An Irregularity in the Solvent Powers of Paraffins

Joel H. Hildebrand

An Irregularity in the Solvent Powers of Paraffins

JOEL H. HILDEBRAND

Department of Chemistry, University of California, Berkeley, California

(Received July 17, 1950)

The solubility relations of n-heptane with f-heptane, iodine, sulfur, stannic iodide, and phosphorus are all accounted for within the usual limits of accuracy for regular solution theory by a solubility parameter 8.1 instead of the value 7.45 derived from its energy of vaporization per cc. Solutions of 2,2,4-trimethyl pentane with f-heptane and with iodine are similarly accounted for by the empirical value 7.45 instead of 6.85. Such an adjustment for paraffins is a practical alternative to the treatment used by Simons and Dunlap for the system n-pentane, "pentforane," which they recently reported upon, and is, at the same time, consistent with their assumption that the exceptional behavior of paraffins is to be attributed to an irregularity in their mutual repulsions.

IT has been known for some time[1] that the solubility of iodine in paraffin hydrocarbons is somewhat less than would be expected from the theory of regular solutions using values of solubility parameters derived from heats of vaporization. Recently, Simons and Dunlap[2] have reported that the mutual solubility of n-pentane and n-perfluoropentane, "n-pentforane," is *less* than would be expected from the same theory. At the time this paper appeared, Benesi, Fisher, and I[3] had submitted a paper for publication in which we reported a similar discrepancy for solutions of n-perfluoroheptane with n-heptane and with 2,2,4-trimethyl pentane, "*iso*-octane." They form two liquid phases at 50° and 24°, respectively, whereas, according to theory, they should not unmix till cooled far below zero. We stated therein our conclusion that this irregularity is to be attributed to an energy rather than an entropy effect, and could be accounted for by assigning to the paraffins a larger solubility parameter than the one based upon the heat of vaporization. The purpose of this communication is to show the quantitative internal consistency that is brought into the solubility relations of n-heptane by so doing.

Because of the large molal volume of perfluoroheptane, (I shall call it f-heptane) I add the Flory-Huggins term to the regular solution equation to give the more general equation,

$$\ln a_2 = \ln \varphi_2 + \varphi_1 \left(1 - \frac{V_2}{V_1}\right) + \frac{V_2 \varphi_1^2 (\delta_2 - \delta_1)^2}{RT}. \quad (1)$$

The equation for the critical solution temperature derived from this[3] is

$$RT_c = \frac{2V_1 V_2}{(V_1^{\frac{1}{3}} + V_2^{\frac{1}{3}})^2} (\delta_2 - \delta_1)^2. \quad (2)$$

The symbols have the following meanings: a is activity referred to pure liquid, φ is volume fraction, V is molal

volume, T_c is critical solution temperature, and δ is "solubility parameter," $(\Delta E^v / V)^{\frac{1}{2}}$, where E is molal energy of vaporization and V is molal volume. I shall compare the solvent power of n-heptane with that of carbon tetrachloride for five other substances, f-heptane,[3] iodine,[1] sulfur,[4] stannic iodide,[5] and phosphorus,[6] which are designated as component 2. Component 1 is n-heptane and 1' is carbon tetrachloride. The data used are the critical solution temperature, in the case of f-heptane, and the solubility of the solid form of the other substances at 25°. In these cases, the activities are those of the solid, $a_2{}^s$, referred to the supercooled liquid. Any uncertainties in the values of $a_2{}^s$ are canceled out by the method of calculation used, so do not affect the comparison. Table I gives the differences, $\delta_2 - \delta_1'$ and $\delta_2 - \delta_1$, calculated from the solubility data for each second component and in the case of f-heptane, the experimental values of T_c are given in Table II, along with the values of V at the same temperatures.

The last row in Table I shows that all of these solutions agree in indicating that the solubility parameter of n-heptane should be taken as from 0.3 to 0.5 less than that of carbon tetrachloride instead of 1.15 less, as given by their energies of vaporization per cc., 7.45 and 8.6, respectively. If we assume 8.6 for carbon tetrachloride as a standard for comparison, then the value 8.1 for n-heptane would obviously be consistent, within the usual limits of error, with its solvent powers for all of the substances here considered. It should be remembered that a variety of disturbing factors unite to cause variations of from 0.1 to 0.2 in the δ-values for any one substance by means of Eqs. (1) and (2).

The paraffin, 2,2,4-trimethyl pentane, is, similarly, a better solvent for iodine[1] and a poorer solvent for f-heptane[3] than its value of $(\Delta E^v / V)^{\frac{1}{2}} = 6.85$ would lead one to expect. With iodine, $\delta_1' - \delta_1 = 0.7$ and with

[1] H. A. Benesi and J. H. Hildebrand, J. Am. Chem. Soc. 70, 3978 (1948).

[2] J. H. Simons and R. D. Dunlap, J. Chem. Phys. 18, 335 (1950).

[3] Hildebrand, Fisher, and Benesi, J. Am. Chem. Soc. (September, 1950).

[4] J. H. Hildebrand and C. L. Jenks, J. Am. Chem. Soc. 43, 2172 (1921).

[5] M. E. Dorfman and J. H. Hildebrand, J. Am. Chem. Soc. 49, 729 (1927). See, also, *Solubility of Nonelectrolytes* (Reinhold Publishing Corporation, New York) 1950 for the data cited in references 4–7.

[6] C. Groot and J. H. Hildebrand, J. Am. Chem. Soc., 70, 3815 (1948).

TABLE I. Difference between solubility parameters of CCl_4 and $n\text{-}C_7H_{16}$ from their solubility data with common solutes.

	C_7F_{16}	I_2	S_8	SnI_4	P_4
V_2		59.0	135	151	70.4
$100x_2$ in CCl_4		1.147	0.500	1.46	1.58
$100x_2$ in C_7H_{16}		0.679	0.141	0.553	1.24
$\delta_2-\delta_1'$	−2.98	5.74	4.26	3.05	5.94
$\delta_2-\delta_1$	−2.62	6.21	4.80	3.53	6.26
$\delta_1'-\delta_1$	0.36	0.47	0.54	0.48	0.32

TABLE II. Critical solution figures for n-heptane with f-heptane (2) and carbon tetrachloride (1′).

	T_c	V_1	V_1'	V_2
n-Heptane—f-heptane	332	152	—	239
Carbon tetrachloride—f-heptane	323	—	101	235

f-heptane it is −0.5. The proper value for this octane should evidently be about 7.45 instead of 6.85.

It is, of course, quite reasonable to obtain δ-values from solubility data themselves rather than from heats of vaporization. I have noted a similar displacement in the case of chloroform,[7] where a variety of solubility data are consistent with a parameter 9.0 instead of the value 9.3 from $(\Delta E^v/V)^{\frac{1}{2}}$.

The explanation offered by Simons and Dunlap in connection with their investigation of the two pentanes, i.e., that hydrocarbon molecules can interpenetrate and yield a liquid with unusually small free volume seems

quite reasonable. This implies that the slope of the repulsive branch of the curve of potential energy vs. distance in the case of paraffin molecules differs markedly from that of most other molecular species, and the repulsive branch plays a larger role in the small separations involved in mixing with another liquid than it does in the large separations involved in vaporization.

The figures cited in this paper seem to show that a simple, practical means of dealing with the solubility relations of paraffins is to derive their solubility parameters from known solubility data with a reasonable expectation that values so derived will prove applicable to new cases.

[7] J. H. Hildebrand, Chem. Revs. 44, 37 (1949).

LCAO Self-Consistent Field Calculation of the π-Electron Energy Levels of cis- and *trans*-1,3-Butadiene*

ROBERT G. PARR† AND ROBERT S. MULLIKEN
Department of Physics, University of Chicago, Chicago 37, Illinois
(Received June 6, 1950)

The π-electrons of the molecules cis- and trans-1,3-butadiene are treated by the method of antisymmetrized products of molecular orbitals, the molecular orbitals being taken as linear combinations of $2p\pi$-Slater atomic orbitals with effective charge 3.18. The *best* ground state *LCAO* molecular orbitals obtainable from these are found by application of a method recently proposed by Roothaan which is based on the variational theorem, and the π-electron energy of the ground state is calculated. Including a correction for nuclear repulsions, the *trans*- form is computed to be 0.12 ev more stable than the *cis*-form. Using the ground state orbitals to build up excited state wave functions, the energies of four singly excited singlet states and the corresponding triplet states are calculated, there resulting for the average of the lowest singlet and triplet states the excitation energy 5.4 ev for *cis*- and 5.7 ev for *trans*-, the experimental value for the lowest singlet state (probably for *trans*-) being 6.0 ev. The first ionization potential is computed to be 9.7 ev for both *cis*- and *trans*-, whereas the observed value is 9.1 ev. No extra-geometrical empirical data are used except in the calculation of ionization potentials, where the value −11.28 ev based on atomic spectroscopic data is used for the energy of a $2p\pi$-electron in a carbon atom in its valence state.

INTRODUCTION

RECENT calculations[1,2] have indicated that electronic excitation and ionization energies of un-

[1] For example, R. G. Parr and B. L. Crawford, Jr., J. Chem. Phys. **16**, 526 (1948); C. C. J. Roothaan and R. G. Parr, J. Chem. Phys. **17**, 1001 (1949).

[2] R. S. Mulliken, Parts II–III of "Report on molecular orbital theory," J. de Chim. Phys. **46**, 497 (1949)—see 1947–8 ONR

saturated organic compounds can be computed with fair accuracy by the method of antisymmetrized products of molecular orbitals (in *LCAO* approximation) with the introduction of no extra-geometrical empirical factors. In most cases so far treated the molecular orbitals have been determined by symmetry considerations alone. In the present paper we consider a molecule (1,3-butadiene) where the orbitals can *not* be so de-