[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

The Orthobaric Surface Tensions and Thermodynamic Properties of the Liquid Surfaces of the *n*-Alkanes, C_5 to C_{28}

BY JOSEPH J. JASPER, E. ROBERT KERR AND FREDERICK GREGORICH

RECEIVED APRIL 8, 1953

In the following paper there is briefly described the procedure for measuring orthobarically the surface tensions of the *n*-alkanes, C_5 to C_{18}, furnished by the American Petroleum Institute Research Project 44. The capillary rise method was employed, and a precision capillarimeter, specially designed for this project, was used for the measurements. Surface tension-temperature data are presented in a table together with the constants of the least-square equations which relate the variables. From these data the entropies, latent heats and enthalpies of the liquid surface were calculated. The entropies and enthalpies are plotted graphically against the number of carbon atoms per molecule for the different compounds of the series.

The surface tension is a fundamental thermodynamic property of the liquid surface, which, due to its origin in intermolecular attraction, has served as a convenient and accurate index of the relative magnitudes of other properties of liquids. It has become of increasing importance in numerous aspects of theoretical and industrial chemistry, and in recent years considerable study has been given to its application in the determination of molecular structure, and the structure of surface films on liquid substrates. Since the surface tension of a liquid is influenced markedly by the presence of small amounts of capillary-active impurities, reliable data for its numerous applications can be expected only from very pure compounds.

The purpose of this investigation was to obtain orthobaric surface tension data of the *n*-alkanes, C_5 to C_{18}, over an appreciable range of temperature, and to formulate empirical equations relating these variables. The compounds used were of a high degree of purity, and were made available by the American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology from the series of API research samples of hydrocarbons purified by the American Petroleum Institute Research Project 6 from source materials supplied as follows: *n*-tridecane, *n*-pentadecane and *n*-heptadecane, from the API Research Project 42 at the Pennsylvania State College; *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, *n*-undecane, *n*-dodecane, *n*-tetradecane, *n*-hexadecane and *n*-octadecane from the API Research Project 6.

The uncertainties, inherent in the capillary rise method and in all surface tension methods involving curved liquid surfaces, are reflected in the capillary constant. These can be reduced to negligible proportions by adhering rigorously to certain structural and dimensional specifications in designing the capillarimeter. The accurate experiments of Richards and Carver[1] indicate that the major errors in the capillary constant can be reduced to a minimum if (a) the radius of the capillary is sufficiently small[2] and (b) the reference surface of the liquid differs but slightly from that of a geometric plane.

Experimental

Description of the Apparatus.—A capillarimeter was designed[3] to conform with the structural and dimensional requisites of a precision instrument and which possessed the additional advantage of requiring no greater volume than 12 ml. of liquid for its operation. In this investigation it was desired to measure the surface tensions of the hydrocarbons with a precision of 0.01 dyne cm.$^{-1}$, and calculations based on this predetermined precision indicated that variations in the capillary radius should not exceed one part in two thousand. Since one of the chief requisites of the designed capillarimeter was a capillary tube of small and constant bore, much time and effort were devoted to its selection. A short length of capillary tube was subsequently found with a 3-cm. section which had an average radius of 0.012299 cm. with a variation less than that required for the desired precision. Etched lines encircling the tube indicated the limits of the section. The procedure employed in the preliminary treatment of the capillary tube and the determination of the radius and constancy of bore, was similar to that of Harkins and Brown.[4] A horizontally mounted Gaertner microscope slide cathetometer was used which could be read directly to 0.0001 cm. Equal care was used in selecting the larger tubing for the section of the capillarimeter in which the reference surface was to be established. Since it is important that the inner and outer walls be parallel and cylindrical in order to minimize optical distortion, special tubing, having an inside diameter of 50 mm. was obtained which was ground and polished to produce a right cylinder of uniform wall thickness.

Procedure.—Since the hydrocarbons were supplied in sealed glass ampoules it was necessary to transfer them to and from the capillarimeter in a dry inert atmosphere. This was accomplished in an air-tight steel chamber within which there was maintained an atmosphere of dry nitrogen. Under these conditions the ampoules were opened and the hydrocarbons transferred to the reservoir bulb of the capillarimeter through a side arm which carried half of a mercury seal. This was closed by a glass cap, ground to fit the joint, and the capillarimeter then removed and connected to the nitrogen-filled vacuum system. The liquid was then solidified and the system evacuated. Following this the capillarimeter was sealed off from the vacuum line. During all subsequent manipulations the compound was under its own vapor pressure.

The capillary rise measurements were made in a highly-insulated constant temperature water-bath having heat resistant (herculite) plate glass windows. These were tested for optical distortion with negative results. The thermoregulator maintained a constant temperature to 0.04°, while the exact temperatures were measured with NBS certified thermometers of short range having scale divisions of 0.01°. A horizontal knife edge, vertically adjustable, and located between the capillarimeter and the fluorescent light source, provided optical contrast at the reference surface.

The capillary heights were measured at approximately ten-degree intervals with the Gaertner cathetometer mounted vertically. At each temperature a minimum of 30 minutes was allowed for the attainment of thermal equilibrium. Several times during a series of measurements at each temperature, the liquid in the capillary was forced to flow to a level above its normal equilibrium position by tipping the instrument to an angle of about 60° from the vertical. Upon the resumption of the vertical position the liquid in the capillary spontaneously dropped to its equilibrium position with a receding contact angle. Under these conditions the probability of zero contact angle is greater.[5] The readings for

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(1) T. W. Richards and E. K. Carver, THIS JOURNAL, **43**, 827 (1921).

(2) Under these conditions the shape of the liquid meniscus closely approximates that of a hemisphere and can be treated as such in correcting the capillary rise.

(3) J. J. Jasper and K. D. Herrington, THIS JOURNAL, **68**, 2142 (1946).

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

(5) W. D. Harkins, "The Physical Chemistry of Surface Films," Reinhold Publ. Corp., New York, N. Y., 1952, p. 66.

TABLE I

THE SURFACE TENSIONS AND LEAST-SQUARE FACTORS *a* AND *b* FOR THE *n*-ALKANES, C_5 TO C_{18}

Compound	Temperature, °C.										
	0	10	20	30	40	50	60	70	80	*a*	*b*
n-Pentane	18.27	17.19	16.09	15.00						18.27	0.10891
n-Hexane	20.50	19.46	18.41	17.37	16.32	15.28	14.24			20.50	.10439
n-Heptane	22.31	21.30	20.28	19.27	18.25	17.24	16.22			20.31	.10148
n-Octane	23.75	22.77	21.78	20.80	19.82	18.84	17.85			23.75	.09826
n-Nonane	24.84	23.90	22.96	22.01	21.07	20.13	19.19			24.84	.09417
n-Decane	25.73	24.81	23.89	22.98	22.06	21.14	20.22			25.73	.09190
n-Undecane	26.57	25.68	24.78	23.89	23.00	22.10	21.21	20.31	19.42	26.57	.08935
n-Dodecane	27.24	26.36	25.48	24.60	23.73	22.85	21.97	21.09	20.21	27.24	.08788
n-Tridecane	27.87	27.00	26.13	25.26	24.39	23.52	22.65	21.78	20.90	27.87	.08707
n-Tetradecane	28.42	27.56	26.69	25.83	24.97	24.11	23.24	22.38	21.52	28.42	.08625
n-Pentadecane	28.87	28.02	27.12	26.32	25.46	24.61	23.76	22.91	22.06	28.87	.08515
n-Hexadecane	29.32	28.48	27.64	26.79	25.95	25.11	24.27	23.42	22.58	29.32	.08424
n-Heptadecane	29.74	28.90	28.06	27.22	26.38	25.55	24.71	23.87	23.03	29.74	.08389
n-Octadecane	30.09	29.26	28.42	27.59	26.75	25.92	25.09	24.25	23.42	30.09	.08339

TABLE II

THE LATENT HEAT OF THE SURFACE AND THE LEAST-SQUARE FACTORS *c* AND *d* FOR THE *n*-ALKANES, C_5 TO C_{18}

Compound	Temperature, °C.										
	0	10	20	30	40	50	60	70	80	*c*	*d*
n-Pentane	30.76	31.84	32.93	34.01						30.76	0.1084
n-Hexane	28.56	29.58	30.60	31.61	32.63	33.65	34.67			28.56	.1018
n-Heptane	27.69	28.70	29.71	30.73	31.74	32.75	33.76			27.69	.1012
n-Octane	26.83	27.82	28.80	29.79	30.77	31.76	32.74			26.83	.0985
n-Nonane	25.77	26.70	27.64	28.57	29.50	30.43	31.37			25.77	.0933
n-Decane	25.10	26.02	26.94	27.86	28.78	29.70	30.62			25.10	.0920
n-Undecane	24.39	25.29	26.18	27.09	27.98	28.88	29.77	30.67	31.56	24.39	.0897
n-Dodecane	24.00	24.88	25.76	26.65	27.52	28.40	29.28	30.16	31.04	24.00	.0881
n-Tridecane	23.79	24.66	25.53	26.40	27.27	28.14	29.01	29.88	30.75	23.79	.0871
n-Tetradecane	23.55	24.41	25.28	26.15	27.01	27.88	28.74	29.60	30.46	23.55	.0864
n-Pentadecane	23.27	24.12	24.97	25.82	26.67	27.52	28.37	29.22	30.08	23.27	.0851
n-Hexadecane	23.00	23.84	24.69	25.54	26.38	27.23	28.07	28.91	29.75	23.00	.0844
n-Heptadecane	22.87	23.72	24.56	25.44	26.27	27.11	27.95	28.79	29.63	22.91	.0840
n-Octadecane	22.79	23.62	24.45	25.28	26.12	26.95	27.79	28.62	29.45	22.79	.0832

the various temperatures, were repeated on successive days until a high degree of concordance was obtained between successive sets. These were finally averaged and tabulated as the capillary rise for the respective temperatures. The maximum variation in the temperature was no greater than 0.02° over the entire temperature range. Each value of the temperature and of the surface tension tabulated in the table which follows, is the average of from 20 to 65 readings.

Results

The data were applied in the following form of the capillary-rise equation

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

where r is the radius of the capillary, h the observed capillary rise, d_l the density of the liquid, d_v the density of the vapor and g the gravitational factor (980.316 for Detroit). 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 properties of hydrocarbons published 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 principal of least squares was applied to the surface tension–temperature data, and the resulting equations were of the linear form, $\gamma = a - bt$, The surface tension–temperature data together with the *a* and *b* factors of the least squares equations, are presented in Table I.

Discussion

The surface tension has been defined as the area derivative of the free surface energy at constant temperature and pressure. It is a fundamental thermodynamic property and represents the work required to increase the surface area by one cm.^{2}. The mechanism of this area extension involves the transfer of molecules to a position of higher potential energy, and if the process is isothermal a quantity of heat must be added equivalent to the kinetic energy transformed during the transfer of the molecules. It is evident, therefore, that the enthalpy of the surface is the sum of the free surface energy, γ, required to extend the surface, and the latent heat, Q, required to maintain isothermal conditions.

The thermodynamic equation of Clapeyron, which was first applied to surfaces by Lord Kelvin, takes the following form when applied to liquid surfaces

$$-(\partial\gamma/\partial T) = Q/T \qquad (1)$$

and from this the latent heat, and the entropy, s, can be calculated. To calculate the enthalpy, h, equation 1 is combined with the free surface energy as

$$h = \gamma + Q = \gamma - T(\partial\gamma/\partial T) \qquad (2)$$

From reference to equation 1 it is seen that the entropy of surface formation is equal to the negative temperature coefficient of the surface tension, and since the values of this property are tabulated as the *b* factors for the *n*-alkanes in Table I, the data necessary to calculate *Q* and *h* are available. The temperature–latent heat relations for the *n*-alkanes 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 tabulated in Table II.

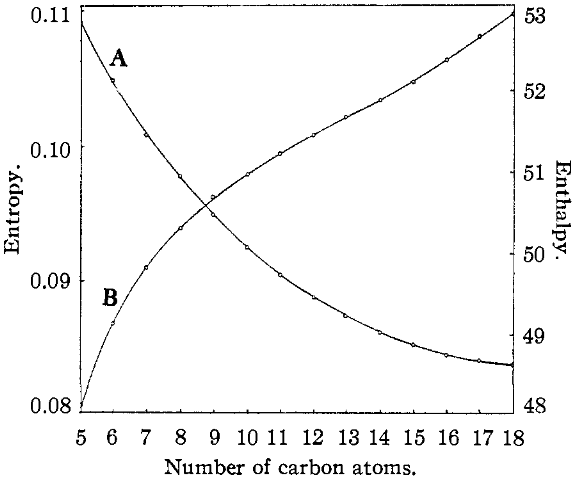

Fig. 1.—A, the entropies of surface formation; B, the enthalpies of surface formation as a function of the number of carbon atoms per molecule.

The least squares equation relating the entropy and the number of carbon atoms per molecule, *n*, is given by the following power series

$$s = 0.14024 - 0.007921n + 0.0003674n^2 - 0.00000568n^3$$

The plot of the entropies calculated from this equation are shown in Fig. 1a, and the enthalpies are shown in Fig. 1b.

From reference to the tables it is evident that while γ decreases and *Q* increases with the temperature for each of the compounds, *h*, the sum of these, and *s*, which is (Q/T), are independent of the temperature. The curves (a) and (b) of Fig. 1 show that the enthalpies increase and the entropies decrease with increasing molecular weights of the compounds, and that the latter appears to be approaching a limiting value of about 0.0830.

DETROIT, MICH.

[JOINT CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, DUKE UNIVERSITY AND CORNELL UNIVERSITY]

Statistical Mechanics of Dilute Polymer Solutions. V. Evaluation of Thermodynamic Interaction Parameters from Dilute Solution Measurements[1]

BY W. R. KRIGBAUM AND P. J. FLORY

RECEIVED MAY 28, 1953

Accurate osmotic pressure measurements are reported for benzene solutions of four well-fractionated polyisobutylene samples, varying in molecular weight from 102,000 to 720,000, at three temperatures in the vicinity of the Θ temperature at which the second virial coefficient in the expansion of the osmotic pressure vanishes. As evaluated from these data, Θ = 297.5°K., independent of the molecular weight. The entropy of dilution parameter ψ_1, calculated from the change in the second virial coefficient with temperature at $T = \Theta$, is 0.34 ± 0.02. Further examination of the values obtained from the second coefficient reaffirms the previous observation that the theoretical pair interaction function $F(X)$ derived in a recent treatment of dilute polymer solutions varies too slowly with X (which depends on the segment–solvent interaction, and the molecular configuration.) The parameters Θ and ψ_1 for polyisobutylene in benzene have been evaluated independently from measurement of the critical consolute temperatures, T_c, for four fractions. The Θ values deduced by the two methods are in excellent agreement; however, ψ_1 obtained by the precipitation temperature method is twice that deduced from A_2. On the other hand, the ψ_1 value reported for the same system by Fox and Flory from intrinsic viscosity measurements is only half that calculated from the second virial coefficient.

Introduction

According to the statistical treatment of dilute polymer solutions,[2,3] the second coefficient, A_2, in the virial expression for the osmotic pressure

$$\pi = RT[A_1c + A_2c^2 + A_3c^3 + \ldots] \qquad (1)$$

takes the form

$$A_2 = (\bar{v}^2/V_1)(1 - \Theta/T)\psi_1F(X) \qquad (2)$$

where $\bar{v}$ and V_1 are the partial specific volume of polymer and the molar volume of solvent, respectively. The standard state entropy of formation of a polymer–solvent contact pair is given by $k(\psi_1 - {}^1/_2)$, k being Boltzmann's constant, and Θ is the critical temperature for which the second coefficient vanishes. The segment–solvent contact-pair heat parameter, κ_1, is given in terms of the foregoing by $\psi_1\Theta/T$.[4] As given by theory, the function $F(X)$ appearing in equation 2 is equal to unity for all molecular weights at the unique temperature Θ, but under all other conditions varies with molecular weight, temperature and the thermodynamic parameters characterizing the polymer–solvent interaction.

Earlier statistical treatments,[5,6] which disre-

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(1) The experimental work reported in this paper was carried out at Cornell University under sponsorship of the Government Research Program on Synthetic Rubber, Synthetic Rubber Division, Reconstruction Finance Corporation.

(2) P. J. Flory, *J. Chem. Phys.*, **17**, 1347 (1949).

(3) (a) P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950); (b) W. R. Krigbaum and P. J. Flory, *ibid.*, **20**, 873 (1952).

(4) These parameters are discussed more fully in ref. 3a; see also, "Thermodynamics of High Polymer Solutions," by P. J. Flory and W. R. Krigbaum, a chapter in the "Annual Review of Physical Chemistry," Vol. 2, 1951; published by Annual Reviews, Inc., Stanford, California.

(5) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

(6) (a) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); (b) **12**, 425 (1944).