Discussion

The results of the measurements of interfacial surface tension variations against aqueous solutions of HCl, KOH, ZnCl₂, CaCl₂, CdBr₂ indicate that for very dilute solutions of the salts, there is an increase in the surface tension and finally decrease with change in concentration giving a maximum of interfacial surface variations, just as in the case of such measurements of soap solutions against liquids such as n-butyl acetate, iso amyl acetate, sec. octyl alcohol etc. (J. Ind. Chem. Soc. 1953, 30, 209). The details are shown in Table No. 1. When however, such measurements have been carried out with salts like HgCl₂, HgBr₂, CoCl₂, the results indicate that two maxima in interfacial surface tensions variations with change in salt concentration are obtained. (Table No. 2).

The results of interfacial tension measurements of iso amyl acetate against aqueous solutions of cupric chloride with varying salt concentrations indicate that there are five maxima in interfacial tension values. The work of previous investigators have shown that the ions such as CuCl₃, CuCl₄ and hydrated Cu⁺⁺ ions exist in solution as a result of an auto-complexing process.

In light of this knowledge, it is presumed that the proportion of dissociated to undissociated salt goes on increasing with successive dilution in the following manner and the complex ions exist in solution due to auto complex formation.
The equilibrium sequence may be presumed to shift with change in salt concentration in aqueous solution in the following manner:

\[
\begin{align*}
3 \text{CuCl}_2 & \rightleftharpoons \text{Cu}^{++} + (\text{CuCl}_3)_2^- \\
5 \text{CuCl}_2 & \rightleftharpoons \left\{ \begin{array}{l}
\text{Cu}^{++} + (\text{CuCl}_3)_2^- \\
\text{Cu}^{++} + (\text{CuCl}_4)^{--}
\end{array} \right. \\
2 \text{CuCl}_2 & \rightleftharpoons \text{Cu}^{++} + (\text{CuCl}_4)^{--} \\
3 \text{CuCl}_2 & \rightleftharpoons \left\{ \begin{array}{l}
\text{Cu}^{++} + (\text{CuCl}_4)^{--} \\
\text{Cu} + 2 \text{Cl}^-
\end{array} \right. \\
\text{CuCl}_2 & \rightleftharpoons \text{Cu}^{++} + 2 \text{Cl}^-
\end{align*}
\]

The five peaks in interfacial surface tension variations may be due to five different changes in the ionisation character of the salt with successive dilution as illustrated in the sequence and the existence of complex anions due to the auto-complexing process may account for the sequence.
In case of CdI₂, the measurements have been repeated with number of liquids such as n-butyl, i-amyl, n-hexyl and sec. octyl alcohols, methyl, ethyl, n-propyl, n-butyl, and i-amyl acetates, methyl and ethyl salicylates and hexane. It is evident from the results and interfacial tension -- concentration curves (Table No. 4-6, Fig. 1-2) that two peaks appear in the case of liquids Type I, viz. hexyl and sec. octyl alcohols, ethyl, n-propyl, n-butyl and i-amyl acetates, while no such peak is observed with liquids Type II, viz, n-butyl, i-amyl alcohols, methyl acetate, methyl and ethyl salicylate and hexane.

The variations in the interfacial tension values with increasing concentration of cadmium iodide in water are explained in the following manner.

For dilute solutions, the ionisation of cadmium iodide in water is in the following manner:

\[ \text{CdI}_2 \xrightarrow{\text{Cd}^{++} + 2 \text{I}^-} \]  \hspace{1cm} (1)

At higher concentrations, existence of complex anion (CdI₄)⁻⁻ has been postulated to account for abnormal transport number data (Hittorf, Ann. Physik, 1859,106,513; Jahn, Z. Physikal Chem. 1901,37,673). Therefore, the ionisation is expected in the following manner:

\[ 2 \text{CdI}_2 \xrightarrow{\text{CdI}_4} \xrightarrow{\text{Cd}^{++} + \text{CdI}_4} \]  \hspace{1cm} (2)

For extremely dilute solution, when the ionisation is of the type (IQ, a kind of ionic layer is preferentially adsorbed at the oil droplet interface with diffuse ionic layer of
opposite kind in the body of the solution, thus setting up electrical double layer with corresponding interfacial potential. With increasing concentration of the electrolyte, however, this potential value is presumed to decrease with decrease in charge density at the interface. When this happens, the interfacial tension value increases and reaches maximum, when the double potential practically annulled. With further increase in the electrolyte concentration, a double layer of opposite kind to the original is presumed to be formed at the interface having again some potential, which increases with concentration increase. When this happens, the interfacial tension falls. The unstable H-bond ring structure of liquids—Type I is considered to be mainly responsible for the reversal of electrical double layer. No such reversal is presumed to take place in case of liquids Type II, having no such unstable structure. Methyl or ethyl salicylate has comparatively stable H-bond, because the distance, through which it operates, is small (Huggins. J. org. Chem. 1936, 407). Therefore, its structure is not so unstable as to be sensitive enough to suffer the reversal of the double layer. It is only the unstable nature of H-bond that is responsible for such a reversal.

For dilute solutions of cadmium iodide, when the concentration increase is of lower order, the first peak indicates the reversal during course of ionisation, shown in (1). At higher concentrations of the salt, however, the auto-complex formation takes place and so rearrangement in ionic atmosphere is necessitated thus:

\[ 2 \text{CdI}_2 \xrightarrow{\text{L}} 2 \text{Cd}^{++} + 4 \text{I}^- \xrightarrow{\text{L}} \text{Cd}^{++} \text{I}_4^{-} \]

This effect leads to different type of preferential
adsorption of ionic layer at the interface and thereby brings up entirely new set up of electrical double layer potential and corresponding interfacial tension values follow the similar sequence with increase in salt concentration, indicating a second peak, at which reversal of double layer again takes place. It therefore appears that the unstable H-bond ring structure acts as a sensitive indicator of any change in ionisation character of an electrolyte. In case of liquids—Type IIII having no such unstable ring structure, the interfacial tension merely goes on decreasing with increase in salt concentration.

It may be possible that at higher concentration of salts—CoCl₂, HgCl₂, HgBr₂, the autocomplex formation may be taking place. For dilute solutions, of these salts the ionisation would be of the type:

\[ MX_2 \rightarrow M^{++} + 2X^- \]

where \( M \) stands for metal and \( X \) for the halogen. At higher concentration existence of complex anion \( (MX_4)^{2-} \) has been postulated and so the ionisation may be expected to occur in the following manner

\[ 2 MX_2 \rightarrow M^{++} (MX_4)^{2-} \]

In the system HgCl₂—KCl, it is evident that there are seven peaks corresponding to 6, 8, 12, 18, 24, 36 and 48 cc of KCl solution when the concentration of KCl was varied systematically, and also seven peaks corresponding to 6, 8, 12, 16, 24, 36 and 48 cc of HgCl₂ solution, when its concentrations was systematically varied, keeping that of the other constant in each case (vide Table No. 9-10 and fig. 4). It is evident that stoichiometric relations
are maintained and that molecular ratios between the two salts at these peaks correspond to the formation of compounds of molecular formulae (a) 4 KCl. HgCl₂, (b) 3 KCl. HgCl₂, (c) 2 KCl. HgCl₂, (d) 3 KCl. 2 HgCl₂, (e) KCl. HgCl₂, (f) 2 KCl. 3 HgCl₂ and (g) KCl.2HgCl₂. Thus seven complexes appear in mixed solutions, prepared from stock solutions M/80 and M/40. However, only six complexes appear in mixed solutions similarly prepared from M/4 each of potassium and mercuric chlorides. The complex (b) 3 KCl. HgCl₂ disappears in the case of series prepared from M/4 stock solutions. The same six complexes also appear in comparatively higher concentrations of mixed salts solutions, prepared from M/2 potassium and M/8 mercuric chloride solutions. With comparatively still higher concentrations of mixed salts solutions, prepared from M/1 potassium and M/4 mercuric chloride solutions, only three complexes (c), (e) and (g) appear (vide Table No. 7-8, fig. 3). Thus, the extent of concentration of salts in mixed solutions determines largely the number of complexes formed; at comparatively lower concentrations, the formation of greater number of complexes appears to be favoured.

The results, obtained with the HgCl₂-NH₄Cl system, are parallel to those obtained with KCl-HgCl₂-KCl system, with respect to the number of complexes, their molecular composition and range of salt concentrations. Three, six and seven complexes appear to be favoured with decreasing extent of salt concentrations in mixed solutions (Table No.11-12, fig. 5). They are (1) a,b,c, d,e,f, and g ; (2) a,c,d,e,f, g and (3) c,e, and g, indicated in fig 5.

In the HgCl₂- NaCl, the formation of three, six and
seven complexes appears to be favoured with decreasing extent of salt concentrations in mixed solutions as in the case of other two systems (Table No. 13-14, fig. 6). However, it is interesting to observe that formation of complex 3 NaCl.HgCl₂ is preferentially favoured with the disappearance of complex 4 NaCl. HgCl₂, when six complexes altogether are formed, while with KCl and NH₄Cl system, the opposite is the case.

One is inclined to take the view that the formation of these complexes corresponds to:

\[ M₄(HgCl₆) \overset{M_2(HgCl₄)}{\rightleftharpoons} M_2(HgCl₄) \overset{M(HgCl₃)}{\rightleftharpoons} \]

\[ M_2(HgCl₄) \overset{2HgCl₂}{\rightleftharpoons} M(HgCl₃) \]

--- sequence resulting from changes in interionic character, due to variations in electrolyte concentration. The complex 3 MCl. HgCl₂ is interpreted in the ratio 6 MCl.2 HgCl₂ for the sequence. The complex 2 MCl. 3 HgCl₂ is expressed as \( M₂(HgCl₄) \) and not as \( 2M(HgCl₃) \) HgCl₂, because in that case the interionic character would not suffer such significant change from that of (7) as to warrant maximum tension, corresponding to the peak in the curves. (M stands for K, NH₄, or Na)

The results, obtained with HgCl₂-LiCl system, reveal the formation of only three and six complexes with progressive dilution of the mixed salt solution (Table 15-fig 7). Their molecular composition are similar to those obtained with potassium
and ammonium chloride systems. The formation of the complex

\[ 3 \text{LiCl} \cdot \text{HgCl}_2 \]

is not favoured.

In the system HgBr\textsubscript{2} - KBr, it is evident that there are seven peaks corresponding to 6, 8, 12, 16, 24, 36 and 48 cc. of HgBr\textsubscript{2} solution, when its concentration was systematically varied, keeping that of KBr constant (24 cc M/80) in the series. (table No. 16, fig. 8). The stoichiometric relations are maintained and molecular ratios between two salts at these peaks correspond to the formation of compounds of molecular formulae; (a) 4 KBr.HgBr\textsubscript{2}, (b) 3 KBr.HgBr\textsubscript{2}, (c) 2 KBr.HgBr\textsubscript{2}, (d) 3 KBr.2 HgBr\textsubscript{2}, (e) KBr.HgBr\textsubscript{2}, (f) 2 KBr.3 HgBr\textsubscript{2} (g) KBr.2 HgBr\textsubscript{2} (curr. sci. 1953, 22, 15).

The complex (b) 3 KBr.HgBr\textsubscript{2} disappears in case of the data as given in Table No. 16 and fig. 8, and complex (c) 2 KBr.HgBr\textsubscript{2} (e) KBr.HgBr\textsubscript{2} and (g) KBr.2 HgBr\textsubscript{2} only appear in case of data as given in Table no. 16 and fig. 8. Thus, the range of salt concentrations in mixed solutions is a fundamental factor affecting the degree of complex formations. The formation of greater number of complexes is facilitated at comparatively lower concentrations.

The results of HgBr\textsubscript{2} - NH\textsubscript{4}Br system are parallel to those obtained with the potassium bromide system, as regards the number of complexes their molecular formulae and range of salt concentrations (Table No. 18-19, xx xx). They are (1) a, b, c, d, e, f, g, (2) a, c, d, e, f, g, and (3) c, e, g. as indicated in fig 9.
In HgBr$_2$ - NaBr system, with decreasing concentration of mercuric bromide and sodium bromide, three, six and seven complexes, a, b, c, d, e, f, and g, are found in solution (Table No. 20-21). When six complexes are evident, the complex (a)4 NaBr.HgBr$_2$ disappears in this system, while in the other two complexes (b) 3 NaBr.HgBr$_2$ has been found to disappear (Fig 10). In other respects the results are parallel to those of the other two systems. Further, the range of concentrations of both the salts to obtain three, six and seven complexes has to be comparatively lowered in this system.

The results of HgBr$_2$ - LiBr system reveal the only formation of three and six complexes with progressive dilution of the mixed solution (Table No. 22). They are (i) a, c, d, e, f, and g (ii) c, e, g, as indicated in Fig 11. The formation of the complex 3 LiBr.HgBr$_2$ is not favoured. To obtain maximum number of complexes, dilution of alkali salt solution should be progressively increased in the order; Li > Na > K, in view of the greater polarizing effect of the smaller cation, just as in the case of chloride system.

Copper chloride - alkali chlorides and cobalt chloride - alkali chloride systems: - The results obtained with both the systems are similar with respect to the number of complexes, their molecular composition and range of salt concentrations. Two and four complexes appeared to be favoured with decreasing extent of salt concentrations in mixed solutions (CuCl$_2$ system, Table No. 23-27, Fig. 12-15; CoCl$_2$ system, Table No. 28-31, Fig. 16-19).
They are (a) 3 MCl. CuCl₂, (b) 2 MCl. CuCl₂, (c) MCl. CuCl₂, (d) MCl. 2 CuCl₂ and (b) 2 MCl. CuCl₂ and (c) MCl. CuCl₂ — where M stands for K, NH₄, Na or Li. Similar results as regards the complexes are obtained with the cobalt chloride system.

In the cadmium iodide — alkali iodide system, only two complexes appear to be formed either at higher or lower concentrations of the salts in the mixed solutions. They are 2 Ml. CdI₂ and Ml. CdI₂ (Table No. 32-37, fig 20-23).

Lead nitrate — alkali nitrate system: —

It is evident from the Table no.38-39 and fig 24 that there are three peaks corresponding to 5, 10 and 20 cc of lead nitrate when its concentration was varied systematically; in each case, keeping that of potassium nitrate and ammonium constant. The molecular ratios between the two salts at these peaks in each system corresponds to the formation of complexes of the formulae

KNO₃·Pb(NO₃)₂, 2 KNO₃·Pb(NO₃)₂, 4 KNO₃·Pb(NO₃)₂;

NH₄NO₃·Pb(NO₃)₂, 2 NH₄NO₃·Pb(NO₃)₂, 4 NH₄NO₃·Pb(NO₃)₂.

These results confirm the findings of Nayar and others (loc. cit). Further, sec. octyl alcohol behaves as sensitively as n-butyl acetate in the indication of complex formation in solution.

As the sensitivity of interfacial surface tension measurements with n-butyl acetate against the system HgCl₂ in the indication of complex formation was observed, it was thought interesting to see whether complex formation indication would be obtained with the Pb(NO₃)₂—NaNO₃ system. These measurements throw light on the existence of complexes in solution in definite
stoichiometric relation.

It is evident from Table No. 40 and fig. 24, that there are three peaks corresponding to 5, 10 and 20 cc of lead nitrate solution, when its concentration varied systematically and also three peaks corresponding to 5, 10 and 20 cc of sodium nitrate solution, when its concentration was systematically varied, keeping that of the other constant in either case. It is evident that stoichiometric relations are maintained and that molecular ratios between the two salts at these peaks correspond to the formation of complexes of molecular formulae:

\[ \text{NaNO}_3 \cdot \text{Pb(NO}_3\text{)}_2, \ 2 \text{NaNO}_3 \cdot \text{Pb(NO}_3\text{)}_2, \ 4 \text{NaNO}_3 \cdot \text{Pb(NO}_3\text{)}_2. \]

These results are in conformity with the conclusion arrived by Lewis and others (loc. cit). This method of interfacial tension measurements of a liquid with unstable H-bond ring structure being extremely sensitive, opens a wide field in the investigations of existence of complex salts in solutions, in as much as it reveals that definite complexes, obeying stoichiometric laws, also seem to exist in \( \text{Pb(NO}_3\text{)}_2 - \text{NaNO}_3 - \text{H}_2\text{O} \) system, just as in the case of such potassium and ammonium nitrate systems. One is inclined to take the view that the following equilibrium sequence exists

\[ \text{M Pb(NO}_3\text{)}_3 \rightleftharpoons \text{M}_2 \text{ Pb(NO}_3\text{)}_4 \rightleftharpoons \text{M}_4 \text{ Pb(NO}_3\text{)}_6, \]
as a result of changes in interionic character, due to variations in electrolyte concentration; where M is either potassium, ammonium or sodium in the system.

These measurements using n-butyl acetate, were therefore further extended to the system \( \text{Pb(NO}_3\text{)}_2 - \text{LiNO}_3 \) to study the complexity of the solution. It has been observed that
the complexity of the solution changes with variation in salt concentration and so the measurements were carried out starting with five different concentrations (Table No. 41-42).

An examination of various curves (fig. 25-26) indicates that the number of complexes changes from two to three on dilution of the mixed solutions. Within the range starting with stock solution M/30 to M/300 two peaks corresponding to two complexes 2 LiNO₃·Pb(NO₃)₂ and LiNO₃·Pb(NO₃)₂ are only evident at 20 and 40 cc of lead nitrate solution in the curves, while with the stock solutions M/600 to M/1200, three peaks corresponding to three complexes 4 LiNO₃·Pb(NO₃)₂, 2LiNO₃·Pb(NO₃)₂ and LiNO₃·Pb(NO₃)₂ appear at 10, 20 and 40 cc of lead nitrate solution in the curves. For M/600 and M/1200 concentration, the part of the curve at 30 cc of lead nitrate solution is noteworthy, perhaps indicating a slight tendency for the formation of a complex. Thus the alkali metals show the tendency of forming three complexes (1) 4 MNO₃·Pb(NO₃)₂, (2) 2 MNO₃·Pb(NO₃)₂ and (3) MNO₃·Pb(NO₃)₂, where M stands for K, NH₄, Na or Li. But the ease of this tendency is conditioned by the order of alkali metal in the Periodic Table increasing with the atomic volume. It appears that in polar solvents like water high solvation effects at great dilution often permits the existence of highly charged ions. It is also noteworthy that the concentration effects of the salts largely determine the complexity of the mixed solution.

The results of complex formation in lead nitrate -- alkali nitrate and mercuric halide -- alkali halide
systems reveal interesting observation. To obtain maximum possible number of complexes, dilution of alkali salt solution should be progressively increased in the order: - Li > Na > K. Under this condition, the ions get comparatively far apart and interionic attractions between anions and alkali metal ions tend to become negligible. The dilution of a salt involves work against electrostatic attraction and hence the extent of dilution required for this purpose is a measure of the magnitude of electrostatic attraction between anions and alkali metal ions. This binding force between the anions and the metal ions is in the order: Li > Na > K. This is in agreement with decreasing size of the cations (Li⁺ < Na⁺ < K⁺) and correspondingly increasing deformation effect (i.e. the change from electrovalence to covalence) in the order: Li⁺ > Na⁺ > K⁺, in view of greater polarizing effect of the smaller cations.

In such cases of complex formation, there is the possibility of association of ions to a considerable extent by coulombic attraction and it may be that there is a smooth transition between a case of ion association where there is purely physical attraction and the formation of genuine chemical complexes.

The interfacial tension measurements of liquids having H-bond ring structure afford a novel method for the study of complex ions in solution. It opens the possibility to make a direct comparison of the tendency of different metal ions to form complexes under comparable conditions, because lattice forces do not operate in solution. The stability of various complex ions existing in solution may be further investigated. In conjunction with this method, which easily and conveniently indicates the concentrations at which complex ions exist to the maximum extent, if measurements such as adsorption spectra, Raman spectra, con-
conductivity, transference etc. are carried out at these concentrations, they promise to reveal interesting results. Such a coordinated study would, however, require a large scale team work.
EFFECT OF SOAP CONCENTRATION ON THE INTERFACIAL TENSION OF SOME ALIPHATIC ALCOHOLS AND ESTERS

BY

(MISS) H. J. KAZI AND C. M. DESAI

Reprinted from "Current Science", August, 1952, 21, 218
EFFECT OF SOAP CONCENTRATION ON THE INTERFACIAL TENSION OF SOME ALIPHATIC ALCOHOLS AND ESTERS

It is generally observed that the interfacial tension at the oil-water interface decreases with the increasing concentration of soaps, oleates, stearates, etc., in water, till a limiting value is reached. This may be accounted for on the basis of the mono-molecular layer theory of adsorption of fatty acid radical on the interface of the oil droplet.

In our work it has been observed that the interfacial tension for some liquids like hexyl and octyl alcohols, and propyl, butyl, amyl acetates, etc., is initially found to increase with increasing soap concentrations for dilute solutions, followed by usual decrease in interfacial tension with further increase in soap concentration. With saponin, however, such a behaviour as observed with dilute soap solutions, is not observed.

The interfacial tension of liquids against aqueous phase in presence of soaps was measured by the drop number method using a microsyringe (Burrows and Welcome) which gives the volume of a single drop with an accuracy of 0.0004 c.c. The final values for the interfacial tension were obtained by applying Harkin’s Correction Factor for the size of the drop. The effect of soap concentrations on the interfacial tensions of sec. octyl alcohol and normal butyl acetate against sodium oleate solutions is indicated in Fig. 1.

The interesting behaviour of the liquids may be explained on the basis of the reversal of electrical double layer at the oil-water interface and further that these liquids have a ring structure postulated by Smith and McReynolds. They have stated that the data of esterification, saponification, dissociation constants, irregularities in optical rotatory power and other anomalies may be explained on the basis of ring structure through hydrogen bond. The formation of ring structure has been also postulated by Evans and others. This type of ring must, by its very nature, be quite unstable. The details of the experimental results and the discussion will be published elsewhere. Further work along this line on different alcohols, esters, ketons, etc., is also in progress.

Chemistry Dept., M. T. B. College, Surat, February 5, 1952.

(MISS) H. J. KAZI.
C. M. DESAI.

INTERFACIAL TENSION OF ALIPHATIC ALCOHOLS AND AROMATIC LIQUIDS WITH SURFACE ACTIVE AGENTS. PART I

By Miss Hemlata J. Kazi and C. M. Desai

Measurements of the interfacial tension of some alcohols and aromatic liquids have been carried out against soap solutions. The tension at the oil droplet interface with increasing soap concentration is initially found to fall rapidly for dilute solutions, and thereafter reach a limiting value, when further increase in soap concentration has practically no effect, except in cases of n-hexyl and sec.-octyl alcohols which show a maximum in dilute soap solutions, followed by a rapid lowering.

Lowering of interfacial tension of organic liquids brought about by soaps and such substances is generally necessary for their emulsification. Soap solution has a low surface tension which together with the adsorbed interfacial film, contributes to its emulsifying property (Donnan, Kolloid Z., 1910, 208; Bancroft, J. Phys. Chem., 1915, 19, 275; Harkins, J. Amer. Chem. Soc., 1917, 39, 541; Wilson, J. Chem. Soc., 1934, 1360; McBain, "Colloid Science", 1950).

The effect of hydrolysis of soaps has been investigated by various workers (Harkins and Clark, J. Amer. Chem. Soc., 1925, 47, 1854; Powney, Trans. Faraday Soc., 1935, 31, 1510). Traces of free alkali first raise the surface tension to a maximum and then with further increase in alkali concentration, it decreases slowly and almost linearly. Addition of alkali suppresses hydrolysis, and the adsorbed layer consists of neutral soap which gives the maximum tension, while acid soap lowers the tension, as it is more strongly adsorbed than a neutral soap.

Surface tension curves have been classified according to three types (McBain et al., Kolloid Z., 1937, 78, 1). In type I, surface tension of the solvent is increasingly lowered with increasing concentration of the solute. This is the commonest case. In type II, surface tension is increased, though not to a great extent, with increasing concentration of the solute. In type III, there is a very great lowering of surface tension in a very dilute solution, the surface tension thereafter remaining approximately constant, or even, passing through a minimum, followed by a shallow maximum, but still at a value far below that of the solvent. In contrast to surface tension, the interfacial tension between two liquids is often reduced to nearly zero by the addition of a surface active agent. Sometimes, however, the behaviour may be similar to that of the three types mentioned.

E X P E R I M E N T A L

The liquids selected were as follows: n-butyl, isobutyl, isoamyl, n-hexyl and sec.-octyl alcohols and benzyl alcohol, methyl and ethyl benzoates, benzyl benzoate and hexane. Many of the liquids were from reliable manufacturers, such as Schering-Kahlbaum and E. Merck. They were, however, treated with sodium carbonate, washed with distilled water, dried and distilled under reduced pressure and the middle fractions were used for the purpose. The specific gravities of the liquids were determined using a calibrated 25 c.c. bottle and values obtained at 30° were used in the calculation of their interfacial tension. The substances used to lower the surface tension were sodium oleate, potassium oleate, with excess of acid and alkali, and saponin. They were prepared and purified by the usual methods.

The drop volume method using a microsyringe (Burroughs and Wellcome) was adopted throughout to determine the interfacial tension of liquids against water and soap solutions. The syringe was scrupulously cleaned by means of alcohol, soap and distilled water and then dried before each measurement. It was then filled with the liquids and kept vertically with the tip at the definite depth in the aqueous medium in the container. By the careful working
of the screw cap, the drops with maximum possible size were slowly allowed to be formed covering the entire tip. All measurements were taken under identical conditions at a temperature 30° (±1.0). The measurements were thrice repeated and the mean value was corrected by Harkin's factor \( J. \) Amer. Chem. Soc. 1919, 41, 499.

The arrangements of the apparatus is shown in Fig I.

**FIG. I**

The motion of the piston in the barrel (capacity, 1 c.c.) of the syringe is governed by the micrometer screw head. Each division on the barrel corresponds to a volume of 0.04 c.c. and each sub-division on it is further calibrated by means of the micrometer screw to read 0.0004 c.c. The syringe with the liquids was clamped vertically with its tip pointing downwards for liquids heavier than water (Fig. 1), and the tip pointing upwards for those lighter than water. In the latter case, the barrel was fitted in the container holding aqueous medium by means of a tightly fitting rubber bung. In the case of liquids partly miscible with water, if the syringe be filled with such a liquid, the liquid often forms a continuous stream, instead of drops. If, however, the solubility of water in liquid is considerably less than that of liquid in water and water is filled in the syringe, water may give drops, and thus the tension of water against the liquid can be measured.

The variation in the interfacial tension of liquids with change in the soap concentrations ranging from \( 0.234 \times 10^{-3} M \) to \( 14.79 \times 10^{-3} M \) has been studied and the results are shown in Table I and Figs. 2 and 3.

**TABLE I**

<table>
<thead>
<tr>
<th>Sodium oleate, ( M \times 10^3 )</th>
<th>( n\text{-BuOH} )</th>
<th>( \text{isoBuOH} )</th>
<th>( \text{isoAmyl alcohol} )</th>
<th>( n\text{-Hexyl alcohol} )</th>
<th>( \text{sec.-Octyl alcohol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>3.021</td>
<td>2.406</td>
<td>5.231</td>
<td>8.239</td>
<td>10.60</td>
</tr>
<tr>
<td>0.246</td>
<td>---</td>
<td>2.767</td>
<td>2.333</td>
<td>4.863</td>
<td>8.851</td>
</tr>
<tr>
<td>0.938</td>
<td>---</td>
<td>2.537</td>
<td>2.103</td>
<td>4.634</td>
<td>8.239</td>
</tr>
<tr>
<td>1.479</td>
<td>2.410</td>
<td>2.098</td>
<td>4.413</td>
<td>7.769</td>
<td>17.73</td>
</tr>
<tr>
<td>1.908</td>
<td>2.354</td>
<td>1.832</td>
<td>4.195</td>
<td>7.278</td>
<td>16.21</td>
</tr>
<tr>
<td>2.469</td>
<td>2.105</td>
<td>1.788</td>
<td>3.788</td>
<td>---</td>
<td>15.26</td>
</tr>
<tr>
<td>2.950</td>
<td>---</td>
<td>3.659</td>
<td>---</td>
<td>---</td>
<td>13.91</td>
</tr>
<tr>
<td>3.340</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>5.658</td>
<td>---</td>
</tr>
<tr>
<td>4.930</td>
<td>1.935</td>
<td>1.646</td>
<td>3.348</td>
<td>---</td>
<td>11.76</td>
</tr>
<tr>
<td>9.860</td>
<td>---</td>
<td>3.073</td>
<td>---</td>
<td>---</td>
<td>10.60</td>
</tr>
<tr>
<td>14.790</td>
<td>---</td>
<td>2.877</td>
<td>4.401</td>
<td>6.76</td>
<td></td>
</tr>
</tbody>
</table>

The interfacial tension in the aliphatic alcohol series is found to increase in the following order: \( \text{iso-BuOH} < n\text{-BuOH} < \text{isoamylyl alcohol} < n\text{-hexyl alcohol} < \text{sec.-octyl alcohol} \) (Table I, Fig. 2). It is found to be increasing with the increase in the length of the aliphatic chain for all concentrations of sodium oleate. Further, it appears that the magnitude of the lowering of the interfacial tension by soap solution depends on the magnitude of the tension of the liquid against pure water, and it is found to be in the following increasing order: \( \text{iso-butyl} < n\text{-butyl} < \text{isoamylyl} < n\text{-hexyl} < \text{sec.-octyl alcohol} \).
INTERFACIAL TENSION OF ALIPHATIC ALCOHOLS, ETC.

With potassium oleate—neutral, 10% free acid and 10% free alkali, the measurements of the interfacial tension were carried out in the case of iso- and n-butyl alcohols. It was, however, observed that the acidity or alkalinity did not appreciably affect the results and the fundamental behaviour was the same as against sodium oleate.

![Graph showing interfacial tension](image)

**FIG. 2.**

In the case of n-hexyl and sec-octyl alcohols, it was surprising to note that at lower concentrations of soap solutions, i.e., up to $2 \times 10^{-3} M$, the interfacial tension initially increased with the increasing soap concentration and then decreased as usual with further increase in soap concentration. With saponin (Fig. 3), however, at any concentration, this rather unusual behaviour, as observed with soap solution, was not evident. Addison (J. Chem. Soc., 1945, 98; 1944, 477) has shown that there is an almost linear relation between chain length and the surface tension of the aqueous saturated solution of normal alcohols; but sec-octyl alcohol and tert-hexyl alcohol depict an irregular behaviour. It has been therefore suggested that when the structure of alcohol is altered, other factors in addition to solubility factor, might be operative. The interfacial tension curves of hexyl and sec-octyl alcohols do not come under any of three types, already mentioned, as there is an initial rise of interfacial tension in very dilute solutions of soap, followed by a great lowering and thereafter the interfacial tension slowly decreasing and ultimately remaining approximately constant with increasing soap concentration.

In case of aromatic liquids (Fig. 3) it is apparent that groups -CH₂OH, -COOCH₃ and even -COOC₆H₅ reduce the tension against water when compared to that of unsubstituted nucleus (benzene, 34.6 dynes/cm.), while the group COOC₆H₅ considerably enhances it (67.7 dynes/cm.). This surprisingly high interfacial tension of ethyl benzoate may be attributed to the peculiar effect of the ethyl group, which this group often exerts. Further, the magnitude of the surface tension lowering by sodium oleate also appears to depend on the magnitude of the tension of that liquid against water i.e., greater the tension against water, greater is the lowering, but ethyl benzoate is also in this case an exception which shows much less lowering of tension against soap solution in view of its high tension against water.

In case of fatty acids, Szyszykowski's equation (Z. physikal. Chem., 1908, 64, 385) expresses
the relation between the lowering of the tension and concentration of the solute. For very dilute solutions of any solute, the depression of surface tension, caused by the solute, is proportional to its concentration. As the concentration of the solute, however, increases, the lowering of the tension is no longer proportional to the concentration, but increases more slowly than does the concentration. The portions of the curves of liquids depicting interfacial tension lowering in Figs. 2 and 3, however, indicate that the lowering increases much more rapidly than the soap concentration for dilute solutions, but as the concentration of the soap increases, the interfacial tension lowering generally increases less and less slowly and ultimately reaches a nearly zero value, when further increase in the soap concentration has practically no effect. Thus the interfacial tension at the oil droplet interface with soap solution is generally found to decrease to a greater extent initially with the increase in the soap concentration and then reaches a limiting value. This may be accounted for on the basis of the unimolecular theory of adsorption; when the entire surface area of the droplet is covered with the unimolecular layer of surface active agent, the adsorption becomes independent of the concentration of the active agent, and no further decrease in the interfacial tension takes place. With hexane, these measurements using sodium oleate and saponin (Fig. 3) also indicate that there is at first a considerable reduction in the tension and then a limiting value is reached.

The unusual behaviour of hexyl and octyl alcohols is explained in an earlier communication along with that of esters (Desai and Kazi, Curr. Sci., 1952, 21, 218).

The authors are indebted to Dr B. K. Vaidya, Assistant Director, Ahmedabad Textile Industrial Research Association, for his suggestion and interest and also express their gratitude to the college authority for the grant to meet the expense incurred in the work.

Chemistry Department
M. T. B. College, Surat.

Received August 14, 1952.
INTERFACIAL TENSION OF ALIPHATIC ESTERS WITH SURFACE ACTIVE AGENTS. PART II

By Miss Hemiata J. Kazi and C. M. Desai

The interfacial tension measurements of some aliphatic esters have been carried out against aqueous soap solutions. A number of esters, e.g. propyl, butyl and amyl acetates etc. show an exceptional behaviour in a sense that the tension increases to a sharp maximum initially with increasing soap concentration in dilute solutions, followed by a great lowering and thereafter reaching a limiting value.

In Part I of this series (this Journal, 1953, 30, 209) the authors reported the unusual behaviour of hexyl and sec.-octyl alcohols as regards the increase of interfacial tension over a certain low range of soap concentration. This behaviour is particularly marked with a class of aliphatic esters, viz, ethyl, isopropyl, n-butyl, isobutyl, isoamyl acetates, ethyl acetoacetate and ethyl isovalerate; while methyl acetate and diethyl malonate do not exhibit such a behaviour.

EXPERIMENTAL

The interfacial tension measurements were carried out by the method described in Part I (loc. cit.) using sodium and potassium oleate, sodium and potassium stearate, sodium chloride and acetate, and saponin. In case of methyl and ethyl acetates, which are partly miscible with water, if the syringe is filled with ester, the liquid forms a continuous stream in the water phase, instead of drops. Since the proportionate solubility of water in the esters is considerably less than that of esters in water, when water is filled in the syringe, water forms drops at the tip in the ester phase. In this way the interfacial tension of esters against water was determined.

The substances were either of standard quality or prepared by the usual method and subsequently purified before use. The results are expressed in Tables I—III and Figs. 1 and 2.

The interfacial tension against water in the ester series is found to be in the following order: methyl < ethyl < isopropyl > n-butyl > isobutyl > isoamyl. It appears to be increasing first and then decreasing with the length of the aliphatic chain.

It is also obvious that the extent of the lowering of surface tension by the soap solution depends on its magnitude against water, but isopropyl acetate is an exception, where the relative lowering is much less. In case of all esters, except methyl acetate and diethyl malonate, the interfacial tension increases with increasing soap concentration up to $2 \times 10^{-2}$ M and then diminishes with further increase in the soap concentration, till the limiting value is reached (Table I, Figs. 1 and 2). With saponin, however, it appears to decrease with increasing saponin concentration over the entire range, till the limiting value is reached (Table II). The interfacial tension measurements with isoamyl acetate using sodium chloride and sodium acetate, indicate that the tension initially increases with increase in electrolyte concentration and then diminishes with further increase in
electrolyte concentration (Fig. 2). The measurements with n-butyl acetate using potassium oleate-neutral, acidic and alkaline-, sodium and potassium stearate show the analogous behaviour (Table III). In general, the interfacial tension depression, follow-

### Table I

**Interfacial tension (dynes/cm.).**

| Solute               | Na-oleate | Methyl acetate | Ethyl acetate | isoPropyl acetate | n-Butyl acetate | isoButyl acetate | isoAmyl acetate | Ethyl acetate | Ethyl iso- | Diethyl acetate | Ethyl iso- | Diethyl iso- | Diethyl iso-
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000 M×10^-3</td>
<td>3.099</td>
<td>6.640</td>
<td>13.93</td>
<td>13.88</td>
<td>12.11</td>
<td>2.701</td>
<td>18.14</td>
<td>13.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.246 M×10^-3</td>
<td>2.845</td>
<td>7.119</td>
<td>14.02</td>
<td>18.01</td>
<td>13.89</td>
<td>12.82</td>
<td>3.038</td>
<td>19.32</td>
<td>9.333</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.492 M×10^-3</td>
<td>2.735</td>
<td>7.230</td>
<td>14.21</td>
<td>18.35</td>
<td>14.40</td>
<td>13.32</td>
<td>2.789</td>
<td>21.31</td>
<td>8.654</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.984 M×10^-3</td>
<td>-</td>
<td>-</td>
<td>14.56</td>
<td>18.57</td>
<td>-</td>
<td>11.41</td>
<td>2.649</td>
<td>22.83</td>
<td>7.352</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.476 M×10^-3</td>
<td>-</td>
<td>-</td>
<td>15.24</td>
<td>19.31</td>
<td>12.95</td>
<td>10.17</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.460 M×10^-3</td>
<td>-</td>
<td>-</td>
<td>14.03</td>
<td>17.09</td>
<td>-</td>
<td>8.847</td>
<td>2.345</td>
<td>14.90</td>
<td>6.506</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.950 M×10^-3</td>
<td>-</td>
<td>-</td>
<td>13.72</td>
<td>15.68</td>
<td>9.24</td>
<td>8.023</td>
<td>-</td>
<td>14.06</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.436 M×10^-3</td>
<td>2.275</td>
<td>7.168</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.560 M×10^-3</td>
<td>-</td>
<td>5.421</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.79 M×10^-3</td>
<td>-</td>
<td>-</td>
<td>13.32</td>
<td>6.477</td>
<td>5.94</td>
<td>-</td>
<td>-</td>
<td>6.691</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19.68 M×10^-3</td>
<td>-</td>
<td>-</td>
<td>13.12</td>
<td>6.183</td>
<td>-</td>
<td>5.18</td>
<td>1.635</td>
<td>6.092</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>29.52 M×10^-3</td>
<td>-</td>
<td>-</td>
<td>13.03</td>
<td>5.247</td>
<td>5.36</td>
<td>4.537</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.80 M×10^-3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>4.74</td>
<td>4.319</td>
<td>1.295</td>
<td>5.283</td>
<td>4.455</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>49.20 M×10^-3</td>
<td>-</td>
<td>-</td>
<td>12.93</td>
<td>4.863</td>
<td>4.22</td>
<td>4.17</td>
<td>-</td>
<td>-</td>
<td>4.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>98.40 M×10^-3</td>
<td>-</td>
<td>12.75</td>
<td>4.553</td>
<td>3.08</td>
<td>3.683</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table II

**Interfacial tension (dynes/cm.).**

<table>
<thead>
<tr>
<th>Saponin.</th>
<th>isoPropyl acetate</th>
<th>isoButyl acetate</th>
<th>n-Butyl acetate</th>
<th>isoAmyl acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000 %</td>
<td>13.03</td>
<td>13.22</td>
<td>13.88</td>
<td>12.11</td>
</tr>
<tr>
<td>0.0075</td>
<td>8.502</td>
<td>11.47</td>
<td>9.085</td>
<td>7.608</td>
</tr>
<tr>
<td>0.015</td>
<td>7.595</td>
<td>9.883</td>
<td>7.608</td>
<td>5.845</td>
</tr>
<tr>
<td>0.045</td>
<td>6.577</td>
<td>6.419</td>
<td>5.667</td>
<td>5.371</td>
</tr>
<tr>
<td>0.060</td>
<td>5.991</td>
<td>5.130</td>
<td>4.778</td>
<td>4.528</td>
</tr>
<tr>
<td>0.090</td>
<td>5.680</td>
<td>4.939</td>
<td>4.074</td>
<td>4.112</td>
</tr>
<tr>
<td>0.150</td>
<td>5.069</td>
<td>4.617</td>
<td>3.777</td>
<td>4.015</td>
</tr>
<tr>
<td>0.300</td>
<td>4.757</td>
<td>4.206</td>
<td>3.592</td>
<td>3.792</td>
</tr>
<tr>
<td>0.450</td>
<td>3.464</td>
<td>3.805</td>
<td>3.322</td>
<td></td>
</tr>
<tr>
<td>0.900</td>
<td>3.149</td>
<td>3.805</td>
<td>3.322</td>
<td></td>
</tr>
</tbody>
</table>
INTERFACIAL TENSION OF ALPHATIC ESTERS

ing the maximum tension, increases much more rapidly than soap concentration for dilute solutions, thereafter becomes less and ultimately any more increase in soap concentration has practically no effect on it.

**Table III**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>13.88</td>
<td>13.88</td>
<td>13.88</td>
<td>13.88</td>
<td>13.88</td>
</tr>
<tr>
<td>0.233</td>
<td>14.00</td>
<td>15.25</td>
<td>15.70</td>
<td>15.80</td>
<td>14.88</td>
</tr>
<tr>
<td>0.4666</td>
<td>14.46</td>
<td>15.60</td>
<td>16.90</td>
<td>15.95</td>
<td>17.80</td>
</tr>
<tr>
<td>0.932</td>
<td>15.86</td>
<td>16.25</td>
<td>17.90</td>
<td>16.75</td>
<td>16.76</td>
</tr>
<tr>
<td>1.864</td>
<td>17.53</td>
<td>16.81</td>
<td>19.70</td>
<td>18.65</td>
<td>15.96</td>
</tr>
<tr>
<td>2.336</td>
<td>16.46</td>
<td>16.45</td>
<td>19.00</td>
<td>19.45</td>
<td>14.88</td>
</tr>
<tr>
<td>2.796</td>
<td>15.95</td>
<td>16.00</td>
<td>18.25</td>
<td>18.20</td>
<td>14.60</td>
</tr>
<tr>
<td>4.660</td>
<td>15.57</td>
<td>14.25</td>
<td>15.40</td>
<td>15.55</td>
<td>14.25</td>
</tr>
<tr>
<td>9.320</td>
<td>9.63</td>
<td>10.55</td>
<td>9.96</td>
<td>-</td>
<td>12.82</td>
</tr>
</tbody>
</table>

**Fig. 1**

**Fig. 2**

DISCUSSION

Initial increase in interfacial tension of alcohols and esters over the low increasing range of soap concentrations and then its usual decrease, is explained on the basis of these liquids having a ring structure as postulated by Smith and McReynolds (J. Amer. Chem. Soc., 1939, 61, 1963) and further that the reversal of electrical double
layer at the interface of aqueous medium and such a liquid takes place with the variation in soap concentration. From the data of esterification, saponification and dissociation constants, they have postulated that acids with a chain involving four or more carbon atoms have a ring structure. Further, they have stated that irregularities in optical rotatory power, noted by Pickard and Kenyon for homologous alcohol series (J. Chem. Soc., 1911, 99, 45) could be satisfactorily interpreted in the light of a ring formed through hydrogen bond and also that the ring structure through hydrogen bond may explain other anomalies, particularly the peculiar effect which the ethyl group often exerts. The effect of the nature of carbon chain on the rate of acid catalysed and base catalysed prototropy of phenylalkyl ketones (Evans and Gordon, ibid., 1938, 1434) may be explained by the formation of such a ring containing four carbons as easily as by the three carbon ring. In this connection, Huggins (J. Org. Chem., 1936, 407) has pointed out that in general, hydrogen bonds are more stable when the distances through which the bond operates are small. This type of ring must by its very nature be quite unstable. Liquids, referred to above, should have this type of unstable ring structure through the hydrogen bond. There is formed at the interface of such a liquid and aqueous phase an electrical double layer, as suggested by Helmholtz, Gouy and others (McBain, "Colloid Science", 1950) and correspondingly, there exists a double layer potential.

Much work has been done by Beutner, Loeb and Baur (Z. Elektrochem., 1913, 19, 509; 1926, 32, 547; Z. physikal. Chem., 1923, 104, 472; Rec. trav. chim., 1923, 42, 656) on potential differences existing between organic liquids and aqueous salt solutions. The double layer potential, which is due to the preferential adsorption of one or the other ion on the liquid interface, has been found to change, when the composition of the aqueous phase is changed.

The relation between double layer potential and interfacial tension between mercury and aqueous solution was first studied by Lippmann and others (Ann. chim. phys., 1875, 8, 494; Z. physikal. Chem., 1931, 154, 454; J. Phys. Chem., 1935, 39, 439). With increasing applied potential, the charge on mercury decreases and is then neutralised, the interfacial tension increases while this happens, reaching a maximum, when the charge is annulled. Further increase of potential develops opposite charge on the mercury, and the tension again begins to fall.

In the present work, such a double layer potential between the organic liquid and aqueous phase is presumed to be decreased by increasing ionic atmosphere in very dilute solutions with increase in soap concentration. With the consequent lowering of charge density at the interface, it is accompanied by an increase of surface tension. When the potential of the double layer is completely annulled by the increasing ionic atmosphere, the interfacial tension will be maximum. With increasing soap concentration, however, a double layer of opposite sign to the original will be formed, and the sign of potential is now reversed; with increase in charge density of this layer, now again the interfacial tension goes on decreasing. The development of the reversal of electrical double layer in case of esters and alcohols, referred to, should be ascribed to the unstable ring structure through the hydrogen bond. In case of other liquids, viz, butyl and
amyl alcohols, diethyl malonate and methyl acetate, there should not be H-bonding possibility, and so the reversal of double layer would not take place. Therefore, there is observed a gradual decrease of interfacial tension with increasing soap concentration over the entire range.

The work on interfacial tension variations at the interface between organic liquids, referred to, and mixed aqueous salt solutions viz., KCl-HgCl₂, KNO₃-Pb(NO₃)₂ etc. indicating complex formations between these salts, provides confirmation for this type of explanation. These results will be discussed in later papers.

In the case of isoamyl acetate (Fig. 2) such a behaviour is also observed with a very dilute solution of sodium acetate and sodium chloride, as in the case of colloidal electrolyte, sodium oleate. In a very dilute aqueous solution, soap behaves like an ordinary electrolyte and is considerably ionised into an alkali metal ion and a fatty acid ion. At an appreciable concentration, however, the anions aggregate together to form ionic micelles (McBain).

With the saponin solution (Table II), however, only the decrease in the interfacial tension is observed with its increasing concentration over the entire range, as it would not provide ionic atmosphere like an electrolyte.

The peak in interfacial tension is maximum with n-butyl acetate, ethyl isovalerate and sec.-octyl alcohol, viz., 5.5, 4.69 and 6.83 dynes/cm. respectively and minimum with hexyl alcohol, ethyl acetoacetate and ethyl acetate, viz., 0.87, 0.33 and 0.74 dynes/cm. respectively. It may be possible that the peak might be related to the degree of stability of the ring character through H-bond in these cases. Further work along these lines is in progress.

The authors are indebted to Dr. B. K. Vaidya, Assistant Director, Ahmedabad Textile Industrial Research Association for his suggestions and interest and also they express their gratitude to the college authority for the grant to meet the expenses incurred in the work.

CHEMISTRY DEPARTMENT,
M. T. B. COLLEGE, SURAT.

Received August 14, 1952.

INTERFACIAL TENSION OF LIQUIDS HAVING H-BOND RING STRUCTURE AND COMPLEX FORMATION. PART I.
HgCl₂—KCl—H₂O SYSTEM

By Miss HEMALATA J. KAZI AND C. M. DESAI

Measurements of interfacial tension between n-butyl acetate and solutions containing KCl and HgCl₂ in varying proportions indicate the formation of seven complexes in solution between KCl and HgCl₂ viz., (1) 4KCl. HgCl₂, (2) 3KCl. HgCl₂, (3) 2KCl. HgCl₂, (4) 3KCl. 2HgCl₂, (5) KCl. HgCl₂, (6) 2KCl. 3HgCl₂ and (7) KCl. 2HgCl₂.

The formation of three complexes between HgCl₂ and KCl in solution, namely, KCl. HgCl₂, KCl. 2HgCl₂, and 2KCl. HgCl₂ has been shown by measurements of solubility, conductivity and surface tension (Tichomiroff, J. Russ. Phys. Chem. Soc., 1907, 39, 731; Foote, Amer. Chem. J., 38, 236; Arcay and Marcot, Compt. rend.,
The existence of complex \( K_4(\text{HgCl}_6) \) in solution has been reported by others (Benrath, *Z. anorg. Chem.*, 1908, 56, 258; Dey, *Curr. Sci.*, 1946, 15, 24). Tournoeux's investigations (*Ann. chim. phys.*, 1919, ix, 11, 225) indicate the formation of complexes: (1) \( \text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O} \), (2) \( 2\text{HgCl}_2 \cdot \text{KCl} \cdot \frac{3}{4} \text{H}_2\text{O} \), (3) \( 3\text{HgCl}_2 \cdot 2\text{KCl} \cdot \frac{5}{3} \text{H}_2\text{O} \), (4) \( 2\text{HgCl}_2 \cdot 3\text{KCl} \cdot \frac{3}{5} \text{H}_2\text{O} \) and (5) \( 2\text{HgCl}_2 \cdot \text{KCl} \cdot \text{H}_2\text{O} \). The existence of \( (\text{HgCl}_4)^- \) and \( (\text{HgCl}_6)^- \) ions has been shown in solution by the study of solubility and Raman spectra (Garret, *J. Amer. Chem. Soc.*, 1939, 61, 2714; Nayar and Saraf, this *Journal*, 1943, 20, 312). The viscosity, refractive index and surface tension data (Nayar *et al.*, *ibid.*, 1952, 29, 241-254) obtained by the method of monovariation reveal the formation of six complexes: (1) \( 4\text{KCl} \cdot \text{HgCl}_2 \), (2) \( 2\text{KCl} \cdot \text{HgCl}_2 \), (3) \( 3\text{KCl} \cdot 2\text{HgCl}_2 \), (4) \( \text{KCl} \cdot \text{HgCl}_2 \), (5) \( 2\text{KCl} \cdot 3\text{HgCl}_2 \) and (6) \( \text{KCl} \cdot 2\text{HgCl}_2 \).

In the present investigation the method of monovariation (Nayar, *loc. cit*), which is eminently suited for the study of complexes in solution, has been adopted for interfacial tension measurements by the drop number method (Kazi and Desai this *Journal*, 1953, 30, 209) using n-butyl acetate against a series of mixed solutions of \( \text{HgCl}_2 \) and \( \text{KCl} \).

**Experimental**

The substances used were of A.R. quality (B. D. H.). The ester was further purified by treatment with sodium carbonate solution, washing with water, drying and distilling. The middle fraction was utilised for the purpose. Potassium and mercuric chlorides were further purified by repeated crystallisations from pure distilled water. \( \text{HgCl}_2 \) or \( \text{KCl} \) (24 c.c.) solutions were run into a glass-stoppered 100 c.c. flask from a calibrated burette. The requisite volumes of either \( \text{KCl} \) or \( \text{HgCl}_2 \) were then added and the mixture made up to 100 c.c. with distilled water. The results obtained by measurements of the interfacial tension of the solutions at 30\(^\circ\) are shown graphically in Fig 1 which also gives the results with the system \( \text{HgCl}_2 \cdot \text{NaCl} \cdot \text{H}_2\text{O} \).

**Discussion**

Fig. 1 shows peaks corresponding to the formation of complex compounds of molecular formulae: 4 KCl, \( \text{HgCl}_2 \), 3 KCl, \( 3\text{KCl} \cdot 2\text{HgCl}_2 \), 2 KCl, \( 3\text{KCl} \cdot \text{HgCl}_2 \), 2KCl, \( 3\text{KCl} \cdot 2\text{HgCl}_2 \) and KCl. \( 2\text{HgCl}_2 \). The tendency for complex formation is not evident in \( \text{HgCl}_2 \cdot \text{NaCl} \cdot \text{H}_2\text{O} \) system.

The authors are inclined to take the view that the formation of these complexes corresponds to:

\[
\begin{align*}
K_4(\text{HgCl}_6) & \rightarrow [K_4(\text{HgCl}_6)]^- \\
& \leftarrow [K_2(\text{HgCl}_3)]^- \\
K_2(\text{HgCl}_3) & \leftarrow [K(\text{HgCl}_3)]^- \\
& \leftarrow [2\text{HgCl}_2] \\
\end{align*}
\]

sequence resulting from changes in interionic character, due to variations in electrolyte concentration. The complex 3KCl, \( \text{HgCl}_2 \) is interpreted in the ratio 6KCl, \( 2\text{HgCl}_2 \).
for the sequence. The complex 2KCl, 3HgCl₂ is expressed as \( K_2(HgCl_4) \) and not as \( 2 \text{HgCl}_2 \) \( K \), because in that case the interionic character would not suffer such a significant change from that of (7) as to warrant maximum tension, corresponding to the peak in the curves.

**FIG. 1**

M/25-KCl (c.c.) added to 24 c.c. of M/50-HgCl₂.

The method is likely to prove a very sensitive one, because it reveals the tendency of complex formation in solutions of even very low concentrations. It therefore offers an advantage in the case of sparingly soluble salts or when salts are sparingly available.

The authors are grateful to the college authority for laboratory facilities and a grant to meet the expenses incurred in the work.

**Chemistry Department,**
M. T. B. College, Surat.

Received October 24, 1952.
INTERFACIAL TENSION OF LIQUIDS HAVING H-BOND RING STRUCTURE AND COMPLEX FORMATION. PART II. THE SYSTEMS KNO₃-Pb(NO₃)₂-H₂O AND NH₄NO₃-Pb(NO₃)₂-H₂O

BY MISS HEMLATA J. KAZI AND C. M. DESAI

Measurements of interfacial tension between n-buty] acetate and sec.-octyl alcohol against mixed solutions of KNO₃ (or NH₄NO₃) and Pb(NO₃)₂ indicate the formation of three complexes in the systems KNO₃-Pb(NO₃)₂-H₂O and NH₄NO₃-Pb(NO₃)₂-H₂O respectively.

The complex formation between Pb(NO₃)₂ and KNO₃ in solution has been indicated from the study of solubility and cryoscopic measurements (Le Blanc and Noyes, Z. physikal. Chem., 1890, 6, 386; Kanitz, ibid., 1897, 22, 347). Glasstone and others (J. Chem. Soc., 1923, 123, 2134; 1925, 2846) also added evidence of complex formation and indicated the probable existence of a double salt, viz. 2KNO₃·Pb(NO₃)₂. The existence of the complex 2NH₄NO₃·Pb(NO₃)₂ was indicated by Malquori (Chem. Zentr., 1928, II, 517; Atti R. Acad. Lincei, 1929, 9, 231; Gazzetta, 1929, 59, 355) from the study of conductivity and viscosity data of solutions of lead and ammonium nitrates. Recently, Nayar and Pande (Proc. Ind. Acad. Sci., 1948, 27A, 285, 353; 1949, 30A, 251; this Journal, 1951, 28, 112) showed by the study of viscosity, surface tension, E.M.F., transport number, magnetic susceptibility and thermometric titration measurements of mixtures of aqueous solutions of the above nitrates, the formation of complexes:

(a) KNO₃·Pb(NO₃)₂; 2KNO₃·Pb(NO₃)₂; 4KNO₃·Pb(NO₃)₂.
(b) NH₄NO₃·Pb(NO₃)₂; 2NH₄NO₃·Pb(NO₃)₂; 4NH₄NO₃·Pb(NO₃)₂.


The interfacial tension measurements of n-buty] acetate against mixed aqueous solutions of mercuric chloride and potassium chloride (this issue, Part I, p. 287) have indicated the formation of seven complexes in solution. The present investigation deals with the study of the systems (a) and (b) studied by Nayar and others (loc. cit.) by the authors' method. For the procedure, n-buty] acetate was selected for the system (a), and sec.-octyl alcohol for (b) to see whether it behaved in an analogous manner to n-buty] acetate, as it also seems to have an unstable H-bond ring structure (cf. Miss Kazi and Desai, Curr. Sci., 1952, 21, 218).

Experimental

The method of procedure adopted in preparing solutions of the nitrates was that of Nayar and Pande (loc. cit.); KNO₃, NH₄NO₃ and Pb(NO₃)₂, pure quality (E. Merck), were further purified by repeated crystallisations from distilled water. sec.-Octyl alcohol (Scheri}g-Kahlbaum) was distilled and the middle fraction was utilised for interfacial tension measurements.
Either KNO₃ or NH₄NO₃ solutions (20 c.c.) were pipetted into a flask, different volumes of Pb(NO₃)₂ solution were added and the mixture was made up to 60 c.c. with distilled water.

The interfacial tensions were measured by the method described earlier. The results obtained at 30° are shown graphically in Fig. 1.

**Discussion**

The figure shows peaks corresponding to the formation of the following complexes:

(a) KNO₃·Pb(NO₃)₂; 2KNO₃·Pb(NO₃)₂; 4KNO₃·Pb(NO₃)₂
(b) NH₄NO₃·Pb(NO₃)₂; 2NH₄NO₃·Pb(NO₃)₂; 4NH₄NO₃·Pb(NO₃)₂.

These results confirm the findings of Nayar and others (loc. cit.). Further, sec-octyl alcohol behaves as sensitively as n-butyl acetate in the indication of complex formation in solution.

The authors are grateful to the college authority for laboratory facilities and a grant to meet the expenses incurred in the work.

Chemistry Department,
M. T. B. College, Surat.

Received October 24, 1952.
It was observed by Le Blanc and Noyes (Z. physikal. Chem., 1890, 6, 386) that solubility of Pb(NO₃)₂ in water at ordinary temperature was increased by the presence of KNO₃, but decreased by NaNO₃. The same conclusion was arrived at by Kanitz, Glasstone and others (ibid., 1897, 22, 347; J. Chem. Soc, 1923, 123, 2134). The difference in the behaviour of the potassium salt from that of sodium salt was ascribed to the formation of its potassium double salt with lead nitrate in solution. Lewis and others (Dissert. Breslau, 1908; J. Chem. Soc. 1923, 123, 2134; Trans. Faraday Soc. 1907, 2, 199; Z. elektrochem., 1904, 10, 77; Z. anorg. Chem., 1898, 17, 327) however, observed that the addition of either KNO₃ or NaNO₃ to a solution of Pb(NO₃)₂ caused a considerable decrease in plumbous ion concentration, thus indicating complex formation in each case, though to a greater extent with potassium salt. The conductance, viscosity and thermometric measurements (Proc. Ind. Acad. Sci., 1948, 27A 293; this Journal, 1951, 28, 112) led Nayar and Pande to conclude that no complex formation took place between NaNO₃ and Pb(NO₃)₂, but transport number measurements (Proc. Ind. Acad. Sci., 1948, 27A, 359) indicated a tendency for the formation of complex, as originally pointed out by Lewis. They, however, observed that definite complexes obeying stoichiometric laws did not seem to exist in NaNO₃—Pb(NO₃)₂—H₂O system.

The authors have examined the possibility of complex formation by the method of interfacial tension measurement.

**Experimental**

Lead nitrate and sodium nitrate (E. Merck) were recrystallised from distilled water and their stock solutions (M/10) were prepared in distilled water.

**Fig. 1**

![Graph showing interfacial tension changes](image_url)
NaNO₃ solution (20 c.c.) was pipetted into a flask to which different volumes of Pb(NO₃)₂ solution were added and the total volume was made up to 60 c.c. with distilled water. In another set of experiments 10 c.c. of Pb(NO₃)₂ solution were taken and different volumes of NaNO₃ solution were added and the mixture was made up to 60 c.c.

The interfacial tensions were measured in the same manner as described in Part I (this issue, p. 287) at 30°. The results obtained are shown graphically in Fig. 1.

**Discussion**

Fig 1 shows peaks corresponding to the formation of the following complexes; NaNO₃. Pb(NO₃)₂; 2NaNO₃. Pb(NO₃)₂; 4NaNO₃. Pb(NO₃)₂. These results are in conformity with the conclusions (qualitative) arrived at by Lewis and others (loc. cit). This method of interfacial tension measurements of a liquid with unstable H-bond ring structure being extremely sensitive, opens a wide field in the investigations of the existence of complex in salt solutions, in as much as it reveals that definite complexes, obeying stoichiometric laws, also seem to exist in NaNO₃—Pb(NO₃)₂—H₂O system, just as in the case of analogous potassium and ammonium nitrate systems. The authors consider that the following equilibrium sequence exists:

\[
M [\text{Pb(NO₃)₂}] \leftrightarrow M_2 [\text{Pb(NO₃)₄}] \leftrightarrow M_4 [\text{Pb(NO₃)₆}]
\]

as a result of changes in the interionic character, due to variations in electrolyte concentration, where M is either potassium, ammonium or sodium in the system.

The authors are grateful to the college authority for laboratory facilities and a grant to meet the expenses incurred in the work.

**Chemistry Department,**

**M. T. B. College, Surat**

*Received October 24, 1952.*
INTERFACIAL SURFACE TENSION AND COMPLEX FORMATION IN SALT SOLUTIONS

BY

(Miss) HEMILATA J. KAZI AND C. M. DESAI

Reprinted from "Current Science," January, 1953, 22, 18
INTERFACIAL SURFACE TENSION AND COMPLEX FORMATION IN SALT SOLUTIONS

Nayar and co-workers\textsuperscript{1,2} have shown the formation of complexes in various systems, such as Pb(NO\textsubscript{3})\textsubscript{2}-KNO\textsubscript{3}-H\textsubscript{2}O, by the presence of anomalous values of physical properties at concentrations corresponding to their formation. Similar peaks are also found in the curves obtained by plotting interfacial tension of liquids having unstable H-bond ring structure against the concentration of any one variant. Using the drop number method,\textsuperscript{3} the authors have found peaks in the surface tension-concentration curve with the system CdI\textsubscript{2}-KI-H\textsubscript{2}O, corresponding to the complexes CdI\textsubscript{2}.2KI and CdI\textsubscript{2}KI. Further, seven complexes in case of the system HgCl\textsubscript{2}-KCl-H\textsubscript{2}O, seven in HgBr\textsubscript{2}-KBr-H\textsubscript{2}O and three in case of the system Pb(NO\textsubscript{3})\textsubscript{2}-NaNO\textsubscript{3}-H\textsubscript{2}O seem to be formed. In other cases, the results of Nayar, et al., are confirmed. Auto-

complex formation in case of salts like cadmium iodide, cupric chloride, etc., is evident from the results of such interfacial tension measurements. Experimental details of the study of all these systems with full discussion of the theory of reversal of electrical double layer at interface of liquids, referred to, will be published elsewhere.

Chemistry Dept., \textit{(Miss) HEMLATA J. KAZI.} 
M. T. B. College, \textit{C. M. DESAI.} 
Surat, \textit{October 1, 1952.}