of the temperature coefficients of surface tension obtained from these lines are presented in Table II.

TABLE II

TEMPERATURE COEFFICIENTS OF SURFACE TENSION

$\gamma_t = \gamma_{800°} - k(t - 800°)$

$BaCl_2$ mole, %	$\gamma_{800°}$ (dynes/cm.)	$-k$ (dynes/cm. per °C.)	$BaCl_2$, mole, %	$\gamma_{800°}$ (dynes/cm.)	$-k$ (dynes/cm. per °C.)
0.0	96.2	0.072	37.3	114.3	0.061
3.9	98.4	.078	42.3	117.0	.044
8.4	101.7	.079	47.7	121.5	.066
13.5	102.8	.071	62.3	133.0	.077
24.4	108.9	.060	82.1	144.2[a]	.076
29.4	111.0	.064	100.0	162.6[a]	.078
34.0	112.8	.061			

[a] Extrapolated values.

Discussion of Results

The consistency of the results obtained in this investigation gives confidence in their accuracy. The fact that the curves of surface tension *versus* temperature show a linear decrease with increasing temperature is in accord with the generally observed relationship between these variables. Furthermore, the measurements made on the pure salts gave values which agree with those of Jaeger[8] for potassium chloride and of Motylewski[9] for barium chloride. The termination of the curve of surface tension *versus* composition at 62.3 mole per cent. barium chloride is due to the higher melting points of the 82.1 mole per cent. mixture and of pure barium chloride.

The values for the temperature coefficient of surface tension do not show a simple variation with composition. There is considerable scatter in the plot of this quantity *versus* composition which makes the interpretation of this variation uncertain.

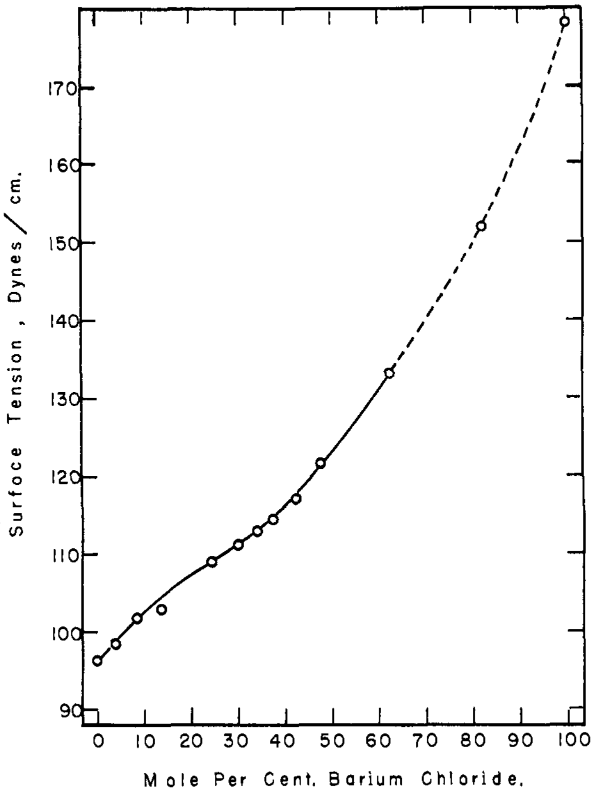

Fig. 3.—Surface tensions of KCl–$BaCl_2$ mixtures at 800°.

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(8) F. M. Jaeger, *Z. anorg. Chem.*, **101**, 1 (1917).

(9) S. Motylewski, *ibid.*, **38**, 410 (1904).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

The Orthobaric Surface Tensions and Thermodynamic Properties of the Liquid Surfaces of a Series of 1-Alkenes, C_6 to C_{16}, and of *n*-Decylcyclopentane, *n*-Decylcyclohexane and *n*-Decylbenzene

BY JOSEPH J. JASPER AND E. ROBERT KERR

RECEIVED JANUARY 4, 1954

This is the second of a series of three papers on surface tension measurements of hydrocarbons briefly describing the procedure for measuring orthobarically the surface tensions of a series of 1-alkenes and of *n*-decylcyclopentane, *n*-decylcyclohexane and *n*-decylbenzene. Surface tension–temperature data are presented in tables together with the constants of the least squares equations which relate the variables. From these data the entropies, enthalpies and latent heats of the liquid surfaces were calculated and tabulated in the tables.

The surface tension, which is the resultant of a differential attraction across a liquid–vapor interface, has proved to be an important and convenient index for comparing the magnitude of other physico-chemical properties of pure liquids which depend upon intermolecular attraction. It is a measure of the free energy of formation of unit area of the surface and from its application in the two-dimensional forms of the fundamental thermodynamic equations[1] it is possible to determine the magnitude of the thermodynamic properties which are of such importance in the study of the nature of liquid surfaces. In recent years the purely theoretical concepts related to the surface properties of liquids now find their implementation in many technological processes to a most unexpected de-

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(1) W. D. Harkins, "The Physical Chemistry of Surface Films," Reinhold Publ. Corp., New York, N. Y., 1952, Chap. 1 and 2.

Table I

The Surface Tensions and Least Square Factors *a* and *b* for the Series of 1-Alkenes and for *n*-Decylcyclopentane, *n*-Decylcyclohexane and *n*-Decylbenzene

Compound	Temperature, °C. 0	10	20	30	40	50	60	70	80	90	100	*a*	*b*
1-Hexene	20.58	19.55	18.52	17.49	16.46	15.43	14.40	...	...	...	...	20.58	0.10300
1-Heptene	22.40	21.41	20.42	19.43	18.44	17.45	16.46	15.47	14.49	...	...	22.40	.09893
1-Octene	23.83	22.87	21.91	20.95	19.99	19.03	18.08	17.12	16.16	15.20	14.24	23.83	.09590
1-Nonene	24.98	24.05	23.12	22.19	21.26	20.33	19.40	18.47	17.54	16.61	15.68	24.98	.09300
1-Decene	25.97	25.05	24.14	23.22	22.30	21.39	20.47	19.55	18.64	17.72	16.81	25.97	.09165
1-Undecene	26.79	25.89	24.98	24.08	23.18	22.28	21.37	20.47	19.57	18.67	17.76	26.79	.09025
1-Dodecene	27.48	26.59	25.71	24.82	23.94	23.05	22.17	21.28	20.40	19.51	18.63	27.48	.08853
1-Tetradecene	28.64	27.77	26.90	26.03	25.16	24.29	23.43	22.56	21.69	20.82	19.95	28.64	.08691
1-Hexadecene	...	...	...	27.01	26.16	25.31	24.45	23.60	22.75	21.90	21.04	29.57	.08525
n-Decylcyclopentane	31.29	30.40	29.51	28.62	27.73	26.84	25.95	25.06	24.17	23.29	22.39	31.29	.08898
n-Decylcyclohexane	31.67	30.81	29.95	29.09	28.23	27.37	26.51	25.65	24.79	23.93	23.07	31.67	.08596
n-Decylbenzene	31.92	31.12	30.33	29.53	28.73	27.93	27.14	26.34	25.54	24.75	23.95	31.92	.07969

gree, and in these concepts the surface tension plays an important role. High precision methods, however, will give surface tension values only with a degree of accuracy commensurate with the purity of the liquids available. Small amounts of capillary-active impurities profoundly influence the surface tension, therefore, reliable and reproducible data can be obtained only from the purest compounds.

The purpose of this investigation was to obtain surface tension data over an appreciable temperature range, of a series of 1-alkenes, C_6 to C_{16}, and of *n*-decylcyclopentane, *n*-decylcyclohexane and *n*-decylbenzene under orthobaric conditions. The compounds were of a high degree of purity and were made available by the American Petroleum Institute through the API Research Project 44 at the Carnegie Institute of Technology. The samples were purified by the API Research Project 6 from materials supplied by the following laboratories: 1-hexene, 1-heptene, 1-nonene, 1-undecene, *n*-decylcyclopentane, *n*-decylcyclohexane and *n*-decylbenzene by the API Research Project 45, at the Ohio State University, Columbus, Ohio; 1-octene, 1-decene, 1-dodecene, 1-tetradecene and 1-hexadecene by the API Research Project 6 at the Carnegie Institute of Technology, Pittsburgh, Pennsylvania.

Experimental

Description of the Apparatus.—The capillarimeter used in this investigation was specially designed for this project and has been described in former reports.[2,3] It was desired to obtain surface tension data with a precision of 0.01 dyne $cm.^{-1}$, and the parts of the capillarimeter were selected in accord with the requirements of this predetermined precision. The procedure employed in selecting the capillary tubing and testing it for constancy of bore was similar to that of Harkins and Brown.[4] Since the requisites for high precision include that the reference surface of the liquid be plane, 50-mm. tubing, specially ground and polished, was used for the construction of the reference chamber of the capillarimeter. After its construction the apparatus was carefully annealed and subsequent tests showed no optical distortion. The cathetometer used for the readings was capable of horizontal and vertical mounting and could be read directly to 0.0001 cm.

Procedure.—The hydrocarbons were supplied in sealed glass ampoules, and since it was necessary to protect these compounds both from moisture and from the air, they had to be transferred to and from the capillarimeter in a dry inert atmosphere. This was accomplished in an air-tight steel change box within which was maintained an atmosphere of dry nitrogen. Subsequent manipulations were carried out with equal care and every effort was made to preserve the purity of the compounds and to prevent the formation of oxidation products. The transfer procedure and all subsequent manipulations were the same as previously described.[3] The capillary-height measurements were made in a specially designed and constructed water-bath with heat-resisting plate glass windows which gave no optical distortion. The temperatures were read from NBS certified thermometers with two-degree ranges and 0.01 degree scale divisions. A vertically adjustable brass plate having a narrow horizontal slit, was placed between the fluorescent light source and the capillarimeter. When the slit was adjusted to the proper position the reference surface was seen in sharp silhouette. The capillary heights were measured at approximately ten-degree intervals. At each temperature a minimum of 30 minutes were allowed for the capillarimeter and contents to reach thermal equilibrium with the water-bath. To ensure that the readings were taken with a receding contact angle, the cathetometer was tilted to an angle of about 60 degrees from the vertical thus forcing the liquid within the capillary to flow to a level above its normal equilibrium position. The instrument was again clamped upright and the meniscus observed through the telescope. When no further change in its position was noted readings were resumed.

A series of readings at the various temperatures were repeated on successive days until a high degree of concordance was obtained between them. The average of these was recorded as the capillary rise for the given temperature. Each value of the surface tension and of the temperature recorded in Table I is the average of twenty readings.

Results

The data were applied in the following form of the capillary height equation

$$\gamma = \frac{r\left(h + \frac{r}{3}\right)(d_l - d_v)g}{2}$$

where r is the radius of the capillary, h the observed capillary height, d_l and d_v the densities of the liquid and vapor, respectively, and g the gravitational factor. The effective density $(d_l - d_v)$, for each compound, was determined with the aid of the density data of the liquid hydrocarbons and the Antoine constants which were tabulated in the tables of selected values of the properties of hydrocarbons pub-

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(2) J. J. Jasper and K. D. Herrington, This Journal, **68**, 2142 (1946).

(3) J. J. Jasper, E. R. Kerr and F. Gregorich, *ibid.*, **75**, 5252 (1953).

(4) W. D. Harkins and F. E. Brown, *ibid.*, **41**, 499 (1919).

TABLE II

THE LATENT HEAT OF THE SURFACE AND THE c AND d FACTORS FOR THE SERIES OF 1-ALKENES AND FOR n-DECYLCYCLOPENTANE, n-DECYLCYLOHEXANE AND n-DECYCLBENZENE

Compound	Temperature, °C.											c	d
	0	10	20	30	40	50	60	70	80	90	100		
1-Hexene	28.14	29.18	30.21	31.23	32.26	33.29	34.32	...	...	...	...	28.15	0.1030
1-Heptene	27.03	28.01	29.00	30.00	30.99	31.97	32.96	33.95	34.94	...	...	27.03	.09888
1-Octene	26.20	27.15	28.11	29.08	30.04	31.00	31.95	32.91	33.87	34.83	35.79	26.20	.0959
1-Nonene	25.41	26.34	27.27	28.20	29.13	30.06	30.99	31.92	32.85	33.78	34.71	25.41	.0930
1-Decene	25.04	25.96	26.87	27.79	28.71	29.62	30.54	31.45	32.37	33.28	34.20	25.04	.0916
1-Undecene	24.66	25.11	26.46	27.36	28.27	29.17	30.07	30.97	31.88	32.78	33.68	24.66	.0902
1-Dodecene	24.19	25.08	25.96	26.84	27.73	28.61	29.50	30.38	31.27	32.16	33.04	24.19	.0885
1-Tetradecene	23.74	24.61	25.48	26.35	27.22	28.09	28.96	29.83	30.70	31.57	32.44	23.74	.0870
1-Hexadecene	...	...	...	25.85	26.70	27.55	28.41	29.26	30.11	30.97	31.82	23.29	.08529
n-Decylcyclopentane	24.31	25.20	26.09	26.98	27.87	28.76	29.65	30.54	31.43	32.32	33.21	24.31	.0890
n-Decylcyclohexane	23.48	23.34	25.20	26.06	26.92	27.78	28.64	29.50	30.36	31.22	32.08	23.48	.0860
n-Decylbenzene	21.77	22.57	23.36	24.16	24.96	25.76	26.55	27.35	28.15	28.94	29.74	21.77	.0797

lished by the American Petroleum Institute, Project 44. The probable error of the derived values of the surface tensions were calculated and found to be no greater than 0.01 dyne cm.$^{-1}$. The principle of least squares was applied to the surface tension data, and the resulting equation was of the linear form, $\gamma = a - bt$. The surface tension data, together with the a and b factors of the linear equation, are tabulated in Table I.

Discussion

By applying the two-dimensional form of the thermodynamic equation of Clapeyron[3] it is possible to calculate the entropy of surface formation. This is found to be the negative temperature coefficient of the surface tension and is tabulated as the b factor in Table I. These values in turn enable the calculation of the enthalpy h and the latent heat of the surface Q. The temperature–latent heat relations for the compounds take the form of the linear equation, $Q = c + dt$. The Q values together with the c and d factors of the least squares equations, are recorded in Table II. The enthalpy of the surface is given by the relation, $h = \gamma + Q$, and from reference to the tables it is seen that h has a constant value over the temperature range employed. The entropy of the surface, represented by the b factor of Table I, is measured by the slope of the surface tension *vs.* temperature curve. This has a constant value, and, therefore, it is evident that both the enthalpy and the entropy of the surface are independent of the temperature.

DETROIT, MICHIGAN

[CONTRIBUTION NO. 40 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

The Chemical Thermodynamic Properties of Thiacyclohexane from 0 to 1000°K.[1]

BY J. P. MCCULLOUGH, H. L. FINKE, W. N. HUBBARD, W. D. GOOD, R. E. PENNINGTON, J. F. MESSERLY AND GUY WADDINGTON

RECEIVED OCTOBER 29, 1953

As part of a program of investigations of the thermodynamic properties of organic sulfur compounds, an experimental and computational study was made of the properties of thiacyclohexane. The entropy of the liquid at saturation pressure at 298.16°K., 52.16 cal. deg.$^{-1}$ mole^{-1}, was computed from measured values of the heat capacity in the solid and liquid states (13 to 341°K.) and the heats of transition (262.4 and 1858.3 cal. mole^{-1} at 201.4 and 240.02°K., respectively) and fusion (585.2 cal. mole^{-1} at the triple point, 292.25°K.). Experimental results obtained for the heat capacity of the liquid [C_{satd}], the heat of vaporization [ΔH_v], the heat capacity in the ideal gaseous state [C_p°], and the second virial coefficient [$B = (PV - RT)/P$] are accurately represented by the empirical equations: [1] $C_{\text{satd}}(\text{liq.}) = 112.057 - 0.8324\ T + 2.865 \times 10^{-3}T^2 - 3.0 \times 10^{-6}T^3$, cal. deg.$^{-1}$ mole^{-1} (292–342°K.); [2] $\Delta H_v = 14{,}355 - 13.871\ T$, cal. mole^{-1} (350–415°K.); [3] $C_p^\circ = -13.82 + 0.15037\ T - 6.648 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1} (399–483°K.); and [4] $B = -1040 - 2.25 \exp(2000/T)$, cc. mole^{-1} (350–483°K.). From determinations of the heat of combustion, the standard heat of formation [ΔH_f°(liq.)] of thiacyclohexane from graphite, hydrogen and rhombic sulfur was found to be -25.18 kcal. mole^{-1} at 298.16°K. Calorimetric, spectroscopic and molecular structure information were used to compute the functions $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)$, S° and C_p° at selected temperatures to 1000°K. One spectroscopically unobserved vibrational frequency was selected to fit the calorimetric entropy datum. Parameters required to compute the contributions of anharmonicity and "chair-boat" tautomerism were evaluated from the experimental vapor heat capacity data. Values of ΔH_f°, ΔF_f° and $\log_{10} K_f$, for the formation of thiacyclohexane in the ideal gaseous state from graphite, hydrogen and gaseous diatomic sulfur, were computed from the calculated thermodynamic functions and appropriate calorimetric data.

A comprehensive series of investigations of the thermodynamic properties of organic sulfur compounds is being conducted in this Laboratory to provide relatively complete data for those compounds important in petroleum production and refining processes. Thorough studies are made of

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(1) This investigation was part of American Petroleum Institute Research Project 48A on the "Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.