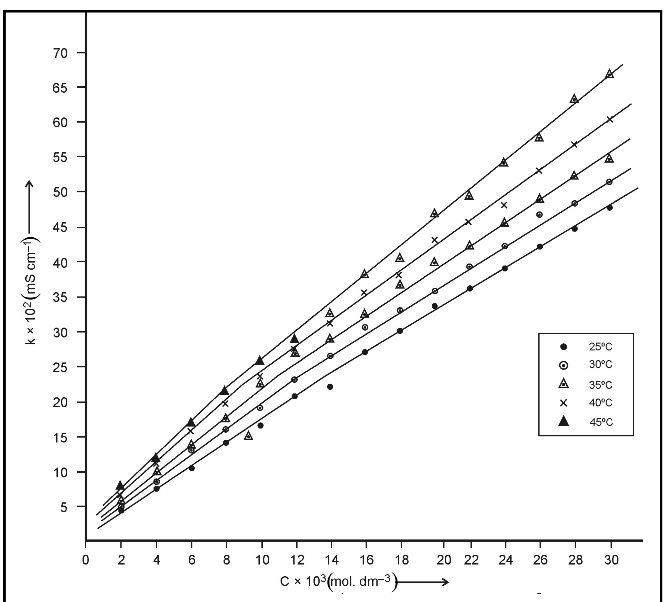

Fig. 5 : Plots of specific conductance, k (mS cm^{-1}) vs. concentration, C (mol. dm^{-3}) at Potassium laurate-Potassium dodecylsulphate (K laurate-KDS) mixed aqueous micellar systems at different temperatures (25-45^{0}C)

refer to main surfactant system.

The determination of critical micelle concentration, cmc is an age old significant ploy used to hint at a better quality surfactant product. Mixed micellar systems involving ionic–nonionic and ionic–ionic (*viz.* anionic–cationic; cationic–cationic; anionic–anionic) surfactant systems have of late drawn interest from researchers so as to observe synergistic effects. The outcome of the present exhaustive experimental work may summarily be stated by observing the fact that the micellisation of pure surfactant systems under study comprising of the aqueous solutions of dodecylsulphates of lithium, sodium, potassium (*viz.* LiDS, NaDS, KDS) is facilitated by introducing to these systems the microquantities (1.0 x 10^{-4}mol.dm^{-3}) of various anionic surfactants (Table 2) *i.e.* cmc of the pure surfactant systems (*i.e.* in absence of additives) is lowered in presence of the different surfactant additives.

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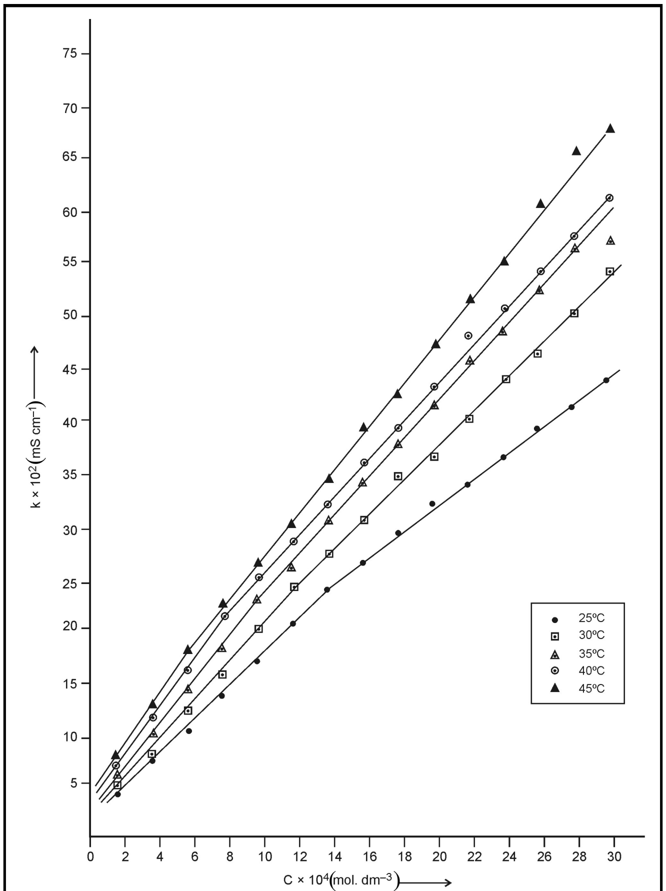

Fig. 7 : Plots of specific conductance, k (mS cm^{-1}) vs. concentration, C (mol. dm^{-3}) at Lithium dodecylsulphate- Sodium dodecylsulphate (LiDS-NaDS) mixed aqueous micellar systems at different temperatures (25-45^{0}C)

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