THERMODYNAMIC STUDIES ON SOME SURFACTANTS AND THEIR MODEL COMPOUNDS IN AQUEOUS AND MIXED AQUEOUS SOLVENTS

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BY
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TO

MY MOTHER

CERTIFICATE

This is to certify that the thesis entitled "THERMODYNAMIC STUDIES ON SOME SURFACTANTS AND THEIR MODEL COMPOUNDS IN AQUEOUS AND MIXED AQUEOUS SOLVENTS" being submitted by Mr. Nirupam Roy Choudhury to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bona fide research work carried out by him. Mr. Roy Choudhury has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis which, to my knowledge, has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

I. I. T., Delhi
May 29, 1981

(J.C. Ahluwalia)
Professor
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N. Roy Choudhury

ABSTRACT

This work describes the thermodynamic investigations carried out on some surfactants in aqueous solutions. The compounds chosen for the present study were sodium decanoate, sodium dodecanoate, sodium dodecyl sulfate, and some lower members of the sodium carboxylate series viz., sodium formate, sodium acetate, sodium propionate, and sodium butyrate. The thermodynamic parameters determined experimentally were the integral enthalpies of solution at infinite dilution, from which the heat capacities of dissolution values were evaluated. An isoperibol submarine calorimeter was employed for determination of integral enthalpy of solution.

The integral enthalpies of solution at infinite dilution, ΔH_s^o, of sodium decanoate, sodium dodecanoate, and sodium dodecyl sulfate in water were determined at various temperatures from 288.15 to 338.15 K. The heat capacities of dissolution, ΔC_p^o, of these solutes in water at various temperatures were computed from ΔH_s^o values. The ΔC_p^o values thus obtained were combined with the estimated values of intrinsic heat capacity, $C_{p_{IN}}$, and of heat capacity of pure solute, $C_{p_2}^*$, to obtain the partial molal heat capacities, $\bar{C}_{p_2}^o$, and the structural heat capacities, $\bar{C}_{p_2}^o$ (str) of these solutes in aqueous solutions. The results indicate that the ΔC_p^o, $\bar{C}_{p_2}^o$, and

$\overline{C}^{o}_{p_2}$ (str) values for all these solutes decrease with increase in temperature. These observations have been interpreted in terms of the decrease in hydrophobic hydration with increasing temperature. The role of the size of the solute and of the nature of the hydrophilic polar group attached to the hydrophobic group has also been emphasized.

In order to examine the effect of tert-butyl alcohol (TBA) on the solution properties of the surfactants, the integral enthalpies of solution at infinite dilution of sodium dodecanoate and sodium dodecyl sulfate in aqueous TBA solutions have been determined at 298.15 and 308.15 K by varying the TBA concentration from 0.02 to 0.20 mole fraction. Enthalpies and heat capacities of transfer of these solutes from water to aqueous TBA solutions have been computed from the ΔH^{o}_{s} values. With a view to understand the effect of the size of the solute on these transfer functions, similar measurements have also been done with sodium formate, sodium acetate, sodium propionate, and sodium butyrate. The results obtained have been explained by considering the effects of the constituent hydrophobic and hydrophilic groups of the solute molecules separately on the structure of the mixed solvent. It is observed that at lower concentrations of alcohol (upto ca. 0.02 mole fraction of TBA), the structure of the mixed solvent increases. At higher concentrations of TBA, on the other hand, the overall structure of the mixed solvent collapses. It has further been suggested that the hydrophobic portion of the solute molecule causes an enhancement of the structure (upto ca. 0.02 mole fraction TBA) the effect being increased with increasing solute size and that the hydrophilic polar portion of the molecule has the opposite effect, viz., the breakdown of the structure of the mixed solvent.

Further, with a view to understand in more detail the interaction of urea with the surfactants in aqueous solutions, the enthalpies and heat capacities of transfer of sodium decanoate and sodium dodecyl sulfate from water to 2m and 6m aqueous urea solutions and of sodium dodecanoate from water to 2m aqueous urea solution have been determined from the measurements of integral enthalpies of solution. The results indicate that urea causes the breakdown of the structure of water and that the hydrophobicity of the surfactants decreases in aqueous urea solution. This decrease in hydrophobicity is seen to be more pronounced with the larger hydrophobic solutes. With increase in urea concentration from 2m to 6m, this effect is observed to increase suggesting that the structure-breaking ability of urea increases with increase in its concentration at least upto 6m.

Due acknowledgement has been made wherever the work described is based on the findings of other investigators. The author apologizes for any omission or mistake which might have creeped in due to oversight.

GLOSSARY OF SYMBOLS AND ABBREVIATIONS

α-ABA	α-aminobutyric acid
Am_4NBr	tetraamylammonium bromide
Bu_4NBr	tetrabutylammonium bromide
c	molar concentration
CMC	critical micellization concentration
$C^*_{p_2}$	heat capacity of pure solute
$\bar{C}^o_{p_2}$	partial molal heat capacity of the solute at infinite dilution
$\bar{C}^o_{p_2}(str)$	structural heat capacity of the solute
$C_{p_{IN}}$	intrinsic heat capacity of the solute
$C_{p_{liq}}$	heat capacity of the liquid
ΔC^o_p	heat capacity of dissolution at infinite dilution
$\Delta C_{p_{tr}}$	heat capacity of transfer
ϕ^o_c	apparent molal heat capacity of the solute at infinite dilution
ΔG	free energy change
H	enthalpy
H^o_1	enthalpy of the solvent
H^*_2	enthalpy of the solute

$\bar{H}_1$	partial molal enthalpy of the solvent
$\bar{H}_1^o$	partial molal enthalpy of the solvent at infinite dilution
$\bar{H}_2$	partial molal enthalpy of the solute
$\bar{H}_2^o$	partial molal enthalpy of the solute at infinite dilution
ΔH	enthalpy change
ΔH^E	excess enthalpy
ΔH_h	enthalpy of hydrolysis
$\Delta H_{ionz.}$	enthalpy of ionization
ΔH_m	enthalpy of micellization
Δh_s	heat evolved or absorbed by the dissolution of the solute
ΔH_s	integral enthalpy of solution per mole of the solute
ΔH_s^o	integral enthalpy of solution at infinite dilution
ΔH_{tr}	enthalpy of transfer
$\Delta H_{tr}(max)$	maximum enthalpy of transfer
I	current in amperes
K_a	dissociation constant of the acid
K_h	hydrolysis constant

K_w	ionization constant of water
m	molality
M	molarity
MC	Monte Carlo Simulation
MD	molecular dynamics simulation
mf	mole fraction
mol dm^{-3}	moles of solute per cubic decimeter solution
mol kg^{-1}	moles of solute per kilogram solvent
n_1	moles of solvent
n_2	moles of solute
NaC_1	sodium formate
NaC_2	sodium acetate
NaC_3	sodium propionate
NaC_4	sodium butyrate
NaC_{10}	sodium decanoate
NaC_{12}	sodium dodecanoate
NaDDS	sodium dodecyl sulfate
NTABr	n-nonyltrimethylammonium bromide
R	resistance of the calibration heater in ohms
ΔS	entropy change
ΔS_h	entropy of hydration
t	time in seconds
TBA	tertiary butyl alcohol

THAM	tris(hydroxymethyl)-aminomethane
ΔT_c	corrected change in temperature during calibration of the calorimeter
ΔT_s	corrected change in temperature during dissolution of the solute
y_{ij}, y_{ijj}, etc.	pair, triplet, etc. interaction coefficients of like (if $i = j$) or unlike (if $i \neq j$) species corresponding to enthalpy ($y = h$), heat capacity ($y = c$), etc.
α	degree of hydrolysis

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