The Dipole Moments of Fulvene and Azulene

G. W. Wheland and D. E. Mann

Articles you may be interested in

CASSCF and CASPT2 studies on the structures, transition energies, and dipole moments of ground and excited states for azulene
J. Chem. Phys. **120**, 1245 (2004); 10.1063/1.1631914

Dipole Moments of the Excited States of Azulene
J. Chem. Phys. **50**, 1684 (1969); 10.1063/1.1671258

Dipole Moment, Microwave Spectrum, and Electronic Structure of Fulvene
J. Chem. Phys. **49**, 5542 (1968); 10.1063/1.1670085

Determination of ExcitedState Dipole Moments of Azulene
J. Chem. Phys. **35**, 464 (1961); 10.1063/1.1731953

Dipole Moments
Am. J. Phys. **18**, 532 (1950); 10.1119/1.1932663

$= 1.123$ K cal./mole, and $C = 0.197$ K cal./mole. The minimum corresponding to the C_2 configuration is computed at $\phi = 117.1°$ instead of $\phi = 120°$, and the force constants for the C_2 and C_{2h} configurations obtained from the curvature of the potential function are $9B + 13.5C - A/2$ and $A + 9B$, respectively.

For small amplitudes of vibration the potential energy of C_{2h} dichloroethane is $V = (A + 9B/2) \cdot \phi^2$ and the kinetic energy is $T = 2 \times \frac{1}{2} \times (I)/(2) \cdot \dot{\theta}^2$ where I is the least moment of inertia and $\dot{\theta}$ is the angular velocity about the least axis. The relation between θ and ϕ is given by

$$\theta = \phi \left\{ \frac{\sin\beta}{\tan(\pi/2 - \beta)} + \cos\beta \right\}$$

where β is the angle the axis of least moment of inertia makes with the $C-C$ axis $= 49° \, 25'$. Although the torsion vibration occurs in a symmetry class with three other vibrations its frequency may be evaluated approximately from

$$\omega^2 = \frac{4(A + 9B)}{I} \cdot \frac{1}{\left\{ \frac{\sin\beta}{\tan(\pi/2 - \beta)} + \cos\beta \right\}^2}.$$

Assuming tetrahedral angles and the values of the internuclear distances given above, it is found that

$I = 34.3 \times 10^{-40}$ c.g.s. The torsion frequency is then calculated as $\nu_{12} = 101$ cm^{-1}. This agrees as well as can be expected with the value chosen (80 cm^{-1}) for this frequency from the experimental data.[3]

Gwinn and Pitzer have calculated the torsion frequency of the C_2 molecule from the curvature of their potential function and found 79 cm^{-1}. Since the frequency is proportional to the square root of the force constant, use of the potential function constants in this paper leads to the calculated frequency of $\nu = (12.40/9.95)^{\frac{1}{2}} \times 79 = 88$ cm^{-1}. This compares as well as can be expected with the observed value of 124 cm^{-1}.[**]

Other halogen substituted ethanes are being treated in the same manner.

[**] Recently Gordon and Giauque (J. Am. Chem. Soc. **70**, 1506 (1948)) have given the barrier for ethyl chloride as 4700 cal. for entropy data. Using this value to obtain the magnitude of the constant for HCl interaction gives AHCl $= 20.0 \times 10^5$. With AH$_2 = 4.65 \times 10^5$ and AHCl $= 20.0 \times 10^5$ the ACl$_2$ constant is calculated as 63.3×10^5. This leads to values of A, B, C, in the potential function equal to 0.76, 1.48, 3.67 K cal./mole respectively.

The force constant for C_2 dichloroethane calculated from the curvature of the potential function with these values of the constants leads to a value for $\nu = (62.3/9.95)^{\frac{1}{2}} \times 79 = 198$ cm^{-1}. This frequency is much higher than that observed at 124 cm^{-1} and serves as a suitable criterion to reject these high values for A, B, C. It would seem that the observed barrier of 4700 cal. for C_2H_5Cl is too high. Using the constants obtained from the barrier in CH_3CCl_3 the computed barrier in C_2H_5Cl (after suitable correction for the second order interaction) is 2700 cal./mole.

The Dipole Moments of Fulvene and Azulene[*]

G. W. Wheland and D. E. Mann[**]
Department of Chemistry, University of Chicago, Chicago, Illinois
(Received August 24, 1948)

The dipole moments of fulvene and azulene have been calculated theoretically by the LCAO MO method, and have been obtained from experimental data. The experimental results support the theoretical predictions.

ON the basis of the molecular-orbital (MO) calculations of Coulson and Longuet-Higgins,[1] fulvene (Fig. 1, with $R' = R'' = H$) should have a
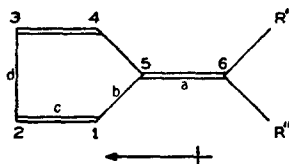

FIG. 1.

dipole moment of about 4.7 D, and azulene (Fig. 2) should have a dipole moment of about 6 D. (In Figs. 1 and 2, the negative end of the dipole is indicated by the head of the arrow.) Refinements in the calculations, which are described in the mathematical appendix to this paper, reduce the predicted moment of fulvene to about 1.5–2 D. (See column 4 of Table VI, below.) These refinements, if applied to

[*] The material in this paper is taken from the dissertation submitted by D. E. Mann to the Division of the Physical Sciences of the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
[**] Du Pont Predoctoral Fellow (1946–1948). Present address: School of Chemistry, University of Minnesota, Minneapolis, Minnesota.
[1] C. A. Coulson and H. C. Longuet-Higgins, Rev. Sci. Inst. **85**, 927 (1947).

TABLE I. 6,6-Dimethylfulvene in benzene at 23.7°C.

w	ϵ_{12}	d_{12}	p_{12} (cc/g)	P_2 (cc)
0.0	2.275	0.8743	0.3412	——
0.02608	2.340	0.8744	0.3530	84.4
0.03250	2.355	0.8744	0.3559	84.3
0.03926	2.372	0.8742	0.3589	84.1

TABLE II. 6,6-Diethylfulvene in benzene at 23.7°C.

w	ϵ_{12}	d_{12}	p_{12} (cc/g)	P_2 (cc)
0.0	2.275	0.8743	0.3412	——
0.02412	2.319	0.8743	0.3493	91.0
0.02752	2.325	0.8742	0.3504	90.6
0.03268	2.333	0.8742	0.3519	89.8
0.03968	2.346	0.8741	0.3542	90.0
0.04283	2.351	0.8741	0.3553	90.0

TABLE IV. 6,6-bis-(p-chlorophenyl)fulvene in benzene at 23.7°C.

w	ϵ_{12}	d_{12}	p_{12} (cc/g)	P_2 (cc)
0.0	2.275	0.8743	0.3412	——
0.02560	2.288	0.8811	0.3409	98.6
0.02612	2.290	0.8812	0.3412	102
0.03314	2.292	0.8833	0.3409	99.2
0.04013	2.296	0.8850	0.3408	99.4
0.04023	2.297	0.8851	0.3410	100

azulene, would probably reduce its moment (given above) to about 1–2 D. Since even the revised moments are unusually large for hydrocarbons, it was desirable to obtain experimental evidence in support of the theoretical results. Moreover, these experimental data provide a test of the validity[2] of the results obtained by the application of the MO method to the calculation of charge distributions and related quantities.

Since fulvene itself has not been obtained in a pure state,[3] it is necessary to estimate its probable experimental moment from the moments of various substituted fulvenes. The fulvenes used for this purpose are 6,6-dimethylfulvene, 6,6-diethylfulvene, and 6,6-diphenylfulvene. Their moments were measured by the optical-solution method,[4] and were found to be respectively 1.48±0.03 D, 1.44±0.03 D, and 1.34±0.04 D. If it is assumed that these solution moments are 10–20 percent lower than the corresponding "true" or vapor-phase moments, and if it is assumed that the moments of 6,6-dimethyl-, 6,6-diethyl-, and 6,6-diphenylfulvene are a few tenths of a Debye unit larger than the moment of fulvene itself, then we may assume that 1.2 D is a reasonable, vapor-phase moment for fulvene. The agreement between this probable experimental value and the theoretical result given above is better than we have a right to expect. It has also been shown that the negative end of the fulvene dipole resides in the five-membered ring. This conclusion, which is predicted by the MO treatment, follows at once from a consideration of the vector relationships of the dipole moments in the 6,6-diphenylfulvene, 6,6-bis-(p-chlorophenyl)fulvene, and chlorobenzene molecules. (It is assumed that the phenyl-carbon-phenyl

angle in the diaryl fulvenes is the same as that reported for 1,1-diphenylethylene.[5]) Unfortunately, however, there seems to be no way in which either the numerical results of the MO calculations or the measured moments can be explained *nonmathematically* in terms of resonating structures or otherwise.

The dipole moment of azulene has been measured by the optical-solution method, and is 1.0±0.05 D. This result, taken together with the fulvene results given above, makes clear the verification and substantiation of the MO predictions for these molecules.

EXPERIMENTAL

The fulvenes were prepared by the general method of Thiele.[3] A few minor modifications of the general procedure were required in order to prepare 6,6-bis-(p-chlorophenyl)fulvene, which has not been reported in the literature. It was prepared from p,p'-dichlorobenzophenone and freshly distilled cyclopentadiene, with sodium ethoxide as condensing agent. Dioxane, instead of absolute alcohol,[3] was used as solvent. The crude fulvene was recrystallized first from 30–60°C petroleum ether, and then six or seven times from 1:1 methanol-ether, from which it separates in the form of red plates. The melting point (by the usual capillary-tube method) of purified 6,6-bis-(p-chlorophenyl)fulvene varies widely (95–110°C) with the rate and duration of heating. Its melting point is estimated* to be 116±1°C. Analytical:—Calculated for $C_{18}H_{12}Cl_2$: C, 72.1 percent; H, 4.0 percent; Cl, 23.7 percent; M.W., 299.2. Found: C, 72.3 percent; H, 4.2 percent; Cl, 23.7 percent;[6] M.W., 307.

TABLE III. 6,6-Diphenylfulvene in benzene at 23.7°C.

w	ϵ_{12}	d_{12}	p_{12} (cc/g)	P_2 (cc)
0.0	2.275	0.8743	0.3412	——
0.02456	2.306	0.8784	0.3453	117
0.03319	2.317	0.8800	0.3467	117
0.04915	2.337	0.8826	0.3493	117

[2] C. A. Coulson and G. S. Rushbrooke, Proc. Camb. Phil. Soc. **36**, 198 (1940).
[3] J. Thiele, Ber. d. D. chem. Ges. **33**, 671 (1900); J. Thiele and H. Balhorn, Ann. d. Chim. **348**, 5 (1908).
[4] See for example, R. W. J. Le Fèvre, *Dipole Moments* (Methuen and Company, Ltd., London, 1938).

FIG. 2.
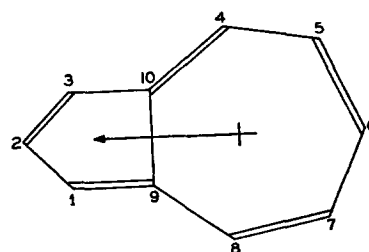
[5] G. E. Coates and L. E. Sutton, J. Chem. Soc. (2), p. 567 (1942).
[6] All analyses were performed by Mr. W. Saschek.

TABLE V. Azulene in benzene at 23.7°C.

w	ϵ_{12}	d_{12}	p_{12} (cc/g)	P_2 (cc)
0.0	2.275	0.8743	0.3412	——
0.01565	2.296	0.8765	0.3442	68.5
0.02143	2.303	0.8775	0.3451	67.0
0.03291	2.317	0.8789	0.3472	67.1

Azulene was prepared by the method of Plattner and Wyss.[7] It was shown spectroscopically[8] that there is no more than 0.5 percent of naphthalene present in our samples of purified azulene. This amount of impurity is negligible so far as this investigation is concerned. The methods and apparatus used to determine the dipole moments have been described by Goldsmith and Wheland.[9] The molar refractions, R_2^D, of 6,6-dimethylfulvene and 6,6-diethylfulvene are literature values[10,11] which were checked in this laboratory. The values of R_2^D for 6,6-diphenylfulvene and 6,6-bis-(p-chlorophenyl)fulvene were computed from atom and group refractions,[12,13] with the assumption of an exaltation of 2 cc. The molar refraction of azulene is assumed to be that of naphthalene.

6,6-Dimethylfulvene (b.p. 72°C at 38 mm).[14]—The experimental data for this substance are given in

TABLE VI. Charge distribution in fulvene.[a]

Atom[b]	1	2	2a	3	3a	3b	4[c]
6	+0.378	+0.251	+0.213	+0.061	+0.138	+0.043	+0.135
5	-0.047	-0.036	-0.032	+0.057	-0.025	+0.042	+0.008
1, 4	-0.092	-0.058	-0.048	-0.043	-0.022	-0.035	-0.0415
2, 3	-0.073	-0.049	-0.042	-0.016	-0.035	-0.007	-0.030
μ	4.7 D	3.1 D	2.6 D	1.1 D	1.8 D	0.7 D	1.9 D

[a] The charge distribution is given in terms of net charge (in e.u.) for each atom of the conjugated system in fulvene. At the head of each column of figures is given the number of the calculation to which the figures apply, and at the left of each row is given the number of the atom to which the net charge refers.
[b] The numbering of the atoms in fulvene is that given in Fig. 1.
[c] The figures in this column refer to the results of the so-called self-consistent first order perturbation calculation.

[7] Joachim Wyss, Thesis, *Synthesen Einfacher Azulene* (Zürich, 1941), p. 27 ff.
[8] By Drs. J. R. Platt and H. B. Klevens, who used the 2205A naphthalene peak for identification purposes. Cf. also E. Heilbronner and K. Wieland, Helv. Chim. Acta **30**, 951 (1947).
[9] M. Goldsmith and G. W. Wheland, J. Am. Chem. Soc. **70**, 2632 (1948).
[10] K. v. Auwers and F. Eisenlohr, J. prakt. Chem. (2) **84**, 53 (1911).
[11] R. Willstätter and M. Heidelberger, Ber. d. D. chem. Ges. **46**, 522 (1913).
[12] Whereas the dialkyl fulvenes do not appear to absorb close enough to the region of the sodium D lines to give abnormal exaltations, solutions of the diaryl fulvenes probably absorb close to this region since exaltations of the order of magnitude of 7 cc are observed. For 6,6-dimethylfulvene the observed exaltation is about 2.7 cc, and for 6,6-diethylfulvene the exaltation is about 2 cc.
[13] A. Weissberger, *Physical Methods of Organic Chemistry* (Interscience Publishers, Inc., New York, 1945), p. 673.
[14] All melting and boiling points are uncorrected.

TABLE VII. Bond orders in fulvene.

Bond[a]	1	2	2a	3	3a	3b	4
a	1.759	1.835	1.857	1.674	1.700	1.708	——
b	1.449	1.381	1.358	1.206	1.204	1.189	——
c	1.778	1.838	1.858	1.676	1.703	1.706	——
d	1.520	1.440	1.409	1.244	1.240	1.222	——

[a] The designation of the bonds in fulvene is given in Fig. 1. It should also be noted that the figures given here are for total bond orders, which are defined by $(1+p_{rs})$ (see reference 18).

TABLE VIII. Bond lengths[a] in fulvene.

Bond	1	2	2a	3	3a	3b	4
a	1.37	1.36	1.355	1.39	1.38	1.38	——
b	1.43	1.44	1.45	1.48	1.48	1.49	——
c	1.37	1.36	1.355	1.39	1.38	1.38	——
d	1.42	1.43	1.44	1.47	1.47	1.48	——

[a] Bond lengths were read from Coulson's curve, and are given in angstrom units.

Table I, where w is the weight fraction of solute, ϵ_{12} is the dielectric constant of the solution, p_{12} is the specific polarization of the solution, and P_2 is the total molar polarization of the solute. The data $P_2^\infty = 85 \pm 1$ cc, $R_2^D = 38.2 \pm 1$ cc, and $T = 296.9°$K lead to $\mu = 1.48 \pm 0.03$ D.

6,6-Diethylfulvene (b.p. 77°C at 17 mm).—The data $P_2^\infty = 92 \pm 1$ cc, $R_2^D = 47 \pm 1$ cc, and $T = 296.9°$K lead to $\mu = 1.44 \pm 0.03$ D. (Cf. Table II.)

6,6-Diphenylfulvene (m.p. 80–81°C).—The data $P_2^\infty = 117 \pm 1$ cc, $R_2^D = 76.5 \pm 1$ cc, and $T = 296.9°$K lead to $\mu = 1.34 \pm 0.04$ D. (Cf. Table III.)

6,6-Bis-(p-chlorophenyl)fulvene (m.p. 116±1°C, but see above).—The data $P_2^\infty = 100 \pm 1$ cc, $R_2^D = 87 \pm 1$ cc, and $T = 296.9°$K lead to $\mu = 0.68 \pm 0.1$ D. (Cf. Table IV.)

Azulene (m.p. 97–98°C).—The data $P_2^\infty = 68 \pm 1$ cc, $R_2^D = 44.4 \pm 1$ cc, and $T = 296.9°$K lead to $\mu = 1.0 \pm 0.05$ D. (Cf. Table V.)

TABLE IX. First order perturbation calculation of the variation of charge distribution in fulvene.[a]

δ_6	+0.213	+0.061	+0.1	-0.1	+1	-1	+0.135
δ_5	-0.035	+0.057	0.0	0.0	0	0	+0.008
$\delta_1 = \delta_4$	-0.048	-0.043	0.0	0.0	0	0	-0.0415
$\delta_2 = \delta_3$	-0.042	-0.016	0.0	0.0	0	0	-0.030
$r = 6^b$	+0.077	+0.194	+0.159	+0.268	-0.333	+0.759	+0.135
5	+0.047	-0.034	+0.001	-0.064	+0.293	-0.357	+0.008
1, 4	-0.043	-0.036	-0.047	-0.049	-0.036	-0.060	-0.0415
2, 3	-0.016	-0.044	-0.0325	-0.052	+0.057	-0.142	-0.030
μ	1.2 D	2.4 D	2.0 D	3.2 D	-3.7[c] D	9.1 D	1.9 D

[a] In each column of figures is listed a given set of δ_r's (rows 1–4), then the net charges (in e.u.) derived from this set of δ_r's (rows 5–8), and last, the dipole moment calculated with the use of the net charges given in rows 5–8.
[b] The numbering of the atoms in fulvene is that given in Fig. 1.
[c] The minus sign on the dipole moment indicates that the direction of the moment is the opposite of that given in Fig. 1.

MATHEMATICAL APPENDIX

The jth MO for fulvene is $\psi = \sum_n c_n \theta_n$, where the c's are numerical coefficients, and the functions θ_n are defined in terms of the atomic orbitals as follows:[15] $\theta_1 = \phi_6$, $\theta_2 = \phi_5$, $\theta_3 = (\phi_1 + \phi_4)$, $\theta_4 = (\phi_2 + \phi_3)$, $\theta_5 = (\phi_1 - \phi_4)$, $\theta_6 = (\phi_2 - \phi_3)$. The secular equation for fulvene has the form[16]

$$\begin{vmatrix} (\zeta_6 y + \delta_6) & \rho_{56} & 0 & 0 & 0 & 0 \\ \rho_{56} & (\zeta_5 y + \delta_5) & 2\rho_{15} & 0 & 0 & 0 \\ 0 & \rho_{15} & (\zeta_1 y + \delta_1) & \rho_{12} & 0 & 0 \\ 0 & 0 & \rho_{12} & (\zeta_2 y + \delta_2 + \rho_{23}) & 0 & 0 \\ 0 & 0 & 0 & 0 & (\zeta_1 y + \delta_1) & \rho_{12} \\ 0 & 0 & 0 & 0 & \rho_{12} & (\zeta_2 y + \delta_2 - \rho_{23}) \end{vmatrix} = 0.$$

The corresponding 10×10 secular equation for azulene is set up in the same way.

Calculation 1.—In the simplest treatment (given by Coulson and Longuet-Higgins[1]) all ζ's = 1, all δ's = 0, and all ρ's = 1. The results of this and the following calculations are given in Tables VI–X.

Calculation 2.—The preceding calculation for fulvene is refined by taking into account, by the Lennard-Jones method,[17] the variation of the bond integrals with bond length. The bond lengths are determined from the Coulson curve,[18] with the aid of the bond orders obtained from Calculation 1. All δ's and overlap integrals are set equal to zero.

Calculation 2a.—To refine the preceding calculation, new bond lengths are determined from the Coulson curve, with the aid of the revised bond orders obtained from Calculation 2. These revised bond lengths are used to calculate new values of the ρ's. The other assumptions are the same as before.

Calculation 3.—In this calculation the bond lengths are determined from the bond orders obtained from the preceding calculation. It is assumed that the δ's *are equal* to the *net* charges (in electron units) on the corresponding atoms. The net charges actually used are those obtained from Calculation 2a. It is easily seen that the δ-values thus obtained are of a reasonable order of magnitude, and show the correct qualitative dependence[16] on the electron affinities of the corresponding unsaturated carbon atoms in fulvene. Furthermore, the assumption which leads to these values is simple and easy to apply.

Calculation 3a.—Here the charge distribution and bond orders obtained from Calculation 3 are used to determine respectively the δ's and the ρ's for the secular equation.

Calculation 3b.—The results of the preceding calculation are used to evaluate the δ's and the ρ's for the secular equation.

Calculation 4.—The last refinement applied to the MO treatment of fulvene is a first order perturbation calculation, with the δ's as perturbation parameters. The unperturbed secular equation is taken as that of Calculation 2a. The q_r's[19] are thus obtained as linear functions of the four δ's, as follows.

$$q_6 = 0.78674 + 0.54620\delta_6 - 0.32466\delta_5 - 0.022832\delta_1 - 0.19870\delta_2,$$
$$q_5 = 1.03194 - 0.32468\delta_6 + 0.34922\delta_5 - 0.048968\delta_1 + 0.02436\delta_2,$$
$$q_1 = q_4 = 1.04819 - 0.011414\delta_6 - 0.024486\delta_5 + 0.34087\delta_1 - 0.30495\delta_2,$$
$$q_2 = q_3 = 1.04246 - 0.099346\delta_6 + 0.012186\delta_5 - 0.30494\delta_1 + 0.39208\delta_2.$$

Finally, the q_r's in these equations are replaced by the corresponding $(1 - \delta_r)$ terms. (This substitution is equivalent to the assumption that the δ's are equal to the corresponding net charges in electron units.) The resulting set of four, linear, simultaneous equations is solved for δ_6, δ_5, δ_1, and δ_2. The values thus obtained are listed in the last column of Table IX. These δ's are now used to obtain the corresponding q_r's. This set of δ_r's and q_r's is then said to be *self-consistent*. The moment calculated from this self-consistent set is about 1.9 D. (Cf. the last column of Table IX.)

Calculation 5.—The calculation for azulene was not carried beyond the simple treatment of Coulson and Longuet-Higgins.[1] The results, which are

TABLE X. Charge distribution in azulene.

Atom[a]	q_r	Net charge (in e.u.)
2	1.047	−0.047
1, 3	1.173	−0.173
9, 10	1.027	−0.027
4, 8	0.855	+0.145
5, 7	0.986	+0.014
6	0.870	+0.130

[a] The numbering of the atoms is that given in Fig. 2.

[15] The subscripts on the ϕ's, and the subscripts used in the secular equation below, refer to the numbering system given in Fig. 1.

[16] The methods and nomenclature are given by G. W. Wheland, J. Am. Chem. Soc. 64, 900 (1942).

[17] J. E. Lennard-Jones, Proc. Roy. Soc. (London), A158, 280 (1937).

[18] C. A. Coulson, Proc. Roy. Soc. (London), A169, 423 (1939).

[19] The quantity q_r represents the average number of π-electrons on the rth carbon atom.

analogous to those obtained for fulvene by Calculation 1, are listed in Table X.

Finally, a word should perhaps be said in regard to the significance of calculated charge distributions, dipole moments, bond orders, and bond lengths which differ as markedly as do those listed in Tables VI–IX. In Table VI, for example, the numerical values given in columns 1, 2, $\cdots$4 represent successive approximations, with those in the last column presumably the most reliable. Table IX, which illustrates the application of the perturbation method, brings out two different points of interest.

Thus, the δ_r's listed in rows 1–4 of the last column are indeed self-consistent (cf. the last column of Table VI) since they are respectively equal to the q_r's listed in rows 5–8. However, the δ's given in the six preceding columns are clearly not self-consistent. In the second place, it is seen that the use of unreasonable values for the δ's, as in columns 6 and 7, leads to unreasonable charge distributions and to unreasonable moments. This fact lends some support to the otherwise arbitrary fundamental assumption (see above) that the δ's are equal to the corresponding net charges.

The Thermodynamics of High Polymer Solutions. IV. Phase Equilibria in the Ternary System: Polymer—Liquid 1—Liquid 2*

Robert L. Scott‡

Department of Chemistry, University of California, Berkeley, California

(Received July 12, 1948)

Two approximate methods of calculating equilibrium phase diagrams in ternary systems of polymer and mixed liquids have been compared with exact phase diagrams based upon the Flory-Huggins equations. Both a "single liquid approximation" and a "complete immiscibility approximation" are worthless except for the crudest qualitative considerations. Analytical expressions for the plait points of such ternary systems (a maximum of ten) have been derived. A consideration of the solubility of polymers in mixed solvents leads to

the conclusion that a polymer may be completely soluble in certain mixtures of non-solvents if its internal pressure (cohesive energy density) lies between those of the two liquids and if the two liquids are themselves completely miscible. The position of the phase boundary is nearly independent of the molecular weight of the polymer for molecular weights above 10,000. Osmotic pressures in mixed solvents are discussed, and Gee's suggestion that the osmotic pressure is zero at the critical solubility limit is confirmed.

INTRODUCTION

IN Articles I and II of this series[1,2] a first attempt was made to treat the multicomponent system involved in the fractionation of high polymers. In particular, we assumed that·"solvent mixtures can be treated with a fair degree of accuracy assuming the mixture of two solvents to behave as a homogeneous liquid with respect to the polymer," this new "liquid" having average thermodynamic properties. We did not suppose this treatment, which we shall call the "single liquid approximation," to be very accurate, but used it to obtain valuable qualitative information concerning the fractionation of high polymers. The present paper attempts to consider in further detail the problem of phase equilibria in a three-component system consisting of a long-chain polymer and two ordinary liquids, with a view to determining, among other results, the limitations of such a "single liquid approximation."

THE HEAT OF MIXING OF A TERNARY SYSTEM

Van Laar,[3] Scatchard,[4] and Hildebrand[5] have shown that, in many cases, the heat absorbed in mixing two substances may be represented by the expression:

$$\Delta H_{12}{}^M = V_m A_{12}\phi_1\phi_2, \tag{1}$$

when V_m is the volume of the mixture, ϕ_1 and ϕ_2 are the volume fractions of the respective components, and A_{12} is a constant characteristic of the system. Scatchard[6] has shown that if one makes entirely equivalent assumptions for a three-component system, one obtains

$$\Delta H_{123}{}^M = V_m(A_{12}\phi_1\phi_2 + A_{13}\phi_1\phi_3 + A_{23}\phi_2\phi_3), \tag{2}$$

where the A's are the constants for the corresponding binary systems.

Differentiation leads to the partial molal heats

[1] R. L. Scott and M. Magat, J. Chem. Phys. 13, 172 (1945).
[2] R. L. Scott, J. Chem. Phys. 13, 178 (1945).

[3] J. J. van Laar, "Sechs Vortrage," Zeits. f. physik. Chemie 72, 723 (1910).
[4] George Scatchard, Chem. Rev. 8, 321 (1931).
[5] J. H. Hildebrand, *Solubility of Non-electrolytes* (Reinhold Publishing Corporation, New York, 1936).
[6] G. Scatchard, Trans. Faraday Soc. 33, 160 (1937).