153. *The Adsorption of Alcohols at Hydrocarbon–Water Interfaces.*

By F. Franks and D. J. G. Ives.

The dependence of the interfacial tension between a pure hydrocarbon and water upon temperature indicates that ΔH and ΔS for interface formation pass through a pronounced maximum at about 34° c. Small additions of methanol, ethanol, or n-propanol, but not of n-butanol, produce elevations in interfacial tension at 10° and 25°, but not at 40°: further additions lead to normal "Gibbsian adsorption" at the interface with accompanying depression of interfacial tension. These effects are discussed in terms of current views on the structure of water and its modification by solutes.

The process of forming a liquid–liquid interface involves the transfer of two substances from initial bulk-phase states to a final "interfacial state." Studies of this process should be capable of providing information about any of these states, providing that difficulties of interpreting experimental results can be overcome. Thus, when an interface is formed, two sets of interactions between like molecules are partially replaced by interactions between unlike molecules, which may establish preferred orientations and confer a degree of organised structure upon the interfacial zone. The systems are complex, and the study of *one* process can hardly be expected to provide intelligible information about *three* states (two bulk and one interfacial) simultaneously: only with prior knowledge of two of them can reliable conclusions conceivably be reached about the third. It is doubtful if this desirable situation has yet been attained. Water, more often than not, is one of the components of the two-phase liquid systems which are of principal interest. But water is a very anomalous liquid with a structure of its own which alters with temperature in a way not yet fully understood. If the second liquid consists of polar molecules carrying functional groups, it may present its own structural problem, and what happens at the interface may be as much a function of the dissimilar structures of the two liquids as of specific interactions operating across the interface. A further complication arises from the fact that no two liquids are completely immiscible and there is the possibility that each may be significantly modified by the amount of the other that it is able to dissolve. These may be the reasons why there is at present little information about the thermodynamic functions of interface formation; there are no clear-cut questions which thermodynamics might be expected to answer. It may also be significant that it is an exacting experimental task to determine these functions, for accurate measurements of interfacial tension over a range of temperatures are needed. Few of the accepted methods of measuring surface tension are readily adaptable to the study of interfaces, particularly under the rigorous conditions needed to exclude the vitiating effects of traces of surface-active impurities.

It is perhaps not surprising that data of the requisite kind are scanty and present a picture of inconsistency or, alternatively, of specific effects of potential interest. Thus Harkins *et al.*[1] measured interfacial tensions between many organic liquids and water and found that, as a general rule, there was a linear variation with temperature. There were cases, however, in which the tension reached a maximum between 30° and 40° (heptaldehyde, non-1-yne, " higher paraffin "). In contrast with the bulk of Harkins's results, later work [2] has shown that the tensions of halogenated benzenes and toluenes against water lead to curves concave to the temperature axis.

Progress would seem to depend on simplifying the experimental systems. If water is retained as one principal phase, the other must be the simplest kind of liquid which is immiscible with it, and the obvious choice is a paraffin hydrocarbon of low molecular weight. But once the interfacial tensions have been measured over a temperature range, there is little else that can be done with this system unless it is adopted as a standard of reference with which others may be compared. This is the procedure which has been used in the present work, the changes in behaviour resulting from the addition of a third component to the standard system being followed systematically. At first sight it might seem that the use of a third component would only add complication and introduce new effects to cloud the issue further. But the idea has been so to choose the third component that it might serve as an " indicator " of the state of affairs at the interface and perhaps in the aqueous phase as well. It should therefore not be highly surface active, it should be predominantly soluble in the aqueous phase and be as " compatible " with it as possible; it should be used in extremely low concentrations and should lend itself to setting up non-standard systems differing from the standard one in a graded and systematic way. Only the lower aliphatic alcohols meet these requirements, and their suitability is further indicated by the fact that they are known to have a perceptible effect upon hydrocarbon–water interfaces at very low concentrations.[3] The use of an electrolyte as an " indicator " in this way might be of great interest, but would involve complications arising from the electrical double layers set up in response to electrostatic forces. It may well be that such considerations cannot be excluded, since studies of the electrophoresis of hydrocarbon

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[1] Harkins and Humphrey, *J. Amer. Chem. Soc.*, 1916, **38**, 246; Harkins, Clarke, and Roberts, *ibid.*, 1920, **42**, 700; Harkins and Cheng, *ibid.*, 1921, **43**, 35.

[2] Jasper and Wood, *J. Phys. Chem.*, 1955, **59**, 541; Jasper and Seitz, *ibid.*, 1958, **62**, 1331.

[3] Jordan and Taylor, *Trans. Faraday Soc.*, 1952, **48**, 346.

droplets has shown that the oil phase in contact with an aqueous medium carries a negative charge[3] for which there is no well-established explanation.[4]

It was not to be expected that any very clear-cut results would emerge, but there is an obvious need for studies of this kind conducted at various temperatures. The only extensive investigations[5,6] of the effects of alcohols of low molecular weight on oil–water interfaces have been carried out at a single temperature and cannot give any information about enthalpy and entropy effects.

In the present work, the drop-volume method has been applied, in a manner described in the experimental section, to the determination of interfacial tensions, with a probable error of ±0·04 dyne cm.$^{-1}$ between 10° and 40° C. The method has the advantages that a fresh interface is created for each determination, that the results are independent of contact angle at the glass–liquid interface or, below a critical limit, of rate of drop-growth, and that it is relatively easy to maintain the high standards of purity required. The water used had a conductance about twice that due to self-ionisation, and every effort was made to achieve and maintain similar standards of purity for the other components, all of which were stored and manipulated under an atmosphere of pure nitrogen. Under these conditions it was possible to reproduce all the measurements within the limits of error of one experiment, provided that the liquid phases were always thoroughly equilibrated with each other, and to obtain significant results for a range of alcohol concentrations between 10^{-12} and 10^{-2} mole l.$^{-1}$. The hydrocarbon phase used was initially a large stock of purified "hexane fraction from petroleum, special for spectroscopy," but in the later work pure n-octane and pure n-hexane were used with no alteration in the nature of the results.

FIG. 1.

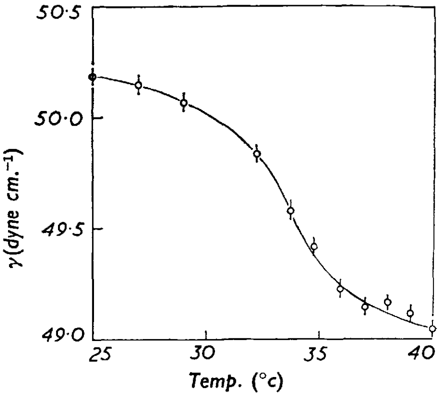
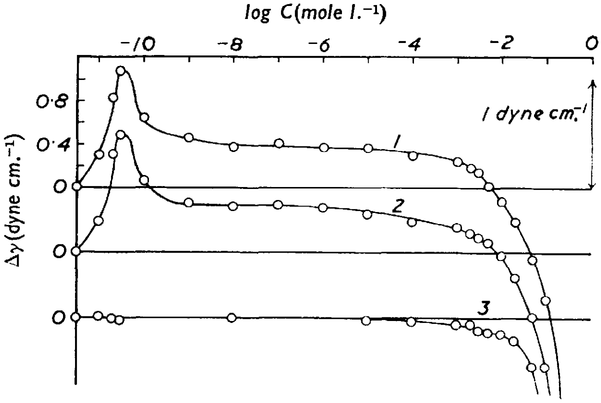


FIG. 2. *Methanol*: 1, 10°; 2, 25°; 3, 40°.



The first result of major interest is illustrated in Fig. 1, which shows the interfacial tension between n-hexane and water from 25° to 40°; it is seen that the experimental points (each the mean of at least ten determinations) give, within the indicated experimental error, a smooth curve of very characteristic shape. It is obvious that the entropy of interface formation passes through a very pronounced maximum at about 34°. This effect has already been reported;[7] it is much more likely to be due to the water than the hydrocarbon layer and calls to mind suggestions that have been made[8] that there may be a change in the structure of water near this temperature.

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[4] Taylor and Wood, *Trans. Faraday Soc.*, 1957, **53**, 523.
[5] Bartell and Davies, *J. Phys. Chem.*, 1941, **45**, 1321.
[6] Hutchinson and Randall, *J. Colloid Sci.*, 1952, **7**, 151.
[7] Franks and Ives, *Nature*, 1959, **183**, 316.
[8] Feates and Ives, *J.*, 1956, 2798.

Results for hexane–aqueous alcohol systems are recorded in Figs. 2—6, in terms of the differences of interfacial tension, $\Delta\gamma$, from that of the standard, alcohol-free system. Their remarkable nature is clearly apparent. Thus, the addition of a trace of methanol (10^{-11} mole l.$^{-1}$) to the hexane–water system causes a marked elevation of interfacial tension at 10° and at 25°, but not at 40°; $\Delta\gamma$, after passing through a peak of about +1·2 dyne cm.$^{-1}$ (which is about 30 times the experimental error), levels off at about +0·4 dyne cm.$^{-1}$ before becoming negative and embarking upon normal, " Gibbsian " behaviour. At 40° these outstanding effects have vanished, and they are also abolished by the presence of hydrochloric acid in the aqueous phase. The ethanol–water system shows similar behaviour, but the peak is not so high, and has been displaced to a higher alcohol concentration. The n-propanol–water system continues the trend established by the two lower members of the homologous series; an additional curve, relating to n-octane as the hydrocarbon, provides evidence that the phenomena are not adventitious functions of some

FIG. 3. *Ethanol*: 1, 10°; 2, 25°; 3, 40°.

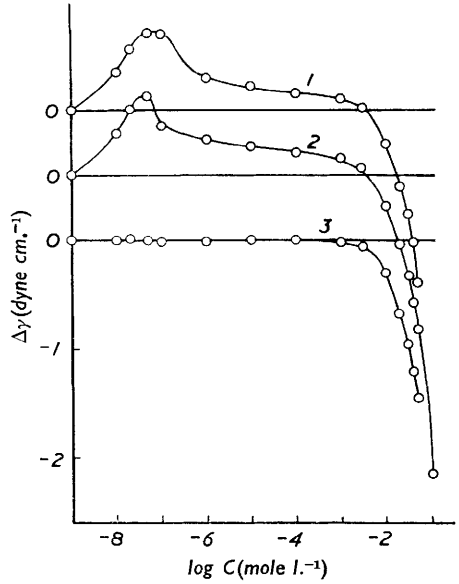


FIG. 4. *n-Propanol*: 1, 10°; 2, 25°; 3, 25°. *n-Octane*: 4, 40°.

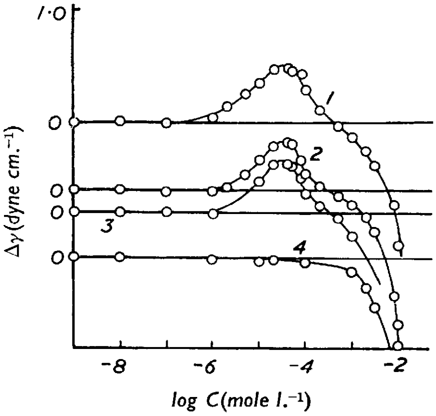


FIG. 5. *n-Propanol in* 0·1N-*hydrochloric acid*: 1, 10°; 2, 25°; 3, 40°.

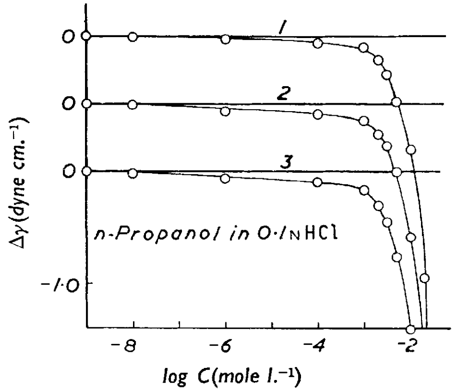
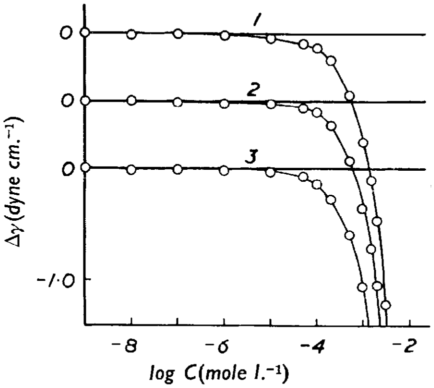


FIG. 6. *n-Butanol*: 1, 10°; 2, 25°; 3, 40°.



impurity in this phase. It has also been found that the presence of hydrochloric acid again dispels the abnormalities in this system (Fig. 5). The n-butanol–water system shows none of these effects; at all three temperatures there is no elevation of interfacial tension, and the curves may be regarded as "normal."

The validity of these results might be questioned on the grounds that the concentrations of hexane, and of nitrogen, dissolved in the aqueous phase exceed those of the alcohols, at least in the ranges where the abnormalities occur. But these are constant factors common to all the cases, whether there are abnormalities or not, and the objection can hardly be sustained in view of the regularity of the maximum elevations of interfacial tension, and of the threshold concentrations of alcohol above which $\Delta\gamma$ becomes negative. This can be seen from the data assembled in Table 1. There can be no reasonable doubt that here is an interesting phenomenon which, however difficult it may be to interpret, at once suggests that there is a radical difference between the state of the hexane–water interface at 15° and its state at 40°. The same conclusion could be drawn from the direct study of this interface, in absence of any third component, as inspection of Fig. 1 clearly indicates.

TABLE 1.

Alcohol	Maximum $\Delta\gamma$ (dyne cm.$^{-1}$)		Threshold concn. (mole l.$^{-1}$)	
Temp.	10°	25°	10°	25°
MeOH	1·08	1·08	$6·7 \times 10^{-3}$	$8·5 \times 10^{-3}$
EtOH	0·70	0·72	$3·0 \times 10^{-3}$	$4·0 \times 10^{-3}$
PrOH	0·49	0·43	$0·55 \times 10^{-3}$	$0·3 \times 10^{-3}$

In order to evaluate thermodynamic functions for interface formation, measurements spaced more closely on the temperature scale are desirable, but the labour involved in simultaneously filling in the concentration scale equally adequately for a number of systems is very great. The hexane–aqueous propanol system has therefore been selected for this more detailed study, since it shows all the features of interest in a concentration range normally considered "accessible," where the experimental difficulties are correspondingly less. The measurements concerned are shown in Table 2, together with the data used in plotting Fig. 1, and some derived thermodynamic functions are assembled in Table 3, for temperatures between 25° and 40°.

TABLE 2. *Interfacial tensions* (*dyne cm.*$^{-1}$).

Hexane–water		Hexane–water + n-propanol				
			Concn. of n-propanol (mole l.$^{-1}$)			
Temp.	γ	Temp.	10^{-6}	10^{-5}	6×10^{-5}	10^{-4}
		10°	51·17	51·48	51·88	51·42
		15	50·91	51·23	51·33	51·14
		20	50·67	50·97	51·08	50·87
25°	50·19	25	50·42	50·70	50·83	50·58
27	50·15	27	50·32	50·60	50·73	50·48
29	50·07	29	50·22	50·50	50·63	50·39
32·2	49·84	32	50·08	50·32	50·47	50·19
33·7	49·58	33	50·03	50·26	50·40	50·13
34·75	49·42	34	49·98	50·18	50·33	50·07
35·9	49·23	35	49·91	50·09	50·24	49·99
37	49·15	36	49·85	49·96	50·04	49·91
38	49·17	37	49·81	49·88	49·92	49·85
39	49·12	39	49·74	49·75	49·77	49·75
40	49·05	40	49·72	49·71	49·72	49·70

The behaviour of these systems so far recorded suggests that it is permissible to regard this temperature interval as one within which some transition of state takes place. For the standard hexane-water system (on the left of Table 3), it appears that the transition is quite sharp, and is marked by a very large enhancement of ΔH and ΔS for interface formation, which strongly suggests that some sort of " melting " accompanies this process. The same effect is seen when n-propanol is added to the system, but it becomes rather less pronounced, and it is noteworthy that *outside* the rather narrow transition region the presence of the alcohol itself enhances ΔH and ΔS. It is as if the alcohol rather " smeared out " the melting process. These effects are clearly seen in Fig. 7, where ΔH is plotted against temperature; the curves for ΔS, with adjustment of scale, are practically superposable on these curves.

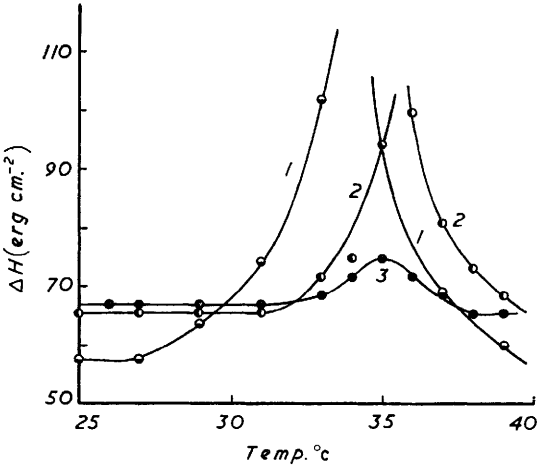
TABLE 3. *Thermodynamic functions of interface formation.*

Concn. of n-propanol (mole l.$^{-1}$)

	0				6×10^{-5}				10^{-4}			
Temp.	ΔG	ΔH	$T\Delta S$	ΔS	ΔG	ΔH	$T\Delta S$	ΔS	ΔG	ΔH	$T\Delta S$	ΔS
25°	50·19	57·7	7·5	2·5	50·83	65·7	14·9	5·0	—	—	—	—
26	—	—	—	—	—	—	—	—	50·52	67·0	16·5	5·5
27	50·15	57·7	7·5	2·5	50·73	65·7	15·0	5·0	50·47	67·0	16·5	5·5
29	50·07	63·7	13·6	4·5	50·63	65·7	15·1	5·0	50·36	67·0	16·6	5·5
31	49·96	74·3	24·3	8·0	50·52	65·7	15·2	5·0	50·24	67·0	16·7	5·5
33	49·72	101·8	52·1	17·0	50·40	71·8	21·4	7·0	50·13	68·5	18·4	6·0
34	—	—	—	—	50·33	75·0	24·7	8·0	50·07	71·6	21·5	7·0
35	49·37	94·1	44·7	14·5	50·24	93·9	43·7	14·5	49·99	74·7	24·7	8·0
36	—	—	—	—	50·04	99·5	49·5	16·0	49·91	71·6	21·6	7·0
37	49·15	69·3	20·2	6·5	49·92	80·9	31·0	10·0	49·85	68·5	18·6	6·0
38	—	—	—	—	49·84	73·2	23·3	7·5	49·79	65·4	15·6	5·5
39	49·07	60·0	10·9	3·5	49·72	68·5	18·7	6·0	49·74	65·4	15·6	5·5

ΔG, ΔH, and $T\Delta S$ are in erg. cm.$^{-2}$; ΔS in erg. cm.$^{-2}$ deg.$^{-1}$.

FIG. 7. 1, *Hexane–water*; 2, 6 × 10^{-5}M-*propanol*; 3, 10^{-6}M-*propanol*.



DISCUSSION

In general, it can hardly be disputed that these phenomena must be derived from the peculiarities of the aqueous phase, but there is some difficulty in deciding whether they are to be attributed to the bulk phase or are characteristic of the interface, and what rôle is to be assigned to the alcohol. It is desirable first to consider the relevant information in the literature.

" Discontinuities " in surface tension–concentration curves for solutions have been observed before,[9-11] and it has been shown by Prigogine and Defay[12] that surface-tension

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[9] Ramsay and Shields, *Phil. Trans.*, 1893, *A*, **184**, 622.

[10] Ramsay and Aston, *Trans. Roy. Irish Acad.*, 1902, **32**, *A*, 93.

[11] Morgan and Scarlett, *J. Amer. Chem. Soc.*, 1917, **39**, 2280.

[12] Prigogine and Defay, *Bull. Soc. chim. belges*, 1944, **53**, 115.

and vapour-pressure deviations from ideality should have opposite signs. If this principle is applicable to interfacial tensions against a hydrocarbon phase, the positive deviations from ideality now observed suggest that very dilute alcohol–water systems should show negative deviations from Raoult's law. But within the range of compositions within which these systems have been studied, the deviations are positive; then if the inference is acceptable, the partial vapour pressure curves must cross the Raoult's law line at some very low concentration. This is not forbidden by the Duhem–Margules equation, and the opinion may be held that it is very likely. There is no doubt that alcohols interact with water by hydrogen bonding and it is possible that at very low concentrations the molecules of the alcohol may be able to " build in " to the water structure; this is almost certainly true of methanol, which is the least abnormal of the alcohols in regard to its entropy of vaporisation from aqueous solution.[13] If this can be accepted, then in the lower temperature range, where there can be little doubt that water has a co-operative, pseudo-crystalline structure, a sudden breakdown might be expected within quite a narrow range of conditions, in particular, of alcohol concentration. Such a breakdown, occurring when the water structure can no longer tolerate an increasing alcohol content, might well be marked by a transition from negative to positive deviations. The partial molar volumes of alcohols in water are notorious for their irregularities, but have not yet been determined for the very low concentrations which would be of greatest interest; attention is being given to this matter. In general, there is evidence that in many systems containing alcohols particular interest attaches to the low alcohol end of the concentration range,[14,15] and it seems to be the case that for aqueous-alcoholic systems in particular no comprehensive physical picture from the structural point of view is available. This uncertainty obscures the application of the Gibbs equation to the interfacial tension problem, for it would have to be applied in the form $\Gamma_i = -\,\partial\gamma/\partial\mu_i$, and there is no knowledge of how the chemical potential, μ_i, varies as a function of concentration at the dilutions concerned. The Gibbs–Duhem equation allows $\partial\mu_i/\partial c_i$ to become infinite at zero concentration, and there is evidence that activity coefficients indeed assume extreme values at high dilutions.[16]

Little progress can therefore be made without directing attention to the properties of water in the bulk phase, and very particular interest attaches to possible changes between 25° and 40°. A case has been made [8] that some sort of collapse of order occurs, involving a transition, without loss of cohesion or extensive breaking of hydrogen bonds, from what may be called a pseudo-crystalline structure of the kind suggested by Bernal and Fowler,[17] to a more randomised state, in which entropy and energy are enhanced by the bending of hydrogen bonds, such as that pictured by Lennard-Jones and Pople.[18] The strongest evidence for this was provided by the dependence of heat capacity [19] and of the pressure coefficient of viscosity [20] upon temperature. This may now be supplemented by evidence from the thermal conductance of water,[21] which appears to be quite differently dependent upon temperature on either side of 30°. It is of special interest that surface and interfacial tension effects are consistent with this hypothesis. Fig. 8 shows values for ΔH and $T\Delta S$ for the formation of the water–air interface, calculated from the unsmoothed surface tensions measured at 1° intervals by Moser; [22] they are quite remarkable and suggest that above 35° a more disordered surface is produced than below this temperature. A somewhat different effect can be found in the measurements of Howard and McAllister [23] of

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[13] Frank and Wen, *Discuss. Faraday Soc.*, 1957, No. 24, 133.

[14] Barker, *J. Chem. Phys.*, 1952, **20**, 794.

[15] Moelwyn-Hughes and Missen, *J. Phys. Chem.*, 1957, **61**, 518.

[16] Butler, *Trans. Faraday Soc.*, 1937, **33**, 229.

[17] Bernal and Fowler, *J. Chem. Phys.*, 1933, **1**, 515.

[18] Lennard-Jones and Pople, *Proc. Roy. Soc.*, 1951, *A*, **205**, 155.

[19] Ginnings and Furukawa, *J. Amer. Chem. Soc.*, 1953, **75**, 552.

[20] Bridgman, " The Physics of High Pressures," Bell, London, 1949, p. 346.

[21] Trontasev, *Doklady Akad. Nauk S.S.S.R.*, 1956, **111**, 1014.

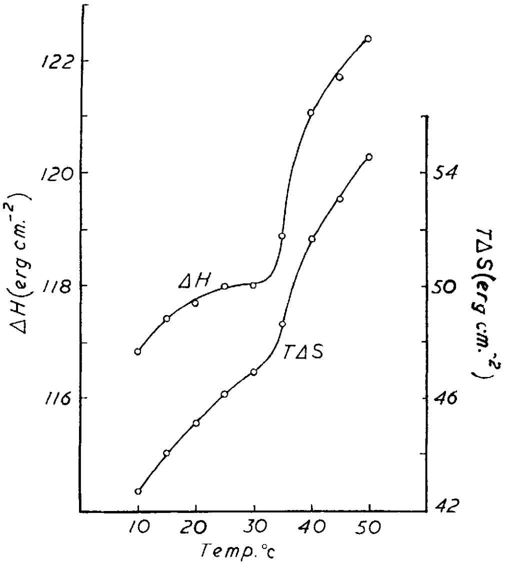
[22] Moser, *Ann. Phys.*, 1927, **82**, 993.

[23] Howard and McAllister, *A.I.Ch.E. Journal*, 1957, **3**, 325.

surface tensions of acetone–water mixtures; for dilute acetone solutions, the entropy of surface formation rises from 0·10 erg cm.$^{-2}$ deg.$^{-1}$ at 20° to 0·22 at 35°, and decreases to a level value of 0·14 erg cm.$^{-2}$ deg^{-1} above 40°.

No effects of this kind can be seen in the measurements of interfacial tensions between n-paraffins and water made by Hassan, Nielson, and Calhoun [24] or by Michaels and Hauser,[25] but in this case ΔS is small, and rather high accuracy of measurement is needed to observe its dependence on temperature; certainly a very marked effect is apparent in the present work. But the influence of pressure on the interfacial tension between n-decane and water gives a decisive indication; [25] at 23·55°, the isotherm passes through a maximum near 400 atm., and then falls, so that at 700 atm., the tension is *lower* than its normal value at 1 atm. All the other isotherms, above 50°, however, are uniformly rising curves. With the benzene–water system, on the other hand, the isotherms have positive slopes at the lower temperatures, negative at the higher. Although these effects are embarrassingly various, they all go to confirm the complexity of the water structure problem and support the view that the temperature range 30—40° is a critical one within which something rather decisive happens.

Fig. 8.



The work of Frank and Evans [26] on the hydration of nonpolar molecules in aqueous solution is relevant to the present problem. In order to explain the very large entropies of evaporation of such solutes, it was necessary to conclude that they promote the natural tendency of water to be ice-like, so that each solute molecule can be pictured as forming a nucleus for an " iceberg "; no specific hydration forces are involved, but only a stabilising effect whereby the open structure of the " iceberg " is packed out and protected from the crushing effect of thermal bombardment. This kind of solute–solvent interaction is quite abnormal and peculiar to water in the lower range of temperatures; with rising temperature the abnormality decreases and there is a tendency for a transition to the normal solute–solvent interaction (which tends to depress ΔS of vaporisation of the solute) to occur. This change in the interactions with temperature may well explain the minima that have

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[24] Hassan, Nielson, and Calhoun, *J. Petr. Technol.*, 1953, **5**, 399.
[25] Michaels and Hauser, *J. Phys. Colloid Chem.*, 1951, **55**, 408.
[26] Frank and Evans, *J. Chem. Phys.*, 1945, **13**, 507.

been reported for partial molar volumes [27] and solubilities [28] of hydrocarbons in aqueous solution, plotted against temperature.

Frank and Evans's theory provided a basis for the linear relationship, observed by Barclay and Butler,[29] between the entropy and enthalpy changes associated with the evaporation of a solute from dilute solution. The available data lead to three linear plots: one for non-polar solutes, one for polar solutes, and another for alcohols (and amines). The " alcohol line " has a characteristic slope, suggesting a mode of interaction with water peculiar to the alcohols. The alcohols fall upon the line in the order of the homologous series, the point for methanol falling near to that for the evaporation of pure water, through which the line passes. At the other end, the line approaches that for nonpolar solutes, and n-pentyl alcohol falls on both. It is thus indicated that the lowest member of the series, methanol, is indeed rather water-like, but with increasing length of hydrocarbon chain, the alcohol molecules tend to assume hydrocarbon-like properties.

These ideas lend themselves to application to our own results, and lead to the following interpretation of them.

The pure hexane–water system being considered first, the most striking result is the indication of some sort of melting process, with large ΔH and ΔS, which accompanies, and is a function of, interface formation. It occurs over quite a narrow temperature range, centred on 34°, so that at both lower and higher temperatures, no such melting is involved when interface is generated. Comparison of Figs. 7 and 8 shows that there is no such melting in the surface formation of water; ΔH and ΔS do not pass through a peak with rising temperature, but they do show a great inflection. This is entirely consistent with the view that below about 34° there is an increase in order when the surface of water is formed; it might be said that a freezing process, liberating heat, depresses the positive value of ΔH and, involving a decrease in entropy, depresses the positive value of ΔS. What might otherwise be regular curves thus develop large kinks by being " pushed down " at temperatures below 34°. The picture may be completed by noting that for the n-hexane–air interface, ΔH is a linear function of temperature between 0° and 60°, and ΔS is constant.[30]

The question arises, why does water behave so differently when it makes an interface with the two ostensibly inert phases, hydrocarbon and air? The simplest answer is that one is a condensed phase and the other is not.

At the lower temperatures, it is suggested that the hydrocarbon–water interface is covered by an " icy " layer of water molecules entirely similar in nature to Frank and Evans's icebergs which are known to surround hydrocarbon molecules in aqueous solution. This is but an extrapolation of Frank and Evans's idea, and has already been suggested for another kind of interface.[31] This is supported by the fact that ΔH and $T\Delta S$ (or ΔS) at, say, 25° (cf. Table 3) are very low in value, far lower than for the surface formation of water at the same temperature (cf. Fig. 8). Then it may be supposed that the hydrocarbon phase stabilises the ice-likeness of water in its vicinity mainly by a sort of packing-out, or reinforcement, lending protection against thermal disruption. It is very important to note that what might be called, in general, the " Frank and Evans effect " in no way depends upon any interaction forces operating between unlike molecules; only water–water forces are concerned. This is emphasised by Claussen's [32] exercises in synthesising model clathrate cages by building together primary tetrahedral water–associate units, which correspond so well with " icebergs " and with known crystalline hydrates. Thus, the suggested icy layer over the hydrocarbon phase does not depend on any hydrocarbon–water forces; rather the contrary.

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[27] Masterton, *J. Chdm. Phys.*, 1954, **22**, 1830.
[28] Bohon and Claussen, *J. Amer. Chem. Soc.*, 1951, **73**, 4181.
[29] Barclay and Butler, *Trans. Faraday Soc.*, 1938, **34**, 1445.
[30] Jasper, Kerr, and Gregorich, *J. Amer. Chem. Soc.*, 1953, **75**, 5252.
[31] Grahame, *J. Chem. Phys.*, 1955, **73**, 1725.
[32] Claussen, *ibid.*, 1951, **19**, 259, 662, 1425.

Another important point is that the primary tetrahedral unit of water association, and all the more complex cages or sheets that further association may form, involve a degree of " contra-association "; in the simplest terms the water molecules do not all point one way, molecular dipoles are not all aligned so as to give each other the maximum support. This is why the dielectric constant of water is increased under high pressures.[33]

Now, if one considers interaction between the hydrocarbon phase and water *molecules*, it is obvious that these will be maximal at some preferred orientation of the water molecules with respect to the surface of the phase; what it actually is (hydrogens inwards, hydrogens outwards ?) is quite secondary. The point is that such an interaction, which must be quite considerable (for work of adhesion is far from negligible), will, to minimise potential energy, require *all* the water molecules to adopt the same orientation and point in the same direction. This is inconsistent with the arrangement of the water molecules in the icy layer, in which, by the dictates of " tetrahedral hydrogen bonding," some will point inwards and some outwards. This may be why, over a narrow temperature range only, interface formation may involve an " unfreezing," or what might be called a " rotational melting," occurring when non-co-operative hydrocarbon–water interactions overcome co-operative water–water interactions. A similar thing could not happen at the water–air interface because the air phase is too " dilute " and cannot exert any significant forces on anything.

It is relevant that the fact that the entropy of interface formation is positive (with some notable exceptions) has led to a statement [34] that the interfacial layer is more disordered than the bulk phase from which it was generated. This is untenable, for a reversible process can be imagined in which an idealised surface is generated with no change in degree of order; it would be endothermic and would necessarily involve an increase in entropy. If a standard ΔS for such an idealised process were known, then greater values *would* indicate increased disorder. For associated liquids at least, there is little doubt that surface zones tend to be more ordered than bulk phases.[35]

To attempt an interpretation of the behaviour of alcohol-containing systems, it is first noted that abnormalities in the interfacial tension–concentration isotherms disappear (*a*) at about 35°, (*b*) with increase in alcohol concentration, (*c*) with increase in length of the hydrocarbon chain of the alcohol, and (*d*) on addition of a large excess of the strong electrolyte, hydrochloric acid. These salient facts can be considered in turn.

(*a*) The outstanding effect of very low concentrations of the three lower alcohols is to increase ΔG for interface formation, and there can be little doubt that in this region the alcohol molecules are effectively repelled from the interface. This must mean that they are preferentially retained in the bulk of the aqueous phase. The enhancement of surface tensions by ionic solutes is interpreted in this way; Harkins and MaLaughlin [36] have calculated that in dilute electrolyte solutions there is a solute-free surface layer one molecule thick, into which ions may be forced as the concentration is increased. No information is available about possible preferred orientations in the surface layer or about the effect of temperature. In this case it is the forces of solvation of ions which are responsible. For the case of the alcohols, the forces of hydrogen bonding come to mind, but these are very much weaker. Something more seems to be needed, and is found in the suggestion that the lower alcohols can, at low enough concentrations, be tolerated as components of the *co-operative* water structure. Then, over quite a narrow range of rising temperatures, release of the alcohol molecules might be expected. Alternatively, similar arguments might be presented that alcohol molecules locked in Frank and Evans's " icebergs " are naturally very hydrophilic, but cease to be so when, with rising temperature, this abnormal solute–solvent interaction weakens and disappears. In either case, a marked change in

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[33] Hamann, " Physico-chemical Effects of Pressure," Butterworths, London, 1957, p. 104.

[34] Stephan, *Wied. Ann.*, 1896, **29**, 655.

[35] Good, *J. Phys. Chem.*, 1957, **61**, 810.

[36] Harkins and McLaughlin, *J. Amer. Chem. Soc.*, 1925, **47**, 2083.

solute–solvent interaction at about 35° is postulated, and evidence for it is provided by heat capacity–composition isotherms which, for alcohol–water mixtures, undergo a complete change of shape at about this temperature.[37] A simpler explanation of the effective repulsion of the alcohol molecules from the interface is that the supposed ice-like layer acts as a barrier which is vulnerable to rising temperature. It is clear that evidence is wanting to decide between these conjectures.

(*b*) With increasing alcohol concentration, the interfacial tension isotherms, for the two lower members, pass through a peak and then descend to a plateau where $\Delta\gamma$ is still positive. It is likely that two influences are needed to explain this, one raising and the other lowering the free energy of interface formation. On the other hand, the comparative sharpness of the peak suggests that it is caused by something akin to a phase transition, or order–disorder transformation, perhaps leading to a modified interface. In this case, the whole of the curve after the peak has been traversed could be regarded as normal, but shifted with respect to a horizontal axis which is no longer relevant. Against this, however, is the fact that at 10° and at 25° the interfacial tension in this " normal " section is appreciably higher than that for the alcohol-free system, in contrast to what is found at 40°. It has been suggested that the lower alcohols can " build in " to the water structure with a difficulty which increases with the number of carbon atoms in the molecule. This might also apply to the kind of ordered water layer which is believed to exist at the hydrocarbon surface; the peak might then represent a re-arrangement of this layer to admit alcohol molecules to a limited number of sites. If so, the results are consistent with a greater tolerance for the more water-like alcohol, and a reason is perhaps found for the decreased sharpness of the " melting point " of the layer (cf. Fig. 7), and the increased values of ΔH and ΔS outside the melting range.

(*c*) Sooner or later, with rising alcohol concentration, preferred, " Gibbsian " adsorption at the interface supervenes, just as if a barrier to it had been overcome, or as if the alcohol molecules had been released from bondage in the aqueous phase. The tendency for this adsorption to occur must, however, be present all the time and must exert some effect at all concentrations, the more the higher the alcohol. With n-butanol it appears to be strong enough to be decisive, and with the other alcohols, to play a part consistent with their chain length, as shown by the " threshold concentrations " noted in Table 2.

(*d*) It is well known that the kind of order promoted by ionic solutes in aqueous solution is incompatible with the ordinary water structure and that, outside of their hydration zones, ions have a structure-breaking effect. That a heavy excess of strong electrolyte abolishes all the abnormal effects that have been observed supports the view that they are to be explained in some such way as has been attempted.

EXPERIMENTAL

The Drop-volume Apparatus.—The interfacial-tension measurements were made by means of the apparatus illustrated in Fig. 9, based upon a design due to Taylor.[38] The clean dry apparatus was set up in its rigid mounting frame and the tap *S*2 alone was lubricated with a thin film of Apiezon L grease; no liquids came into contact with this tap. The barrel of the " Agla " micrometer syringe was attached by means of a Polythene sleeve, and the whole apparatus was flushed out with purified nitrogen for 30 min. The reservoir containing the equilibrated phases was attached to *B* by means of a glass spiral and nitrogen pressure was used to fill *B* with hexane, the unlubricated tap *S*1 being kept closed. The reservoir was then connected to the top of *D* and the aqueous phase forced into the apparatus until it overflowed at the syringe barrel. The syringe plunger was at this moment inserted and, simultaneously, tap *S*2 opened, so that the vessel *C* filled with the aqueous phase. When it was nearly full, *S*2 was closed and the connection at *D* loosened, so that bulb *A* filled. The reservoir was then removed and *D* stoppered.

Next, the joint *Q* was loosened and hexane allowed to fill the rest of the apparatus from *B*;

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[37] Staveley, Hart, and Tupman, *Discuss. Faraday Soc.*, 1953, No. 15, 130.

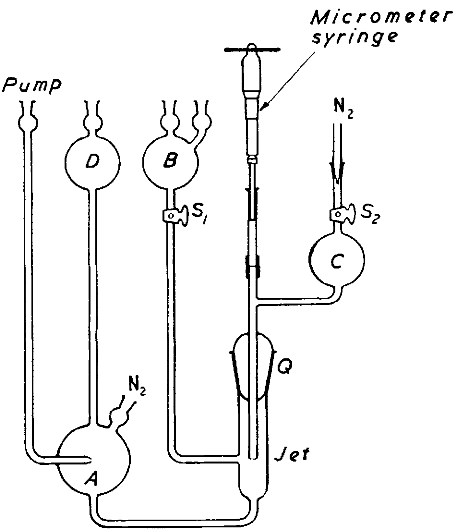
[38] Taylor, Thesis, London, 1952.

when the joint was wetted with hexane, it was secured. By loosening the stopper at *D*, more hexane was allowed to flow until the interface between the phases was some 3 cm. below the jet. Finally excess of aqueous phase was withdrawn from *A*, the nitrogen supply connected to *A*, and the whole apparatus was transferred to the thermostat bath which was regulated to better than ±0·02° c.

The jet consisted of a length of thick-walled Pyrex tubing which was polished with jeweller's rouge on a high-speed lathe, until the diameter was constant to within 0·001 cm. The end of the tube was set in an alloy of low melting point and ground with carborundum powder on a high speed drill, until microscopical examination showed freedom from flaws. The jet satisfied the requirement[39] that V/r^3 should lie between 1·2 and 2·6.

Method of Measurement.—To measure the drop volume, the nitrogen flow at *A* was stopped, and a drop was grown by opening tap *S*2. Before the drop broke away, the tap was closed and the jet examined by means of a cathetometer for perfect wetting. Growth was then continued by use of the micrometer at a rate of 0·012 ml. min.$^{-1}$, until the drop broke away; the micrometer reading was then taken. Another drop was then grown quite rapidly to about 2/3 of its break-away volume, again by use of the micrometer, and was left suspended for a period ranging from 3 min. to 24 hr. The length of this period was found to have no effect upon the final drop-volume, thus showing the absence of slow, surface-ageing effects.

FIG. 9.



Density Determinations.—These were carried out using a modified Sprengel pyknometer having a volume of 15 ml. Before it was filled, dry, purified nitrogen was passed through it for 15 min. The solution under test was introduced by nitrogen pressure from the reservoir, which was suspended in the thermostat bath.

Preparation of Solutions.—Alcohol solutions were made up by weight in conductance water and allowed to reach equilibrium with hexane in the thermostat. The volume ratio of aqueous to organic phase was kept constant at about 10 : 1. It was assumed throughout that the alcohol concentration in the equilibrium solution was the same as in the solution originally prepared,[40] since the partition coefficient of ethyl alcohol is 20 and that of butyl alcohol >5. The air in the equilibrium reservoir was displaced by nitrogen and the reservoir placed in the thermostat for 24 hr. and gently agitated.

Interfacial tensions were evaluated by means of the relation

$$\gamma = \frac{Vg\,(D - d)}{r} \cdot \phi\left(\frac{V}{r^3}\right)$$

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[39] Adam, " The Physics and Chemistry of Surfaces," Oxford University Press, 1941, p. 378.

[40] Washburn *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 1454.

where D and d are the respective densities of the aqueous and oil phases, V is the drop volume and $2r$ is the outside diameter of the jet. $\phi\left(\frac{V}{r^3}\right)$ is a correction factor obtained by interpolation from the results of Harkins and Brown.[41] A typical set of measurements is shown in Table 4.

TABLE 4. *Interfacial tension between hexane and water at* 25·00° ± 0·02°.

Micrometer readings, cm.^{3} × 5 × 10^3	Residuals, x	x^2	Micrometer readings, cm.^{3} × 5 × 10^3	Residuals, x	x^2
1487	−3	9	1490	0	0
1477	−13	169	1490	0	0
1498	+8	64	1485	−5	25
1484	−6	36	1490	0	0
1488	−2	4	1490	0	0
1499	+9	81	1491	+1	1
1500	+10	100			
			1490	±4	489

$$\text{Probable error} = \pm 0{\cdot}6745\sqrt{[x^2/n(n-1)]} = \pm 1{\cdot}2 \sim \pm 0{\cdot}08\%.$$
$$V/r^3 = 0{\cdot}2980/0{\cdot}1250 = 2{\cdot}384;\ \phi(V/r^3) = 0{\cdot}26332;\ (D-d) = 0{\cdot}3275$$
$$\gamma = 0{\cdot}2980 \times 981{\cdot}2 \times 0{\cdot}3275 \times 0{\cdot}2633/0{\cdot}5000 = 50{\cdot}43 \pm 0{\cdot}04 \text{ dyne cm.}^{-1}.$$

Purification of Materials.—Hexane. As n-hexane was not readily available, most measurements were carried out with British Drug Houses Ltd. "Hexane fraction from petroleum, special for spectroscopy." A sample of each batch used was tested by ultraviolet absorption spectrum. Absence of absorption between 210 and 700 mμ indicated freedom from unsaturated halogen derivatives, alcohols, phenols, and ethers. The material was shaken with concentrated sulphuric acid, then with a 0·1N-solution of potassium permanganate in 10% sulphuric acid and finally with a 0·1N-solution of potassium permanganate in 10% sodium hydroxide. It was washed with water, dried over sodium wire, and distilled. The fraction boiling between 65° and 70° was collected.

Shortly after commencing the experimental work, it was found that successive batches of hexane varied in density. Evans [42] found that the interfacial tension of this particular grade of hexane against water varies by as much as 0·3 dyne. cm.$^{-1}$ for different batches. A gas–liquid chromatogram was run on several batches and varying amounts of several isomers of hexane and heptane could be identified. Several batches were therefore mixed and the stock mixture used for all interfacial tension determinations.

n-Octane. Laboratory reagent grade n-octane was treated with chlorosulphuric acid for 2 days and fractionated (b. p. 125°).

Methanol. "AnalaR" methanol was treated with sodium hydroxide solution containing iodine. The mixture was set aside for 1 day and then poured into a quarter of its volume of 10% silver nitrate solution, shaken for several hours, and finally distilled after the silver oxide had settled. The alcohol was dried by heating it under reflux with 3 g./l. of aluminium amalgam until the whole of the aluminium had reacted. It was then slowly distilled (2 drops/sec.), the first 50 ml. and the last quarter being rejected. The column used for all alcohol purifications was a 200 cm. × 2 cm. column packed with Fenske helices. A stream of purified nitrogen was passed through the apparatus and the alcohol was stored over nitrogen (b. p. 64·5°/758 mm.).

Ethanol. "AnalaR" ethanol was distilled with 5 ml. of concentrated sulphuric acid and 20 ml. of water per litre. The distillate was refluxed with 10 g. of silver nitrate and 1 g. of potassium hydroxide per litre for several days and finally distilled. The alcohol was dried by refluxing it over 600 g. of freshly ignited calcium oxide per litre and subsequently shaking the mixture for 24 hr. at room temperature. The alcohol was then fractionally distilled (b. p. 78·2°/756 mm.).

n-Propanol. As no "AnalaR" grade material was available, commercial n-propanol was refluxed with 5 g. of concentrated sulphuric acid and 20 ml. of water per litre. The alcohol was distilled and refluxed with 10 g. of silver nitrate and 1 g. of potassium hydroxide per litre for several days. It was then dried with aluminium amalgam and fractionally distilled (b. p. 97·2°/771 mm.).

n-Butanol. "AnalaR" n-butanol was treated with sodium hydrogen sulphite solution and

[41] Harkins and Brown, *J. Amer. Chem. Soc.*, 1919, **41**, 499.
[42] Evans, *Trans. Faraday Soc.*, 1937, **33**, 794.

then boiled for 4 hr. with a 10% solution of sodium hydroxide. The separated alcohol was washed with water and all remaining alkali was neutralised with hydrochloric acid. The product was dried by refluxing it with 600 g. of freshly ignited calcium oxide per litre and subsequently shaking the mixture for 24 hr. at room temperature. The alcohol was then fractionally distilled (b. p. 117·7°/762 mm.).

Water. Ordinary laboratory distilled water was first redistilled over alkaline potassium permanganate and then over phosphoric acid. Spray was centrifuged off from the steam by forcing it at speed through a spiral. The steam was condensed in a quartz condenser and the distillate collected in a seasoned Pyrex flask. The whole operation was carried out as a continuous process and the distillation from the phosphoric acid and subsequent condensation were carried out in an atmosphere of purified nitrogen. Water prepared by this method had a conductance of about 1×10^{-7} ohm^{-1} cm.$^{-1}$. The water-still used had the advantage that the conductance cell was placed in such a position that the resistance of the water could be measured both before it was collected and also before it was withdrawn from the storage flask for experimental runs.

Hydrochloric acid. " AnalaR " sodium chloride was freed from bromide and iodide impurities by adding chlorine water to a solution in conductance water. The solution was then boiled until all the liberated bromine and iodine had been expelled. The recrystallised product was treated with concentrated sulphuric acid. The liberated hydrogen chloride was passed through a cold trap and absorbed in conductance water. The solution was then boiled to give constant-boiling hydrochloric acid.

Nitrogen. Nitrogen from a cylinder of " oxygen-free nitrogen " was first freed from dust by filtering through cotton wool. It was then passed over soda lime and bubbled through a solution of potassium hydroxide and then through phosphoric acid. Finally it was scrubbed with conductance water.

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