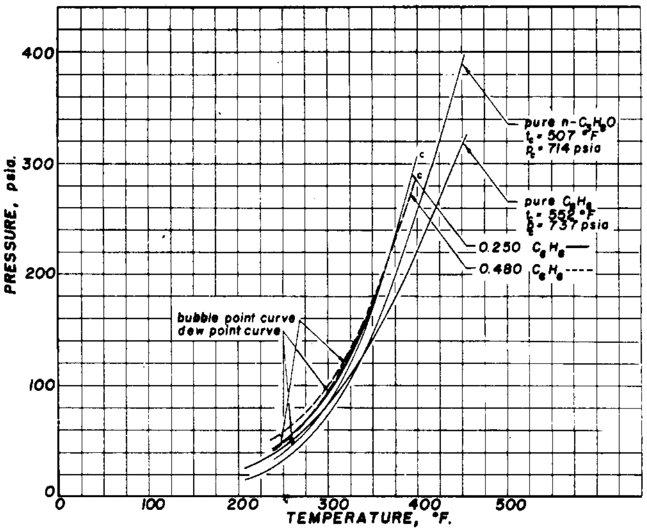

Figure 3. Pressure-temperature diagram, benzene–1-propanol system

the mixture curves end at lower temperatures because of the lower critical points. The solid lines in Figure 3 represent the bubble and dew point curves for the 25.0 mole % benzene system. These curves coincide from about 367° F. to the critical point. This indicates that azeotropic conditions exist over this temperature range. Similar azeotrope formation exists for the 48.0 mole % system (shown as dotted lines in Figure 3) starting approximately at the same temperature. This behavior is also evident from the flat isotherms in the two-phase region in Figures 1 and 2 above about 367° F.

ACKNOWLEDGMENT

The Organization of American States provided the financial aid for this study.

NOMENCLATURE

C = critical point
C_p = specific heat at constant pressure, B.t.u./(lb.)(° F.)
Δh = enthalpy correction, B.t.u./lb.
H = enthalpy of binary mixture referred to $H = 0$ for the pure components as saturated liquids at 77° F., B.t.u./(lb. of mixture)
L_f = heat of vaporization of Freon-11, B.t.u./lb.
ΔH_c = enthalpy difference between entrance and exit conditions of the calorimeter, B.t.u./lb.
ΔH_m = heat of mixing at 77° F., B.t.u./(lb. of mixture)
p = pressure, p.s.i.a.
p_c = critical pressure
t = temperature, ° F.
t_c = critical temperature
W_f = mass of Freon-11 sample, lb.
W_s = mass of mixture sample, lb.

LITERATURE CITED

(1) Eubank, P.T., Smith, J.M., J. CHEM. ENG. DATA **7**, 75 (1962).
(2) "International Critical Tables," Vol. **5**, p. 158, McGraw-Hill, New York, 1929.
(3) McCracken, P.G., Smith, J.M., *A.I.Ch.E. J.* **2**, 498 (1956).
(4) Organick, E.I., Studhalter, W.R., *Chem. Eng. Progr.* **44**, 847 (1948).
(5) Storvick, T.S., Smith, J.M., J. CHEM. ENG. DATA **5**, 133 (1960).
(6) Watson, K.M., *Ind. Eng. Chem.* **35**, 398 (1943).

RECEIVED for review September 17, 1962. Accepted December 26, 1962.

Thermodynamics of Liquid Surfaces

Surface Tension of *n*-Hexane–Cyclohexane Mixtures at 25°, 30°, and 35° C.

H. LAWRENCE CLEVER and WILLIAM E. CHASE, Jr.
Department of Chemistry, Emory University, Atlanta 22, Ga.

A single parameter equation reproduces the experimental surface tensions of *n*-hexane–cyclohexane mixtures with an average deviation of 0.05 dyne/cm. at temperatures of 25°, 30°, and 35° C.

THE SURFACE TENSION of several *n*-hexane-cyclohexane mixtures has been measured at 25°, 30°, and 35° C. The single parameter equation:

$$\exp(-41.74\gamma/T) = X_1 \exp(41.74\ \gamma_1/T) + X_2 \exp(-41.74\ \gamma_2/T \quad (1)$$

reproduces the data at the three temperatures with a mean deviation of 0.05 dyne/cm. In the equation, γ is the mixture surface tension, γ_1 and γ_2 are the surface tensions of pure *n*-hexane and pure cyclohexane, respectively (Table I); X_1 and X_2 are the respective mole fractions, and T is the absolute temperature.

EXPERIMENTAL

Materials. Both the *n*-hexane and cyclohexane were Phillips Petroleum Pure Grade (99 mole %). Both were shaken with concentrated sulfuric acid, washed, dried over sodium, and distilled through a 20-plate packed column. The purified samples were stored over sodium until used. Density, refractive index (*8*), and surface tension (*5-7, 10*) checked well with accepted values.

Surface Tension. The surface tensions were measured by the maximum bubble pressure technique on apparatus built and described by Quayle (*5*). The bubble pressure air was

Table I. Surface Tensions of Some *n*-Hexane–Cyclohexane Mixtures

Cyclohexane, Mole Fraction	Surface Tension, Dyne/Cm. 25° C.	30° C.	35° C.
0.0	17.99	17.36	16.89
0.075	...	17.69	...
0.080	18.35	...	...
0.212	...	18.30	...
0.252	19.15	...	...
0.254	...	..	18.20
0.490	20.36	...	...
0.498	...	19.93	...
0.584	...	...	19.90
0.751	...	21.57	21.05
0.753	22.07	...	...
0.887	23.14	22.54	...
1.000	24.27	23.71	23.06

presaturated with the mixture vapor to minimize evaporation loss during the measurement. The mixtures were prepared by weight. Their densities were measured in a 5-ml. pyncrometer that had been calibrated with distilled water.

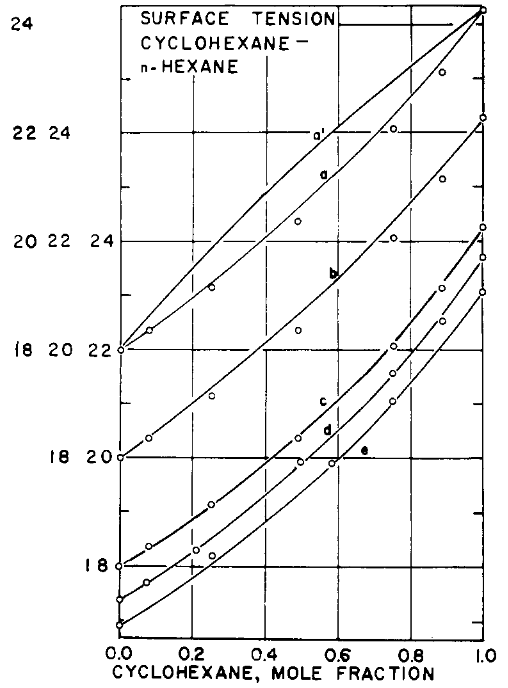

Figure 1. Surface tension vs. mole fraction cyclohexane

a, a' = regular solution equation fit at 25° C.; $a = 34.1 \times 10^{-16}$; $w = 36.1 \times 10^{-16}$

b = ideal equation fit at 25° C.; $a = 34.1 \times 10^{-16}$

c, d, e = empirical equation fit at 25°, 30°, and 35° C., respectively

RESULTS AND DISCUSSION

The surface tensions are given in Table I and in Figure 1, curves *c*, *d*, and *e* for 25°, 30°, and 35° C. respectively. The circles representing the surface tensions in the figure are drawn with a diameter equivalent to 0.1 dyne/cm. The lines are calculated from Equation 1 and fit the data with an average deviation of 0.05 dyne/cm.

Wolf has obtained *n*-hexane–cyclohexane surface tensions at 20° C. [reported by Timmermans (*9*)]. His *n*-hexane surface tension is about 1 dyne/cm. higher than that reported by most other workers (*5*, *6*, *10*). This suggests the mixture surface tensions may also be high. Wolf's data parallel our data fairly well between 0.5 and 1.0 mole fraction cyclohexane but appear high in the 0 to 0.5 mole fraction range.

Curve *b* of Figure 1 shows the fit of the Guggenheim (*1*, *2*) ideal solution equation to the data at 25° C. The equation is of the same form as our empirical Equation 1 with the numerical constant theoretically equal to a/k where a is the average surface area per molecule and k is the Boltzman constant. Assuming a spherical molecule, the surface area per molecule is the ⅔ power of the molar volume divided by Avogadro's number. Surface areas are 36.3×10^{-16} and 31.9×10^{-16} sq. cm. per molecule for *n*-hexane and cyclohexane, respectively. Curve *b* was calculated using the average a of 34.1×10^{-16}. Our empirical equation implies an a of 57.6×10^{-16}. The *n*-hexane-cyclohexane system shows a definite negative deviation from ideal behavior.

Curves *a* and *a'* show a test of the Guggenheim regular solution equations (*1*, *2*):

$$\gamma = \gamma_1 + \frac{kT}{a} \ln \frac{X_1'}{X_1} + (X_2'^2 - X_2^2)\frac{lW}{a} - mX_2^2 \frac{W}{a} \qquad (2)$$

and

$$\gamma = \gamma_2 + \frac{kT}{a} \ln \frac{X_2'}{X_2} + (X_1'^2 - X_1^2)\frac{1W}{a} - mX_1^2 \frac{W}{a} \qquad (3)$$

In addition to symbols already defined, X_1' and X_2' are mole fractions in the surface layer, l and m are geometrical factors for the type of packing in the liquid, and W is an interaction energy between the two molecules that make up the mixture. The test was made using physically real values of a and W. The interaction energy, W, can be estimated from the heat of mixing at half mole fraction. Both Mathieson and Thynne (*3*) and Mathot (*4*) report a heat of mixing of 52 cal./mole at half mole fraction which gives an interaction energy of 36.1×10^{-16} ergs per molecular pair. Assuming a close packed lattice with $l = ½$ and $m = ¼$, the average a of 34.1×10^{-16} sq. cm. per molecule, and W of 36.1×10^{-16} ergs per molecule, the pair of equations has been solved simultaneously for the mixture surface tension and the surface layer composition at 25° C. Curve *a'* gives the surface composition and curve *a* the surface tension. The fit to the data is improved about 0.1 dyne/cm. over the ideal equation fit at half mole fraction. No better fit is obtained if a simple cubic lattice is assumed.

An interaction energy of 160×10^{-16} ergs per molecular pair would force a fit at 0.5 mole fraction.

LITERATURE CITED

(1) Guggenheim, E.A., "Mixtures," Chap. IX, Clarendon Press, Oxford, 1952.
(2) Guggenheim, E.A., *Trans. Faraday Soc.*, **41**, 150 (1945).
(3) Mathieson, A.R., Thynne, J.C. J., *J. Chem. Soc.*, **1956**, 3708.
(4) Mathot, V., *Bull. soc. chim. Belg.*, **59**, 111 (1950).
(5) Quayle, O.R., *Chem. Rev.*, **53**, 439 (1953).
(6) Quayle, O.R., Day, R.A., Brown, G.M., *J. Am. Chem. Soc.*, **66**, 938 (1944).
(7) Robinson, A.E., Ph.D. thesis, Emory Univ., Atlanta, Ga., 1950.
(8) Rossini, F.D., Pitzer, K.S., Taylor, W.J., Ebert, J.P., Kilpatrick, J.E., Beckett, C.W., Williams, M.G., Werner, H.G., "Selected Values of Properties of Hydrocarbons," Natl. Bur. Standards (U.S.) Circ. **C461**, 1947.
(9) Timmermans, J., "Physico-Chemical Constants of Binary Systems," Vol. **I**, Interscience, New York, 1959.
(10) Vogel, A.I., *J. Chem . Soc.*, **1946**, 136.

RECEIVED for review September 27, 1962. Accepted January 7, 1963. This work is part of a research program supported by NSF G-7357. Mr. Chase was an Undergraduate Research Participant supported by NSF G-15672.