NOMENCLATURE

d_4^{30} = density at 30° C. with reference to water at 4° C.
n_D^{30} = refractive index at 30° C., using sodium D-line
x_A = mole fraction of ethylbenzene in toluene and ethylbenzene mixtures
x_B = mole fraction of carbon tetrachloride in benzene and carbon tetrachloride mixtures
Δ = difference between present h^E results and values obtained by use of the equation of Larkin and McGlashan (*4*) for the benzene and carbon tetrachloride system, J. mole^{-1}
n = integer
A_n = constant
h^E = excess enthalpy of mixing, J. mole^{-1}
a = number of experimental points
δ_i = difference between experimental h^E and the h^E predicted for ith point
χ_H = Flory-Huggins enthalpy interaction parameter
ϕ = volume fraction of ethylbenzene

LITERATURE CITED

(1) Amaya, K., Fujishiro, R., *Bull. Chem. Soc. Japan* **29**, 270 (1956).
(2) Flory, P.J., "Principles of Polymer Chemistry," Chap. **XII**, p. 508, Cornell University Press, New York, 1953.
(3) Gray, D.F., Watson, I.D., Williamson, A.G., *Australian J. Chem.* **21**, 379 (1968).
(4) Larkin, J.A., McGlashan, M.L., *J. Chem. Soc.* **1961**, p. 3425.
(5) Tager, A.A., Kargin, V.A., *Kolloidn. Zh.* **14**, 395 (1952).
(6) Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Vol. **II**, pp. 100, 102, Elsevier, Amsterdam, N. Y., 1965.
(7) Weissburger, A., Ed., "Technique of Organic Chemistry," Vol. **VII**, pp. 73, 319, 324, Wiley, New York, 1958.

RECEIVED for review March 3, 1969. Accepted July 14, 1969.

Molar Volume of Supercooled Naphthalene at 25° C.

E. L. HERIC and JAMES M. BERRYMAN[1]
Department of Chemistry, The University of Georgia, Athens, Ga. 30601

The molar volume of naphthalene in near-ideal solutions in ethylbenzene from 0 to 0.2 mole fraction is 123.98 ml. per mole at 25.000° ± 0.005° C.

NAPHTHALENE is frequently involved in chemical studies. At the standard temperature of 25° C., naphthalene is about 55° C. below its normal melting point. Precise interpretation of volume-dependent phenomena in liquid mixtures containing naphthalene requires a dependable value for the molar volume of that compound in the dissolved state—i.e., the supercooled liquid state.

Extrapolation of the density of liquid naphthalene to 25° C. from above the normal melting point yields a value of 125.9 ml. per mole (*4*). The calculated liquid molar volume is uncertain to ±0.1 ml. per mole at temperatures in the region moderately above the normal freezing point (*4*), and the uncertainty is quite indefinite at 25° C.

Lumsden (*5*) reported 124.25 ml. per mole for naphthalene dissolved in toluene at 25° C. at a single solute mole fraction of 0.09. The value was determined by density measurement, assuming ideal behavior. His additional results (*5*) for naphthalene dissolved in toluene, xylene, and benzene at 15° C., at solute mole fractions of 0.05, 0.10, and 0.20 in each system, indicate that the single value at 25° C. should be considered uncertain to approximately 0.3 to 0.4 ml. per mole.

This note reports the molar volume of supercooled naphthalene, based on a series of density measurements of naphthalene-ethylbenzene solutions. The solubility of naphthalene in ethylbenzene is about 95% of the ideal value (*2*) at 25° C. Moreover, refractive indices in this system are additive in mole fraction at 25° C. (*3*), again indicating near-ideality, as well as near-equal molar volumes for these components as liquids at this temperature. This should be a more reliable value of the molar volume of supercooled naphthalene than presently available.

EXPERIMENTAL

Material. Naphthalene was Baker reagent grade, recrystallized from alcohol. Previous work has shown that further recrystallization causes no measurable change in properties in these mixtures (*2*), so the material was used as received. Ethylbenzene was MCB Spectroquality grade, purified by distillation through a 4-foot-long vacuum-jacketed column at a recovery rate of about 1 ml. per minute. Calcium hydride was used as a drying agent. Only the middle half of the distillate was recovered. For the purified product, the refractive index (sodium D-line at 25.00° ± 0.01° C.) was 1.49300 [lit., 1.49320 (*1*)].

Equipment. Densities were determined with a 25-ml. Weld pycnometer. The pycnometer was calibrated with degassed distilled water to a standard error of ±0.002 ml. Weighings were made with a Mettler single-pan balance with certified weights. Temperature equilibrium was reached in a Sargent Thermonitor-controlled bath at 25.000° ± 0.005° C. Replication indicated an uncertainty in density equivalent to 0.02 ml. in molar volume.

RESULTS AND DISCUSSION

The experimental molar volumes, V°, of the solvent and four mixtures are given in Column 2 of Table I. Assuming ideality

$$V^\circ = x_1 V_1^\circ + x_2 V_2^\circ \qquad (1)$$

where x is the mole fraction, and the subscripts 1 and 2 refer, respectively, to solvent (ethylbenzene) and solute (naphthalene). By rearrangement of Equation 1 into

$$V^\circ = V_1^\circ + (V_2^\circ - V_1^\circ)x_2$$

$V_2^\circ - V_1^\circ$, and thus V_2°, may be evaluated as the slope

---

[1] Present address: Department of Chemistry, West Georgia College, Carrollton, Ga.

Table I. System Naphthalene-Ethylbenzene at 25° C.

x_2, Mole Fraction Naphthalene	V°, Ml. per Mole Exptl.	V°, Ml. per Mole Calcd.
0	122.83	122.83
0.0420	122.87	122.88
0.0840	122.91	122.92
0.1250	122.98	122.98
0.1723	123.05	123.04

of a plot of V° *vs.* x_2. This was done by the method of least squares, forcing the regression line to pass through $V^\circ = V^\circ_1$ at $x_2 = 0$. This requirement was imposed on the principle that density determination on the pure solvent involved fewer sources of error.

A value of 123.98 ml. per mole was found for V°_2. For the four mixtures, the experimental and calculated values of V° are compared in Table I. The agreement is within experimental error for all mixtures.

The experimental value of V°_1, 122.83 ml. per mole, differs from the literature value of 123.06 (*1*) by about 0.2%. Both this and the refractive index indicate a measurable impurity in the solvent. Previous work (*2*) has shown, however, that the effect thereof should be negligible.

When the interaction between mixture components is sufficiently small, Henry's law behavior at low solute concentrations coincides experimentally with Raoult's law behavior. The upper limit of concentration observed here is about 0.2 mole fraction of naphthalene, which extends beyond the usual limit of the Henry's law region. As the volumetric data at the high concentration agree with those at the lower concentration, this is taken to indicate that V°_2 reported here does represent the molar volume of pure supercooled naphthalene, rather than an apparent molar volume.

LITERATURE CITED

(1) Forziati, A.F., Rossini, F.D., *J. Res. Natl. Bur. Std.* **43**, 473 (1949).
(2) Heric, E.L., Posey, C.D., J. CHEM. ENG. DATA **9**, 35 (1964).
(3) *Ibid.*, **10**, 75 (1965).
(4) "International Critical Tables," Vol. III, p. 30, McGraw-Hill, New York, 1928.
(5) Lumsden, J.S., *J. Chem. Soc.* **91**, 24 (1907).

RECEIVED for review April 17, 1969. Accepted August 2, 1969.

Heat of Reaction and Dissociation Energy for the C—C Bond in 1,2-Dimethoxy-1,1,2,2-tetraphenyl Ethane

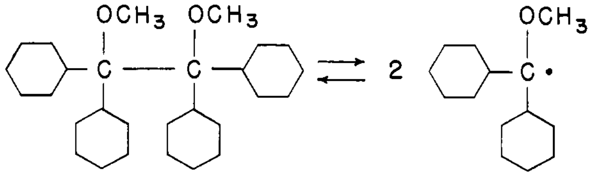
B. R. LOY[1], H. B. GEIGER, F. W. HEATH, T. A. JOHNSON, and J. V. NEERING
Saginaw Valley College, University Center, Mich. 48710

The dissociation energy for the $\phi_2(OCH_3)C—C(OCH)\phi_2$ bond, as determined by ESR, is 30.0 ± 0.6 kcal. per mole. The activation energy for the recombination of α-methoxydiphenylmethyl radicals is approximately zero.

CONTINUING their interest in the physical properties of the α-methoxydiphenylmethyl radical (*3*), the authors have measured the equilibrium constant of the

$$R—R \rightleftharpoons 2R\cdot$$

reaction over the temperature range of 77° to 120° C. by measuring the radical concentration with ESR.



Below 77° C. the signal-to-noise ratio is low, and at 120° C. the steady state radical concentration decays by means of side reactions, with a half-life of 25 minutes.

At intermediate temperatures, the system is sufficiently stable to permit reliable equilibrium measurements. The change in radical concentration follows the temperature change so closely that no activation energy can be observed for the recombination of radicals, as is the case with the trityl radical(*2*). Therefore, the heat of reaction is assumed to be the dissociation energy of the $\phi_2(OCH_3)C—C(OCH_3)\phi_2$ bond.

The calculated data in Table I were obtained from a least squares fit to the equation

$$K_{eq} = \exp\left[\frac{(-15109 \pm 303)}{T} + 17.93 \pm 0.82\right]$$

from which

$$\Delta H = D[\phi_2(OCH_3)C—C(OCH_3)\phi_2] = R \times \frac{d(\ln K_{eq})}{d(1/T)} = 30.0 \pm 0.6 \text{ kcal. per mole}$$

The substitution of methoxy groups for phenyl in trityl increases the C—C bond strength by 12 kcal. per mole, which is substantially the same as suggested by Conant (*1*) when a phenyl group is replaced by hydrogen.

---

[1] Present address: Physical Research Laboratory, The Dow Chemical Co., Midland, Mich. 48640