# Temperature–Interfacial Tension Studies of Some 1-Alkenes Against Water

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**The interfacial tensions of 1-tridecene, 1-tetradecene, 1-pentadecene, and 1-hexadecene against water have been measured at five temperatures over a range of 25° to 65° C. Equations were formulated relating the interfacial tensions to the temperature. The entropy of formation of unit area of interface, together with the latent heat and total energy, were calculated and recorded in a table.**

THE REGION (*2*) which separates contiguous immiscible liquids, commonly known as the dineric interface, may be regarded as a transitional phase containing both molecular species, since it is improbable that, for a two-phase liquid system, an absolute discontinuity exists. Therefore, the magnitude of the interfacial tension is determined by the degree of dissimilarity of the molecular species of the component liquids.

Interfacial tension studies have proved to be of fundamental importance in many phases of theoretical and industrial chemistry. Measurements of this thermodynamic property have been valuable in the investigation and interpretation of properties of colloidal systems, interfacial monolayers, and many others.

Since intermolecular attraction is the agency underlying interfacial phenomena, the temperature would be expected to have a marked influence on the interfacial tension. An increase in the temperature of the present olefin-water systems is attended by a corresponding increase in the mutual miscibility of the component liquids and also in their mean molecular kinetic energies. As both of these contribute in decreasing the interfacial tension, data obtained over a temperature range enable a more complete evaluation of the thermodynamic properties of the interfacial region.

The present paper is the first of a projected series of interfacial tension studies of highly purified *n*-alkanes and 1-alkenes with water as the arbitrarily chosen standard liquid.

## EXPERIMENTAL

**Materials.** The compounds used in this study were 1-tridecene, 1-tetradecene, 1-pentadecene, and 1-hexadecene. Olefins of the best quality were obtained from the Humphrey Chemical Co. and each was tested with a Dual-Column Programmed Temperature Gas Chromatograph packed with 5% polyglycol (molecular weight 20,000) on 35/80 Chromosorb P. The chromatograms showed the compounds were of exceptional purity and suitable for the proposed study. To obtain water of the highest possible purity, doubly distilled water was first passed through a Barnstead block tin conductivity still and finally distilled in an all-quartz double chamber Heraeus-Quarzschmelze still. The final product had a conductivity of $10^{-6}$ mho.

**Apparatus.** The drop-weight apparatus used for measuring the interfacial tensions was similar to that described by Harkins and Alexander (*3*). The apparatus assembly consisted of a helical spring of DuPont teflon (T.F.E.) tubing of 2- to 3-mm. I.D. The helix consisted of 5 coils, 25 cm. in diameter which ensured a large vertical motion with no apparent change in volume. The upper end of the spring was attached to a calibrated measuring pipet and the lower to a capillary tube of borosilicate glass upon which the drops were to form. A series of tips were constructed with one end ground to a plane surface with a series of grinding powders. These were applied with the aid of a jeweler's sapphire faceting apparatus. The finished tips had sharp edges with no flaws prominent enough to be visible under a magnification of 14 diameters. A receiving container, within which the tip was inserted, was connected to the capillary tube with a ground-glass joint. Thus, the helical spring served to connect the pipet and tip components of the system.

In the operation, the drop-forming liquid is forced to flow from the measuring pipet through the helical spring and then to the tip by increasing the hydrostatic head.

A device, constructed of brass, was designed to actuate the vertical motion of the measuring pipet. This consists essentially of a circular plate supporting a vertical rod to form a ringstand. The receiving container is clamped to the rod at the desired height above the base. The measuring pipet is attached to a brass block which has a fine-pitch threaded opening. A correspondingly threaded shaft, attached to the rod, passes through this opening. By rotating a knurled knob at the top, a precisely controlled vertical motion is imparted to the pipet.

A series of interchangeable tips and measuring pipets permitted the measurement of a variety of liquids of different density.

To maintain constant temperatures during the measurements, a thermostat bath, with heat-resistant plate glass windows was used. The walls were insulated with polyurethane foam with openings on opposite sides of the bath to permit the operator to observe the apparatus during experimentation. The stirring apparatus operated with sufficient efficiency and the thermoregulator was sensitive enough to maintain a temperature constant to ±0.01° between 25° and 65° C. Actual temperatures were determined at any given time by an NBS certified resistance thermometer-Mueller bridge system.

## PROCEDURE

Preliminary experiments proved that the aqueous phase wet and spread much more readily on the ground surface of the tip than the organic phase; therefore, the former was selected as the drop-forming liquid. Since the aqueous phase was the more dense, the tip had to be arranged so that the drops formed vertically downward within the organic liquid and subsequently became detached.

In the present study, the experimental procedure involved the determination of drop-volumes rather than drop-weights, since the former can be measured more directly. The apparatus was mounted on the base of the brass stand, with the receiving container and tip clamped to the vertical rod and the measuring pipet to the movable block. This assembly was immersed in the water bath and the helical spring coiled. The aqueous phase was then introduced into the measuring pipet with the aid of a hypodermic syringe until the pipet and coiled spring were filled. By partially uncoiling the spring, a portion of the aqueous phase was transferred to form a layer in the lower part of the receiving container. Enough of the saturated organic phase was introduced into the receiving container just to cover the capillary tip. This was accomplished by carefully adjusting the level of the organic phase while observing the interface through the telescope of a traveling microscope. The drops were made to form slowly on the tip under conditions approaching static equilibrium. As the volume of the drop depends primarily on the rate of its formation, the final stage of development should be very slow. By careful manipulation of the knurled knob, each drop was formed and became detached in 1 minute, the maximum rate recommended by Harkins and Brown (*4*).

The pure component liquids were saturated with each other by frequently shaking them together in a long-necked flask. The flask and contents were then suspended in the thermostat bath for a minimum of 18 hours before use. Samples were readily withdrawn from the respective layers and introduced into the pycnometers and interfacial tension apparatus, while each was suspended in the bath at the same temperature. Since all measurements were carried out isobarically, the authors assumed that each pure liquid was saturated with air.

Since the densities of the mutually saturated liquids appear in the interfacial tension equation as explicit variables, they must be measured directly and as accurately as possible. The pycnometers used in this investigation were similar to the Type D described by Weissburger (*9*) but with necks 8 cm. in length. Three were constructed, one each for the respective mutually saturated liquids and the third for a counterpoise. The first two of these had volumes of 8.6470 and 8.5486 ml., respectively. All volume calibrations were made both with pure water and with spectro-quality benzene. The densities of the mutually saturated liquids at the five temperatures are given in Table I.

Table I. Densities of the Mutually Saturated Liquid Compounds

| $t$, ° C. | $d_w$ | $d_o$ |
|---|---|---|
| 1-Tridecene | | |
| 25 | 0.9977 | 0.7620 |
| 35 | 0.9937 | 0.7546 |
| 45 | 0.9896 | 0.7474 |
| 55 | 0.9854 | 0.7397 |
| 65 | 0.9811 | 0.7326 |
| 1-Tetradecene | | |
| 25 | 0.9984 | 0.7694 |
| 35 | 0.9937 | 0.7604 |
| 45 | 0.9896 | 0.7528 |
| 55 | 0.9857 | 0.7441 |
| 65 | 0.9818 | 0.7382 |
| 1-Pentadecene | | |
| 25 | 0.9972 | 0.7732 |
| 35 | 0.9937 | 0.7656 |
| 45 | 0.9897 | 0.7578 |
| 55 | 0.9860 | 0.7514 |
| 65 | 0.9814 | 0.7444 |
| 1-Hexadecene | | |
| 25 | 0.9973 | 0.7769 |
| 35 | 0.9940 | 0.7699 |
| 45 | 0.9901 | 0.7638 |
| 55 | 0.9859 | 0.7581 |
| 65 | 0.9818 | 0.7529 |

The number of drops collected for each of the four compounds varied between 20 and 27. Measurements were made at five temperatures over a range of 25° to 65° C.

## RESULTS

The interfacial tension is a measure of the interfacial free surface energy per square centimeter of the dineric interface. The magnitude of this property, together with the temperature coefficients, enable the calculation of all other thermodynamic properties of the interfacial region. The following equation of Harkins and Cheng (*5*) was applied in calculating the interfacial tensions.

$$\gamma_i = \frac{vg(d_w - d_o)}{2\,\pi r F} \tag{1}$$

in which $\gamma_i$ represents the interfacial tension in ergs per square centimeter, $v$, the average drop volume in milliliters; $d_w$ and $d_o$, the densities of the water and organic phases, respectively; $r$, the radius of the tip; $g$, the gravitational factor; and $F$, the Harkins and Brown correction factor (*4*).

The thermodynamic equation of Clapeyron can be applied to the dineric interface when written in the two-dimensional form (*2*),

$$-\frac{d\gamma_i}{dT} = \frac{L_i}{T\Delta A} = \Delta S_i$$

whence

$$L_i = T\Delta S_i = -\ T\Delta A\,\frac{d\gamma_i}{dT} \tag{2}$$

Since these properties are intensive variables, $\Delta A$ is equal to unity and $L_i$ and $\Delta S_i$ represent, respectively, the latent heat and entropy of formation of unit area of interface under isobaric and isothermal conditions. The total energy of formation of unit area of interface $U_i$ is given by the relation,

$$U_i = \gamma_i + L_i \tag{3}$$

Therefore, with the aid of these equations, all thermodynamic properties of the interfacial region can be calculated.

Empirical equations expressing the interfacial tension as a function of the temperature were formulated and used to calculate the interfacial tensions for the temperature range indicated. These, together with the values of the entropy, latent heat, and total energy, are recorded in Table II as ergs per square centimeter.

1-Tridecene: $\gamma_i = 49.9600 - 0.001789t - 0.001007t^2$
1-Tetradecene: $\gamma_i = 47.8993 + 0.0003846t - 0.0002209t^2$
1-Pentadecene: $\gamma_i = 47.8771 + 0.004562t - 0.0005378t^2$
1-Hexadecene: $\gamma_i = 47.3157 + 0.02834t - 0.0008273t^2$

Plots of the interfacial tensions as functions of the temperature give curves (not shown) which are concave to the temperature axis. This direction of the deviation from linearity has been observed in all such studies carried out by the author (*6, 7, 8*) and appears to be typical of interfacial tension–temperature relations. Some variation from linearity is to be expected, since the kinetic energy of the molecules in the interfacial region and the mutual miscibility of the component liquids increase. The latter of these leads to increasing deviation from linearity with the temperature, and the studies of Donahue and Bartell (*1*) appear to bear this out.

Table II. Interfacial Tensions of the 1-Alkene–Water Systems—Thermodynamic Properties of the Interfacial Region

| $t$, ° C. | $\gamma_i$ | $-(d\gamma_i/dt)$ | $L_i$ | $U_i$ |
|---|---|---|---|---|
| | | 1-Tridecene | | |
| 25 | 49.29±0.13 | 0.0521 | 15.53 | 64.82 |
| 35 | 48.66±0.13 | 0.0723 | 22.29 | 70.95 |
| 45 | 47.92±0.13 | 0.0924 | 29.40 | 77.32 |
| 55 | 46.82±0.14 | 0.1126 | 36.95 | 83.77 |
| 65 | 45.59±0.14 | 0.1327 | 44.87 | 90.46 |
| | | 1-Tetradecene | | |
| 25 | 47.77±0.13 | 0.0107 | 3.19 | 50.96 |
| 35 | 47.64±0.13 | 0.0151 | 4.65 | 52.29 |
| 45 | 47.47±0.13 | 0.0195 | 6.20 | 53.67 |
| 55 | 47.25±0.13 | 0.0239 | 7.84 | 55.09 |
| 65 | 46.99±0.13 | 0.0283 | 9.57 | 56.56 |
| | | 1-Pentadecene | | |
| 25 | 47.66±0.13 | 0.0223 | 6.65 | 54.31 |
| 35 | 47.38±0.13 | 0.0331 | 10.20 | 57.58 |
| 45 | 46.99±0.13 | 0.0438 | 13.94 | 60.93 |
| 55 | 46.50±0.14 | 0.0546 | 17.92 | 64.42 |
| 65 | 45.90±0.14 | 0.0654 | 22.12 | 68.02 |
| | | 1-Hexadecene | | |
| 25 | 47.51±0.13 | 0.0130 | 3.88 | 51.39 |
| 35 | 47.29±0.13 | 0.0296 | 9.12 | 56.41 |
| 45 | 46.92±0.13 | 0.0461 | 14.67 | 61.59 |
| 55 | 46.37±0.13 | 0.0627 | 20.58 | 66.95 |
| 65 | 45.66±0.13 | 0.0792 | 26.78 | 72.44 |

Table II shows that the entropy and the latent heats of the interfacial region increase with the temperature. Changes in this direction are to be expected. The increasing entropy reflects the increasing disorder within the interfacial region. If the theory underlying the latent heat of formation of unit area of liquid-gas interface (2) is accepted as valid for the dineric interface, then the given quantity of heat for each given temperature may be regarded as that required to extend the interfacial region by unit area, and this quantity is proportional to the temperature.

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# Adsorption of Carbon Dioxide and Nitrogen on Charcoal at 30° to 50° C.

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**Isotherms for carbon dioxide and nitrogen on metal impregnated and nonimpregnated charcoal were obtained in the temperature range of 30° to 50° C. Isosteric heats of adsorption were also determined. Carbon dioxide was more favorably adsorbed in all cases. The more favorable adsorbent for carbon dioxide was shown to be a function of temperature while the nonimpregnated charcoal was more favorable for nitrogen over the range studied.**

MOST DATA which have been reported on the physical adsorption of carbon dioxide and nitrogen on various charcoals are at temperatures of 20° C. and lower. Many of these data have been summarized and compared (*5*). Recently, Major, Sollami, and Kammermeyer (*4*) reported adsorption data for $CO_2$ at 1 atm. on 15 different carbons at 23° to 27° C. Charcoals used in the present work are relatively new products of Pittsburgh Coke and Chemical Co. for which no $CO_2$ or $N_2$ data have been reported previously at any temperature.

## EXPERIMENTAL

**Materials.**

| Charcoal type | BPL | ASC (metal impregnated BPL) |
|---|---|---|
| Surface area | 1050–1150 m.$^2$/gram | 800–850 m.$^2$/gram |
| Apparent Density | 0.50 grams/cc. | 0.58–0.60 grams/cc. |
| Mesh | 12 × 30 | 12 × 30 |
| Carbon Dioxide | 99.995% pure | |
| Nitrogen | 99.4% pure (0.6% $O_2$) | |

**Equipment.** A static gravimetric adsorption apparatus of the McBain and Bakr type (*3*) with a 30-cm. adsorption chamber was used. The weight of gas adsorbed was measured by the extension of calibrated quartz spring. Pressures were measured by mercury manometers. All height or distance measurements were made using 40-cm. Eberbach cathetometers. Temperature was maintained by circulating heated air outside the adsorption chamber located within an insulated container. Heat was furnished by a hot air blower and was controlled to approximately ±½° C. with a bimetallic control switch. Details of the experimental unit are given in (*5*).

**Procedure.** Charcoal adsorbent was placed in a small sample holder suspended from the quartz spring. The surface of the charcoal was evacuated by applying a vacuum $\ll 1$ mm. of Hg while heating the exterior of the adsorption chamber to an excess of 200° C. by means of Electro-thermal heating tapes. This process was continued for more than an hour; tapes were removed and the chamber was allowed to come to the desired temperature level. Prior to making equilibrium measurements, the charcoal was contacted with the gas and the evacuation procedure repeated several times. The adsorbate then was admitted to the adsorption cham-

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