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Surface and Interfacial Tensions and Their Combined Properties in Seven Binary, Immiscible Liquid–Liquid–Vapor Systems

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The interfacial tension between two liquids and surface tensions of respective liquids in contact with their common, saturated vapors in equilibrium have been measured, by use of the pendant-drop method, for each of the following systems: *n*-pentane–water, *n*-hexane–water, isopentane–water, R 113 ($C_2Cl_3F_3$)–water, *n*-pentane–glycerol, furan–glycerol, and water–methylphenyl silicone oil. The temperature range covered by the measurements for each system was from 15 or 20 °C up to near the saturation temperature, under atmospheric pressure, of the more volatile one of the two liquids. The data obtained were used to deduce the following composite properties: a pair of final spreading coefficients, work of adhesion, and surface pressure at the less volatile liquid surface. All properties were correlated respectively by linear functions of temperature.

Introduction

Some kinds of heat-transfer processes are intrinsically related to three-phase, two-component systems each consisting of two immiscible liquids and their common vapors. Examples follow: condensation of a binary vapor mixture of immiscible liquids on a cooled wall (e.g., ref *1*); and direct-contact heat-exchange processes in which either two immiscible liquids come into contact, resulting in vaporization of the more volatile one of the two (*2*, *3*), or a liquid and a vapor of different components come into contact, resulting in condensation of the vapor (*4*, *5*). In these operations the manner of contact of the two liquids and consequently the heat-transfer characteristics are strongly influenced by the relations among the three boundary tensions: surface tensions of the two liquids in contact respectively with their common vapors, and interfacial tension between the two liquids. (In this paper, we customarily refer to an interfacial tension between a liquid and a vaporous phase (a pure vapor or a vapor/vapor mixture or a vapor/gas mixture) as "surface tension".) Very insufficient effort has been made so far, however, to obtain systematic data on these three kinds of tensions in systems of industrial importance, as is briefly outlined below.

Over 50 years, surface chemists have occasionally measured surface tension of some liquids (mostly water) in contact with vapors of immiscible, more volatile liquids at constant temperatures and varying pressures primarily to deduce adsorption isotherms (e.g., ref *6*-*14*). Also found in the literature are interfacial tension values mostly for water-organic liquid combinations (e.g., ref *15*-*20*). Those measurements are limited to specific combinations of substances and, in most cases, to narrow temperature ranges or only to room temperatures. In this situation, some researchers of direct-contact heat transfer have attempted to measure, for themselves, surface and interfacial tensions in systems of their own interest in simple ways mostly at room temperatures (*2*, *4*, *21*). The accuracy of these measurements cannot be considered high.

This work is the first attempt to present simultaneously, on the basis of reasonably precise measurements, the values of the three kinds of tensions in each system of interest in some heat-transfer problems. In fact, we selected, disregarding systematic composition considerations, seven systems that had been employed in previous direct-contact heat-transfer researches and/or have potential applicabilities to practical heat-transfer operations. In each one of the seven systems which involves two fluid substances (say, more volatile fluid 1 and less volatile fluid 2), we tried to measure, under equilibrium conditions, the surface tension of the saturated liquid of fluid 1 in contact with the saturated common vapors of fluid 1 and fluid 2, σ_1; the surface tension of the saturated liquid of fluid 2 in contact with the saturated common vapors, σ_2; and the interfacial tension between the two liquids, σ_{12}. (Note that we generally abbreviate hereafter "fluid 1 in the liquid state" to "liquid 1" and "fluid 2 in the liquid state" to "liquid 2". Sometimes "fluid 1 (or fluid 2)" and "liquid 1 (or liquid 2)" may be used alternatively without clear distinction.) The system temperature was varied generally from 15 or 20 °C up to near the normal boiling point (saturation temperature under atmospheric pressure) of a more volatile fluid in each system. The results of the tension measurements enabled us to deduce some composite interfacial properties such as final (or equilibrium) spreading coefficients

$$S_{1/2} = \sigma_2 - \sigma_1 - \sigma_{12} \qquad S_{2/1} = \sigma_1 - \sigma_2 - \sigma_{12} \tag{1}$$

work of adhesion

$$W = \sigma_1 + \sigma_2 - \sigma_{12} \tag{2}$$

and surface pressure at the less volatile liquid surface

$$\Pi_2 = \sigma_{20} - \sigma_2 \tag{3}$$

where σ_{20} denotes the surface tension of pure liquid 2 in contact with its own vapor. Of particular interest from an engineering viewpoint may be the pair of spreading coefficients which could play a critical role in some heat-transfer operations (*1*-*4*).

Experimental Section

From among many methods for measuring surface or interfacial tension we selected the pendant-drop method primarily taking account of the following advantages: (a) successive, perfectly static measurements are possible which are desirable for binary systems in which some aging effects (*18*, *19*) may exist; and (b) the method is essentially free from any contact-angle problem, which is particularly favorable for liquid–liquid interfacial tension measurements. The method itself is well-known, and general techniques are described by, for example, Ambwani and Fort (*22*) and Patterson and Ross (*23*). In the present work, however, we had to devise some auxiliary techniques in order to deal with binary systems at elevated temperatures. We therefore restrict detailed description to such matters which may be unique to our measurements. All details of the experiments are given elsewhere (*24*).

Apparatus. The main portion of the apparatus consisted of a Nikon microscope illuminator (6 V, 30 W) as a light source, a vertical ground-glass plate as a light diffuser, a rectangular glass cell filled with water as a heat filter, a specially designed

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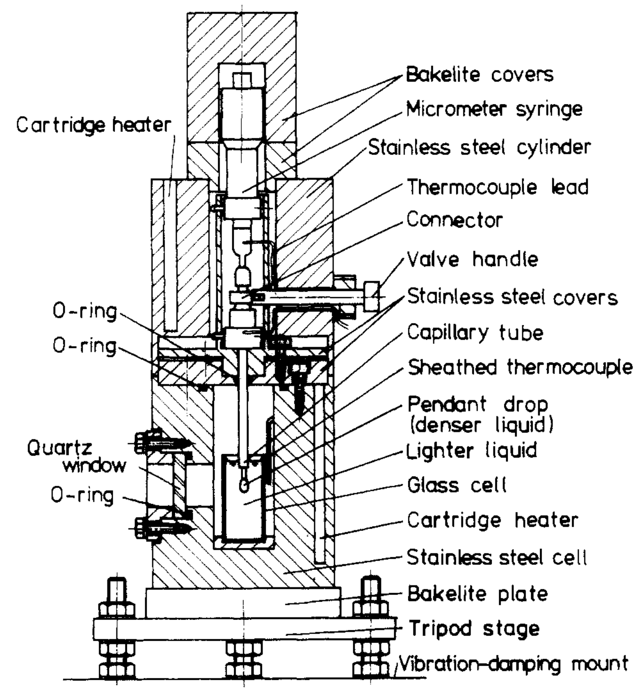
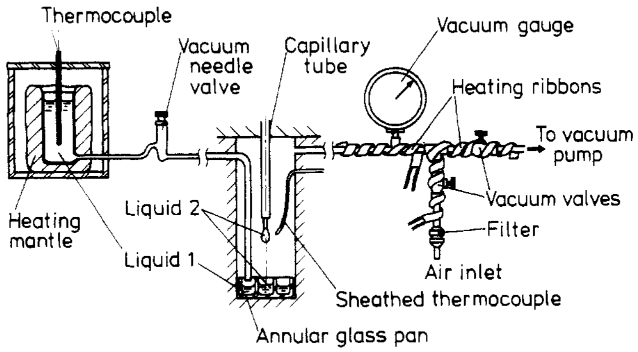


Figure 1. Construction of the pendant-drop cell and syringe assembly for liquid–liquid interfacial tension measurement.



(Not to scale)

Figure 2. Setup of the pendant-drop cell and the auxiliary equipment for surface tension measurement.

pendant-drop cell with syringe assembly, and a Canon FTb 35-mm camera with a Canon 100-mm f 4 macrographic lens and a Canon Auto-Bellows. All of these components were securely aligned and rigidly fixed on a massive cast iron surface plate which was then mounted on a desk equipped with pressurized air supports regulated by an automatic level controller to minimize the possible effect of ambient vibrations.

The construction of the pendant-drop cell and syringe assembly is shown in Figure 1. The setup of the pendant-drop cell illustrated here is for liquid–liquid interfacial tension measurement. An alternative setup for surface tension measurement is illustrated in Figure 2. The pendant-drop cell was a cylindrical stainless steel (SUS 304) cell of 100-mm o.d., 36-mm i.d., 130-mm height, and 110-mm inside depth. A capillary tube was inserted into the cell along its central axis through top airtight stainless steel covers. The cell had three polished quartz windows. Two of them were on the axis of the light beam for photography. The third was at right angles to the other two for observing the capillary tube, while adjusting it to an exactly vertical position.

The capillary tube was prepared in triplicate for alternate use. Each was a Pyrex capillary tube, 6-mm o.d. and 0.5-mm i.d., which was ground, for over 10 mm from its tip, to approximately 3-mm o.d. with an out-of-roundness of 1 μm or less. The tip face was also carefully ground perpendicular to the axis so that the tip had a sharp-edged circular periphery which the pendant-drop periphery was to meet.

The liquid which formed the drops was forced into the capillary tube from a micrometer syringe of 2-cm^3 capacity (Gilmont Instruments Inc., Great Neck, NY) through Omnifit connecting arrangements, with a pressure-resisting valve, made of Teflon and Tefzel. The syringe assembly was enclosed in a stainless steel (SUS 304) cylinder mounted on the cell and with removable Bakelite covers. The temperature in the pendant-drop cell as well as that of the syringe assembly could be elevated by four 200-W cylindrical cartridge heaters and four 150-W ones imbedded respectively in the wall of the cell and the stainless steel cylinder, and was monitored by three copper–constantan thermocouples (one in the cell and the other two around the syringe assembly).

In the liquid–liquid interfacial tension measurement, a rectangular optical Pyrex glass cell was put into the stainless-steel cell to hold the lighter liquid into which a pendant drop of a denser liquid was to be formed. In the surface tension measurement, it was replaced by an annular Pyrex glass pan which was to collect the pendant-drop liquid in the core section and to contain in its annular section another liquid which was to be supplied from an external temperature-controlled reservoir connected to the pendant-drop cell. The reservoir and the connecting tube equipped with a needle valve were all made of Pyrex glass except the Teflon needle of the valve. Also connected to the cell was the assembly by which air inside the cell could be evacuated and alternatively, if necessary, filtered air could be supplied to the cell.

Procedure. The procedure of surface tension measurement is outlined here. First, we filled the micrometer syringe with a liquid (say, liquid **2**; presaturated with the other liquid at a desired temperature) and the external reservoir with another liquid (say, liquid **1**), both of them being shut off from the cell. The cell and the syringe assembly were heated to the desired level, followed by an evacuation of the cell to a sufficient vacuum. Subsequently, with the cell shut off from the evacuation assembly, some of liquid **1** was sucked into the cell from the external reservoir by manipulating the needle valve. Liquid **1** now in the annular section of the glass pan filled the cell with the saturated vapor on the establishment of equilibrium. The vapor–liquid equilibrium in the cell was confirmed by the thermocouple and the vacuum gauge readings. Then the valve of the syringe assembly was opened. By manipulation of the micrometer syringe, liquid **2** was supplied to the capillary tube. First several drops of liquid **2** were dropped into the core section of the glass pan and one drop was left at the capillary tip forming a pendant drop; some fraction of liquid **2** (either collected in the pan or forming the pendant drop) would evaporate in the cell, resulting in the formation of a binary saturated vapor mixture in simultaneous equilibrium with the two liquid phases. After about 1 h the pendant drop at the capillary tip was dropped off, and another drop was formed to an adequate size for measurement. After another 10 min or so the drop was photographed for the first time; then the same drop was photographed a few times in succession every 3 min, the drop volume being changed a little each time by manipulating the micrometer syringe. This photographic operation was repeated with several newly formed drops; thus about 15 photographs were taken for determining the surface tension at each temperature.

The procedure of liquid–liquid interfacial tension measurement was generally simpler than the one described above, and its description is omitted here. Final results were about 15 photographs for each of σ_1, σ_2, and σ_{12} at each of four or, in most cases, five different desired temperatures for each system.

The negative films (Kodak TRI-X) developed were analyzed on a film analyzing system consisting of a Master Hi-Lux 35-mm

Table I. Comparison of Results of Preliminary Measurements in the Benzene-Water System with Literature Values

ref	T, °C	$\sigma_1{}^a$	$\sigma_2{}^a$	$\sigma_{12}{}^a$	$S_{1/2}{}^a$	method
present study	20	28.68	62.26	34.05	−0.47	pendant drop
6	25	28.2	62.1	33.9	0.0	drop weight
7	25	28.36	61.8	33.64	−0.2	capillary rise
35	20	28.82	62.36	35.03	−1.49	drop weight
23	20	28.69	62.15	34.08	−0.62	pendant drop

[a] Units: mN/m.

film projector with an F = 130 mm lens (Rikagaku Seiki Co., Ltd., Tokyo) and a screen box (with built-in X-Y traveling cross hairs linked to a digital readout device) of a Filmotion F-107A film analyzer (J. Osawa & Co., Ltd., Tokyo). Surface and interfacial tensions were determined by the conventional method of the selected plane (*22*) with the aid of equations by Misak (*25*) for the dimensionless shape factor.

Fluid Samples and Their Properties. We selected seven systems for which temperature dependences of interfacial properties were to be studied: these are n-pentane-water, n-hexane-water, isopentane-water, R 113 ($C_2Cl_3F_3$)-water, n-pentane-glycerol, furan-glycerol, and water-methylphenyl silicone oil (the first substance in each system is the more volatile one designated as fluid **1**). In addition, the benzene-water system was used in a preliminary experiment performed only at 20 °C. Benzene, n-pentane, n-hexane, isopentane, furan, and R 113 were of reagent grade and were distilled once before use. Glycerol of reagent grade and methylphenyl silicone oil (KF 54 fluid prepared by Shin-Etsu Kagaku Co., Ltd., Tokyo, which has intermediate properties between Dow Corning 550 and 710 fluids) were used as received from the manufacturers. Water was taken from an Auto-Still WAR-30 apparatus (Yamato Scientific Co., Ltd., Tokyo) which comprises a reverse osmosis device and an ion-exchange device as well as an all-glass distillation unit.

In determining the surface and interfacial tensions, one must know the density difference between the pendant-drop liquid and the surrounding medium. Densities of two liquid phases in each system were taken from previously published data on respective pure liquids assuming the effect of mutual dissolution as negligible except the water-saturated silicone oil KF 54, whose density we measured with a pycnometer at elevated temperatures. The density of the vapor phase in each system was approximated by that of the pure saturated vapor of fluid **1** considering the vapor pressure of fluid **2** low enough in the range of the present measurements. The saturated-vapor densities were either directly taken from published data or calculated by use of either the ideal gas law or, if possible, the virial equation of state based on published data of vapor pressures and of virial constants. Data sources were Kell (*26*) for liquid density of water, International Critical Tables (*27*) for liquid density of glycerol, Vargaftik (*28*) for vapor density of n-hexane, Downing (*29*) for liquid and vapor densities of R 113, Guthrie et al. (*30*) for liquid density and vapor pressure of furan, and API 44 Tables (*31*) for all other properties.

Results

Preliminary Measurements. Prior to measuring σ_1, σ_2, and σ_{12} in the seven aforementioned systems, some preliminary measurements were performed, to check the reliability of our apparatus and procedure, with pure water and n-hexane at elevated temperatures and then with the benzene-water system at 20 °C. The data obtained on water surface tension agreed with the values recommended by the IAPS (*32*) within a deviation of 0.26 mN/m over the range between 15 and 60 °C. The data of surface tension of n-hexane obtained at 20 and 50 °C agreed with those given by Jasper (*33*) within 0.14 mN/m. The benzene-water system was the only one for which some different sources for data on the set of σ_1, σ_2, and σ_{12} at room temperature were found in the literature. Comparison of our data with them is made in Table I. Our data are in good agreement with the others, particularly with the latest ones by Patterson and Ross (*23*). On the basis of the aforementioned, we judged that our apparatus and procedure were reliable enough, and proceeded to the main measurements, whose results are presented below.

Measurements in the Seven Systems. Table II gives the major results obtained in this work, those for seven binary systems plus the surface tension of pure water and glycerol, the latter being necessary for calculating surface pressure Π_2. Each numerical value is an arithmetic mean of about 15 data; the magnitude of deviation will be shown later in terms of the standard deviation from a correlation. The possible errors in those data due to the uncertainties in densities of fluids and due to the errors in meausring pendant-drop dimensions have been evaluated by using the calculus of variations according to Ambwani and Fort (*22*); the error due to the uncertainty in gravitational acceleration was neglected, since we used the value measured precisely on our campus, 9.797 45 m/s^2. This error analysis yielded the maximum uncertainty in each tension, over the temperature range of its measurement, which is given in the right-hand column of Table II.

We encountered some difficulties in measurements of σ_1 and σ_{12} in the R 113-water system and σ_1 in the water-silicone oil KF 54 system. We could not form a pendant drop of R 113 with an adequate configuration at the capillary tip in the vaporous medium becuase the density difference was too large (or, to be more exact, the capillary constant was too small). Thus, in the R 113-water system σ_1 was not measured. As for σ_{12} in this system, measurement was performed only in a less reliable manner. The R 113 did not spread, displacing water, up to the edge of the capillary tip because of high wettability of the glass with water, and thus the pendant drops of which σ_{12} was measured may not have had a completely circular base. In this case, the possible error in σ_{12} may surpass the uncertainty given in Table II. In the water-silicone oil KF 54 system we could not get reproducible data of σ_1 at higher temperatures (>60 °C). This is probably due to an occasional formation of a duplex film of silicone oil on the surface of the pendant drop of water which was presaturated with the silicone oil at approximately the same temperature as the one to be maintained in the cell. (The solubility of silicone oil in water increases with an increasing temperature. Therefore, when the temperature in the presaturation operation was slightly higher than the desired temperature, the water possibly became supersaturated in the cell and resulted in the formation of a duplex film of silicone oil on its surface.) At lower temperatures the data of σ_1 were obtained with a good reproducibility. They agree, contrary to our intuitive expectation, with the surface tension of pure water, σ_{10}, within possible experimental error. In other words, the surface pressure on water given by σ_{10}-σ_1 turns out as small as 0.42-0.63 mN/m, which is within the sum of respective uncertainties of σ_1 and σ_{10}.

Correlations of Surface and Interfacial Tensions. It is known that for the great majority of liquid compounds surface tension can be considered a linear function of temperature over a fairly wide temperature range provided they are highly pure and in contact solely with their own vapors (*33*). By a simple analogy to this fact, we tried to express our results of surface

Table II. Results of Surface and Interfacial Tension Measurements

	surface or interfacial tension, mN/m											max uncertainty	
	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	60 °C	70 °C	90 °C	mN/m	%
						Water							
	73.49	72.72	71.89	71.15	70.15	69.55		67.85	66.13			±0.36	±0.5
						n-Pentane–Water System							
σ_1	16.47	15.98	15.49	14.99	14.54							±0.08	±0.05
σ_2	62.51	62.22	61.99	61.72	61.50							±0.36	±0.6
σ_{12}	48.61	48.41	48.18	47.96	47.74							±0.44	±0.9
						n-Hexane–Water System							
σ_1		18.33	17.86	17.27		16.36		15.37	14.37			±0.09	±0.5
σ_2		64.24		62.96		61.65		60.26	58.91			±0.36	±0.6
σ_{12}		49.46		48.40		47.40		46.45	45.35			±0.50	±1.0
						Isopentane–Water System							
σ_1	15.29	14.75	14.33	13.80								±0.09	±0.6
σ_2	58.59	58.16	58.14	57.82								±0.36	±0.6
σ_{12}	48.50	48.03	47.64	47.05								±0.50	±1.0
						R 113–Water System							
σ_2		58.29	58.08	58.01		57.79	57.57					±0.36	±0.6
σ_{12}		44.57	44.64	44.47		43.79						±0.59	±1.3
						Glycerol							
	62.48		61.81	61.33	60.99							±0.74	±1.2
						n-Pentane–Glycerol System							
σ_1	16.46	15.97	15.52	15.02	14.47							±0.14	±0.9
σ_2	42.36	42.15	42.10	41.95	41.65							±0.74	±1.8
σ_{12}	27.84	27.84	27.79	27.78	27.76							±0.68	±2.4
						Furan–Glycerol System							
σ_1	24.53[a]	24.06	23.37	22.62								±0.14	±0.6
σ_2	41.10	39.70	38.51	37.22								±0.74	±1.9
σ_{12}	15.46[a]	15.38	15.25	15.13								±0.82	±5.3
						Water–Silicone Oil KF 54 System							
σ_1		72.23		70.68		69.13		67.22				±0.36	±0.5
σ_2		24.59				23.60		23.02		21.91	20.98	±0.11	±0.4
σ_{12}		39.48				39.21		39.14		38.78	38.51	±0.77	±2.0

[a] Measured at 15.7 °C.

and interfacial tensions in binary systems as linear functions of temperature, say

$$\sigma_1 = a + bT \tag{4}$$

where *T* is the temperaure in degrees Celsius, and *a* and *b* are constants to be determined by least-squares fitting of the values given in Table II. Table III indicates the least-squares constants, *a* and *b*, thus obtained and the standard deviations of the data (not the mean values used to determine *a* and *b* but the raw data of multiple measurements) from the correlations. For every tension the standard deviation is smaller than the uncertainty in the data as given in Table II. This fact indicates that the above simple way of preparing correlations is satisfactory for the present objective.

Derivation of Composite Properties. The composite properties at each specified temperature in each system were generally obtained by substituting into eq 1–3 the values of σ_1, σ_2, σ_{12}, and σ_{20} given in Table II with a few exceptions. In the R 113–water system σ_1 was not measured successfully, as described before. Therefore, the correlation for surface tension of pure R 113 in contact with its own vapor by Watanabe and Okada (*34*) was tentatively used to predict σ_1, which was then substituted into eq 1 and 2; this was based on the assumption that the surface tension of R 113 is not appreciably affected by saturation with water. Both σ_1 and σ_{12} in the furan–glycerol system were measured at 15.7 °C instead of 15.0 °C; thus σ_1 and σ_{12} at 15.0 °C were extrapolated by the correlation given in Table III and then substituted into eq 1 and 2. In the water–silicone oil KF 54 system, the values of σ_1 at 70 and 90 °C were also extrapolated by the prepared correlation to calculate composite properties at those temperatures. As all the tensions were successfully correlated by linear functions of temperature, the composite properties defined in eq 1–3 are also representable by some linear functions as given in eq 4. The constants, *a* and *b*, for the composite properties were determined by least-squares fitting of the values calculated as stated above and are listed also in Table III. The uncertainty of each of such correlations is, in principle, a sum of those of two or three tensions given in Table II. This means that some spreading coefficients whose absolute values are calculated at 1 mN/m or less have relative uncertainties on the order of 100% or more and thus may have the wrong signs.

Discussion

Comparison with Previously Reported Data. In an extensive survey of the literature, we have found very limited data on the seven systems dealt with in the present work. Some of them are those obtained by crude or unspecified techniques in the course of research on heat transfer (e.g., ref *2* and *4*) or bubble dynamics. We assume that they are not worthy to be discussed here. The rest are of σ_{12} in the *n*-pentane–water system (*15*, *17*) and of σ_2 (*8*, *23*) and σ_{12} (*15*–*17*, *20*, *23*) in the *n*-hexane–water system. They are data obtained exclusively at either 20 or 25 °C except those of Aveyard and Haydon (*17*) on σ_{12} in the *n*-hexane–water system. As for σ_{12} in those systems the data obtained by the pendant-drop method (*15*, *23*) agree with ours within 0.8 mN/m. Other data obtained by dynamic methods (*16*, *17*, *20*) give higher values than ours by 0.9–1.8 mN/m. The differences in σ_2 are more appreciable. The previous data (*8*, *23*) are higher than ours by 2.1–4.2 mN/m. It should be noted that they are data obtained by use of equipment with no air-evacuation device. A possible un-

Table III. Least-Squares Constants (a and b)[a] of Correlations for Properties in the Form of Linear Functions of Temperature in Degrees Celsius, and Standard Deviations of Measured Values from the Correlations

	σ_1	σ_2	σ_{12}	$S_{1/2}$	$S_{2/1}$	W	Π_2
			n-Pentane–Water				
a	17.92	63.25	49.28	-3.95	-94.60	31.89	12.76
b	-0.0970	-0.0504	-0.0438	0.0904	-0.0028	-0.1036	-0.1146
SD	0.06	0.12	0.10				
			n-Hexane–Water				
a	20.32	66.95	51.48	-4.80	-98.16	35.74	9.12
b	-0.0992	-0.1336	-0.1017	0.0663	0.1371	-0.1301	-0.0312
SD	0.08	0.25	0.20				
			Isopentane–Water				
a	16.74	59.23	49.94	-7.46	-92.42	26.03	16.62
b	-0.0978	-0.0466	-0.0948	0.146	0.0436	-0.0496	-0.1104
SD	0.04	0.26	0.21				
			R 113–Water				
a		58.79	45.57	-6.79	-84.36	33.09	17.14
b		-0.0263	-0.0419	0.1295	-0.0457	0.0933	-0.1340
SD		0.27	0.34				
			n-Pentane–Glycerol				
a	17.95	42.85	27.92	-3.01	-52.81	32.89	20.78
b	-0.0986	-0.0324	-0.0046	0.0706	-0.0618	-0.1266	-0.0430
SD	0.06	0.21	0.06				
			Furan–Glycerol				
a	26.69	44.91	15.84	2.38	-34.18	55.76	18.72
b	-0.1343	-0.2566	-0.0234	-0.0989	0.1506	-0.3675	0.1814
SD	0.07	0.13	0.07				
			Water–Silicone Oil KF 54				
a	75.62	25.64	39.78	-89.73	10.17	61.46	
b	-0.1658	-0.0523	-0.0140	0.1272	-0.0991	-0.2037	
SD	0.35	0.08	0.20				

[a] a in mN/m. b in mN/(m·K).

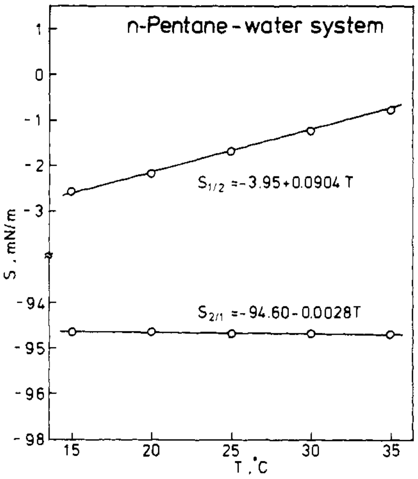


Figure 3. Temperature dependence of spreading coefficients in the *n*-pentane–water system.

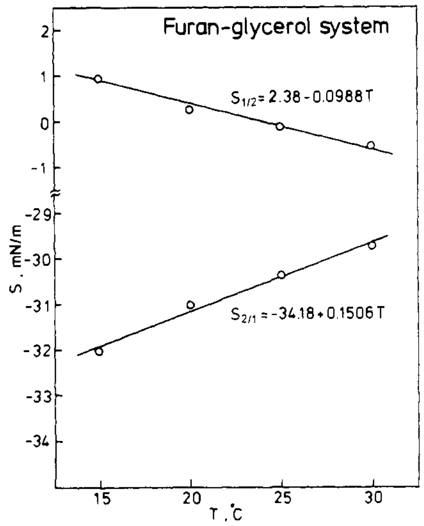


Figure 4. Temperature dependence of spreading coefficients in the furan–glycerol system.

dersaturation of air, adjacent to the water surface in such equipment, with *n*-hexane vapor may have given values of σ_2 which were too high.

Signs and Temperature Dependences of Spreading Coefficients. In order to facilitate the understanding of the temperature dependences of spreading coefficients, three typical results are exemplified in graphical form in Figures 3–5, wherein the determined correlations are shown together with points representing the values to which the correlations were fitted. Five systems other than the furan–glycerol and water–silicone oil KF 54 systems exhibit features similar to those represented in Figure 3 for the *n*-pentane–water system. As temperature increases, $S_{1/2}$ increases and $S_{2/1}$ either increases or decreases in a more moderate manner. A simple extrapolation of $S_{1/2}$ in each system to higher temperatures beyond the range of the present work indicates that its value will change from negative to positive as the temperature increases to several degrees higher than the normal boiling point of fluid 1 (except in the isopentane–water system, in which $S_{1/2}$ will change to positive at a much higher temperature excess over the boiling point).

Figure 4 for the furan–glycerol system shows that $S_{1/2}$ decreases with an increase of temperature, changing its sign from positive to negative at a moderate temperature ($\simeq$24 °C). Such a tendency of the temperature dependence of $S_{1/2}$ seems true, though the critical temperature for $S_{1/2} = 0$ is ambiguous to a great extent because of the uncertainty of our correlation being as large as ±1.7 mN/m.

Figure 5 illustrates that the water–silicone oil KF 54 system is distinguished from other systems by such a relation as $S_{1/2}$

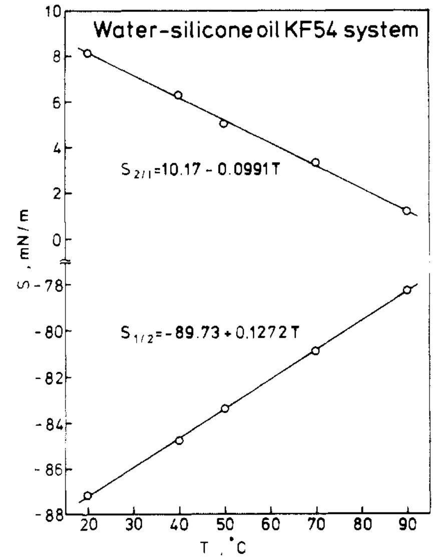


Figure 5. Temperature dependence of spreading coefficients in the water-silicone oil KF 54 system.

$< 0 < S_{2/1}$ over the temperature range of this work. A simple extrapolation indicates that $S_{2/1}$ will change its sign from positive to negative at a temperature not widely different from the normal boiling point of water.

In conclusion, the results of the present work suggest that one of the two spreading coefficients, $S_{1/2}$ and $S_{2/1}$, in each system could have positive values in some temperature range. This conclusion conflicts with the conventional notion that final spreading coefficients must generally be negative (*35-38*), while the latter notion has been supported by experimental results with various liquids deposited on water or mercury at room temperature under atmospheric pressure. (Strathdee and Given (*11*), Mori (*21*), and Higeta et al. (*4*) are in the minority giving positive values of final spreading coefficients in some systems. The measuring techniques used in the latter two are less reliable.) In order to settle this problem, more extensive and, if possible, more precise measurements will be required.

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Glossary

a	least-squares constant (property value extrapolated to 0 °C), mN/m
b	least-squares constant (temperature coefficient of the property), mN/(m·K)
$S_{1/2}$	final spreading coefficient of liquid 1 on liquid 2, mN/m
$S_{2/1}$	final spreading coefficient of liquid 2 on liquid 1, mN/m
T	temperature, °C
W	work of adhesion, mN/m
Π_2	surface pressure of monolayer of liquid 1 substance adsorbed on liquid 2 surface, mN/m
σ_1	surface tension of liquid 1 in contact with common vapors of liquid 1 and liquid 2, mN/m
σ_{10}	surface tension of pure liquid 1 in contact with its own vapor, mN/m
σ_2	surface tension of liquid 2 in contact with common vapors of liquid 1 and liquid 2, mN/m
σ_{20}	surface tension of pure liquid 2 in contact with its own vapor, mN/m
σ_{12}	interfacial tension between liquid 1 and liquid 2, mN/m

Registry No. R 113, 76-13-1; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3; isopentane, 78-78-4; glycerol, 56-81-5; furan, 110-00-9.

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