Glossary

c_1, c_2, ..., c_j	coefficients in representation of V^E by eq 1, $cm^3\ mol^{-1}$
m	numer of coefficients used in eq 1
n_D	refractive index for sodium light
V^E	molar excess volume, $cm^3\ mol^{-1}$
V_i^E	partial molar excess volume of component i, $cm^3\ mol^{-1}$
$V_i^{E,\infty}$	limiting value of V_i^E at infinite dilution of component i, $cm^3\ mol^{-1}$
x	mole fraction of 1-decanol

Greek Letters

ρ	density, $g\ cm^{-3}$
σ	standard deviation for fit of V^E, $cm^3\ mol^{-1}$

Subscripts

1	1-decanol component
2	cycloalkane component

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Surface Tension of Mercury between 15 and 50 °C by the Sessile Drop Method

Graeme H. Perry and Noel K. Roberts*

Chemistry Department, University of Tasmania, Hobart, Tasmania, Australia 7001

The surface tension of mercury has been determined by the sessile drop method in vacuo at 15, 20, 25, and 50 °C. Ca. 50 measurements were made at each of the four temperatures, extending over a period of 2 yr. The greatest attention was paid to the purification of the mercury and the estimation of all possible errors in the determination of the surface tension. The surface tension varied linearly with temperature according to the equation $\gamma = 490.8 - 0.2155t$ with a correlation coefficient of 0.9998, where γ = surface tension in $mN\ m^{-1}$ at t °C. This relation is in excellent agreement with the results obtained previously by one of the authors and with that postulated by Jasper from the large number of determinations of the surface tension of mercury, $\gamma = 490.6 - 0.2049t$. The temperature coefficient obtained in this study is in slightly better agreement with the average of all previous experimental measurements, $-0.224\ mN\ m^{-1}\ K^{-1}$, than with the value recommended by Jasper, $0.2049\ mN\ m^{-1}\ K^{-1}$.

Introduction

The surface tension of mercury is an important quantity, as indicated in the lengthy review on the surface properties of mercury by Wilkinson (*1*). Even so there is still some uncertainty about its value. Wilkinson (*1*) reports that the range of values obtained during the three decades preceding his review (1942–1972) is still exceptionally large. The average of all of these values is 469.7 ± 34.3 $mN\ m^{-1}$. Jasper (*2*) has carefully analyzed the wide range of values and selected the results of one of the present authors (N.K.R.) (*3*), Kemball (*4*), and Bosworth (*5*) as reference data for the National Bureau of Standards. He proposes a linear relation between the surface tension and temperature of the following form:

$$\gamma = 490.6 - 0.2049t \qquad (1)$$

where γ = surface tension in $mN\ m^{-1}$ at temperature t °C.

The original results of Roberts (*3*) were over a limited temperature range, 16.5–25.0 °C. In this paper we present results from 15 to 50 °C using the sessile drop method in vacuo and involving over 50 measurements at each of the following temperatures: 15, 20, 25, and 50 °C. The sessile drop method avoids a contact angle and therefore has advantages over other methods for measuring surface tension. Furthermore the measurements for all four temperatures extended over a period of 2 yr.

Before proceeding it is necessary to correct a serious error in Wilkinson's otherwise excellent review. On p 582 of the review, referring to the surface tension obtained by Roberts (*3*), he says, "Some recent workers have just added 1 dyne cm^{-1} to a value calculated by means of the Worthington equation [to obtain the surface tension]. It is clear that accurate values cannot be obtained unless recourse is made to equation 2", i.e.

$$\gamma = h^2\rho g/2 - \gamma \int_0^h \sin\phi/x\,dz + 2\gamma h/b \qquad (2)$$

where h = height of the apex of the drop above the maximum cross-sectional area, ρ = density of the liquid (Hg), g = acceleration due to gravity, x = horizontal radius of a given section above the maximum cross-sectional diameter, z = distance between the apex and this horizontal section, ϕ = angle of

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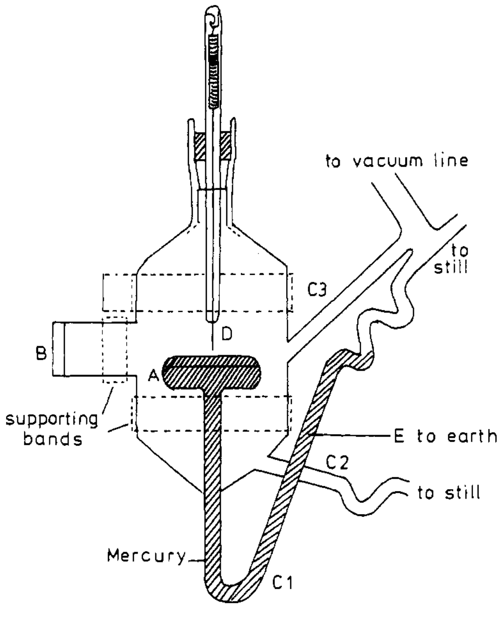

Figure 1. Measuring vessel.

inclination of the normal to the axis, measured on the side of the vertex, i.e., the normal acting at the drop surface, distance x from the axis, and b = radius of curvature at the apex. However Roberts (*3*) states quite clearly (p 1907), "The surface tension of mercury was calculated from Ziesing's (*6*) corrected version of Worthington's (*7*) equation." Ziesing (*6*) has shown that his equation is equivalent to eq 2. Furthermore, on p 1910, it was stated, "Kemball's value for the surface tension of mercury should be increased by 1.1 dyne cm^{-1} owing to the error in the Worthington equation." Obviously Roberts did not "just [add] 1 dyne cm^{-1} to a value calculated by means of the Worthington equation". In fact the error of 1.1 dyn cm^{-1} was calculated by using the radius of the pool of mercury given by Kemball (*4*) (p 531), i.e., 2.52 cm.

Experimental Section

Apparatus. The apparatus used for determining the surface tension of mercury by the sessile drop method in vacuo was similar to that employed by Roberts (*3*). Temperature control was accurate to 0.1 °C at 15, 20, and 25 °C and to 0.2 °C at 50 °C. Figure 1 shows details of the vessel. The measuring vessel consists of the following: (A) A low profile cup with sides of ~1 cm. (B) A viewing tube sealed by a Pyrex window. (C) Tubes leading to the mercury distillation apparatus. C_1 carries mercury to the cup; C_2 drains mercury which has spilt from the cup to the mercury still; C_3 allows evacuation. (D) A tungsten wire which is suspended on an assembly made up of a spring and cylindrical iron core free to move in a glass tube. This glass tube enters the measuring vessel through a ground-glass joint sealed with mercury. A solenoid about the glass tube and above the measuring vessel is connected to a rheostat. Variation of the magnetic field of the solenoid acts on the cylindrical iron core to draw the tungsten point toward or away from the mercury surface. (E) During distillation a large electrical potential builds up in the distillation vessel. To remove this we connected the distilled mercury to earth potential through E. A lowering up to 10 mN m^{-1} in γ can result from failure to earth the mercury. The traveling microscope had a smallest scale division of 0.0002 cm; i.e., h could be read to 0.000 05 cm, or an uncertainty of 0.2 mN m^{-1} in γ.

The wedge angle of the Pyrex window, 30 × 6.5 mm, through which the sessile drop was viewed, was measured with a Taylor-Hobson autocollimator and amounted to 15 ± 0.25 s over the central 10 mm. Kemball's equation (*4*) predicts that such an angle will produce a slight increase in the true value of h of 0.0001 cm. This correction is probably accurate to ±2-3% (*4*), i.e., 2 × 10^{-6} cm or ~0.01 mN m^{-1} uncertainty in γ.

Table I. Summary of Uncertainties Involved in the Measurement of the Surface Tension by the Sessile Drop Method

uncertainty	error in surface tension, mN m^{-1}
setting of lamp to define equator of mercury pool	0.3
optical flatness and level of glass plate over which the traveling microscope was moved to define equator and vertex of mercury pool	0.3
scale divisions of traveling microscope and reliability of wedge angle correction for window	0.2
radius of mercury pool	0.2
total error in surface tension	1.0

The optical flatness of the glass slab, 17.5 × 17.5 × 2.5 cm, over which the traveling microscope was moved, was measured by an interference method using an optically flat plate. The glass slab was flat to within ±0.0001 cm, which leads to an uncertainty in γ of 0.3 mN^{-1}. The level of glass slab was measured with a Cooke, Troughton, and Simms precision level. The uncertainty in the level of the slab was ~10^{-5} cm over the distance that the traveling microscope was moved between reading the vertex and the equator of the sessile drop, i.e., ~2.25 cm. The level was reversed to correct any error in the level itself. The uncertainty of ~10^{-5} cm corresponds to ~0.03 mN m^{-1} in γ. The tungsten pointer over the mercury pool was 3-4 mm off-center, which meant that the error was of the order of 10^{-5} m, i.e., beyond the accuracy of the traveling microscope used. The uncertainty in the height of the lamp used to define the equator pool led to an uncertainty of 0.3 mN m^{-1} in the surface tension. The radius of the mercury pool was 4.49 ± 0.01 cm, which introduces an uncertainty of 0.2 mN m^{-1} into γ. The total uncertainty in the determination of the surface tension of mercury is therefore ±1.0 mN m^{-1}. To this uncertainty must be added the standard deviation of the measurements, which was ±0.1 mN m^{-1}. The various uncertainties involved in the measurement of γ are listed in Table I.

Mercury. Redistilled mercury (150 mL) was added to 200 mL of concentrated sulfuric acid containing 10 g of ferrous sulfate, and air was drawn through the mixture for 8 h. The mercury was then separated from the acid layer, washed, and filtered through a pinhole in a filter paper, washed several times with distilled water, and dried for 1 h at 110 °C. The mercury was then filtered through a pinhole in a filter paper and allowed to fall through a solution of 5% nitric acid. This process was repeated 3 times. Then the mercury was cyclically washed with distilled water several times, dried, filtered once again, and slowly distilled under vacuum 3 times, the last time being into the measuring vessel. The mercury was cyclically distilled in the measuring vessel until a stable surface tension was reached after 7 days.

Results and Discussion

Surface Tension of Mercury. The corrected form of the Worthington equation given by Ziesing (*6*) was used to calculate the surface tension of the mercury at 15, 20, 25, and 50 °C, i.e.

$$\gamma = \tfrac{1}{2}\rho g h^2 + \frac{2\gamma h}{b} - \gamma\frac{4a}{3R}\left(1 - \frac{1}{2\sqrt{2}}\right) \qquad (3)$$

where γ = surface tension (mN m^{-1}), ρ = density of mercury (g cm^{-3}), g = acceleration due to gravity = 980.45 cm sec^{-2} (ref *3*), h = height of the sessile drop (cm) from the equator to the vertex, $2R$ = diameter of the sessile drop = 4.49 ± 0.01 cm, $a = [\gamma/(\rho g)]^{1/2}$ cm^{-1}, and $1/b = (8\pi R/a^3)^{1/2} \times 0.41421$

Table II

temp, °C	density of mercury,[a] g cm^{-3}	no. of determinations over 2 yr	surface tension, mN m^{-1}	SD, mN m^{-1}	uncertainty apart from SD, mN m^{-1}
15	13.558	47	487.6 ± 1.1	0.1	± 1.0
20	13.546	49	486.4 ± 1.1	0.1	± 1.0
25	13.534	70	485.3 ± 1.1	0.1	± 1.0
50	13.473	50	480.0 ± 1.1	0.1	± 1.0

[a] References *4* and *8*.

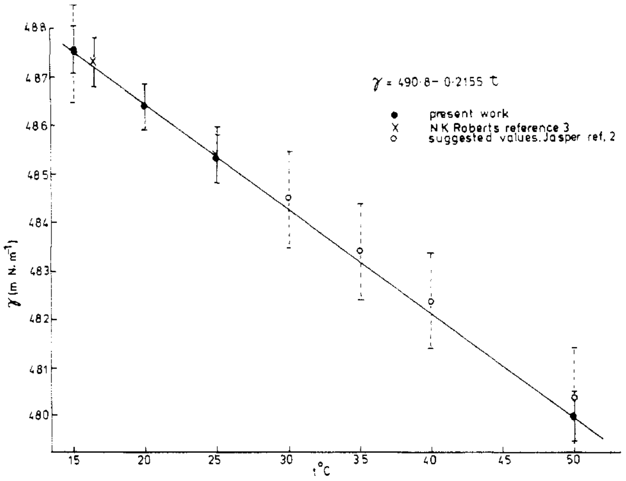

Figure 2. Temperature dependence of surface tension of mercury.

$\times \exp(-R/a + 0.58578)$ cm^{-1}.

The measured height, h, of the sessile drop from the equator to the vertex was subject to two corrections: (a) The wedge angle of the window through which the drop was measured was 15 s; i.e., 0.0001 cm^4 had to be subtracted from h. The wedge angle of the window used here is very much smaller than other wedge angles reported for the sessile drop method. For example, Kemball's two windows had wedge angles of 0.40° and 0.04° leading to corrections of 0.0082 and 0.0010 cm, respectively. In the apparatus used in this study the uncertainty in the wedge angle correction was 2×10^{-6} cm, i.e., beyond the limit of measurement of the traveling microscope. (b) The glass slab over which the traveling microscope was moved to detect the equator and the vertex of the mercury pool was not exactly level. There was a rise of 0.035 mm in 1 m toward the measuring vessel. Since the microscope moved over approximately the radius of the pool, i.e., ~2.5 cm, between readings, 0.8×10^{-4} cm had to be added to the observed height h.

The values for the surface tension obtained over a period of 2 yr are listed in Table II. The results in Table II fit a linear equation of the form

$$\gamma = 490.75 - 0.2155t$$

The correlation coefficient is 0.9998. This equation is in excellent agreement with that suggested by Jasper (*2*) from a bewildering array of experimental data for the surface tension of mercury (*1*), viz.

$$\gamma = 490.6 - 0.2049t$$

The results are shown in Figure 2 with the results obtained previously by one of the authors (*3*) and selected values suggested by Jasper (*2*).

The temperature coefficient obtained in this work, −0.2155 mN m^{-1} K^{-1}, is in slightly better agreement with the average of all previous experimental values (*1*), −0.224 mN m^{-1} K^{-1}, than with the value selected by Jasper (*2*), −0.2049 mN m^{-1} K^{-1}. It is difficult to draw any worthwhile conclusions from this comparison. A much more extended temperature range would be required to decide on the exact value of the temperature coefficient of the surface tension of mercury.

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Molar Excess Volumes of Mixing of Tetrahydrofuran with Some Aliphatic Compounds Having Different Functional Groups

S. K. Suri* and B. Chawla

Department of Chemistry, Indian Institute of Technology, New Delhi 110016, India

Excess volumes of mixing for binary mixtures of tetrahydrofuran with a variety of aliphatic organic compounds containing different functional groups, namely, chloroform, carbon tetrachloride, 1,2-dichloroethane, acetonitrile, nitromethane, acetone, methyl formate, and ethyl acetate, have been determined from the experimental density measurements at 298.15 K over the entire composition range. The data do not indicate any obvious relationship between V^E and the electron donor–acceptor abilities of the solution constituents.

Introduction

The unlike interactions between different functional groups in the molecules of a binary mixture dictate the behavior of the system not only in the liquid phase but also in the gaseous and solid state (*1*, *2*). The strength of these interactions relative to the average of the strengths of the interactions in the two pure unmixed components can, to a fair extent, be predicted from the magnitude of the molar excess thermodynamic function (*3*–*5*).

A perusal of the literature revealed that the thermodynamic studies on the binary mixture containing tetrahydrofuran, a most commonly used organic solvent, are scanty. Recent communications from our laboratory reported excess volumes for the binary mixtures of tetrahydrofuran with aliphatic alcohols and amides (*6*, *7*). As an extension to these studies, excess volumes of mixing for the binary mixtures of tetrahydrofuran with some aliphatic organic compounds, namely, chloroform, carbon tetrachloride, 1,2-dichloroethane, acetonitrile, nitromethane, acetone, methyl formate, and ethyl acetate, have been deter-

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