

THE CONSTITUTIVE NATURE OF THE POLYMER BOND

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ABSTRACT.—A new constitutive effect is proven to be necessary to differentiate between solutions of monomers and solutions of polymers in work using additive-constitutive properties. Numerical results are presented for some typical examples. A brief discussion of the implications of the new effect is presented.

Additive and constitutive properties have long been used to deduce structural information concerning molecules (Partington, 1951). In general, contributions from atoms, groups, and chemical structure are used to determine the value of the property being studied for a given molecule. That is,

$$P = \Sigma P_g + \Sigma P_s \quad (1)$$

where P is the property being studied (e.g. parachor, molar refraction, etc.), P_g is the value of that property for a group or atom, and P_s is the value of that property for a specific type of chemical structure. The adjective *additive* refers to the contributions, P_g ; the adjective *constitutive* refers to the contributions, P_s . Usually the terms P_s arise from multiple bonds, semipolar bonds, and various types of rings.

If, instead of studying the pure specie, the molecule is in solution, then *additive* is used in a second context; *viz.*, the value of the property, P , for the solution is found by adding, in their proper ratios, the

P values for the components of the solution. In equation form

$$P = x_1 P_1 + x_2 P_2 \quad (2)$$

where x is mole fraction and the subscripts, 1 and 2 refer to the solvent and solute, respectively.

The primary purpose of this work is to determine whether or not a constitutive contribution is necessary for a bond linking two or more identical molecules. For example, should the hydrogen bond in an acetic acid dimer give a constitutive contribution? Secondly, this paper presents a generalization of parachor work of Bhagwat and Toshniwal (1942). The generalized proof formalizes the intuitive feeling that if one does not attribute a constitutive nature to the polymer bond, then there is no way to differentiate (on the basis of additive-constitutive properties) between monomers and polymers in solution.

Before proceeding with the proof and calculations, some further notational remarks should be made. Each additive-constitutive property may be written as proportional to the solution molecular weight, M , *viz.*,

$$P \propto M$$

or

$$P = AM \quad (3)$$

where the proportionality constant, A , contains experimentally measured information. For example, the parachor, $[P]$, is given by

$$[P] = \frac{\gamma^{1/4}}{d_l - d_v} M \quad (4)$$

where γ is the surface tension, dl is the density of the solution, and d_v is the density of the vapor. The molar refraction, $[R]$, is given by

$$[R] = \frac{n^2 - 1}{n^2 + 2} \frac{1}{d_l} M \quad (5)$$

The property values for the solvent, P_1 , and the solute, P_2 , may also be found from formulas such as those given by Equations (4) and (5) if d_l is taken as the density of the pure liquid and the corresponding experimental values (surface tension or refractive index) are those of the pure liquid.

Throughout this paper the property value calculated with known atomic and structural values (Equation (1)) is designated by a subscript, C , e.g. P_C , and the property value found from experimental values is designated (Equation (3)) by a subscript, E , e.g. P_E . In order to distinguish between monomeric, dimeric, and polymeric units, an additional subscript is used. The additional subscript is m , d , or p when the discussion involves monomer, dimer, or polymer, respectively. For example, P_{Cm} is a calculated property value of a monomer and P_{2p} is a property value for polymeric solute.

THE NECESSARY CONDITION

Suppose a particular solute is dissolved in a solvent and, further,

suppose that it is not known whether the solute in solution contains monomeric, dimeric, or polymeric units. If the solute is in monomeric form, one writes Equation (2) as

$$P_{Cm} = x_{1m}P_1 + x_{2m}P_{2m} \quad (6)$$

where the mole fractions in terms of the moles of solvent, n_1 , and the moles of solute, n_2 , are given by

$$x_{1m} = \frac{n_1}{n_2 + n_1} \quad x_{2m} = \frac{n_2}{n_2 + n_1} \quad (7)$$

and the terms P_1 and P_{2m} are found from tables of the property value. On the other hand, if the solute exists in solution in polymeric form, then Equation (2) becomes

$$P_{Cp} = x_{1p}P_1 + x_{2p}P_{2p} \quad (8)$$

where, in terms of the moles of polymeric solute, n_2' ,

$$x_{1p} = \frac{n_1}{n_2' + n_1} \quad x_{2p} = \frac{n_2'}{n_2' + n_1} \quad (9)$$

If there are p monomeric units forming the polymer, then, by stoichiometry

$$n_2' = \frac{1}{p} n_2 \quad (10)$$

Further, if the bonds linking the monomeric units contribute no new constitutive information (as is usually assumed), then

$$P_{2p} = pP_{2m} \quad (11)$$

Substituting Equation (10) into Equation (9) and putting that result plus Equation (11) into Equation (8), one obtains

$$P_{Cp} = \frac{pn_1}{n_2 + pn_1} P_1 +$$

$$\frac{n_2}{n_2 + pn_1} pP_{2m} \quad (12)$$

Combining Equations (17), (18), and (19) one obtains

$$P_{Ep} = \frac{p(n_2 + n_1)}{n_2 + pn_1} P_{Em} \quad (20)$$

or

$$P_{Cp} = \frac{p}{n_2 + pn_1} [n_1P_1 + n_2P_{2m}] \quad (13)$$

The right-hand side of Equation (13) is not changed upon multiplication by 1, where

$$1 = \frac{n_2 + n_1}{n_2 + n_1}$$

The result is

$$P_{Cp} = \frac{p(n_2 + n_1)}{n_2 + pn_1} [x_{1m}P_1 + x_{2m}P_{2m}] \quad (14)$$

then, using Equations (15) and (20), one obtains

or, combining Equation (14) with Equation (6),

$$P_{Cp} = \frac{p(n_2 + n_1)}{n_2 + pn_1} P_{Cm} \quad (15)$$

$$\frac{p(n_2 + n_1)}{n_2 + pn_1} P_{Cm} = \frac{p(n_2 + n_1)}{n_2 + pn_1} P_{Em} \quad (22)$$

It is usually true in solution experiments that the molecular weight is an additive function, i.e.

$$M = x_1M_1 + x_2M_2 \quad (16)$$

where M_1 and M_2 are the molecular weights of the solvent and solute, respectively. Since Equation (16) is simply a particular case of Equation (2), it follows that

$$M_{Cp} = \frac{p(n_2 + n_1)}{n_2 + pn_1} M_{Cm} \quad (17)$$

Equation (3) specialized for the monomer is

$$P_{Em} = AM_{Cm} \quad (18)$$

and specialized for the polymer is

$$P_{Ep} = AM_{Cp} \quad (19)$$

Equation (22) gives no further information than the usual assumption for monomers

$$P_{Cm} = P_{Em} \quad (23)$$

The implication of Equation (22) is that no matter how weak the interaction between monomeric units, some constitutive information concerning the link must be used if the property value for the polymer is to reflect any additional information than can be obtained from property value information of the monomer. Intuitively the result is obvious but the preceding derivation puts the intuition on firm footing. Previously Bhagwat and Toshniwal (1942) proved that the equation of Hamrick and Andrew (1929) held for associated molecules. Whereas that

proof, in a different manner, established the conclusion of Equation (22) for parachors of dimers, the present proof shows the generality of the conclusion for all additive-constitutive properties and extends the conclusion to polymers.

A NEW CONSTITUTIVE CONTRIBUTION

One method of insuring that the property value of the polymer differs from that of the monomer is to specifically introduce a constitutive effect for the link between monomeric units. In the following it is assumed that all monomeric linkages in a given polymer are the same. The new effect is properly introduced by rewriting Equation (11) as

$$P_{2p} = pP_{2m} + qP_B \quad (24)$$

where q is the number of identical linkages or bonds in the polymer and P_B is the new constitutive property value for a bond joining two monomeric units. If Equation (24) is used in the derivation of the preceding section, instead of Equation (11), one obtains in place of Equation (22) (or the equivalent Equation (23))

$$P_{Em} = P_{Cm} + \frac{q}{p} x_{2m} P_B \quad (25)$$

NUMERICAL RESULTS

Equation (24) is tested with selected parachor and molar refraction data for associated liquids dissolved in non-associated liquids. A summary of the results is given in Tables 1 and 2. In these calculations p and

TABLE 1.—Dimer Bond Parachors.¹

Solute-Solvent	x_{2m}	$[P]_{Em}^2$	$[P]_{Cm}^{3,4}$	% Deviation	$[P]_{B}^5$	$[P]_{Cm}^6$	% Deviation
CH ₃ COOH-C ₆ H ₆	.279	186.6	184.74	1.00	13.33	185.8	.42
	.510	168.9	167.06	1.09	7.22	169.0	-.07
	.820	145.6	143.33	1.56	5.54	146.5	-.62
	1.000	131.9	129.55	1.78	4.70	133.4	-1.14
				1.36 ⁷	7.70 ⁷		-0.36 ⁷
C ₂ H ₅ OH-C ₆ H ₆	.237	187.8	186.87	.50	7.85	187.3	.27
	.564	161.4	160.33	.66	3.79	161.4	.00
	.758	145.4	144.59	.56	2.14	146.1	-.48
	1.000	126.0	124.95	.83	2.10	126.9	-.71
			.64 ⁷	3.97 ⁷		-.23 ⁷	
(CH ₃) ₂ CO-C ₆ H ₆	.2993	193.1	191.11	1.03	13.30	192.6	.26
	.5283	182.3	179.63	1.46	10.11	182.3	.00
	.7034	174.1	170.86	1.86	9.21	174.4	-.17
	.8563	166.9	163.20	2.22	8.64	167.5	-.36
	1.0000	160.2	156.00	2.62	8.40	161.0	-.50
			1.84 ⁷	9.93 ⁷		-.15 ⁷	

¹ All values in units of dynes ^{1/4} cm^{-1/4} cm³.

² D. L. Hammick and L. W. Andrew (1929).

³ The bond parachors used in this calculation are the revised values given by Vogel, et al. (1950).

⁴ From Equation (2).

⁵ From Equation (25).

⁶ Calculated from $[P]_{Cm} + \frac{x_{2m}}{2} [P]_{B}$.

⁷ Average values.

TABLE 2.—Dimer Bond Refractions.

Solute-Solvent	x_{2m}	$[R]_{Bm}$	$[R]_{cm}^1$	% Deviation	$[R]_B^2$	$[R]_{cm}^3$	% Deviation
<i>i</i> -C ₈ H ₇ CH- <i>n</i> -C ₆ H ₁₄ ⁴	.17920	27.55	27.54	.04	.112	27.54	.04
	.33283	25.69	25.68	.04	.060	25.69	.00
	.47034	24.02	24.02	.00	.000	24.03	-.04
	.59009	22.58	22.57	.04	.029	22.58	.00
	.69742	21.27	21.28	-.05	-.029	21.29	-.09
	.79276	20.12	20.12	.00	.000	20.13	-.05
	.87858	19.08	19.07	.05	.023	19.09	.05
	1.00000	17.62	17.58	.23	.080	17.60	.11
				.04 ⁵	.034 ⁵		.00 ⁵
CH ₃ OH-CCl ₄ ^{6,7}	.26886	22.477	21.256	5.43	9.083	22.105	1.66
	.51242	18.435	16.872	8.48	6.100	18.491	-.30
	.73074	14.345	12.966	9.61	3.774	15.275	-6.48
				7.84 ⁵	6.319 ⁵		-1.71 ⁵
CH ₃ OH-C ₆ H ₆ ^{6,7}	.25186	21.116	21.650	-2.53	-4.240	21.283	-.79
	.49387	16.559	17.283	-4.37	-2.932	16.564	-.03
	.72871	12.476	13.044	-4.55	-1.559	11.984	3.94
				-3.82 ⁵	-2.910 ⁵		1.04 ⁵
CH ₃ OH-C ₆ H ₆ ^{7,8}	.12988	23.901	23.852	.21	.755	23.876	.10
	.13461	23.798	23.767	.13	.461	23.792	.03
	.25397	21.684	21.612	.33	.567	21.658	.12
	.26234	21.525	21.461	.30	.488	21.509	.07
	.36777	19.642	19.558	.43	.457	19.625	.09
	.36893	19.626	19.538	.44	.477	19.606	.10
	.49280	17.392	17.302	.52	.365	17.392	.00
	.49342	17.288	17.201	.50	.353	17.291	-.02
	.61696	15.155	15.061	.62	.305	15.174	-.13
	.62142	15.076	14.981	.63	.306	15.095	-.13
	.74600	12.828	12.732	.75	.257	12.869	-.32
	.74890	12.776	12.680	.75	.256	12.817	-.32
	.74979	12.755	12.664	.71	.242	12.801	-.36
	.87456	10.501	10.412	.85	.203	10.572	-.68
	.87755	10.446	10.358	.86	.201	10.519	-.70
1.00000	8.231	8.148	1.01	.166	8.331	-1.21	
			.57 ⁵	.366 ⁵		-.21 ⁵	

¹ From Equation (2).² From Equation (25).³ Calculated from $[R]_{cm} + \frac{x_{2m}}{2} [R]_B$.⁴ Experimental data from Böttcher (1952), p. 269.⁵ Average values.⁶ Calculated from experimental data given by Scatchard and Ticknor (1952).⁷ Bond refractions taken from Ref. 3, Table 1.⁸ Calculated from experimental data given by Wood, et al. (1960)

q were assumed to be 2 and 1, respectively. In every case a significant improvement was obtained in the calculated property values. Further, in one case where results from two workers can be compared

(CH₃OH in C₆H₆), the average values of P_B are of the same magnitude. In several cases, P_B shows a definite variation with x_{2m} which might indicate a solvation effect. However, the present data does not warrant

the usual extrapolation to infinite dilution. In fact, the term P_B is equivalent to replacing the finite series defining Scatchard's excess function (Scatchard, 1949) by a single term. The variation of P_B could well correspond to higher order terms in the series.

Batsanov (1961) has also suggested that the difference between experimental and calculated molar refractions can be attributed to hydrogen bond molar refractions. His work applies to both inorganic and organic compounds while the present paper provides the natural extension to solutions. Padova (1964) has calculated solvated molar refractions for electrolytic solutions. The present calculations show that solvation effects may be general for additive-constitutive properties.

THEORETICAL RATIONALE

The inclusion of constitutive effects for these weak bonds does, in fact, have some theoretical basis. Fowler (1937), using statistical mechanics and thermodynamics, has related parachor to a constant, B . The value of B is dependent upon interaction energy between molecules as well as a distribution function which is energy dependent. An omission of hydrogen bonding, charge transfer effects, etc., fails to fully utilize the information in B .

Any interaction, e.g., the dimerization of acetic acid, affects the energy of the system. The perturbation caused by the dimer bond formation alters the polarizability of the molecule. Since the polarizability is proportional to the mole refraction (Pauling and Wilson, 1935), a con-

tribution to $[R]_{Cd}$ must be included. Although it is known that hydrogen bonding affects the dipole orientation, the resulting change in dielectric constant and dipole moment varies both in direction and magnitude (Pimental and McClellan, 1960). Consequently a value of $[R]_{Cd}$ depends upon the particular bond. The present proof emphasizes the consequences of omitting constitutive information, even for weak interactions.

SUMMARY

The material in this paper is divisible into two principal parts. First, a mathematical proof is given concerning the necessity of including a constitutive factor to describe, with additive-constitutive properties, the type of bond linking two identical molecules in solution. One, intuitively, feels this is true when a strong polymer bond is formed. However, the present proof emphasizes the necessity of such a contribution even if the linkage is much weaker, e.g. a hydrogen bond or a charge transfer bond. An extremely important corollary to this proof is the fact that it is not possible to obtain additional independent mathematical conditions by writing equations involving the additive-constitutive properties of dimer, trimer, etc., in addition to the monomer equation.

Second, a new constitutive contribution is defined for systems containing linked identical molecules in solution. Numerical calculations are given to support the new proposal. Finally, a brief theoretical justification is given for the new contribution.

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LITERATURE CITED

- BATSANOV, S. S. 1961. Refractometry and Chemical Structure. Translated by Paul Porter Sutton. Consultants Bureau, New York. 250 pp.
- BHAGWAT, W. V., and P. TOSHNIWAL. 1942. Application of Hammick and Andrew's Formulae for Determining the Parachor of a Solute. *Journal of the Indian Chemical Society* 19; 225-230. 3 tables.
- BÖTTCHER, C. J. F. 1952. Theory of Electric Polarisation. Elsevier Publishing Company, Amsterdam. xiii + 492 pp.
- FOWLER, R. H. 1937. A Tentative Statistical Theory of Macleod's Equation for Surface Tension, and the Parachor. *Proceedings of the Royal Society of London A* 159; 229-246. 2 figures.
- HAMMICK, D. L., and L. W. ANDREW. 1929. Determination of the Parachors of Substances in Solution. *Journal of the Chemical Society* 754-759. 1 figure, 4 tables.
- PADOVA, J. 1964. Solvation Approach to Ion Solvent Interaction. *Journal of Chemical Physics* 40; 691-694. 4 tables.
- PARTINGTON, J. R. 1951. An Advanced Treatise on Physical Chemistry. Volume II. The Properties of Liquids. Longmans, Green and Co. London. xlv + 448 pp.
- PAULING, L., and E. B. WILSON. 1935. Introduction to Quantum Mechanics. McGraw-Hill Book Company, Inc. New York xiii + 468 pp.
- PIMENTEL, G. C., and A. L. MCCLELLAN. 1960. The Hydrogen Bond. W. H. Freeman and Company. San Francisco xii + 475 pp.
- SCRATCHARD, G. 1949. Equilibrium in Non-Electrolyte Mixtures. *Chemical Reviews* 44; 7-35. 16 figures.
- SCRATCHARD, G., and L. B. TICKNOR. 1952. Vapor-Liquid Equilibrium. IX. The Methanol-Carbon Tetrachloride-Benzene System. *Journal of the American Chemical Society* 74; 3724-9. 7 tables.
- VOGEL, A. I., W. T. CRESSWELL, G. J. JEFFREY, and L. LEICESTER. 1950. Bond Refractions and Bond Parachors. *Chemistry and Industry* 358. 1 table.
- WOOD, S. E., S. LANGER, and R. BATTINO. 1960. Refractive Index and Dispersion of the Benzene-Methanol System. *Journal of Chemical Physics* 32; 1389-1393. 3 tables.

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