Binding of Water & Organic Liquid Components (Ethyl Alcohol, Methyl Alcohol, Propyl Alcohol, Formic Acid, Acetone, Pyridine & Glycerol) at Interface & the Gibbs Surface Excess

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With the help of a phase dividing plane, a liquid column containing a mixture of water and an organic liquid may be physically divided into the bulk and interfacial phases. The surface excess Γ_1 of water for this mixture becomes equal to $\Delta n_1' - \Delta n_2' X_1/X_2$ where X_1 and X_2 are the bulk mole fractions of the water and the organic liquid components respectively. $\Delta n_1'$ moles of water may be imagined to be bound to $\Delta n_2'$ moles of the organic liquid thus forming an interfacial phase. From the variation of surface tension of the binary liquid mixture with the change in the partial vapour pressure of water, Γ_1 has been calculated using the Gibbs adsorption equation. For water mixed in varying amounts with an organic liquid such as pyridine, formic acid, methyl alcohol, ethyl alcohol or propyl alcohol, Γ_1 is observed to vary linearly with X_1/X_2 in the wide range of the mole ratio composition of the mixture. From the slope and intercept of this linear plot, $\Delta n_1'$ and $\Delta n_2'$ may be calculated for each liquid mixture. Analysis of the results further indicates that the bound liquid components in the interfacial phase form a monomolecular layer so that the effective cross-sectional area of the oriented organic molecule at the interface may be computed. Validity of the monolayer model for the surface phase allows the calculation of $\Delta n_1'$ and $\Delta n_2'$ even when Γ_1 versus X_1/X_2 plot is non-linear. In the case of glycerol-water and acetone-water mixtures, the organic molecules at the interface are observed to alter their orientations as the water content in the bulk phase is significantly decreased.

WILLARD Gibbs[1] introduced the concept of the surface excess of a component in a multicomponent solution by imaginarily dividing a column of such liquid with the help of a mathematical plane. McBain[2] presented precise experimental evidence in support of this concept. Guggenheim and Adam[3] pointed out some difficulties associated with the physical concepts of the Gibbs surface excess quantity. Guggenheim[4] presented an alternative derivation of the Gibbs adsorption equation assuming certain physical thickness for the interfacial phase. Several workers[5] have estimated the thickness of this phase from the experimental data. Efforts[6,7] have recently been made by various workers to clarify the concepts of the surface excess and the surface phase from different approaches of thermodynamics.

In the present paper, an attempt has been made to evaluate the absolute amount of water and organic liquid components bound to each other in the interfacial phase of a binary solution. The data on the surface tension of various liquid mixtures have been used appropriately for the evaluation of such binding. Following a similar approach[8], the absolute compositions of the interfacial phases

associated with various electrolyte solutions have also been estimated by us previously.

Interfacial Binding

Let us imagine that n_1^t moles of water (component-1) is mixed with n_2^t moles of an organic liquid (component-2) as a result of which a binary solution in the shape of a liquid column $AA'PP'$ (Fig. 1) is formed. Let the vapour phase above
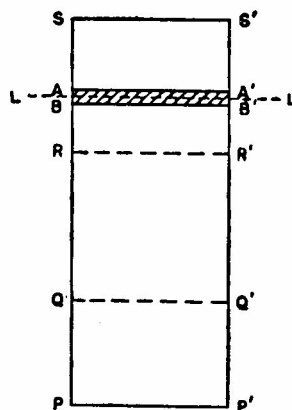

Fig. 1 — Model column for a liquid mixture

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the liquid column be represented $AA'SS'$ and the area of the air-water interface formed at the top of this liquid column be one square centimeter. Because of the existence of the interfacial-free energy, the amount of the two components in the surface region will be different from those present in the bulk of liquid at the bottom and also from those present in the vapour phase. Let C_1 and C_2 stand for the concentrations of the two components in the bulk liquid in moles per unit volume. Similarly $\overline{C_1}$ and $\overline{C_2}$ are concentrations of these components in the vapour phase above the liquid column. According to Defay and Priggogine[6], the balance of the masses of the overall system of this type may lead to Eqs. (1) and (2),

$$n_1^t = \Delta n_1' + C_1 V + \overline{C_1} \overline{V} \qquad \ldots(1)$$

$$n_2^t = \Delta n_2' + C_2 V + \overline{C_2} \overline{V} \qquad \ldots(2)$$

where V and $\overline{V}$ are the volumes of the liquid and vapour phases respectively. $\Delta n_1'$ and $\Delta n_2'$ moles are the absolute amounts of components bound to each other forming the interfacial phase $AA'BB'$. Below this surface bound phase, there exists the entire bulk phase $BB'PP'$ in which n_1 (or C_1V) moles of component-1 is mixed with n_2 (or C_2V) moles of component-2 uniformly throughout the space so that n_1/n_2 becomes equal to X_1/X_2 and

$$n_1 - n_2 \frac{X_1}{X_2} = 0 \qquad \ldots(3)$$

where X_1 and X_2 are the bulk mole fractions of the two components in the mixture. The two components in the bulk phase will be referred to exist in the free state of mixing. The location of the plane BB' is such that the mole ratio composition of the entire bulk liquid region below this plane is X_1/X_2 (or C_1/C_2), whereas above it, the composition in the interfacial region may deviate from this value because of the influence of interfacial energy. In a similar manner, the position of AA' may be defined such that the mole ratio composition of the vapour phase above the plane is uniformly $\overline{C_1}/\overline{C_2}$, whereas below it, the value of this ratio may deviate from $\overline{C_1}/\overline{C_2}$. The composition of the interfacial region thus varies in a gradient manner from C_1/C_2 to $\overline{C_1}/\overline{C_2}$ between the planes AA' and BB' in agreement with the concepts of the interfacial phase according to Tolman[9] and others based on statistical mechanics and thermodynamics[4].

Neglecting the volume of the interfacial phase $AA'BB'$ which is normally infinitesimally small, the total volume V_t of the system may equal $V + \overline{V}$ so that one may write from Eqs. (1) and (2),

$$\Delta n_t' = n_1^t - C_1 V_t + \overline{V}(C_1 - \overline{C_1}) \qquad \ldots(4)$$

$$\Delta n_2' = n_2^t - C_2 V_t + \overline{V}(C_2 - \overline{C_2}) \qquad \ldots(5)$$

Eliminating $\overline{V}$ from Eqs. (4) and (5) and assuming

$$C_1 \ggg \overline{C_1} \text{ and } C_2 \ggg \overline{C_2}$$

one may obtain the relations,

$$n^t - n_2^t \frac{X_1}{X_2} = \Delta n_1' - \Delta n_2' \frac{X_1}{X_2} \qquad \ldots(6)$$

and

$$n_2^t - n_1^t \frac{X_2}{X_1} = \Delta n_2' - \Delta n_1' \frac{X_2}{X_1} \qquad \ldots(7)$$

Here C_1/C_2 has been replaced by X_1/X_2.

Since Willard Gibbs[1] introduced his unique concept of the surface excess, the surface chemists[6,10,11] have accepted the operative definition of the relative excess quantities Γ_1 and Γ_2 of a binary solution given by Eqs. (8) and (9).

$$\Gamma_1 = n_1^t - n_1^t \frac{X_1}{X_2} \qquad \ldots(8)$$

$$\Gamma_2 = n_2^t - n_t^t \frac{X_2}{X_1} \qquad \ldots(9)$$

Combining these relations, it may also be shown that

$$X_1 \Gamma_2 + X_2 \Gamma_1 = 0 \qquad \ldots(10)$$

This is well-known Guggenheim-Adam relation[3] which at once indicates that is at a given X_1/X_2, Γ_1 is calculated with the help of the Gibbs adsorption equation, the value of Γ_2 becomes automatically fixed and it is equal to $-(X_2 \Gamma_1/X_1)$. Γ_1 and Γ_2 are thus interdependent and their signs are opposite to each other. Here Γ_1 and Γ_2 do not stand for the absolute composition of the two components at the interface. The surface excess of a strong adsorbate is positive and its value is believed to be close to the absolute value of this component within the interfacial phase.

The surface chemists even to date have faced difficulties in determining the absolute values $\Delta n_1'$ and $\Delta n_2'$ because in their opinion the actual position of the interfacial plane BB' dividing the interfacial phase from the bulk region cannot be determined with precision[6,10,11]. Following an alternative approach, these workers have divided the liquid column into an imaginary surface and bulk phases by placing a dividing plane at arbitrary position PP', QQ' or RR', etc. Equations (8) and (9) are consistent with this concept of artificial division so that the imaginary surface phase is assumed to be composed of n_1^t and n_2^t moles of the two liquid components. In reality, this composition is related to the formation of the whole liquid column $AA'PP'$ containing both the surface and bulk phases. Further, at a fixed liquid composition, n_1^t and n_2^t may also be varied arbitrarily so that his liquid mixture may enclose lesser volume space $AA'QQ'$ (or $AA'RR'$, etc.). This shows that the expression of the interfacial composition in terms of n_1^t and n_2^t may become imaginary without any physical significance. Because of this, certain conceptual difficulties may occur in some cases if Eq. (8) is used as the expression for the surface excess. This will be discussed in a later section.

In our opinion, Γ_1 and Γ_2 may be most rationally expressed by the relations,

$$\Gamma_1 = \Delta n_1' - \Delta n_2' \frac{X_1}{X_2} \qquad \ldots(11)$$

$$\Gamma_1 = \Delta n_2' - \Delta n_1' \frac{X_2}{X_1} \qquad \ldots(12)$$

These two equations can easily be converted to the forms which are similar to the expressions for the composite isotherms used by Kipling[12], Schay and Nagy[13]. Equations (11) and (12) indicate that a bulk phase $BB'PP'$ (or $BB'QQ'$, etc.) of a given composition X_1/X_2 is associated with a physically defined interfacial phase $AA'BB'$ containing $\Delta n_1'$ and $\Delta n_2'$ moles of liquid components. At a given value of X_1/X_2, $\Delta n_1'$ and $\Delta n_2'$ are definite and independent of the positions PP', QQ', RR', etc. The composition of the interfacial phase is by definition not equal to its bulk composition X_1/X_2, and the bulk and the interfacial phases are separated by a real phase dividing plane BB'.

In Eqs. (6) and (7), Γ_1 and Γ_2 will remain the same whether these quantities are defined by Eqs. (8) and (9) or by more rational Eqs. (11) and (12). The variations of n_1^i and n_2^i in Eq. (9) with the position PP', QQ', RR', etc., are due to the involvement of variable amounts of bulk phases $BB'PP'$, $BB'QQ'$, $BB'RR'$, etc., with the actual interfacial phase $AA'BB'$ thus forming different volumes of the imaginary interfacial phases.

From Eqs. (11) and (12), it is apparent that at a given value of X_1/X_2, $\Delta n_1'$ and Δn_2 and hence Γ_1 and Γ_2 are definite and independent of positions PP', QQ', RR', etc. Each component in the liquid column $AA'PP'$ is existing partly in the surface bound and partly in the bulk (free) states of mixing so that n_1^i and n_2^i in Eqs. (8) and (9) may be replaced by $n_1+\Delta n_1'$ and $n_2+\Delta n_2'$ and

$$\Gamma_1 = \left(\Delta n_1' - \Delta n_2' \frac{X_1}{X_2}\right) + \left(n_1 - n_2 \frac{X_1}{X_2}\right) \qquad ...(13)$$

The last term is zero according to the relation (3) so that unlike n_1^i and n_2^i, Γ_1 and Γ_2 defined by Eqs. (8) and (9) remain invariant to the imaginary position of the dividing plane.

Γ_1 and Γ_2 may be calculated from the experimental data with the help of the Gibbs adsorption equations which at a given temperature will be given by

$$\Gamma_1 = -\frac{a_1}{RT}\frac{d(\gamma)}{da_1} \qquad ...(14)$$

$$\Gamma_2 = -\frac{a_2}{RT}\frac{d\gamma}{da_2} \qquad ...(15)$$

Here a_1 and a_2 stand for the activities of the respective components in the mole fraction scale and γ represents the surface tension of the liquid mixture. R and T are the gas constant and absolute temperature respectively.

From the data of surface tension of liquid mixtures, an attempt has been made in the subsequent sections to evaluate the absolute compositions of the interfacial phase $AA'BB'$ in terms of $\Delta n_1'$ and $\Delta n_2'$.

Evaluation of the Surface Excess

The surface tensions of the following liquid mixtures in the whole range of liquid compositions are considered in this paper: pyridine-water[14] at 50°; formic acid-water[14] at 30°; acetone-water[14] at 25°; propyl alcohol-water[14] at 25°; glycerol-water[14] at 25°; ethyl alcohol-water[3] at 25° and methyl alcohol-water[10] at 30°. The partial vapour pressures

p_2 of the organic liquid for the various compositions of the mixtures of pyridine and water[14] at 50°, formic acid and water[14] at 30°, acetone and water[14] at 25°, glycerol-water[14] at 25°, propyl alcohol and water[14] at 25° have also been taken from the literature. The vapour in contact with the liquid mixture at any given composition may be regarded to behave as an ideal gas mixture so that Eq. (15) may be written in the form[3]

$$\Gamma_2 = -\frac{p_2}{RT}\frac{d\gamma}{dp_2} \qquad ...(16)$$

Values of $d\gamma/dp_2$ for various liquid mixtures at a given p_2 have been obtained by plotting γ against p_2 and determining the slope of the curve by the chord-area method[15]. Γ_2 is then calculated for various values of p_2 (or X_2) using Eq. (16). Γ_2 for methyl alcohol-water and ethyl alcohol-water mixtures calculated in this manner has already been reported in the literature[3,10]. The values of Γ_2 for these two systems have been used by us directly. Using values of Γ_2, X_1 and X_2, the negative surface excess Γ_1 of water in the liquid mixture is estimated as function of X_1/X_2 with the help of Eq. (10).

Evaluation of $\Delta n_1'$ and $\Delta n_2'$

In Figs. 2-4, variation of the negative surface excess Γ_1 of water for different mole ratio compositions X_1/X_2 of the various liquid mixtures are shown graphically. Such a plot for the pyridine-water mixture is linear in the entire range of pyridine mole fractions 0·01 to 0·60 considered by us. The magnitudes of the intercept and the slope values of the linear plot represent the respective values of $\Delta n_1'$ and $\Delta n_2'$ according to Eq. (11). In the range of mole fractions 0·04 to 0·20 for
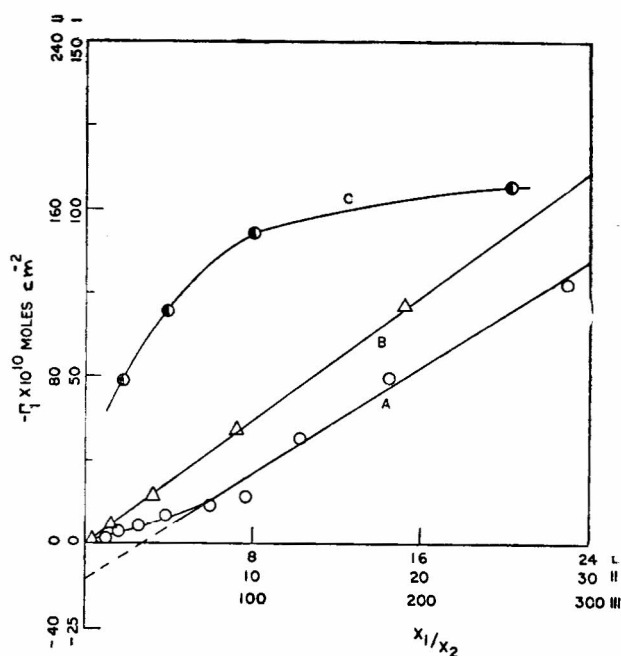

Fig. 2 — Surface excess (Γ_1) of water as a function of the mole ratio composition X_1/X_2 [(A) Formic acid+H_2O, low X_1/X_2 (scale I-I); (B) pyridine+H_2O (scale II-I); and (C) formic acid+H_2O, high X_1/X_2 (scale III-II)]

formic acid, this type of plot is linear with significant positive slope and negative intercept so that $\Delta n_1'$ and $\Delta n_2'$ for this system may also be evaluated. In Fig. 3, Γ_1 is observed to vary linearly with the change in the mole ratio composition for the aqueous mixtures of methyl alcohol,
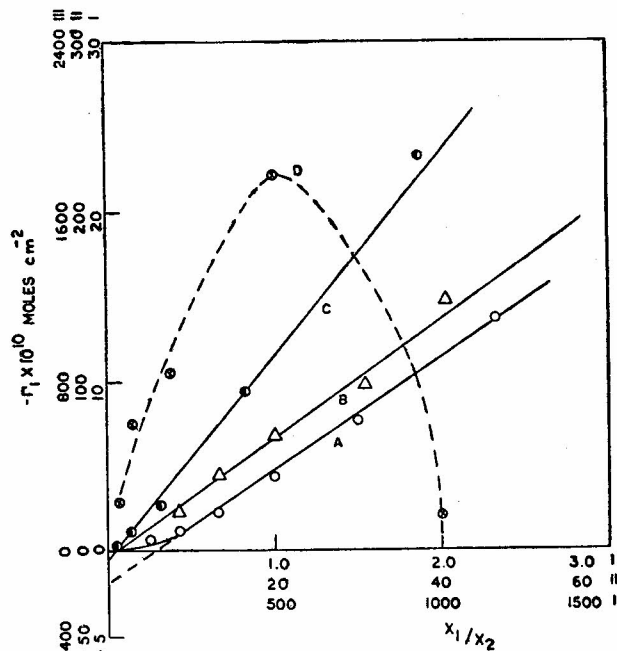
ethyl alcohol and propyl alcohol in the range of mole fractions 0·2 to 0·9, 0·05 to 0·60 and 0·03 to 0·50 for the respective organic components. The values of $\Delta n_1'$ and $\Delta n_2'$ evaluated for all these systems with the help of Eq. (11) along with their standard deviations, are presented in Table 1. It is apparent from Table 1 that $\Delta n_2'$ for all these liquid mixtures are positive and their magnitudes lie in the range 10^{-9} to 10^{-10} mole cm^{-2}. $\Delta n_1'$ for these cases are also positive and the order of their values lies between 10^{-9} and 10^{-11} mole cm^{-2}.

In the light of Eqs. (8) and (11), let us now more critically examine the physical meaning of the two constants evaluated from the linear plot of Γ_1 against X_1/X_2. The feature of this plot indicates that these two constants must be independent of X_1/X_2 so that they cannot be identified with n_1^t and n_2^t according to Eq. (8). This is because of the fact that either n_1^t or n_2^t or both have to vary with changes in X_1/X_2, and Γ_1 versus X_1/X_2 plot should never be linear according to Eq. (8). The linear plot thus indicates that Eq. (8) is

Fig. 3 — Surface excess (Γ_1) of water as a function of the mole ratio composition X_1/X_2 [(A) Ethyl alcohol+H_2O (scale I-I); (B) methyl alcohol+H_2O (scale I-I) (C) propyl alcohol+H_2O, low X_1/X_2 (scale II-II); and (D) propyl alcohol+H_2O, high X_1/X_2 (scale III-III)]

TABLE 1 — VALUES OF $\Delta n_1'$ AND Δn_2 FROM LINEAR PLOTS

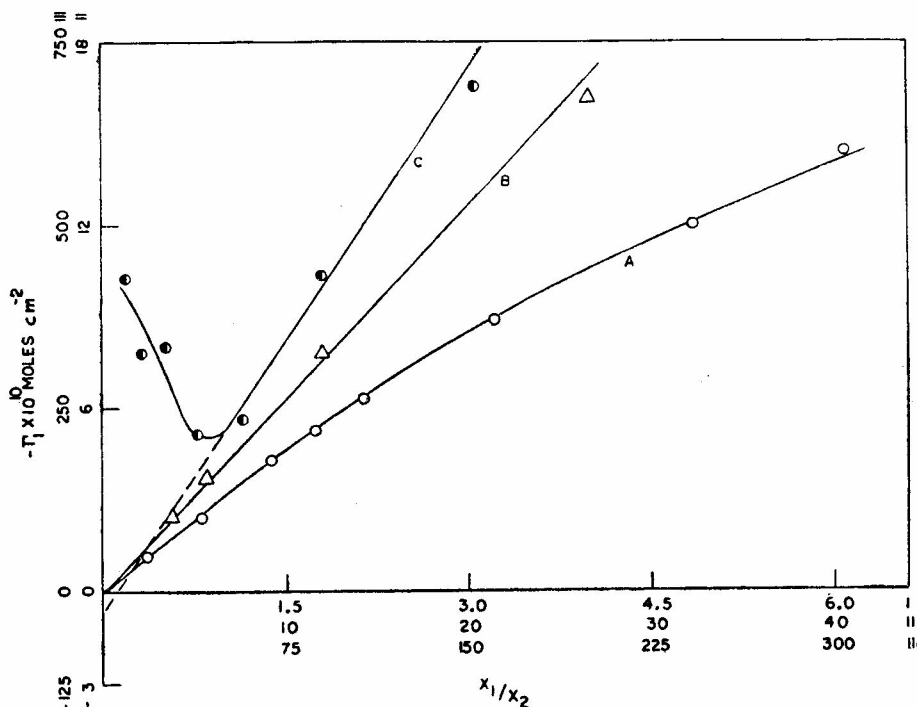| Liquid system	$\Delta n_2' \times 10^{10}$ (mole/cm²)	$\Delta n_1' \times 10^{10}$ (mole/cm²)	$\sigma_2 \times 10^{16}$ (cm²/molecule)
1. Pyridine+H_2O	3·72±0·01	0·20±0·15	44·4
2. Formic acid+H_2O	3·87±0·07	9·38±0·58	18·8
3. Methyl alcohol+H_2O	6·89±0·13	0·44±0·23	24·2
4. Ethyl alcohol+H_2O	6·60±0·20	1·91±0·34	22·4
5. Propyl alcohol+H_2O	5·98±0·47	4·35±0·68	20·0
6. Acetone+H_2O	3·40	5·00	34·5
7. Glycerol+H_2O	0·89	0·60	181·0

Fig. 4 — Surface excess (Γ_1) of water as a function of the mole ratio composition X_1/X_2 [(A) Acetone+H_2O, low X_1/X_2 (scale I-I); (B) acetone+H_2O, high X_1/X_2 (scale III-III); and (C) glycerol+H_2O (scale II-II)]

incorrect and inconsistent for the physical description of the real interfacial phase of constant composition even though the value of Γ_1 expressed by this equation is correct. The two constants evaluated from the linear plot must be free from X_1 and X_2 terms of bulk so that they may be rightly identified with $\Delta n_1'$ and $\Delta n_2'$ according to Eq. (11). The actual composition of the interfacial phase in terms of $\Delta n_1'$ and $\Delta n_2'$ remains thus unaltered with the variation of the composition of the bulk phase. The change of surface energy Υ at constant composition of the interfacial phase possibly indicates that the surface activity coefficient does not remain constant when the composition of the bulk phase is altered.

To make the above conclusion pointedly complete, it is further necessary to demonstrate that the slope and the intercept of the linear plot do not represent some fraction values of the total moles of the two components in the interfacial phase. To prove this proposition, one may divide the actual interfacial phase by placing an imaginary plane LL' within $AA'BB'$ so that $\Delta n_1'$ and $\Delta n_2'$ become respectively equal to $\Delta n_1^f + \Delta n_1^s$ and $\Delta n_2^f + \Delta n_2^s$. Here Δn_1^f and Δn_2^f are moles of components existing in the first layer $AA'LL'$ of interface and Δn_1^s and Δn_2^s are the components present in the second interfacial layer $LL'BB'$. Eq. (11) will then read

$$\Gamma_1 = \left(\Delta n_1^f - \Delta n_2^f \frac{X_1}{X_2}\right) + \left(\Delta n_1^s - \Delta n_2^s \frac{X_1}{X_2}\right) \qquad ...(17)$$

The evaluated constants of our linear plots cannot also be identified with Δn_1^f and Δn_2^f since $\Delta n_1^s / \Delta n_2^s \neq X_1/X_2$ according to our definition of the interfacial phase. The two constants of the linear plot thus represent the absolute compositions $\Delta n_1'$ and $\Delta n_2'$ of the physically defined interfacial phase as a whole. The linear plot also gives experimental evidence that the position of the Gibbs dividing plane is not arbitrary but is fixed at a physically well-defined position BB'. Below this plane, there exists bulk phase of composition X_1/X_2 and above it is the interfacial phase composed of $\Delta n_1'$ and $\Delta n_2'$ moles of the two components.

Monolayer Model

From the geometric standpoint, let us now make an extra-thermodynamic assumption that the bound phase $AA'BB'$ of 1 cm² interfacial area is a monomolecular layer so that one will be permitted to write Eq. (18).

$$N(\sigma_1 \Delta n_1' + \sigma_2 \Delta n_2') = 1 \qquad ...(18)$$

Here σ_1 and σ_2 are the effective cross sectional areas (in cm²) per surface bound water and organic molecule respectively and N is the Avogadro number. σ_1 may be put[16] equal to 10×10^{-16} cm² per molecule so that by inserting appropriate values of $\Delta n_1'$ and $\Delta n_2'$ from Table 1 in Eq. (18), σ_2 for methyl, ethyl and propyl alcohols are calculated to be 24, 22 and 20 Å²/mole respectively. These agree well with the values of σ_2 for the alcohol systems obtained by others after using various surface chemical techniques[11]. Here the hydrocarbon chains are assumed

to be oriented in the vertical direction with respect to the interfacial plane. σ_2 for the formic acid molecule is 19 Å² which is also very reasonable. σ_2 for a surface bound pyridine molecule is as high as 44 Å². This suggests that the large pyridine ring is oriented parallel to the interfacial plane. From all these results, it appears that our assumption about the monolayer nature of the surface bound phase may be essentially valid. Many other workers[11,12] have also shown that the adsorbed phase of the non-electrolytes at the solid-liquid and gas-liquid interfaces are monomolecular in nature.

Thus for mixture of organic liquid and water, the interfacial phase is made up of a monolayer formed by these two components in which water always exists as a negative surface excess. The concentration of organic liquid in water in the interfacial phase may be regarded to be considerably higher than that of the attached bulk phase concentration of the non-aqueous component. However, the average packing of the molecules within the surface layer may be inhomogeneous. Further for different orientations of the adsorbed molecules, varied and significant amounts of the surface void may appear in the interfacial phase. The effects of all these factors are implicitly included in σ_2.

Using the surface tension data of various aqueous solutions of electrolytes, we have previously shown[8] that significant amount of water bound with negligibly small amount of an inorganic electrolyte may form multimolecular layers at the interfacial phase. The number of such interfacial layers may range from 2 to as high as 100 depending upon the nature and valency of the ions composing the electrolyte. Thus, in the presence of KCl, NaNO₃, K₂SO₄, MgCl₂, MgSO₄, Al₂(SO₄)₃ the number of water layers existing in the interfacial phase are shown to be 3, 2, 3, 4, 31 and 19 respectively. In all these cases of electrolyte solutions, water is behaving as positive surface excess. The concentration of the electrolyte in the interfacial water is insignificant compared to the high aqueous concentration of the electrolyte in the bulk.

Binding in the Non-linear Region

The linear plot between Γ_1 and X_1/X_2 according to Eq. (11) will be valid only so long $\Delta n_1'$ and Δn_2 themselves are independent of the mole ratio composition X_1/X_2. When X_1/X_2 is very high or very low, the plots of Γ_1 versus X_1/X_2 for the alcohols and formic acid deviate significantly from linearity (vide Figs. 2 and 3) because of the dependence of $\Delta n_1'$ and Δn_2 on X_1/X_2 in this region of concentration. In the case of propyl alcohol, the plot in the region of high water content becomes dome-shaped because of the significant variation of $\Delta n_1'$ and Δn_2 with X_1/X_2. It may be pointed out here that Eq. (11) may be suitably combined with the Gibbs Eq. (15) so that the resulting equation after replacement of the term a_1 by X_1 (ideal equation) may be integrated at constant values of $\Delta n_1'$ and $\Delta n_2'$ leading to the relation of the form

$$\frac{\Upsilon}{RT} = \Delta n_1' \ln X_1 + \Delta n' \ln(1 - X_1) + \text{constant} \qquad ...(19)$$

TABLE 2 — VALUES OF Δn_1 AND $\Delta n_2'$ IN THE NON-LINEAR REGION

X_1/X_2	$-\Gamma_1 \times 10^{10}$ (mole/cm²)	$\Delta n_2' \times 10^{10}$ (mole/cm²)	$\Delta n_1' \times 10^{10}$ (mole/cm²)	$\sigma_2 \times 10^{16}$ (cm²/molecule)	$\Gamma_2 \times 10^{10}$ (mole/cm²)
		PROPYL ALCOHOL+H_2O			
999·0	163·0	0·18	18·0	20·0	0·16
499·0	1777·5	3·58	10·0	20·0	3·55
199·0	835·6	4·24	8·9	20·0	4·20
82·3	594·9	7·24	2·0	20·0	7·23
37·5	234·4	6·29	4·1	20·0	6·20
		METHYL ALCOHOL+H_2O			
39·0	122·0	3·35	8·60	24·2	3·13
19·0	73·5	4·21	6·58	24·2	3·87
9·0	50·0	5·85	2·65	24·2	5·56
4·0	27·5	6·87	0·44	24·2	6·87
		FORMIC ACID+H_2O			
253·0	170·7	0·74	15·8	18·8	0·67
99·4	148·5	1·64	14·0	18·8	1·49
48·4	110·8	2·54	12·2	18·8	2·29
22·9	77·5	3·80	9·9	18·8	3·37
		GLYCEROL+H_2O			
46·0	22·9	0·83	15·3	181·0	0·50

For very dilute solutions when $X_1 \to 0$, Υ according to Eq. (19) may tend to an absurd value of infinity. It is thus a thermodynamic requirement that the plot $-\Gamma_1$ versus X_1/X_2 should not be linear when X_1 or X_2 tend to zero. For many liquid mixtures considered by us this kind of non-linear feature has been exhibited in Figs. 2-4. For a few other systems, accurate values of Υ for low values of X_1 or X_2 are not available.

Assuming the validity of the monolayer model for the interfacial phase, $AA'BB'$ in the non-linear region also and combining Eqs. (11) and (18), it may be shown that

$$\Delta n_2' = \frac{\dfrac{1}{N\sigma_1} - \Gamma_1}{\dfrac{\sigma_2}{\sigma_1} + \dfrac{X_1}{X}} \qquad ...(20)$$

and

$$\Delta n_1' = \Delta n_2' \frac{X_1}{X_2} + \Gamma_1 \qquad ...(21)$$

Values of Δn_2 and $\Delta n'$ for several compositions of a liquid mixture calculated with the help of Eqs. (20) and (21) are presented in Table 2 assuming plausible values of σ_2. From the scrutiny of the results in Table 2, it appears that $\Delta n_1'$ increases with increase of the water content of the bulk and simultaneously Δn_2 is reduced in appropriate proportions. In the case of ethyl alcohol-water and formic acid-water mixtures, the non-linear behaviour in the low region of X_1/X_2 may be explained in a similar manner.

From Eqs. (11) and (12), it has been noted with interest that

$$\Gamma_1 = \Delta n_1' \left[1 - \frac{X_1/X_2}{\Delta n_1'/\Delta n_2'} \right] \qquad ...(22)$$

$$\Gamma_2 = \Delta n_2' \left[1 - \frac{X_2/X_1}{\Delta n_2'/\Delta n_1'} \right] \qquad ...(23)$$

For relatively strong surface active component such as propyl alcohol, $\Delta n_2/\Delta n_1' \gg X_2/X_1$ so that $s\Gamma_2$ according to Eq. (23) is very close to Δn^2 (vide Table 2). For strong adsorbents, therefore, $\Delta n_2'$ may be replaced by Γ_2 without making any significant error. However, for weak surface active components, viz. methyl alcohol, formic acid and glycerol, Γ_2 is less than Δn_2 because of some contribution of the second term of Eq. (23). For all the liquid mixtures considered here, the term $(X_1/X_2)/(\Delta n_1'/\Delta n_2)$ is significantly greater than unity so that Γ_1 in Eq. (22) is always significantly negative. Γ_1 and Δn_1 thus differ in magnitude and sign. For large value of the second term of Eq. (22), Γ_1 becomes nearly equal to $-(X_1/X_2)/\Delta n_2'$, and Γ_2 becomes again approximately equal to $\Delta n_2'$ in the light of Eq. (10). Values of Γ_1 are very important for the evaluation of $\Delta n_1'$ and $\Delta n_2'$ using Eq. (11).

Molecular Orientation at the Interface

For the range of glycerol mole fractions 0·05 to 0·15, the plot of $-T_1$ against X_1/X_2 appears to be linear (Fig. 4). From the slope and the intercept of this plot, $\Delta n_1'$, $\Delta n_2'$ and σ_2 are calculated in the usual manner. Value of σ_2 is as high as 181 Å² (vide Table 1) which may not be unexpected if the glycerol molecule in the interfacial monolayer is assuming flat orientation with three of its attached hydroxyl groups directed towards the water component in the bulk phase. Values of $\Delta n_1'$ are quite small here and the fraction of the surface area (equal to $N\sigma_1\Delta n_1'$) covered by water molecules is only 0·036. The total surface of 1 cm² area is thus fully covered by glycerol molecules having flat orientation. For $X_2 > 0·15$, the plot of $-\Gamma_1$
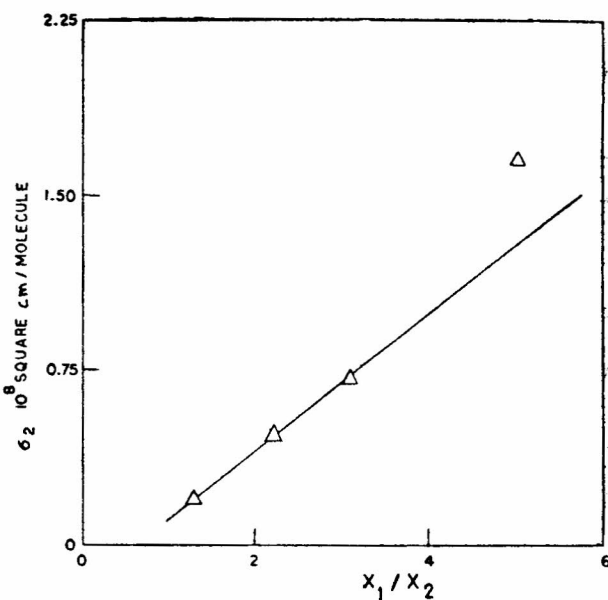

Fig. 5 — Variation of the cross-sectional area (σ_2) of the surface bound organic molecule of glycerol with the mole ratio composition X_1/X_2

against X_1/X_2 is observed to be non-linear. This behaviour can only be explained in terms of the gradual alteration in the orientation of the glycerol molecules within the surface phase $AA'BB'$ as the glycerol mole fraction of the bulk is gradually increased above 0·15. Neglecting $\Delta n_1'$ in Eqs. (11) and (18), calculated value of σ_2 is observed to vary linearly with change of X_1/X_2 (vide Fig. 5). At very low value of X_1/X_2, σ_2 is as low as 20 $Å^2$ which may possibly indicate that the orientation of the hydrocarbon groups of the glycerol molecules in the interfacial phase is nearly vertical at this stage. For $X_2 < 0·05$, $-\Gamma_1$ versus X_1/X_2 plot again deviates from linearity possibly due to the appearance of the significant amount of water in the interfacial phase with subsequent displacement of the bound glycerol molecules (vide Table 2) from it.

In Fig. 4, Γ_1 for acetone-water mixture is observed to vary linearly with X_1/X_2 in the range of acetone mole fractions 0·005 to 0·03. $\Delta n_1'$ and Δn_2 calculated on the basis of these linear plots are given in Table 1. Using Eq. (18), σ_2 for a bound acetone molecule is found to be 34·5 $Å^2$. This high value for σ_2 may also indicate that the acetone molecules in the interfacial phase exist in the flat orientation with respect to the planes AA' or BB'. At $X_2 > 0·03$, $-\Gamma_1$ versus X_1/X_2 plot is non-linear possibly due to the increase in the value of $\Delta n_2'$ as a result of the decrease in the value of $\Delta n_1'$ in the interfacial phase. At very low values of X_1/X_2, most of the water from the interfacial phase is expelled. $\Delta n_2'$ in this region may also increase due to the reduction in the value of σ_2 as a result of the gradual orientation of the bound acetone molecules from the flat to vertical position. In the case of glycerol water interface such orientation effect has been actually observed before.

Thus, from foregoing results it can be concluded that (i) The Gibbs dividing plane necessary to obtain the relative surface excess quantities is not arbitrary. It is fixed and has a position somewhere near the surface.

(ii) With the help of the derived Eqs. (11) and (12) the absolute composition of the surface phase can be found out.

(iii) The surface composition may reveal orientation behaviours of organic compounds at the air-water interface.

Acknowledgement

References

1. *On the equilibrium of the heterogeneous substances in the scientific papers of J. Willard Gibbs*, Vol. 1 (Dover, New York), 1961.
2. McBain, J. W. & Humphrays, C. W., *J. phys. Chem.*, **36** (1932), 300.
3. Guggenheim, E. A. & Adam, N. K., *Proc. R. Soc.*, **139A** (1933), 231.
4. Guggenheim, E. A., *Trans. Faraday Soc.*, **36** (1940), 397.
5. Chattoraj, D. K. & Chatterjee, A. K., *J. colloid interface Sci.*, **21** (1966), 159.
6. Defay, R. & Priggogine, I., Belleman, A. & Everett, D. H., *Surface tension and adsorption* (John Wiley, New York), 1966, 21; 363.
7. Goodrich, F. C., *Trans. Faraday Soc.*, **64** (1968), 3403.
8. Chattoraj, D. K. & Moulik, S. P., in *Adsorption at interfaces*, Ser. 8, edited by K. L. Mittal (American Chemical Society, Washington), 1975, 48.
9. Tolman, R. C., *J. chem. Phys.*, **116** (1948), 758; **17** (1949), 118.
10. Adamson, A. W., *Physical chemistry of surfaces* (Interscience, New York), 1960, 99.
11. Adam, N. K., *The physics and chemistry of surfaces* (Dover, New York), 1968, 50.
12. Kipling, J. J., *Adsorption from solutions of non-electrolytes* (Academic Press, New York), 1965, 28; 194.
13. Schay, G., cited in *Surface and colloid science*, Vol. 2, edited by E. Mattjevic (Wiley-Interscience, New York), 1969, 155.
14. Timmermans, J., *The physico-chemical constants of binary systems in concentrated solutions*, Vol. 4 (Interscience, New York), 1960, 36, 45, 92, 97, 209, 215, 252 and 263.
15. Chatterjee, A. K. & Chattoraj, D. K., *J. colloid interface Sci.*, **26** (1968), 140.
16. Randles, J. E. B., *Advances in electrochemistry and electro-chemical engineering*, Vol. 3, edited by P. Delahay (Interscience, New York), 1963, 1.