Surface Tension of Octamethylcyclotetrasiloxane and Hexamethyldisilazane and Their Solutions with Carbon Tetrachloride and *n*-Hexadecane

RICHARD S. MYERS and H. LAWRENCE CLEVER
Department of Chemistry, Emory University, Atlanta, Ga. 30322

The surface tension and density of octamethylcyclotetrasiloxane and hexamethyldisilazane were measured between 25° and 45° C. The surface tension and density of solutions of hexamethyldisilazane–carbon tetrachloride, octamethylcyclotetrasiloxane–carbon tetrachloride, and octamethylcyclotetrasilaxane–*n*-hexadecane were measured at 30° C. All three solutions show deviations from ideal behavior. All the excess surface tensions are negative. The excess volume of the *n*-hexadecane solutions is positive, while the carbon tetrachloride solutions show negative excess volumes which change to positive values at high silicon compound mole fraction. The Gibbs surface excesses were calculated and are compared for the three solutions.

THE SURFACE TENSION and density of octamethylcyclotetrasiloxane and hexamethyldisilazane were measured at 5° intervals between 25° and 45° C. The surface tension and density of eight concentrations of carbon tetrachloride–hexamethyldisilazane, carbon tetrachloride–octamethylcyclotetrasiloxane, and *n*-hexadecane–octamethylcyclotetrasiloxane were measured at 30° C. It was assumed that the last two solutions were mixtures of spherical-like molecules that differed in molar volume by a factor of 3, and of globular and rodlike molecules of similar molar volume, respectively.

EXPERIMENTAL

Materials. Octamethylcyclotetrasiloxane, $(SiO)_4(CH_3)_8$, General Electric Co. Silicone Products Department, distilled through a 2-foot stainless steel helix-packed column (b.p. 173.0° C.).

Hexamethyldisilazane, $(CH_3)_3SiNHSi(CH_3)_3$, General Electric Co. Silicone Products Department, distilled under a nitrogen atmosphere through a packed column (b.p. 124.0° C.).

Carbon tetrachloride, Fisher certified reagent, refluxed 2 hours over 5% sodium hydroxide, washed with water until neutral, dried over $CaSO_4$ and CaH_2, and distilled through a packed column (b.p. 76.5° C.).

Hexadecane, Eastman practical grade, shaken three times with concentrated sulfuric acid, washed with water until neutral, dried over $CaSO_4$, and distilled at reduced pressure (b.p. 140° C. at 6 mm. of Hg).

Apparatus. Surface tensions were measured by the maximum bubble pressure method on apparatus built and described by Quayle (*9*). The method involves the measurement of the pressure differential developed within the system as bubbles of dry air presaturated with vapor are drawn alternately through two tubes, with different radii, immersed to the same depth in a liquid. The pressure differential is developed by a mercury aspirator and measured on a xylene-filled manometer. The larger tube has a diameter of 0.1624 cm., the smaller tube is not measured, but the bubbler is calibrated with purified samples of benzene, *n*-heptane, and *n*-octane of known surface tension. The bubbler air was dried and presaturated with sample vapor to prevent evaporation and cooling of the sample surface during the measurement. Surface tensions are normally reproducible to 0.03 dyne per cm. There was no evidence of a time effect on the surface tension at different rates of bubble formation. Surface tension equilibrium appears to be established immediately.

Densities were measured in 15-ml. density bottles with a truebore capillary neck of 1.000 ± 0.007-mm. diameter. Solutions were prepared in special weighing and mixing bottles (*1*), and the composition was corrected for material in the vapor phase assuming Raoult's law. The temperature was controlled to ± 0.01° C. by a Bayley Instrument Co. thermoregulator, Model 123, for the surface tension and density measurements. Temperatures were read on a 0.1° graduated thermometer which had been calibrated against a National Bureau of Standards calibrated thermometer.

RESULTS AND DISCUSSION

The surface tensions and densities of octamethylcyclotetrasiloxane and hexamethyldisilazane are shown in Table I. The least squares equations

$$\sigma = 20.44 - 0.0814\,t$$
$$d = 0.97818 - 0.001127\,t$$

Table I. Surface Tension and Density of Octamethylcyclotetrasiloxane and Hexamethyldisilazane

	Octamethylcyclotetrasiloxane		Hexamethyldisilazane	
Temp., °C.	Surface tension, dynes/cm.	Density, g./cc.	Surface tension dynes/cm.	Density, g./cc.
20	18.82	0.95572	...	...
25	18.40	0.94996	18.16	0.77000
30	17.98	0.94438	17.72	0.76546
35	17.56	0.93874	17.28	0.76095
40	17.20	0.93298	16.88	0.75636
45	16.78	0.92760	16.45	0.75179

Table II. Thermodynamic Changes on Forming New Surface, 30° C.

Compound	Gibbs Free Energy, Ergs/ Sq. Cm.	Entropy, Ergs/Deg. Sq. Cm.	Enthalpy, Ergs/ Sq. Cm.	Latent Enthalpy, Ergs/ Sq. Cm.
Octamethylcyclotetrasiloxane	17.88	0.0852	43.81	25.83
Hexamethyldisilazane	17.72	0.0814	42.40	24.68

reproduce the octamethylcyclotetrasiloxane surface tension, σ, to ±0.01 dyne per cm. and the density, d, to ±0.00005 gram per cc. over the temperature range 20° to 45° C. Earlier values of density (*8*) were also reproduced within experimental error by the equation. The least squares equations

$$\sigma = 20.28 - 0.0852\,t$$

$$d = 0.79278 - 0.000910\,t$$

reproduce the hexamethyldisilazane surface tension to ±0.01 dyne per cm. and the density to ±0.00002 gram per cc. Earlier values of density (*2*) were reproduced within experimental error by the equation.

The changes in free energy, σ, entropy, $S = -(\delta\sigma/\delta T)$, enthalpy, $H = \sigma - T\ (\delta\sigma/\delta T)$, and latent heat, $1 = -T(\delta\sigma/\delta T)$, required to form 1 sq. cm. of new surface (*3*) were calculated from the above equations for octamethylcyclotetrasiloxane and hexamethyldisilazane at 30° (Table II).

The surface tension and density for mixtures of octamethylcyclotetrasiloxane with carbon tetrachloride and with hexadecane and of hexamethyldisilazane with carbon tetrachloride at 30° C. are given in Table III. The excess surface

Table III. Surface Tension and Density of Three Solutions Containing a Silicon Compound as One Component, 30° C.

Mole Fraction Organosilicon	Surface Tension, Dynes/Cm.	Excess Surface Tension	Density, G./Cc.	Excess Volume, Cc./Mole
		Carbon Tetrachloride–Octamethylcyclotetrasiloxane		
0.0000	25.95	0.00	1.57421	0.00
0.0789	22.91	−2.40	. . .	. . .
0.1212	22.45	−2.54	1.38214	−0.12
0.2513	20.79	−3.17	1.24888	−0.19
0.3672	19.89	−3.15	1.16515	−0.15
0.4830	19.16	−2.98	1.10223	−0.07
0.6214	18.72	−2.31	1.04456	0.04
0.7316	18.45	−1.70	1.00854	0.09
0.7782	. . .	. . .	0.99524	0.12
0.8056	. . .	. . .	0.98739	0.26
0.8719	. . .	. . .	0.97082	0.31
0.8738	18.14	−0.89	0.97049	0.29
0.9249	. . .	. . .	0.95894	0.29
1.0000	17.98	0.00	0.94429	0.00
		Hexadecane-Octamethylcyclotetrasiloxane		
0.0000	26.70	0.00	0.76643	0.00
0.1181	23.92	−1.75	0.78814	0.18
0.2448	22.14	−2.43	0.81145	0.21
0.3835	20.90	−2.46	0.83656	0.24
0.4876	20.24	−2.21	0.85525	0.22
0.6352	19.46	−1.70	0.88127	0.22
0.7317	19.03	−1.29	0.89814	0.18
0.8688	18.44	−0.68	0.92177	0.14
1.0000	17.98	0.00	0.94429	0.00
		Carbon Tetrachloride–Hexamethyldisilazane		
0.0000	25.95	0.00	1.57421	0.00
0.0438	. . .	. . .	1.50168	−0.02
0.1128	23.34	−1.68	1.40071	−0.05
0.2435	21.42	−2.53	1.24258	0.02
0.3719	20.40	−2.44	1.11527	0.02
0.4991	19.69	−2.15	1.02182	0.06
0.6267	19.08	−1.71	0.93973	0.13
0.7268	. . .	. . .	0.88400	0.28
0.7489	18.60	−1.19	. . .	. . .
0.7944	. . .	. . .	0.85055	0.34
0.8743	18.08	−0.67	0.81484	0.28
1.0000	17.72	0.00	0.76546	0.00

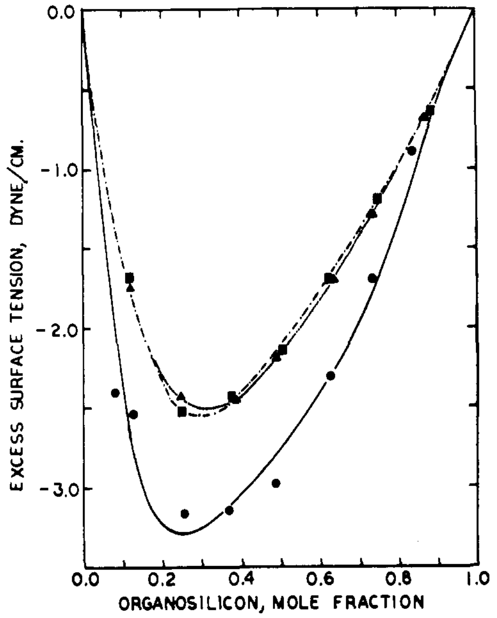

Figure 1. Excess surface tension vs. organosilicon mole fraction

▲ *n*-Hexadecane–octamethylcyclotetrasiloxane
● Carbon tetrachloride—actomethylcyclotetrasiloxane
■ Carbon tetrachloride–hexamethyldisilazane

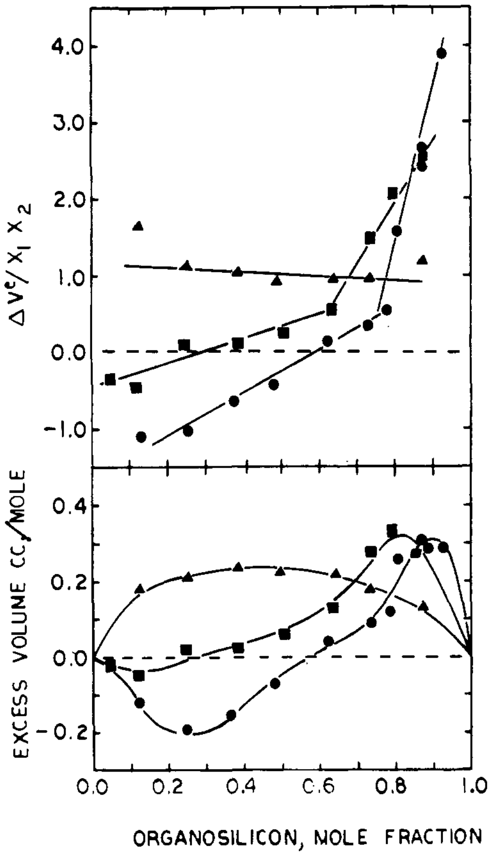

Figure 2. Excess volume functions vs. organosilicon mole fraction

Upper. $\Delta V^e/X_1X_2$ vs. mole fraction
Lower. Excess volume vs. mole fraction
▲ *n*-Hexadecane–octamethylcyclotetrasiloxane
● Carbon tetrachloride–octamethylcyclotetrasiloxane
■ Carbon tetrachloride–hexomethyldisilazane

Table IV. Parameters for Excess Property Equations

Excess Surface Tension			Excess Volume		
n	A_n	Av. dev.	n	A_n	Av. dev.
Carbon Tetrachloride-Octamethylcyclotetrasiloxane					
1	-11.084		1	-0.198	
2	-5.814		2	-1.129	
3	-8.986		3	-1.382	
4	-10.983	0.14	4	-2.536	
			5	5.671	0.02
n-Hexadecane–Octamethylcyclotetrasiloxane					
1	-8.701		1	0.926	
2	-6.156		2	0.112	
3	-4.412		3	0.167	
4	-1.649	0.01	4	0.303	
			5	1.375	0.01
Carbon Tetrachloride–Hexamethyldisilazane					
1	-8.598		1	0.261	
2	-6.942		2	-1.011	
3	-4.986	0.03	3	1.880	
			4	-1.915	0.02

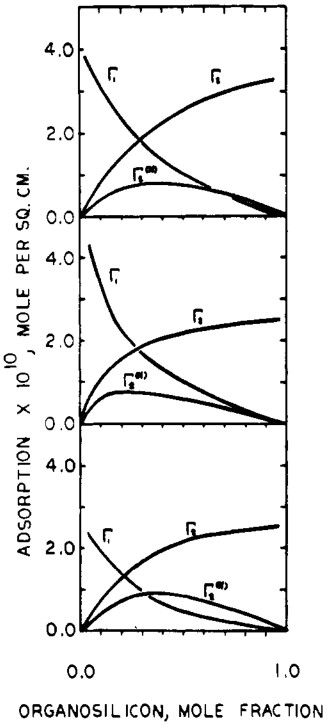

Figure 3. Individual and composite isotherms, 30° C.

Bottom. Carbon tetrachloride–hexamethyldisilazane
Center. Carbon tetrachloride–octamethylcyclotetrasiloxane
Top. n-Hexadecane–octamethylcyclotetrasiloxane

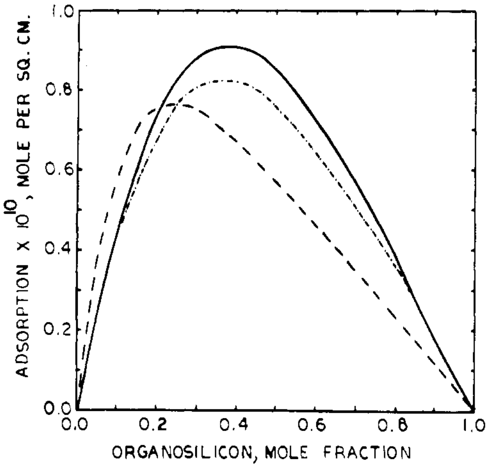

Figure 4. Composite adsorption isotherm for liquid-vapor interface, 30° C.

— n-Hexadecane–octamethylcyclotetrasiloxane
--- Carbon tetrachloride–octamethylcyclotetrasiloxane
— · — Carbon tetrachloride–hexamethyldisilazane

tension was calculated from the data (Figure 1). The excess volume functions were calculated (Figure 2). The top portion shows $\Delta V^e/X_1X_2$ plotted against X_2, the mole fraction of organosilicon. The lower portion shows the excess volume curves, where the solid lines here and in Figure 1 were calculated from the excess properties equation (*7*).

$$\text{Excess property} = X_1X_2\Sigma A_n(1 - 2X_2)^n$$

where X_1 is mole fraction of carbon tetrachloride or hexadecane, X_2 is mole fraction of organosilicon, and A_n are the fitting parameters, given in Table IV.

As expected, all excess surface tensions are negative. However, in the systems with carbon tetrachloride the excess volume undergoes a change in sign from negative at low organosilicon concentration to positive at high concentration. The change in the excess volume of the carbon tetrachloride–octamethylcyclotetrasiloxane is relatively large, from a minimum of −0.19 to a maximum of 0.31 ml. per mole.

A recent report (*6*) of excess volume values from density measurements for octamethyltetrasiloxane–carbon tetrachloride solutions up to 0.6 silicon compound mole fraction is progressively more negative than our values between 0.25 and 0.6 mole fraction. If our solution compositions are not corrected for vapor loss before the calculation of excess volume from the density, we obtain the same results reported (*6*). It is suspected that much of the difference in excess volume values is a measure of the error introduced when the vapor loss correction is not made.

The ideal equation of Hildebrand and Scott (*4*) did not fit the surface tension data well, in each case giving a greater average deviation than obtained with the excess surface tension equations.

The excess surface tension equations were used to calculate the Gibbs surface excesses, Γ_2^N, Γ_1, and Γ_2, which are related (*5, 10*) by the equation

$$\Gamma_2^N = \frac{-X_1X_2}{RT}\,\frac{\delta\sigma}{\delta X_2} = \Gamma_2X_1 - \Gamma_1X_2$$

The equation assumes ideal bulk behavior. Γ_2^N is the excess of solute in the surface of unit area over a region in the bulk liquid containing the same number of total moles of all species and is independent of any model of the surface. Γ_1 and Γ_2 are the moles of component 1 or 2 per unit area in the surface and require a model of the interface and a knowledge of the individual component surface areas. Figure 3 shows the composite, Γ_2^N *vs.* X_2 and individual, Γ_1 and Γ_2 *vs.* X_2, isotherms assuming spherical molecules with the following surface areas per molecule: octamethylcyclotetrasiloxane, 64.79 sq. A.; hexadecane, 62.20 sq. A.; carbon tetrachloride, 29.75 sq. A.; hexamethyldisilazane, 49.67 sq. A. Figure 4 shows a more expanded view of the composite adsorption isotherms. The effect of the size of the solute molecule, especially in the two systems with octamethylcyclotetrasiloxane, can clearly be seen.

ACKNOWLEDGMENT

The authors thank the Emory Biomedical Data Processing and Analysis Center for use of the computer and the General Electric Co. for providing the silicon compounds.

NOMENCLATURE

A_n = fitting parameter in excess properties equation
H = enthalpy of forming new surface, ergs per sq. cm.
d = density, g. per cc.
n = fitting parameter in excess properties equation
R = gas constant
S = entropy of forming new surface, ergs per deg. per sq. cm.
T = temperature, ° K.
X_i = mole fraction of component i
t = temperature, ° C.
Γ_i = individual Gibbs surface excess of component i, mole per sq. cm.
Γ_2^N = composite Gibbs surface excess, mole per sq. cm.
Σ = summation sign
σ = surface tension, dyne per cm. or free energy of forming new surface, ergs per sq. cm.

LITERATURE CITED

(1) Battino, R., *J. Phys. Chem.* **70**, 3408 (1966).
(2) Cerato, C., Lauer, J., Beachell, H., *J. Chem. Phys.* **22**, 1 (1954).
(3) Harkins, W.A., Alexander, E.A., in "Techniques of Organic Chemistry," A. Weissberger, Ed., Vol. **I**, Part 1, Chap. XIV, Interscience, New York, 1959.
(4) Hildebrand, J.H., Scott, R.L., "Solubility of Nonelectrolytes," Chap. 21, Reinhold, New York, 1950.
(5) Kipling, J.J., "Adsorption from Solutions of Nonelectrolytes," Chap. 10, Academic Press, London, 1965.
(6) Marsh, K.N., *Trans. Faraday Soc.* **64**, 883 (1968).
(7) Myers, D.B., Scott, R.L., *Ind. Eng. Chem.* **55**, 43 (1963).
(8) Patnode, W., Wilcock, D., *J. Am. Chem. Soc.* **68**, 358 (1946).
(9) Quayle, O.R., *Chem. Rev.* **53**, 439 (1953).
(10) Schmidt, R.L., Clever, H.L., *J. Colloid Interface Sci.* **26**, 19 (1968).

RECEIVED for review May 1, 1968. Accepted October 18, 1968. Work supported by National Science Foundation Grant GP-5937.

Excess Volumes of Binary Liquid Mixtures of *n*-Alkanes

MARC J. SIMS[1] and JACK WINNICK
Department of Chemical Engineering, University of Missouri, Columbia, Mo. 65201

The excess volume is presented for the binary *n*-alkane systems C_{10}–C_{12}, C_{12}–C_{14}, and C_{12}–C_{16} at 45°, 55°, and 65° C. and the systems C_{10}–C_{14} and C_{10}—C_{16} at 55° and 65° C. A pycnometric technique was used to observe the densities of mixtures and pure components of each system, from which the excess volume was calculated. The excess volume was found to be negative in all cases and to become more negative with increasing temperature. The data reaffirm the principle of congruence and its application to the form of $V(n)$ proposed by Hijmans and Holleman. Deviations from this correlation averaged 0.004 cc. per mole. The mixture volumes were also predicted using Flory's corresponding states theorem. Deviation from the prediction averaged 0.012 cc. per mole. The standard deviation in the experimental excess volumes was 0.007 cc. per mole.

IN AN EARLIER STUDY by Harrison (*4*), the excess volumes of the five binary *n*-alkane systems, C_{10}–C_{12}, C_{12}–C_{14}, C_{12}–C_{16}, C_{10}–C_{14}, and C_{10}–C_{16}, were determined at 25° and 35° C. and of C_{10}–C_{14} and C_{10}–C_{16} at 45° C. In that study the data were correlated using Hijmans and Holleman's equation (*6*), which incorporates an infinite series representation of $V(n)$ (in descending powers of n) and the principle of congruence proposed by Brønsted and Koefoed (*1*). It was shown that the equation was successful in correlating the data within experimental error.

Normal paraffins satisfy the requirements of a law of corresponding states when the concept of "segments" is adopted. A law of corresponding states for the *n*-paraffin liquids has been formulated by Prigogine and coworkers (*7*) from the consideration of a modified cell model and by Hijmans (*5*) from a phenomenological point of view. The partition function derived by Prigogine *et al.* has recently been refined by Flory and coworkers (*2*), and the tractable algebraic equations of state that they have derived can be used to predict the excess volume. These corresponding states treatments exploit the principle of congruence for the prediction of mixture properties.

THEORY

The method of correlating the data with Hijmans and Hollemans' equation and the principle of congruence was presented in an earlier paper (*4*).

To predict the excess volume from the law of corresponding states of Flory (*2*), the reduced volume and temperature of each pure component are required. Also needed are the parameters of hard-core segmental volume, V^*, and the end segment contribution to the total number of segments in a molecule, n_e. An empirical equation given by Flory relates the reduced temperature of a pure component to the chain length and temperature:

$$T = T/T^* = T[A + B/(n + 1)] \qquad (1)$$

---

[1] Present address: Chevron Research Co., Richmond, Calif.