Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Schmidt, Hartland H. , Clark, Ronald K. and Gay, Charles F.(1967) 'Structural Effects and Properties of Oligomers of Interest in Separations', Separation Science and Technology, 2: 1, 65 — 79

To link to this Article: DOI: 10.1080/01496396708049917

URL: http://dx.doi.org/10.1080/01496396708049917

SEPARATION SCIENCE, 2(1), 65–79 (1967)

Structural Effects and Properties of Oligomers of Interest in Separations*,†

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Summary

The contributions of the chain length, chain structure, internal rigidity, segment potential function, and "combinatorial" configurational entropy to the properties of liquid short-chain molecules and their mixtures, as exemplified by the polyphenyl series, are all shown to be significant in terms of general models of simple chain molecules such as those of Prigogine and co-workers and of Flory. The molecular parameters of these systems can be characterized sufficiently well from thermodynamic data on the short polyphenyl isomers and g.l.c. data on benzene dissolved in them so that the application of the models with minimal empirical adjustment can be justified. Fit with experimental data is entirely satisfactory. Simpler models ordinarily used, which include only Flory-Huggins entropy of mixing and regular solution or rigid lattice approximations for the heat of mixing, may thus neglect contributions similar in magnitude to those included. The practical significance of the various contributions to the activity coefficients of small molecules dissolved in larger ones of various sizes and structures is discussed in relation to separations as illustrated by g.l.c.

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* This article will be published later in a volume entitled *Separation Techniques: Proceedings of the Nineteenth Annual Summer Symposium on Analytical Chemistry.*

† This work was supported by Petroleum Research Fund Grant 2183-A5 and by an equipment grant under Contract At(11-1)-34, Project 79, U.S.A.E.C. Division of Reactor Development. It is based upon a paper presented at the Summer Symposium in Analytical Chemistry, Edmonton, Canada, June 1966.

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The thermodynamic properties of primary interest in separations involving distribution of the substances to be separated between two phases are their thermodynamic activities, as solutes, in those phases. The problems of estimating or correlating thermodynamic activities of solutes under varying conditions of temperature, pressure, or solvent type from empirical formulations or semiempirical statistical-thermodynamic models of solution behavior are typified by those in gas-liquid partition chromatography (g.l.c.). Here the specific retention volume at infinite dilution, V_g^∞, is the usual basis for comparison of solute behavior and it is rigorously related to the infinite dilution mole fraction activity coefficient of solute A, γ_A^∞, by the familiar equation (*1*)

$$\gamma_A^\infty = 273R/(M_B f_A^0 V_g^\infty) \tag{1}$$

The subscript B refers to the solvent, M_B is its molecular weight, and f_A^0 is the mole fraction standard-state fugacity of the solute. Higher concentrations could, of course, be treated by an analogous equation and generalization of what is said below if the concentration can be clearly defined, as in the frontal-analysis method.

G.l.c. studies, especially as a function of temperature, provide both the incentive for a study of the factors which contribute to deviations of γ_A^∞ from unity and a method much simpler experimentally than bulk thermodynamic methods for systematic testing of statistical-thermodynamic models, particularly of infinitely dilute small or volatile molecules in large or nonvolatile solvent molecules.

EXPERIMENTAL RESULTS

The experimental precautions necessary for precise g.l.c. determinations of γ_A^∞ by Eq. (1) have been outlined previously (2). Our recent more refined measurements using an F and M Model 700 chromatograph with auxiliary oven thermostating included further runs with benzene in biphenyl and the terphenyls. Materials were the same as previously described. In addition, *o*-quaterphenyl (2,2′-diphenylbiphenyl), *m*-quaterphenyl (3,3′-diphenylbiphenyl), *m*-quinquephenyl (3-phenyl-3-(3-xenyl) biphenyl), and 1,3,5-triphenylbenzene solvent have been used with benzene solute. The two quaterphenyls were obtained from K and K Chemical Laboratories, the *o*-quaterphenyl being zone-refined in a 5-mm I.D. tube through 48 zones, while the *m*-quaterphenyl was column-chromatographed through acid-washed alumina with benzene in a 4-cm I.D. column 16 cm long. The *m*-quinquephenyl was from Aldrich Chemical Co. and was recrystallized twice from an ethanol-petroleum ether mixture and chromatographed on alumina. The 1,3,5-triphenylbenzene from the same manufacturer was twice recrystallized from benzene and zone-refined in 10-mm I.D. tubes through 125 zones.

All results to date are summarized in Table 1, including both γ_A^∞ and $\Delta\bar{H}_A^\infty$, the infinite dilution heat of mixing, in each solvent. The latter quantity for the first three entries has been revised significantly since Ref. (2). More and improved data, a wider range of run temperatures allowed by the fact that several of the liquid polyphenyls can be considerably supercooled on the column with no apparent discontinuity in solvent behavior, and improved methods for treating the data as described below lead to the revised values.

TABLE 1

Properties of Benzene at Infinite Dilution in Polyphenyl Solutes at 90°C from G.L.C. Measurements (Errors in Std. Dev. for All Runs of Solvent)

Solute	Column	m.p., °C	t range, °C	Approx. g solute	No. of runs	γ_A^∞	$\Delta\bar{H}_A^\infty$, cal/mole
Biphenyl	A	69	72–112	0.95	12	1.105 ± 0.004	80 ± 30
	B		72–112	0.77	10		
m-Terphenyl	C		88–125	0.44	32		
	D	87	88–126	0.64	32	1.030 ± 0.005	224 ± 18
	E		70–125	0.55	51		
o-Terphenyl	F		60–125	0.92	21		
	G	56	61–125	1.27	10	0.937 ± 0.005	28 ± 16
	H		22–122	0.79	30		
	I		22–124	0.92	67		
m-Quaterphenyl	J	86	50–157	0.61	43	0.941 ± 0.007	1438 ± 20
o-Quaterphenyl	K	118	89–158	0.72	28	0.890 ± 0.006	517 ± 28
1,3,5-Triphenylbenzene	L	175	180	0.78	3	0.853 ± 0.010	
(at 200°C)[a]	M		188–203	1.26	7		
m-Quinquephenyl	N	113	75–137	0.55	31	0.888 ± 0.006	1078 ± 26

[a] Benzene fugacity at 200° estimated by the method of Pitzer and Curl, *J. Am. Chem. Soc.*, **79**, 2369 (1957).

It is worth noting that the precision of the $\Delta\bar{H}_A^\infty$ calculation can sometimes be considerably improved by considering the temperature dependences of the benzene fugacity and of the specific retention volumes separately rather than determining the temperature dependence of calculated values of ln γ_A^∞. Thus from Eq. (1),

$$R\left(\frac{\partial \ln \gamma_A^\infty}{\partial 1/T}\right)_p = \Delta\bar{H}_A^\infty \tag{2}$$

$$\Delta\bar{H}_A^\infty = -R\left(\frac{\partial \ln f_A^\theta}{\partial 1/T}\right)_p - R\left(\frac{\partial \ln V_g^\infty}{\partial 1/T}\right)_p = \Delta H_A^v - R\left(\frac{\partial \ln V_g^\infty}{\partial 1/T}\right)_p \tag{3}$$

where ΔH_A^v is the solute heat of vaporization to vapor at zero pressure. In the last equality of Eq. (3) we have neglected the small variation of liquid fugacity with pressures below 1 atm.

The advantage of using Eq. (3) rather than (2) is that the heat of vaporization of the solute can ordinarily be measured more accurately calorimetrically than from the temperature dependence of f_A^θ, which is what would be used in applying Eq. (1) at several temperatures. Both terms in the final equality of Eq. (3) vary slowly with temperature while f_A^θ and V_g^∞ vary rapidly. Thus a temperature-by-temperature calculation of ln γ_A^∞ is very sensitive to the absolute accuracy of the gaseous solute data and the temperature of the g.l.c. runs, while Eq. (3) depends primarily upon the relative temperatures of the runs. Using Eq. (3) also gives a clearer picture of the sources of error; both terms of the final equality are of the order of 8 kcal/mole for the systems in Table 1, while their sum is of the order of 0 to 1 kcal/mole. An accuracy of ±10 cal/mole in $\Delta\bar{H}_A^\infty$ requires about 0.1% precision in the heat of vaporization of benzene as well as in the last term of Eq. (3)! Good self-consistent data is available for the pure solute (3).

"COMBINATORIAL" ENTROPY OF MIXING

The only practical solution theories which take into account large differences in sizes of the component molecules are cast in the form of polymer solution models. These make the assumption that the entropy (combinatorial entropy) due to the change in the number of distinct configurations of noninteracting molecules in the mixture, as compared with the number of configurations for molecules of the pure components, can be estimated using a lattice model. Then a separate treatment may be applied to take into account (1) the changes in molecular interaction energy, (2) changes in the entropy of thermal motion, and (3) changes of total volume accompanying the mixing. In the lattice model for the combinatorial entropy deviation from the ideal entropy of mixing, the component molecules are supposed to occupy different numbers of sites in proportion to the number of repeat units in the polymer or, for structurally unrelated molecules of different sizes (pseudopolymers), in proportion to the molecular volume of each species. Three expressions which have been derived for the combinatorial entropy of mixing,[*] $\bar{S}_A^{c\infty}$, contribution to ln γ_A^∞ for infinitely dilute monomers in r_B-mer, denoted ln $\gamma_{\mathrm{II}}^\infty$, are given below along with relationships to the excess Gibbs partial molar free energy $\bar{G}_A^e$.

$$\lim_{x_A \to 0} \bar{G}_A^e = \bar{H}_A^\infty - T\bar{S}_A^{e\infty} = RT \ln \gamma_A^\infty \tag{4}$$

$$= \Delta\bar{H}_A^\infty - T\bar{S}_A^{t\infty} - T\bar{S}_A^{c\infty}$$

$$= RT \ln \gamma_{\mathrm{I}}^\infty + RT \ln \gamma_{\mathrm{II}}^\infty \tag{5}$$

where $\ln \gamma_{\mathrm{II}}^\infty = -\bar{S}_A^{c\infty}/R$. (6)

Miller-Guggenheim approximation (*4*):

$$\ln \gamma_{\mathrm{II}}^\infty = -\ln r_B - (r_B - 1)\,(r_B - q_B)^{-1} \ln (q_B/r_B) \tag{7}$$

Huggins-Miller-Guggenheim open-chain approximation (*5*):

$$\ln \gamma_{\mathrm{II}}^\infty = -\ln r_B - (z/2) \ln[1 - 2/z + 2/(zr_B)] \tag{8}$$

$$q_B z = r_B z + 2 - 2r_B$$

Flory approximation (*6*):

$$\ln \gamma_{\mathrm{II}}^\infty = -\ln r_B + 1 - 1/r_B \tag{9}$$

Equations (7), (8), and (9) can readily be obtained as the $x_A \to 0$ limit of the derivations cited. The superscript *e* refers to excess properties of mixtures (over the ideal solution values), *z* is the number of nearest neighbors to a molecule in a monomer liquid, and $q_B z$ is the number of intermolecular neighbor segments to the r_B-mer. We have calculated segment intermolecular neighbors on

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[*] We have avoided the use of the term "athermal entropy" commonly used in g.l.c. work for what we call the combinatorial entropy, because the latter is more descriptive of the origin of the contribution. Only in the case of certain models such as the regular solution models discussed below is the temperature-independent part of the entropy limited to the combinatorial contribution; e.g., in the corresponding-states models discussed, the last set of brackets of Eq. (14) is also an "athermal" contribution to the entropy, but of a different kind.

the basis of a total of six intra- and intermolecular neighbors in the plane of a segment ring. Partial molar quantities are denoted by the macron, and subscript A refers to monomer. Many lines of evidence (7) suggested that a good value for z in liquids well below their critical points is about 10, and this value is used below, although the results are similar for any choice between 8 and 12.

Even the most general of the three expressions, (7), is rigorously justified only for certain lattice models and only at infinite *polymer* dilution (8). All formally exact three-dimensional treatments are expansions about that concentration limit and are of unknown validity at the infinitely dilute *monomer* limit of most use in g.l.c. Expression (8) is a further specialization to flexible chains of segments with no excluded volume correction for intramolecular over-

TABLE 2

Comparisons of Various Approximations for the Combinatorial Entropy of Mixing at Infinitely Dilute Monomer

	$\bar{S}_A^{c\infty} = -R \ln \gamma_{\text{II}}^{\infty}$, cal/mole deg
Monomer-dimer	
Flory, Eq. (9)	0.386
Huggins-Miller-Guggenheim	
Eq. (7) or (8) with $z = 12, 10, 8$	0.356, 0.332, 0.318
McGlashan,[a] $z = 12$	
1st approx., site pair	0.339
1st approx., site triangle	0.348
1st approx., site tetrahedron	0.354
2nd approx.	0.367
Rushbrooke, Scoins, Wakefield,[b] $z = 6$	0.240
Trevena,[c] $z = 12$	0.358
Monomer-trimer	
Flory, Eq. (9)	0.864
Huggins-Miller-Guggenheim	
Eq. (8) with $z = 12, 10, 8$	0.784, 0.766, 0.738
Miller-Guggenheim	
Eq. (7) with $q_B = 2.4$	0.710
Guggenheim-McGlashan,[d] $z = 12$	0.690

[a] M. L. McGlashan, *Trans. Faraday Soc.*, **47**, 1042 (1951).

[b] Ref. (8).

[c] D. H. Trevena, *Proc. Phys. Soc.*, **84**, 969 (1964).

[d] E. A. Guggenheim and M. L. McGlashan, *Proc. Roy. Soc.* (*London*), **A203**, 435 (1950).

lap ("doubling back"), and expression (9) amounts to the $z \rightarrow \infty$ limit of (7) or (8). Recently Fisher (9) has made some progress in the problem of infinitely dilute monomers on a two-dimensional lattice otherwise filled with dimers, a problem which is already very complex mathematically. Fortunately, the values of ln $\gamma_{\mathrm{II}}^{\infty}$ for the monomer-dimer and monomer-trimer cases by several approximations agree quite well (Table 2), and the reasonableness of fit of quite complete statistical-thermodynamic models and PVT data on the pure species with g.l.c. data on ln γ_A^{∞} and $\bar{H}_A^{\infty}$ using (7), (8), or (9), as discussed below, gives us some confidence in those approximate equations. In any case, these are the approximations available regardless of the models used to evaluate ln $\gamma_{\mathrm{I}}^{\infty}$.

REGULAR SOLUTION MODELS

Two models previously most used for evaluating ln $\gamma_{\mathrm{I}}^{\infty}$ fall under the general class of regular solution models for polymers.

The empirical regular solution theory of Scatchard, Hildebrand, and Scott would predict

$$\ln \gamma_{\mathrm{I}}^{\infty} = (\bar{v}_A/RT)(\delta_A - \delta_B)^2 \tag{10}$$

where $\bar{v}_A$ is the partial molar volume of monomer and δ_A and δ_B are respective solubility parameters calculated from energies of vaporization or PVT data on the pure liquid components. We have made PVT measurements on the oligomers of benzene over a wide T and P range (*10*) and use this single-source of data to calculate (*11*)

$$\delta_i \cong \left(\frac{\partial E_i}{\partial V}\right)_T^{1/2} = \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]^{1/2} \tag{11}$$

The values of ln $\gamma_{\mathrm{I}}^{\infty}$ from (10) can be used with (5) and (7), (8), or (9) to calculate ln γ_A^{∞} as shown in Table 3. These are to be compared with g.l.c. data we have obtained for benzene solute and polyphenyl stationary phases (Table 1).

Also shown in Table 3 are results of applying a "strictly regular" solution model analogous to the Bragg-Williams model for monomer solutions (also called the "zeroth approximation strictly regular solution" model by Fowler and Guggenheim) extended to polymer solutions (*12,13*). This can be considered a rigid lattice model which neglects the effects of thermal motions or thermal expansion

TABLE 3

Regular Solution Predictions of Infinite Dilution Benzene Properties at 90°

Solvent	δ_i^a	Calc.[b] γ_A^∞	Calc.[c] $\Delta\bar{H}_A^\infty$
Benzene	8.65		
Biphenyl	10.09	1.12(1.09)	193(212)
m-Terphenyl	10.50	1.09(1.03)	290(335)
o-Terphenyl	10.63	1.19(1.10)	211(266)
m-Quaterphenyl			355(417)
o-Quaterphenyl			295(377)
1,3,5-Triphenylbenzene (200°C)	(9.10)		
m-Quinquephenyl			426(501)

[a] From PVT data of Ref. (*10*) and more recent data on 1,3,5-triphenylbenzene and Eq. (11). But δ_i for benzene is from calorimetric data of Ref. (*3*); the PVT value of 8.36 would make column 3 considerably larger.

[b] By Hildebrand-Scatchard theory using Eq. (10) and (5) with (7) or (in parentheses) (9).

[c] By strictly regular solution theory using Eq. (13) with (7) or (in parentheses) (9).

but attributes all the heat of mixing to a deviation, θ, from the arithmetic mean rule

$$\theta = [\epsilon_{AB}^* - (\epsilon_{AA}^* + \epsilon_{BB}^*)/2] \times (\epsilon_{AA}^*)^{-1} \tag{12}$$

for interaction between segments on like and unlike molecules. The result of this approximation is

$$\Delta H_A^\infty = RT \ln \gamma_{\mathrm{I}}^\infty = RT \ln \gamma_A^\infty - RT \ln \gamma_{\mathrm{II}}^\infty \tag{13}$$

so that discrepancies between the observed $RT \ln \gamma_A^\infty$ and the combinatorial contribution are all attributed to $\Delta\bar{H}_A^\infty$ (or to $\theta \neq 0$), which can be calculated and compared with the experimental value.

Neither regular solution model appears to give a satisfactory correlation with experiment for all the systems. The lack of fit to Eq. (13) appears to be common for g.l.c. tests, although previous tests were based upon pseudo-polymeric solvents more commonly used for analytical columns with solutes usually not structurally related to the solvent, so that polar, noncentral, or other forms of physical or chemical interactions could be expected to swamp out ΔH_A^∞ effects predicted by the simple model (*14,15*).

Effects which are not contained explicitly in regular solution models but which might be expected to contribute to the observed thermodynamic properties even for very simple oligomer systems such as the polyphenyls [or the alkanes which have been the examples previously most treated *(16–18)*] are:

1. Effects of internal flexibility and shape of the polymer solvent in restricting the freedom of motion of segments and lowering the heat capacity as compared with monomer liquids.
2. Effects of thermal expansion of the liquid or volume changes on mixing in changing the average position of segment nearest neighbors on the pair potential-energy curve.
3. Effects of shape of the solvent molecule in limiting the number of neighbors per segment by intramolecular exclusion.

The relative rigidity of the polyphenyls, their wide liquid stability ranges, and their close approximation to chains of segments with intermolecular segment potential functions close to those of benzene led us to believe that these effects would be most easily observable in this series.

CORRESPONDING-STATES MODELS

All the effects in the last section have been taken into account in several recent detailed models of polymers. Both those of Flory and co-workers *(18)* and Prigogine *(17)* fall under a general class which can be reduced to a corresponding-states theorem *(19)* similar in spirit and assumptions to the theorem of corresponding states of simple liquids and gases. The explicit equation reducing this theorem to the evaluation of ln γ_I^∞ in terms of the properties of benzene and potential function parameters is

$$\begin{aligned}\ln \gamma_\mathrm{I}^\infty = {} & (h_A/RT)(2\theta - 9\rho^2) + (c_{PA}/R)[2\theta(\alpha - \delta\alpha - 1) \\ & + (1-\alpha)(9\rho^2 + \delta - 1) - \tfrac{1}{2}\delta^2(1 - 2\alpha) - \ln \alpha] + (\partial c_{PA}/\partial T)_P \\ & \times (T/R)[\theta(1-\alpha)(1 - \alpha + 2\delta\alpha) + (1-\alpha)(\tfrac{1}{2}\delta^2 - \tfrac{3}{2}\delta^2\alpha + 1) \\ & + (1-\alpha)^2(\tfrac{1}{2} - \delta - \tfrac{9}{2}\rho^2) + \ln \alpha] - \tfrac{3}{2}\rho[\rho(\alpha - \tfrac{1}{4}) + (1-\alpha) \\ & - \alpha(\theta - \tfrac{1}{2}\delta - \tfrac{17}{4}\rho)] \qquad (14)\end{aligned}$$

Although Eq. (14) is messy, it can be considered just an implicit expression for the energy parameter θ defined by (12) as a function of ln γ_I^∞, since all other parameters are derivable from properties of the pure components or from their molecular structure. The quantities h_A, c_{PA}, and $(\partial c_{PA}/\partial T)_p$ are configurational enthalpy and heat capacity functions of liquid benzene, i.e., the difference between the respective functions for the liquid and the ideal gas at the same temperature. For the other parameters,

$$\alpha = c_B q_A / (c_A q_B) \tag{14a}$$

$$\delta = (\epsilon^*_{BB} - \epsilon^*_{AA}) / \epsilon^*_{AA} \tag{14b}$$

$$\rho = (r^*_{BB} - r^*_{AA}) / r^*_{AA} \tag{14c}$$

where ϵ^* and r^* refer to the segment pair intermolecular interaction potential minimum energy and distance for segments on molecule types denoted by the subscripts. The quantity q_i is the number of segments neighboring the r_i-mer divided by z so that $q_A = 1$ for the monomer, while $3c_i$ is the number of external degrees of freedom for motion of the whole molecule i. Previously (*19*) we used the strictly rigid molecule spherical segment values for c_i, which made $c_A = 1$, c_B (linear polymer) = 5/3, and c_B (nonlinear polymer) = 6/3, but more complete data we have taken on the compressibilities of benzene and 1,3,5-triphenylbenzene indicate that benzene can better be treated as a rigid disk ($c_A = 5/3$) [see also a paper by Holleman (*20*)] in comparison with the other oligomers, which in turn behave slightly more flexibly than a rigid segment chain model would indicate. All of this can be derived from *PVT* data on the pure compounds by the method of Ref. (*23*). Only the ratio c_B/c_A

TABLE 4

Values of $\theta = [\epsilon^*_{AB} - (\epsilon^*_{AA} + \epsilon^*_{BB})/2]/\epsilon^*_{AA}$ at 90°C for Benzene Solute as Calculated by Eq. (7) or (9) with (5), (14), and (15) and $z = 10$

Solvent	c_B/c_A	δ	ρ	zq_B	θ[from Eq. (5), (14), and ln γ_A^∞]	θ[from Eq. (5), (15), and $\Delta\bar{H}_A^\infty$]
Benzene[b]	1.0	0.0	0.0	10		
Biphenyl[c]	1.35	0.018	−0.029	18	0.005(0.004)[a] ± 0.001	0.003 ± 0.001
m-Terphenyl[c]	1.77	0.086	−0.041	25	0.013(0.011) ± 0.001	0.003 ± 0.001
o-Terphenyl[c]	1.80	0.110	−0.038	24	0.013(0.009) ± 0.001	0.010 ± 0.001
1,3,5-Triphenylbenzene[c]	2.31	0.174	−0.051	31		

[a] Entries in parentheses are for the Flory ln γ_{II}^∞ approximation, Eq. (9), whereas the first entry used Eq. (7). The estimated error does not take into account uncertainties in this or other parts of the model.

[b] From Ref. (*2*) and (*3*): $h_A = -7300$ cal/mole; $c_{PA} = 12$ cal/mole deg.; $T(\partial c_{PA}/\partial T)_p = -6 \pm 6$ cal/mole deg at 90°C.

[c] Columns 2, 3, and 4 from reworking of *PVT* data of Ref. (*10*) with new data on benzene and 1,3,5-triphenylbenzene, the latter at 200°C.

is experimentally derived. The change in this ratio does not affect the ln γ_A^∞ or θ results because of a compensating change in δ (see "Discussion" section).

A second independent value of θ may be obtained from $\Delta\bar{H}_A^\infty$ data, rather than ln γ_A^∞ data, by Eq. (15), which is the derivative with respect to $1/RT$ of (14):

$$\begin{aligned}\Delta\bar{H}_A^\infty = R(\partial(\ln \gamma_A^\infty)/\partial(1/T))_p &= (2\theta - 9\rho^2)(h_A - Tc_{PA}) \\ &- T^2(\partial c_{PA}/\partial T)_P[\theta(\alpha^2 - 1 - 2\delta\alpha^2) + \delta\alpha(1 - \alpha) + \delta^2\alpha(\tfrac{3}{2}\alpha - 1) \\ &+ \tfrac{1}{2}(1 - \alpha)^2 + (9\rho^2/2)(1 - \alpha^2)] \end{aligned} \tag{15}$$

The comparisons of the values of θ obtained from (14) and (15) using g.l.c. data and the parameters indicated from *PVT* data available at this time on the pure compounds are shown in Table 4. The values of θ are also somewhat constrained by reasonableness, since we would expect them to be around the value dictated by the arithmetic ($\epsilon^*_{AB} = (\epsilon^*_{AA} + \epsilon^*_{BB})/2$ or $\theta = 0$) or geometric ($\epsilon^*_{AB} = (\epsilon^*_{AA}\,\epsilon^*_{BB})^{1/2}$ or $\theta \cong -\delta^2/8$) mean rules. That they agree with both rules within 1 or 2% of $\epsilon^*_{BB}/\epsilon^*_{AA}$, which according to Rowlinson (*21*) is as good as can be expected, even for simple monomeric mixtures, is encouraging.

It is of practical interest to determine to what extent, at typical values of the parameters θ, δ, α, and ρ, variations in the structural parameters q_B, c_B, r_B and potential function parameters ϵ^*_{BB}, r^*_{BB},

TABLE 5

Effects of Variation of Corresponding States Parameters in Eq. (14) upon ln γ_A^∞ According to the Model

θ	ρ	δ	α	$(\partial \ln \gamma_A^\infty/\partial\rho)$	$(\partial \ln \gamma_A^\infty/\partial\theta)$	$(\partial \ln \gamma_A^\infty/\partial\delta)$	$(\partial \ln \gamma_A^\infty/\partial\alpha)$
0.005	−0.0292	0.018	0.748	−6.2	−24	1.7	−2.4
0.014	−0.0408	0.086	0.709	−8.8	−24	2.2	−3.4
0.014	−0.0387	0.110	0.752	−8.1	−25	2.0	−2.9

Contribution to Δ ln γ_A^∞ from:		Δ ln γ_A^∞ (*o*-terph.–biph.)	Δ ln γ_A^∞ (*m*-terph.–*o*-terph.)
to Δ ln γ_{I}^∞	$\Delta\theta$	−0.22	0.00
	$\Delta\rho$	0.07	0.02
	$\Delta\delta$	0.17	−0.05
	$\Delta\alpha$	−0.01	0.13
to Δ ln $\gamma_{\text{II}}^\infty$ {Δq [Eq. (7)]}		−0.19	−0.01
Total		−0.18	0.09
Observed Δ ln γ_A^∞		−0.16	0.09

and θ, as well as the combinational entropy contributions have measurable effects upon γ_A^∞ and $\Delta\bar{H}_A^\infty$. The relevant dependencies from (7), (9), (14), and (15), and their derivatives are shown in Tables 5 and 6 for parameters appropriate to the benzene oligomers investigated thus far.

DISCUSSION

As a consequence of the corresponding-states argument for pure liquid polymers (*19*), the ratio $q_Bc_A(1 + \delta)/(q_Ac_B) = (1 + \delta)/\alpha$ is a constant fixed by variation of the density with temperature for any species B. This ratio can be fixed very accurately from experimental data and it determines the reduced temperature scale. On that same reduced temperature scale, the reduced compressibility at zero pressure determines, less sensitivity, the ratio c_B/c_A. Since all terms in $\ln \gamma_A^\infty$ [Eq. (14)], except the relatively small last term on the r.h.s., are dependent at infinite monomer dilution only upon the reduced temperature of compound B, these terms are invariant at constant $(1 + \delta)/\alpha$, regardless of the choice of c_B/c_A. This is the reason that $\ln \gamma_A^\infty$ and θ calculations are essentially independent of any readjustment of constants based upon compressibilities such as those we have made compared with Ref. (2). This point is illustrated in Table 6 by the partial cancellation of "structural" and "energetic" contribution changes in $\ln \gamma_A^\infty$ caused by inversely proportional c_B/c_A and $(1 + \delta)$ changes. The cancellation is actually complete if cross-terms (structural with energetic) are taken into account, as can be seen from the fact that

$$(1 + \delta)/\alpha = -[\partial \ln \gamma_A^\infty/\partial(\alpha)]/[\partial \ln \gamma_A^\infty/\partial(1 + \delta)]$$

for the parameter values illustrated in Table 5.

The effects upon the benzene solution properties of solvent structure change are best illustrated by the contrast between *o*- and *m*-terphenyls, Table 5, where the smaller value of $\alpha = c_Bq_A/(c_Aq_B)$ for the *meta* isomer, caused by a higher number of intermolecular segment neighbors, zq_B, and a lower c_B, provides the explanation, according to this model, of the higher value of $\ln \gamma_A^\infty$ as opposed to *o*-terphenyl. The same trend in $\ln \gamma_A^\infty$ for the quaterphenyls, Table 1, presumably has the same origin, since 1,3,5-triphenylbenzene has a relatively low q_B, although we do not have

TABLE 6

Contributions to ln γ_A^∞ for a Rigid Nonlinear ($c_B/c_A = 2$) Polymer with $z = 10$ Using the Open-Chain Approximation, Eq. (8), and Configurational Properties of Benzene Monomer; Contributions Are Only Approximately Additive Because of Cross-Terms

Chain length r_B	2	3	4	7	10	40	∞
Huggins-Miller-Guggenheim combinatorial contrib.	−0.166	−0.382	−0.574	−1.006	−1.310	−2.604	$1.12 - \ln r_B$
Structural contribution $\theta = \delta = \rho = 0$	$c_B/c_A = 2$	0.203 0.35[a] 0.15[b]	0.792	2.794	4.944	14.900	$-18 + 9(\ln r_B)$
Energetic contribution $c_B/q_B = c_A/q_A$ $\theta = 0.013$ $\rho = -0.041$		−0.13 for $\delta = 0.086$[a] any r_B 0.01 for $\delta' = 0.226$[b] any r_B					

[a] Value corresponding to $c_B/c_A = 1.77$, $q_B = 2.5$, and $\delta = 0.086$ for *m*-terphenyl, so that $(1 + \delta)/\alpha = 1.53$.

[b] Value corresponding to $c_B/c_A = 2.00$, $q_B = 215$, and $\delta = 0.226$ for *m*-terphenyl, so that $(1 + \delta'')/\alpha = 1.53$.

a c_B for the *o*- and *m*-quaterphenyls. The direction of variation of $\Delta\bar{H}_A^\infty$ between *ortho* and *meta* isomer is as would be expected from changes in q_B, but the effect in the terphenyls is much larger than would be expected. This relatively high $\Delta\bar{H}_A^\infty$ for *m*-terphenyl is the reason for the discordant θ value derived from Eq. (15). The discrepancy may represent the limitations of the model, although considerable improvement in self-consistency could probably be attained by adjusting c_{PA} and its temperature derivative within their large experimental uncertainties. No attempt was made to obtain θ or $\Delta\bar{H}_A^\infty$ for 1,3,5-triphenylbenzene because there is insufficient data on benzene heats of vaporization at high temperatures.

The comparison of contributions to the differences in ln γ_A^∞ of *o*-terphenyl and biphenyl in Table 5 indicate that differences in θ, ρ, δ, and q_B all contribute in a complicated way. This is likely to be the case in comparing polymers of different numbers of segments.

The internal consistency of the results of applying the corresponding-states argument to this series of oligomers where there is a relatively large amount of data on both pure compounds and mixtures of the infinitely dilute monomer in them is quite satisfactory, with the possible exception of the surprisingly high *m*-terphenyl heat of mixing. This fit has been attained with only one adjustable mixing parameter, θ, besides parameters obtained from properties of pure oligomers. The range of compounds investigated covers significant variations in all the parameters and indicates the effects of structural differences among isomers, which are not covered by regular solution models, as well as differences in potential functions and degree of polymerization. All these contributions are of the same order of magnitude within the series.

Certainly this correlation between model and experiment is no direct verification of the assumptions of the model, particularly in light of the uncertainty in the estimate of the combinatorial entropy. It should be noted, however, that the combinatorial entropy enters Eq. (14) but not Eq. (15), so that the comparison of the last two columns in Table 4, in light of the large combinatorial contribution to ln γ_A^∞ (Table 6), constitutes somewhat of a check on ln $\gamma_{\text{II}}^\infty$ within the credibility of the rest of the model. We feel that a systematic study of a series like this one, in addition to studies of the combinatorial problem we are undertaking, will assist in correlating experimental data on very simple polymer series and indicate where weaknesses in various models may exist.

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Received by editor October 3, 1966
Submitted for publication November 17, 1966