ACTA CHEMICA SCANDINAVICA 12 (1958) 1124—1135

Surface Tension of Liquid Mixtures

A Micro-Method Applied to the Systems: Chloroform-Carbontetrachloride, Benzene-Diphenylmethane and Heptane-Hexadecane

JØRGEN KOEFOED and JOHN V. VILLADSEN

Universitetets Fysisk-Kemiske Institut, Copenhagen, Denmark

An apparatus is described which measures surface tension of small samples (10 – 30 μl) with an accuracy better than one in thousand. A glass capillary of 2 mm diameter in the lower end and 0.25 mm in the upper end was inclined to bring the liquid in equilibrium each time at the same position in the capillary.

Experimental results are reported for 10 pure liquids and for three sets of mixtures of varying mole fraction. The applicability of recent theories of the surface tension of regular mixtures is discussed and a new treatment is proposed.

THE APPARATUS

The apparatus was designed for measuring surface tension of some biological fluids which were available in very small quantities only. These measurements will be described elsewhere. For the measurements described in this paper the extreme economy in volume was not particularly advantageous, but did no harm either, even in the work with mixtures because evaporation could be kept correspondingly low.

For adaptation to micro-scale, the capillary rise method is obviously the most suitable. Surfaces of intermediate dimensions ($50 > d > 2$ mm) have a complicated shape and involve awkward correction terms. Usually the reference surface is kept above this interval and treated as a plane surface, but another possibility is to keep both surfaces so small that they can be treated as perfectly spherical. An unfortunate circumstance in this arrangement is that only one of the surfaces can approach the equilibrium position in receding motion. It has, however, been possible to make very accurate measurements.

The laborious search for a capillary of sufficiently constant diameter was saved by measuring to the same narrow region of an ordinary first class capillary. To be able to have both surfaces at prescribed positions in the capillary, gravitational force on the liquid was varied by inclination of the capillary.

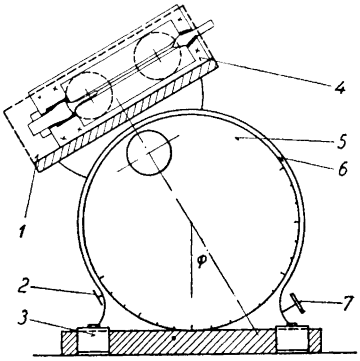

Fig. 1. Sketch of the apparatus. The optical measuring table is solidly clamped to the desk. On the movable table is fixed a U steel, 1, carrying the two microscopes and the Perspex chamber, 4. The fine adjustment screw 7 is engaged or disengaged by turning 2.

The measuring capillary (made to order by F. C. Jacob, Copenhagen) is shown on Fig. 1 together with the Perspex chamber,4, in which it is inserted. Two pieces of Portex tubing (soft PVC) on the two bulbs provide the packing material, the lower one being expanded when the screw is tightened on a thin brass runner. Water is circulated through the chamber from a thermostat. The chamber is fixed to the one side of a length of U-shaped steel,1, (37 × 50 mm) and two microscopes (Hensoldt Metami, 20 ×) are fitted into holes in the other side, focussing on the capillary around its two etched markings which are 50 mm apart. The plane bottom of the U-steel rests against the plane table of an "Optischer Winkel-Mess-Tisch" (Miller, Innsbruck) commercially available from precision-tool dealers. The scale has divisions for every 5′ permitting easy interpolation to 1′.

The horizontal position, read as 0°, is carefully adjusted as the position in which a small mercury drop does not move in the narrow capillary (± 2′).

Although mounting and dismounting of the capillary is very easy, the rinsing and filling is usually made *in situ.* For the filling, the table is moved to bring the tube in an upside down position (—70°), the narrow end is closed with a finger and the liquid is applied as a drop in the wide end of the capillary from a 25 μl capillary pipette. The finger is released until the drop is caught by the narrow part of the capillary and the table is tilted back to a small positive angle (+ 10 — + 15°). The upper surface will now be in the conical part of the tube above the narrow capillary and can be "vacuum-cleaned" for surface impurities through a thin polythene tube.

The capillary is brought to vertical position (+ 90°) and tilted backwards and forwards until the upper surface is at the desired place. The position of both surfaces l_1 and l_2 are read on the ocular scales of the microscopes (0.05 mm divisions). The angle φ is read and the surface tension can be worked out from the following expression, the meniscus to meniscus distance in mm being $50 + l_1 - l_2$:

$$\begin{aligned} \gamma &= Kd(1 + (l_1 - l_2)/50)\sin\varphi \qquad (1) \\ K &= g(50 + (r_1 + r_2)/3) \,/\, (2/r_1 - 2/r_2) \\ d &= d_{\text{liq}} - d_{\text{air}} \end{aligned}$$

Actually, the constant K was determined by standardization on pure benzene and checked on several other substances. The questions of the correction term $(r_1 + r_2)/3$ and of the neglected terms of higher order in r_1 and r_2 have been treated by Højgaard Jensen.[1]

SURFACE TENSION OF SOME PURE LIQUIDS

Ten readings were taken for each liquid. The largest discrepancy was usually within 2 parts in thousand and the accuracy of the mean value should therefore be about 7/10 000. The results are given in Table 1 together with the best values, found in the literature.

The agreement between our measurements and others is very satisfactory. Only diphenylmethane appears not to have been measured before. The measurements on *n*-paraffins by JKG are made in vacuum and seem very accurate, but it is surprising that they report surface tensions of higher paraffins far below the melting point of any reasonably pure sample. Their method gives no proper check on systematic errors in their apparatus and the impressive consistency in their results may depend on their use of the same apparatus throughout. The paraffins used by Vogel appear to have been of moderate purity.

In measuring ethyl ether a small correction (0.23 %) was made for the weight of the air stem in the tube on both sides of the liquid, because the saturation with ether made the air heavier. For the other liquids a similar correction would be smaller than 0.05 % and was neglected.

Table 1. Surface tensions of pure compounds.

	t°C	d g/ml	γ dyn/cm	γ (literature)			
Benzene	25.0	0.8736	[28.24]	28.24	(RC)		
	30.0	0.8683	27.59	27.54	27.61		(T)
Carbontetrachloride	25.0	1.5845	26.14	26.16	26.06		(T)
Chloroform	25.0	1.4799	26.56	26.5	26.67		(T)
n-Heptane	20.0	(0.6836)	20.32	20.28	(JKG)	20.30	(T)
	30.0	(0.6753)	19.30	19.27	(JKG)	19.29	(T)
n-Dodecane	20.0	(0.7492)	25.42	25.48	(JKG)	25.45	(V)
	30.0	(0.7425)	24.52	24.60	(JKG)	24.44	(V)
n-Hexadecane	20.0	(0.7736)	27.42	27.64	(JKG)	27.58	(V)
	30.0	(0.7667)	26.62	26.79	(JKG)	26.87	(V)
Diphenylmethane	30.0	0.9995	38.09				
Methanol	25.0	(0.7566)	22.28	22.18	(T)		
Ethanol	25.0	(0.7077)	21.97	21.85	21.90 (T)		
Ethylether	25.0	(0.7851)	16.50	16.50	(T)		

Density d is $d_{\text{liq}} - d_{\text{air}}$. Values in brackets are taken from the literature.

References: RC: Richards, T. V. and Carver, E. K. *J. Am. Chem. Soc.* **43** (1921) 829.
T: Timmermans, J. *Physico-Chemical Constants of Pure Organic Compounds*, Elsevier 1950.
JKG: Jasper, J. S., Kerr, E. R. and Gregorich, F. *J. Am. Chem. Soc.* **75** (1953) 5253.
V: Interpolated values from Vogel, A. I. *J. Chem. Soc.* **1946** 133.

MATERIALS

Benzene and *carbon tetrachloride*. Merck p.a., dried with silica gel and distilled.

Chloroform. Merck p.a., 1 % alcohol added. Alcohol removed by washing twice with water. Separated. Dried with silica gel and distilled. All samples containing chloroform were stored in dark bottles and measured within a few days from their preparation.

n-*Heptane*. Phillips Petroleum Comp. "more than 99 % pure" (presented by the makers to the late prof. J. N. Brønsted in 1947).

n-*Dodecane* and n-*hexadecane*. Synthetic samples of high purity, as used for the measurements by Brønsted and Koefoed [2].

Diphenylmethane. Fluka, highest purity. 6 times recrystallized, each time discarding about 1/5 as liquid phase, m. p. 26.8°C.

Methanol. Merck p. a.

Ethanol. Alcohol absolutus 99.9 %. Ph. Dan., De Danske Spritfabrikker.

Ethyl ether. Struers, Copenhagen. Best commercial quality, distilled from sodium metal.

SURFACE TENSION OF SOME MIXTURES

Chloroform-Carbontetrachloride. The surface tensions of these mixtures have been measured many years ago by Whatmough [3] and our results agree qualitatively with his. Densities and vapour pressures are known from the work of McGlashan and Prue [4] who showed that the mixtures are regular with the parameter $W = 930$ joule/mole.

Our determinations of densities agree well with those of McGlashan and Prue[4] which are certainly more accurate than ours whereas the values tabulated in *International Critical Tables* appear incorrect. We must have had some losses of chloroform in the making up of the mixtures and we obtained the most consistent results if we based our x-values on the density measurements and not on the weighings.

The experimental results are tabulated in Table 2 and plotted in Fig. 2. In the same figure are plotted values calculated from Guggenheim's equation [5] (2) and from Hoar and Melfords equation [6] (3) for regular solutions:

$$\begin{aligned}\gamma &= \gamma_1 + \frac{RT}{\sigma_1}\ln\frac{x_1'}{x_1} + \frac{W}{\sigma_1}\left(\frac{x_2'^2}{2} - \frac{3x_2^2}{4}\right)\\ &= \gamma_2 + \frac{RT}{\sigma_2}\ln\frac{x_2'}{x_2} + \frac{W}{\sigma_2}\left(\frac{x_1'^2}{2} - \frac{3x_1^2}{4}\right)\end{aligned} \tag{2}$$

$$\begin{aligned}\gamma &= \gamma_1 + \frac{RT}{\sigma_1}\ln\frac{x_1'}{x_1} + \frac{W}{\sigma_1}\left(\frac{x_2'^2}{2} - x_2^2\right)\\ &= \gamma_2 + \frac{RT}{\sigma_2}\ln\frac{x_2'}{x_2} + \frac{W}{\sigma_2}\left(\frac{x_1'^2}{2} - x_1^2\right)\end{aligned} \tag{3}$$

Eqn. (2) corresponds to Guggenheims derivation but σ_1 and σ_2 are not put equal to one another.

The calculations were carried through in the following way: For $x_1 \leqq 0.5$ was inserted: $x_1'/x_1 = 1 + \delta$; $\ln x_1'/x_1 = \delta$; $\ln x'_2/x_2 = - x_1\delta/(1-x_1)$; $(x_1'/x_1)^2 = 1 + 2\,\delta$ and $(x_2'/x_2)^2 = 1 - 2x_1\delta/(1-x_1)$. An explicit expression for δ was developed from each of eqns. (2) and (3). For each of them δ was calculated and inserted in both equations for γ. If the two values of γ agreed, this was taken as evidence for a satisfactory approximation. If not, small corrections were made by iteration until agreement was obtained. After-

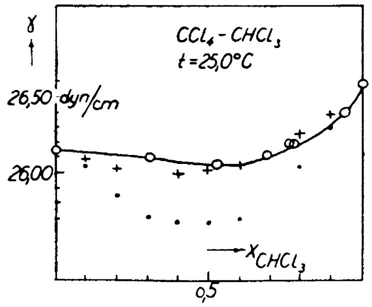

Fig. 2. Surface tension of CCl_4-CHCl_3 mixtures
o experimental values
+ calc. from Guggenheims eqn. (2)
● calc. from Hoar and Melfords eqn. (3)

wards the other halves of the curves, $x_1 > 0.5$, were found by similar sets of equations with x_1 and x_2 interchanged so that $x_2'/x_2 = 1 + \delta'$ *etc.* The reason for using two different expressions is that the terms $x/(1-x)$ get large as x approaches 1 and threaten the successfulness of the approximations.

It is evident from Fig. 2 that Guggenheim's expression gives a much better agreement with the experimental values than Hoar and Melfords. A discussion of the two models is found in the last part of this paper.

Benzene-Diphenylmethane. No measurements of density or surface tension of these mixtures have been published. Everett [7] has mentioned the existence of unpublished density measurements by Duff. From the work of Everett [8] we know the vapour pressures, which follow the rules of "athermal" mixtures.

Our measurements are tabulated in Table 3 and the surface tensions are plotted against mole fraction in Fig. 3. The curve is on the positive side of the right line and plotted against volume fraction it comes out on the negative side. The density measurements show that mixing is accompanied by an appreciable contraction (2.9 % at $x = 0.5$).

In measuring the surface tensions we had to take precautions to prevent evaporation from the surface. The two ends of the tube were connected to a T-tube and the air in the tubes was kept at about the right benzene pressure by evaporation from moistened bits of cotton wool. The solutions rich in diphenylmethane were very viscous and by standing unprotected over night the surface tension approached that of pure diphenylmethane, but a subsequent mixing of the 20 μl lot showed that it was only the surface which had lost an appreciable amount of benzene.

Table 2. Carbontetrachloride-chloroform (25.0°C).

	d g/ml	x (weight)	x (density)	γ dyn/cm
CCl_4	1.5845	0		26.14
Mixture 1	1.5535	0.304	0.310	26.10
2	1.5284	0.526	0.548	26.06
3	1.5092	0.685	0.735	26.12
4	1.5054	0.745	0.766	26.19
5	1.5045	0.760	0.775	26.18
6	1.4854	0.940	0.950	26.40
$CHCl_3$	1.4799	1		26.56

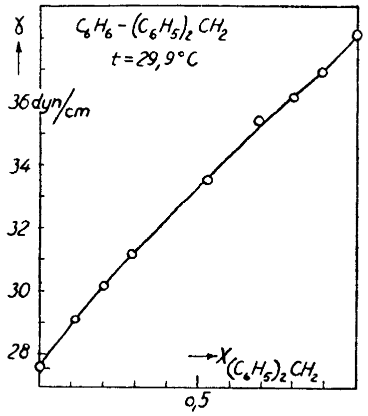

Fig. 3. Surface tension of benzene-diphenylmethane mixtures.

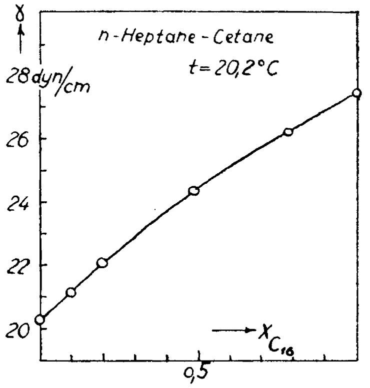

Fig. 4. Surface tension of *n*-heptane-*n*-hexadecane mixtures.

n-*Heptane* — n-*Hexadecane.* Surface tension of paraffin mixtures are not reported in the literature. From earlier, unpublished measurements in this laboratory of densities and volumes of mixing, we know that *n*-paraffins mix under contraction and that the densities correspond as closely to the principle of congruence as it has been possible to ascertain it. The vapour

Table 3. Benzene-diphenylmethane (29.9°C).

	x	d g/ml	γ dyn/cm
Benzene	0	0.86833	27.60
Mixture 1	0.1125	0.89490	29.07
2	0.2038	0.91253	30.15
3	0.2883	0.92683	31.11
4	0.5226	0.95811	33.54
5	0.6864	0.97512	35.38
6	0.8006	0.98479	36.07
7	0.8927	0.99174	36.90
Diphenylmethane	1	0.99954	38.10

Table 4. Heptane-hexadecane.

	x	$x_{\text{vol.}}$	γ (20.2°C)	γ (29.9°C)
Heptane	0	0	20.30	19.31
Mixture 1	0.097	0.177	21.15	20.16
2	0.195	0.326	22.05	21.05
3	0.492	0.660	24.35	23.46
4	0.785	0.879	26.23	25.48
Hexadecane	1	1	27.40	26.63

pressure of n-paraffins have been studied extensively in this laboratory [2] and elsewhere and heats of mixing are known from the work of van der Waals [9]. His results are in moderate agreement with unpublished measurements by Brønsted and Halvard in this laboratory.

The surface tensions were measured at two temperatures and the results are tabulated in Table 4. In Fig. 4 the values at 20°C are plotted against mole fraction. The results at 30°C give exactly the same appearance. The curves are positive and exactly as in the system benzene-diphenylmethane we find on plotting against volume fraction a negative deviation from linear behaviour. For vapour pressures, inversely, the curves are negative when plotted against mole fraction and positive when plotted against volume fraction.

Both of the last two systems are known to deviate rather little from ideality. But starting from Guggenheim's equation for an ideal surface we find that very large deviations from ideal surface behaviour have to be introduced to account for the fact that the curve is much nearer to the straight line than a Guggenheim-ideal surface tension would be. We take this as evidence for the soundness of accepting the straight line relationship as representing ideal behaviour as discussed below.

THE THERMODYNAMICS OF SURFACES

"In the thermodynamics of surfaces there is no theorem more important than that known as Gibbs' adsorption theorem, which determines how the surface tension of a solution varies when the composition is varied at constant temperature. Its derivation by Gibbs has all the logical conviction and elegance characteristic of Gibbs" (Guggenheim[10]).

The situation with regard to this theorem is unsatisfactory in two respects. The existing proofs of the theorem are not irreproachable and the theories of surface tension of binary mixtures lead to disagreement with the theorem as soon as such terms are included in the partition function which take account of the interaction with the bulk phase. Guggenheim's equation, (2), thus is not consistent with Gibbs' theorem. We first thought that the answer to these questions was that Gibbs' theorem was not correct. However elegant Gibbs' proof may be, it involves the use of chemical potentials of molecules in the surface layer with no proper analysis of whatever this may mean. The proof given by Guggenheim [10] involves a hypothetical experiment which is treated as if it were reversible although it most obviously cannot be reversed. It was pointed out to us, however, by H. Højgaard Jensen that it is possible to give a proof which involves nothing more than the second law and the conservation of mass.

A careful analysis of the energetic conditions of molecules in the surface and what could be meant by the chemical potentials of these brought out, then, that it was possible to give a treatment which is inherently consistent with Gibbs' theorem and which leads to a different concept of ideal behaviour with regard to surface tension.

How this result was originally derived from Brønsted's energetic theory and how it relates to other "transport complex" treatments will be discussed elsewhere. We will give here only a short account of its derivation along the lines of Guggenheims *Thermodynamics* [11].

The actual difficulty is in the definition of a chemical potential when other energetic variables are involved than the classical: S, V, N, T, P, μ. The same problem is involved in electrochemistry and in a gravitational field. In surface problems it is the field of the cohesive forces which interferes as a *partly* external force.

If we decide to specify the potential energy of the i'th component with respect to cohesive forces in a gas and in a liquid we can introduce a parameter χ_i. We can split up our ordinary chemical potential accordingly:

$$\mu_i = \mu_i^l + \chi_i^l = \mu_i^g + \chi_i^g \tag{7}$$

and in analogy with the nomenclature for electrochemical and gravitational systems we would refer to μ_i^l and μ_i^g as the "purely chemical potentials" and to our ordinary μ_i as the "cohesion-chemical potential". It will be the latter which determines the equilibrium between two phases in the same way as the electro-chemical and the gravitation-chemical potentials within their fields.

In the bulk phases χ_i is constant but in a surface layer the molecules will move in a field from the cohesive forces. Within a very short distance the potential energy of the van der Waals attraction rises from a large negative value, χ_i^l, in the bulk liquid phase to a value $\chi_i^g \simeq 0$ in the gas. In the same way as in a gravitational field, therefore, the equilibrium conditions are *not* homogeneity in P and the μ_i's but P,μ_i and χ_i are all functions of the position in the surface layer described through a parameter, t, measured along an axis normal to the surface, here supposed to be plane. The condition for equilibrium of a single component, i, is the same as in a mixture in a gravitational field (Guggenheim[11], eqn. 11.07.2):

$$\mathrm{D}\mu_i^t + V_i^t \mathrm{d}P^t + \mathrm{d}\chi_i^t = 0 \tag{8}$$

where $\mathrm{D}\mu_i = \Sigma_s(\partial\mu_i/\partial x_s)\mathrm{d}x_s$ accounts for the variations with composition of the bulk phase (*cf.* Guggenheim[11]). This condition shall be fulfilled for any value of t and therefore also in the bulk phases, whence we have at changing compositions of the bulk phases and hydrostatic pressure P:

$$\mathrm{D}\mu_i^t + V_i^t \mathrm{d}P^t + \mathrm{d}\chi_i^t = \mathrm{D}\mu_i^l + V_i \mathrm{d}P + \mathrm{d}\chi_i^l \tag{9}$$

We have no possibility neither in practise nor in principle to define the functions $\mu_i(t)$, $V_i(t)$, $P(t)$ or $x_i(t)$ in a thermodynamic way. The splitting up of the electrochemical potential in an electric part and a chemical part implies non-thermodynamic and to a certain degree arbitrary assumptions, and the same applies here.

The only entity which is physically measurable is the surface tension:

$$\gamma = \int_l^g (P - P^t)\mathrm{d}t \tag{10}$$

The integral extending from a point $t = l$ which is with certainty in the potential-homogeneous interior of the liquid to a point $t = g$ which is similarly situated in the gas. At both ends therefore $P^t = P$, making the exact positions of l and g immaterial.

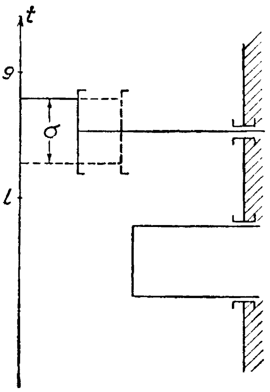

Fig. 5. "Surface piston."

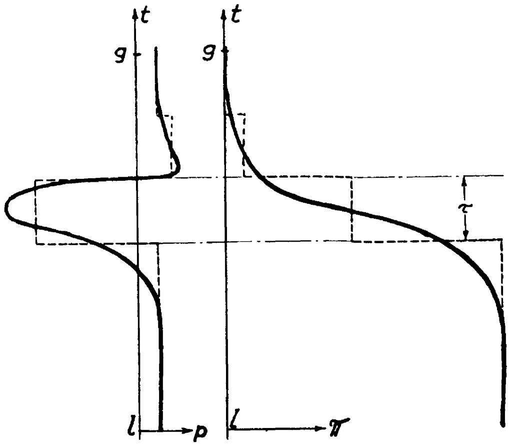

Fig. 6. Hypothetical shape of curves showing changes in pressure, p, and internal pressure, π, in passing from a point in the liquid, l, through the surface to a point in the gas, g.

γ can be measured by a surface piston arrangement (Fig. 5), but any attempt to measure P^t by sliding in pistons with an edge in the zone of potential-inhomogeneity, σ, will imply the creation of new boundary layers and yield no useful information on P^t.

To be able to give our functions definite values we must therefore assume some potential function, χ_i^t, and some equation of state $\Phi_i = \Phi_i(V_i, P, \chi_i) = 0$, and we can imagine that we could get a pressure curve like that of Fig. 6 with a narrow zone of expanded liquid under a large negative pressure and a zone of adsorbed, slightly compressed gas, but such assumptions are obviously outside the domain of thermodynamics, and a further treatment along such a line would fall under the theory of the liquid state and would remind of the classical works of van der Waals and Bakker [12].

To develop thermodynamic equations which are useful for the kind of problems we are dealing with here, we will choose another approach: the monolayer model. We neglect the adsorbed gas-layer and assume that what is different from the bulk phases can be thought of as concentrated in one homogeneous liquid layer of thickness τ. This represents a way of averaging the deviations from bulk phase behaviour by substituting continuous curves as those in Fig. 6 with "square wave" functions. Average values in the monolayer we designate by index s and obtain:

$$\gamma = (P - P^s)\,\tau \qquad\qquad \sigma_i = V_i^s/\tau$$

The equilibrium condition (9) takes the form

$$\mathrm{D}\mu_i^s + V_i^s\mathrm{d}P^s + \mathrm{d}\chi_i^s = \mathrm{D}\mu_i^l + V_i\mathrm{d}P + \mathrm{d}\chi_i^l \tag{11}$$

Neglecting compressibility we can put $V_i^s = V_i$ and imagine a transfer from l to s in a continuous way which allows the integration:

$$\mu_i^s + V_i P^s + \chi_i^s = \mu_i^l + V_i P + \chi_i^l \tag{12}$$

or after insertion of γ and σ_i:

$$\mu_i^s + \chi_i^s - \gamma\sigma_i = \mu_i^l + \chi_i^l \tag{13}$$

Reverting to usual chemical potentials, or cohesion-chemical potentials, we put:

$$\mu_i^s + \chi_i^s = \mu_i' \qquad \text{and} \qquad \mu_i^l + \chi_i^l = \mu_i$$

and derive:

$$\mu_i' - \gamma\sigma_i = \mu_i \tag{14}$$

Our μ_i' is a cohesion-chemical potential and if we want a chemical potential which is the same both in surface and in bulk phases in equilibrium we must interpret the last equation as *defining* a special surface-cohesion-chemical potential, the surface part of which is zero in the bulk phases. Whichever view we take of this equation we can derive the same relations if we work in a consistent way. Equation (14) corresponds to similar relations derived by Defay and Prigogine[14], and the difference from their treatment appears only in the application, when we take into account that μ_i' itself depends on γ, because $\partial\mu_i'/\partial\gamma = -\sigma_i$ corresponding to the usual relation $\partial\mu_i/\partial P = V_i$ as in the surface layer $V_i = \tau\sigma_i$ and $\tau dP^s = -d\gamma$.

The thermodynamic difference between μ_i and μ_i' is:

$$\mu_i' = (\partial F'/\partial n_i')_{T,\gamma,\mathrm{nj}'} \neq \mu_i = (\partial F'/\partial n_i')_{T,A,\mathrm{nj}'}$$

Before we turn to the application of (14) to special cases, we should make its scope and its limitations clear. The introduction of a σ_i- or of a n_i'-parameter will always involve some arbitrary choice which relates closely to the arbitrariness involved for instance in the splitting up of the electro-chemical potential in a chemical and an electrical term. The derivation above indicates clearly that the possibility of introducing a characteristic partial molar surface area σ_i for a component rests on the neglection of the gaseous part of the surface layer. This neglection can be justified only at moderate pressures and far from critical point conditions. To investigate the influence of gas pressure on surface tension or the behaviour of surface tension near the critical point we would have to choose some other approach.

It will be of interest to see what order of magnitude the negative pressure in the surface layer will get. Taking CCl_4 at 25°C, 1 atm. as an example, we derive for close-packed lattice dimensions: $V = 97.07$ ml/mole; $\sigma = 19.5 \times 10^8$ cm^2/mole; $\tau = 5.0$ Å; $P^s = 1 - \gamma/\tau = -500$ atm.

We can also compare the internal pressures $\pi = (\partial E/\partial V)_T$ in liquid and in monolayer, relating the latter to the surface energy $E' = (\partial E/\partial A)_T$. We have the two thermodynamic equations of state:

$$P + \pi = T(\partial P/\partial T)_V \tag{15}$$

$$-\gamma + E' = -T(\partial\gamma/\partial T)_A \tag{16}$$

The latter we can interpret as:

$$(P - P^s)\tau + (\pi - \pi^s)\tau = T\ (\partial(P - P^s)/\partial T)_V\,\tau \tag{17}$$

In CCl_4: $\pi = 3\,310$ atm (Hildebrand and Carter[16]) and $E' = 65.6$ dyn/cm giving $\pi - \pi^s = 1\,300$ atm and $\pi^s = 2\,010$ atm.

MONO-LAYER SURFACES OF IDEAL AND REGULAR MIXTURES

Having derived the condition $\mu_i' - \gamma\sigma_i = \mu_i$ we can directly write down the expressions for μ' and μ corresponding to the model of regular solutions or we can construct partition functions and derive the μ's from these. We will differ from previous treatments in two respects: by letting the potential of the forces from the bulk phase, χ_i^b, contain not only a quadratic term but also a linear term in the mole fraction of the bulk phase and by appreciating that μ'_i depend on the surface tension. With a constant term $2\gamma_1\sigma_1$ in χ_1^b adjusted to fit in the limit $x_2 = 0$ we get for component 1:

$$\mu_1 - \mu_1^\circ = RT\ln x_1 + Wx_2^2 \tag{18}$$

$$\mu_1' - \mu_1^\circ = RT\ln x_1' + W'x_2'^2 + \chi_1^b - \sigma_1\gamma \tag{19}$$

$$\chi_1^b = 2\sigma_1\gamma_1 + \alpha_1 x_2 + W''x_2^2 \tag{20}$$

These expressions and the analogous for component 2 are in agreement with Gibbs' theorem which incidentally is identical with the Gibbs-Duhem condition applied to the mono-layer phase:

$$\begin{aligned} 0 &= x_1'\mathrm{d}\mu_1' + x_2'\mathrm{d}\mu_2' \\ &= x_1'\mathrm{d}\mu_1 + x_2'\mathrm{d}\mu_2 + (x_1'\sigma_1 + x_2'\sigma_2)\mathrm{d}\gamma \\ &= \left\{RT\left(\frac{x'_1}{x_1} - \frac{x'_2}{x_2}\right) - 2W(x_1' - x_1)\right\}\mathrm{d}x_1 + (x_1'\sigma_1 - x_2'\sigma_2)\mathrm{d}\gamma \\ &= 0\mathrm{d}x_1' + \{\alpha_2 x_2' - \alpha_1 x_1' - 2W''(x_1' - x_1)\}\,\mathrm{d}x_1 - (x_1'\sigma_1 + x_2'\sigma_2)\mathrm{d}\gamma \end{aligned} \tag{21}$$

The general relation between the surface tension of the mixture, γ, and those of the pure components, γ_1 and γ_2 is then:

$$\begin{aligned} \gamma &= \gamma_1 + \frac{1}{2\sigma_1}\left\{\alpha_1 x_2 + RT\ln\frac{x_1'}{x_1} + W'x'^2_2 - (W - W'')x_2^2\right\} \\ &= \gamma_2 + \frac{1}{2\sigma_2}\left\{\alpha_2 x_1 + RT\ln\frac{x_2'}{x_2} + W'x'^2_1 - (W - W'')x_1^2\right\} \end{aligned} \tag{22}$$

To derive Guggenheim's equation for regular mixtures we put $\alpha_1 = \alpha_2 = 0$, $\sigma_1 = \sigma_2 = A/2$ and $W = 2W' = 4W''$. Guggenheim's ideality requires further $W = 0$. Similarly Hoar and Melford's eqn. (18) appears if $\alpha_1 = \alpha_2 = 0$, $W = 2W'$ and $W'' = 0$. It is only in a formal way that (22) is brought to agree with these other expressions by doubling the surface area.

Since μ' contains a χ-term, there is no reason why α_1 and α_2 should be zero. Hence a more natural choice of what to define as an ideal or perfect surface will be:

$$\alpha_1/\sigma_1 = -\alpha_2/\sigma_2 = \gamma_2 - \gamma_1 \tag{23}$$

$$W = W' = W'' = 0 \tag{24}$$

which implies the relations:

$$x_1'/x_1 = \exp(\sigma_1(\gamma - \gamma_1)/RT) \tag{25}$$

$$\gamma_{id} = x_1\gamma_1 + x_2\gamma_2 \tag{26}$$

which give exactly the same distribution between bulk phase and monolayer as previous treatments. The difference is the rectilinear dependence of surface tension on mole fraction.

The same concept of ideal surface behaviour has been advanced before. Defay and Prigogine [13,14] use it, but only as an approximation which may be reasonable when γ_1 and γ_2 are not too different from each other.

Passing to regular solutions it is reasonable to maintain the α-values (23) and introduce values for W, W' and W'' corresponding to Guggenheim's model. This leads to the same distribution of the components as Guggenheim's own expressions, eqn. (2) above. The surface tension, however, comes out as the mean between the ideal value, γ_{id}, from eqn. (26) and the γ as calculated from Guggenheim's equation (2). This improves the agreement with our experiments in the region of low chloroform concentrations, but makes it worse in the other end.

The reason why our results for chloroform-carbontetrachloride mixtures corresponded quite well to Guggenheim's regularity is probably that the two components not only form regular mixtures but also have about the same surface tensions.

More experimental data are needed, particularly on regular mixtures of components with widely different surface tension.

The thermodynamic derivations in this paper draw heavily on ten years old discussions with Dr. Th. Rosenberg, now at the Danish Atomic Energy Research Station, Risø, and on recent discussions with professor H. Højgaard Jensen. The experimental work was carried out in collaboration with Dr. T. A. Bak and K. Andersen, who measured the viscosities of the same mixtures (to be published later).

REFERENCES

1. Jensen, H. Højgaard *Acta Chem. Scand.* **12** (1958) 1024.
2. Brønsted, J. N. and Koefoed, J. *Kgl. Danske Videnskab. Selskab, Mat. fys. Medd.* **22** (1946) No. 17.
3. Whatmough, W. H. *Z. physik. Chem.* **39** (1901) 157.
4. Mc Glashan, M. L., Prue, J. E. and Sainsbury, E. J. *Trans. Faraday Soc.* **50** (1954) 1284.
5. Guggenheim, E. A. *Trans. Faraday Soc.* **41** (1945) 150 or *Mixtures*, Oxford U.P. 1952.
6. Hoar, T. P. and Melford, D. A. *Trans. Faraday Soc.* **53** (1957) 318.
7. Everett, D. H. *Discussions Faraday Soc.* **15** (1953) 258.
8. Everett, D. H. and Penney, M. F. *Proc. Roy. Soc.* **A212** (1952) 164.
9. van der Waals, J. H. *Diss.* Amsterdam 1950.
10. Guggenheim, E. A. *J. Chem. Phys.* **4** (1936) 689.
11. Guggenheim, E. A. *Thermodynamics*, North Holland Publ. 1949.
12. *Handbuch der Experimentalphysik.* Bd 6.
13. Defay, R. and Prigogine, I. *Bull. soc. chim. Belges* **53** (1944) 115.
14. Defay, R. and Prigogine, I. *Tension superficielle.* Dunod 1957.
15. Prigogine, I. *et al. J. chim. phys.* **47** (1950) 33, 807; *J. Colloid Sci.* **7** (1952) 122 etc.
16. Hildebrand, J. H. and Carter, J. M. *J. Am. Chem. Soc.* **54** (1932) 3592.

Received February 26, 1958.