Influence of Neighbor Bonds on Additive Bond Properties in Paraffins

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of H. This two-to-two contact between neighboring molecules causes greater London dispersion forces,[9] than the one-to-one contact only possible in the tetrachloride.

Acetone-Water.—There is a maximum of velocity and minimum compressibility. This is again a case of dynamical interaction, when effective depolymerization of water is produced due to the opposing tendencies for the formation of water-water and water-acetone associations. But acetone-water associations may also be formed in some measure, as there is no opposing action of formation of acetone-acetone associations.

Acetic Acid-Water.—The maximum of velocity and minimum of compressibility is caused by the dynamical equilibrium producing effective depolymerization of both the components due to the mutually opposing tendencies of acid-acid, water-water, and acid-water associations. While the depolymerization of water may be thought to be complete, especially at the middle ranges, that of the acid is not expected to be so, on account of the much greater strength of the acid association than that of water.

Sodium Chloride+Water+Alcohol.—The system is of course very complex. But as the minimum of compressibility of water alcohol mixtures was derived to be due to depolymerization, it was surmised that by depolymerizing the water used for the mixture, say by dissolving a salt like sodium chloride in it, the minima of compressibility would be reduced in depth and shift towards the extreme of 100 percent salt water. This is actually found to be so, and there is left no minimum at all for 3N salt water.

From the foregoing it follows that maxima of velocity and minima of compressibility would be produced when an associated liquid is depolymerized by another associated liquid (water-alcohol) or by an unassociated but dipolar and active liquid (water-acetone). Minima of velocity and maxima of compressibility would be produced in a mixture whose components cannot have comparable mutual interactions to that in the pure state of each component, because of diversity of and mutual non-reactivity of elements in their molecular structures.

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Influence of Neighbor Bonds on Additive Bond Properties in Paraffins

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LEAST-SQUARES empirical formulas have been worked out for the variations among acyclic paraffin isomers in molar refractivities, molar volumes, heats of formation, and boiling points to fit the beautiful data in the API Tables of Properties.[1] The fit is about as good as that in the analyses of Taylor, Pignocco, and Rossini

(TPR),[2] but it is believed that the physical significance of the present parameters is clearer.

The properties of the bonds are conceived to be strictly additive, but the contribution of each $C-C$ or $C-H$ bond is supposed to be slightly altered by the influence of its next $C-C$ or $C-H$ neighbors, by its second neighbors, third neighbors, and so on to the tips of the molecular skeleton. For the αth $C-C$ bond, the contribution p_α to the property G is

$$p_\alpha = p_0 + p_1 f_{\alpha 1} + p_2 f_{\alpha 2} + \cdots + q_1 g_{\alpha 1} + q_2 g_{\alpha 2} + \cdots.$$

For the βth $C-H$ bond, the contribution s_β is

$$s_\beta = s_0 + s_1 i_{\beta 1} + s_2 i_{\beta 2} + \cdots + r_1 h_{\beta 1} + r_2 h_{\beta 2} + \cdots,$$

where p_j is the effect of a jth neighbor $C-C$ bond on the $C-C$ property, q_j of a $C-H$ bond on the $C-C$, r_j of a $C-C$ on the $C-H$, s_j of a $C-H$ on $C-H$; and where there are $f_{\alpha j}$ of the $C-C$ bonds at a distance of j bonds along the skeleton from the αth $C-C$, etc.

Summing these contributions for the whole molecule, the total property G can be shown to be of the form

$$G = A + a_0(N-1) + a_1 \sum_\alpha f_{\alpha 1} + a_2 \sum_\alpha f_{\alpha 2} + \cdots,$$

where the $a_1, a_2, \cdots$ are linear combinations of the p_j, q_j, etc., and where N is the number of carbon atoms.

Additional quadratic terms were found to be necessary to obtain a good fit:

$$G = A + a_0(N-1) + a_1 \sum_\alpha f_{\alpha 1} + a_2 \sum_\alpha f_{\alpha 2} + a_3 \sum_\alpha f_{\alpha 3}$$
$$+ a_{11} \sum_\alpha f_{\alpha 1}^2 + a_{12} \sum_\alpha f_{\alpha 1} f_{\alpha 2} + a_{22} \sum_\alpha f_{\alpha 2}^2.$$

The expressions for $\sum f_{\alpha 2}$ and $\sum f_{\alpha 1} f_{\alpha 2}$ will be found to correspond to the coefficients of TPR's k_1 and k_2. The least-squares parameters obtained from the data on the C_5 to C_8 paraffins by use of this last formula are shown in Table I, together with a comparison of the deviations from experimental values obtained with this analysis and with TPR's.

TABLE I. Neighbor-sum parameters.

	R ml/mole at 20°C	V ml/mole at 20°C	BP °C at 760 mm	H_f° kcal/mole at 25°C (for gas from graphite and H_2)
A	6.448	48.45	—	−17.584
a_0	4.744	15.68	(about 45° near C_8)	− 2.116
a_1	.0239	1.090	−8.23	− 1.570
a_2	−.0741	− .505	−2.34	− .545
a_3	−.0015	+ .160	−1.43	− .140
a_{11}	−.0039	− .120	+ .76	+ .120
a_{12}	+.0070	− .100	+1.03	+ .235
a_{22}	−.0020	− .035	+ .14	+ .070
Deviations, C_5–C_8				
TPR				
M.D.	±.013	± .16	± .55	—
σ	±.016	± .20	± .70	—
Max. dev.	.037	.49	1.71	—
Neighbor-sums				
M.D.	±.0106	± .22	± .67	± .19
σ	±.012	± .26	± .85	± .24
Max. dev.	.022	.60	2.41	.75

TABLE II. Predicted deviations of C_1 to $n-C_4$ from line of homologues.

	$\Delta\Sigma f_{\alpha1}$	$\Sigma f_{\alpha2}$	$\Sigma f_{\alpha3}$	$\Sigma f_{\alpha1}{}^2$	$\Sigma f_{\alpha1}f_{\alpha2}$	$\Sigma f_{\alpha2}{}^2$	R	V	δ	BP	δ	$H_f{}^\circ$	δ
C_1	2	4	6	6	10	12	$-.235$	-1.02		-17.86	2.53	-2.25	$-.30$
C_2		2	4	2	6	8	$-.136$	-1.49		-1.58	2.26	$.56$	$-.54$
C_3			2		2	4	$.003$	$-.02$	$(-.38)$	$-.24$	$.00$	$.47$	$-.10$
C_4						2	$-.004$	$-.07$	$(-.20)$	$+.28$	$-.17$	$.14$	$.16$

The n-paraffin molar volumes require an additional exponential term in the formula as follows,

$$\delta V = 10^{(1.989-.387N)},$$

to take account of the thermal enlargement of the lighter molecules. The n-paraffin boiling points are not additive. They lie within $\pm.17^\circ$ of the curve

$$BP = 936.43^\circ - \frac{1162.91^\circ}{1+.074189 N^{.85}};$$

and the formula for G can only be used for differences among isomers.

The fit in the neighbor-sum solution is better than the TPR fit for R, even when applied to the older data used by TPR, and it is within the claimed experimental error for $\Delta H_f{}^\circ$. It is worse for the "phase properties" V and BP, indicating perhaps that these properties require the more detailed description of local structure furnished by the TPR analysis. Conversely, the descriptive advantage of the present scheme lies in its ignoring such details, so that its parameters do not multiply so rapidly with increasing N. Still more important, additional parameters such as TPR introduced, are not needed here to handle special cases such as methane and ethane and molecules with maximum branching.

The a_j values for BP and H seem to fall off smoothly, about $1/j^2$. Reversals of sign are present in R and V, which conceivably indicate steric effects between second neighbors.

The quadratic terms behave qualitatively like a saturation effect, if we consider that the influence of the $C-C$ bonds on each other is the dominant effect. With this in mind, we would set

$$p_\alpha = p_0 + (p_1 f_1 + p_2 f_2) - \eta(p_1 f_1 + p_2 f_2)^2$$
$$= p_0 + p_1 f_1 + p_2 f_2 - \eta p_1{}^2 f_1{}^2 - 2\eta p_1 p_2 f_1 f_2 - \eta p_2{}^2 f_2{}^2.$$

The a_{11}, a_{12}, a_{22}'s are indeed in the ratio $p_1{}^2 : 2p_1 p_2 : p_2{}^2$ within about 10 percent. But the ratio $p_1 : p_2$ so determined does not fit the $a_1 : a_2$ by factors of 2 and more; and a more general treatment is required to obtain a good fit.

The value of a_0 does not represent the whole increment between successive n-paraffins, since the $\Sigma f_{\alpha j}$ and $\Sigma f_{\alpha j} f_{\alpha k}$ all depend on N. Below C_5 this dependence is not linear, and the more distant neighbor sums successively become zero. Consequently, C_1 to C_4 should deviate from the line of the higher n-paraffins by the amounts shown in Table II. The columns marked δ give the additional correction necessary to match the experimental value. The big deviations in BP and $\Delta H_f{}^\circ$ of methane are predicted almost within the original accuracy of fit of the neighbor-sum solution on the C_5 to C_8 isomers. Such a prediction was not possible from the TPR analysis.

Tabulations of the neighbor sums and expressions for the relations between the $\Sigma f_{\alpha j}$, $\Sigma g_{\alpha j}$, etc., and their relations to branching in the molecule will be given in detail in a forthcoming paper.

[1] American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Tables 1a–4a, 1b–4b, dated June 30, 1945; 1p–3p, April 30, 1945 and November 30, 1946.
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