

Evaluation of Interactions between Polymers and Low Molecular Weight Compounds by GLC II: Thermodynamics and Elucidation

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Abstract □ Raoult's law activity coefficients, obtained by GLC procedures for systems consisting of polymers used in packaging as solvents, bacteriostatic agents, and organic solvents as solutes, were related to the Gibbs free energies, enthalpies, and entropies of mixing. Solution theories were employed for elucidating the factors and mechanisms operative in the polymer-low molecular weight compound interactions. The main factor favoring miscibility was the configurational entropy arising from molecular size difference of the components. For the major part of the systems, the contact interactions were unfavorable to mixing in varying degrees. The data strongly indicated that the parabens interacted as aggregates, most probably pairs, participating in dispersion-type interactions; thus, the contact interactions were more favorable to mixing with polyethylene than with polyvinyl chloride. Alternatively, the retention values obtained from GLC were related to the partition coefficients which were used to compare the sorption-desorption propensities of the low molecular weight compounds with respect to the polymers. Heats of solution and vaporization not previously reported were also derived from the data. Agreement with results from other sources is presented.

Keyphrases □ Polymer-low molecular weight compound interactions—sorption-desorption thermodynamic equations, GLC □ Sorption-desorption thermodynamic equations—polyethylene and polyvinyl chloride, 13 low molecular weight compounds, GLC □ Package-content interactions—polymers and low molecular weight compounds, GLC method for evaluating sorption-desorption thermodynamics □ Plastics—interactions of packaging materials with low molecular weight compounds evaluated by GLC, sorption-desorption thermodynamic equations □ GLC—evaluation of polymer-low molecular weight compound interactions, sorption-desorption thermodynamic equations

Raoult's law activity coefficients for systems comprised of polymers used in packaging and low molecular weight compounds were obtained by GLC and employed for relative grading of interaction affinities as described previously (1). These coefficients were further applied in this work for evaluating and elucidating the interaction thermodynamics. Thus, they were linked to the thermodynamics of binary solutions where the polymers, polyethylene and polyvinyl chloride, were the solvents and the low molecular weight compounds, including organic solvents and bacteriostatic agents, were the solutes.

The equations employed for evaluating the excess partial molar functions of mixing were (2-5):

$$\overline{\Delta G^E} = RT \ln \gamma \quad (\text{Eq. 1})$$

$$\overline{\Delta H^E} = \left[\frac{d(\overline{\Delta G^E}/T)}{d(1/T)} \right]_p = R \left[\frac{d(\ln \gamma)}{d(1/T)} \right]_p \quad (\text{Eq. 2})$$

$$\overline{\Delta S^E} = \frac{\overline{\Delta H^E} - \overline{\Delta G^E}}{T} \quad (\text{Eq. 3})$$

where $\overline{\Delta G^E}$ is the Gibbs free energy, $\overline{\Delta H^E}$ is the enthalpy, $\overline{\Delta S^E}$ is the entropy, γ is the activity coefficient, and T is

the absolute temperature. These experimentally determined quantities were interpreted by applying solution theory. The enthalpy was attributed to the balance of contact intermolecular interactions between the "like" and the "unlike" molecules from the Hildebrand-Scatchard "regular solution" theory (6, 7). The Flory-Huggins (8, 9) theory was used to compute the configurational entropy arising from molecular size difference of the system components. The theory of Prigogine *et al.* (10), which considers the free volume dissimilarity between the low molecular weight compound and the polymer as a factor contributing a negative enthalpy and more significantly a negative entropy to the free energy, was also employed.

RESULTS AND DISCUSSION

The excess free energies derived through Eq. 1 from the activity coefficients in Part I (1) express the interaction affinities in energy units¹. Their main utility in the work was for revealing the factors contributing to the interactions through the enthalpy and entropy terms of the Gibbs equation. The excess enthalpies were derived from Eq. 2 using the regression plots of the activity coefficients *versus* temperature. The enthalpies and entropies are shown in Table I. Figures 1 and 2 present the interrelation among the thermodynamic quantities within the Gibbs equation. Since the criterion for miscibility is a negative free energy change, the $-T \Delta S$ term is the main factor favoring mixing for most systems. The enthalpies that are mostly positive reduce the negative quantity for the free energy. The balance between these opposing energy contributions determines the level of the Gibbs free energy. Negative enthalpies were obtained only for the alkane-polyethylene and the butyl acetate-polyvinyl chloride systems; thus, the enthalpy and entropy terms are additive toward a negative free energy. For the propylparaben-polyethylene system, the enthalpy and the entropy are both negative. The negative free energy in this case is due to the negative enthalpy, while the positive entropy term reduces the energy favorable to mixing.

According to theory, the entropy receives contributions from the configurational factor due to molecular size difference (8, 9) and from the free volume dissimilarity (10). The configurational entropy was calculated on the basis of the Flory-Huggins theory (8, 9), using the derivations of Ashworth and Everett (11) and of Martire (12), since the literature does not provide indications for preference between them. The entropies obtained according to *Reference 11* were somewhat larger than the ones from *Reference 12*, but the difference did not alter the rationale for interpreting the interactions. The difference between the experimental and the configurational entropies contained the free volume dissimilarity contribution. The configurational entropies were also used to compute the "size-corrected" activity coefficients (4), which reflect the true intermolecular interactions since they contain only the contact interactions and the volume dissimilarity contributions. The values derived are shown in Table II. Comparing the size-corrected coefficients with the experimental ones (1), at the same temperature, reveals a large increase in values for the former. Therefore, the contact interactions and volume dissimilarity contributed

¹ The free energies at varying temperatures are presented in the dissertation.

Table I—Excess Partial Molar Enthalpies and Entropies of Mixing

	On Polyethylene		On Polyvinyl Chloride	
	$\Delta\bar{H}^E$ ^a	$\Delta\bar{S}^E$ ^b	$\Delta\bar{H}^E$	$\Delta\bar{S}^E$
<i>n</i> -Butanol	5.6	17.2	3.9	15.8
2-Nitropropane	5.7	19.7	1.7	11.9
<i>tert</i> -Butanol	4.6	17.2	6.7	22.7
Butyl acetate	2.1	11.6	-0.2	6.2
Methyl isobutyl ketone	0.2	6.9	1.9	11.9
Toluene	0.1	8.3	0.3	8.1
Octane	-1.8	3.0	4.5	15.0
Hexane	-2.0	2.3	3.4	13.1
Chlorobutanol	5.2	19.1	3.7	15.6
Benzyl alcohol	1.1	8.5	0.5	8.3
Methylparaben	0.9	2.9	4.1	13.7
Phenol	0.1	7.0	1.3	10.5
Propylparaben	-0.3	-0.4	5.2	14.9

^a $\Delta\bar{H}^E$ in kilocalories per mole. ^b $\Delta\bar{S}^E$ in calories per mole degree.

energy unfavorable to mixing in varying degrees. The major factor favoring miscibility was the configurational entropy due to molecular size difference. Only for the hydrocarbon-polyethylene systems are the size-corrected coefficients smaller than unity. These are due to the negative enthalpies which, in view of the contact similarity of the components of these systems, result most probably from negative volume changes. This is in agreement with Flory *et al.* (13) who worked with similar systems.

The entropies containing the free volume dissimilarity show a number of negative values which conform with the concepts of Prigogine *et al.* (10). The agreement is clearly illustrated by the alkane-polyethylene systems since hexane would be expected to exhibit a greater free volume dissimilarity with polyethylene than octane. With the polyvinyl chloride systems, for the most part, there is a parallel reduction of values for the size-corrected activity coefficients and the entropies containing the free volume dissimilarity effect, the latter reaching into the negative range. Therefore, as the contact interaction energy increases, the solutes undergo a greater reduction in free volume to fit the intersegmental distances of the polymer. Systems that do not conform to this pattern will be discussed further.

The contact interactions may be considered through the characteristics of the polymers and their relation to the individual solutes. Polyethylene participates exclusively in dispersion-type interactions. Since these are weak, mixing would be favored only when the forces between the like molecules of the solute are also dispersion type. The size-corrected activity coefficients, the entropies containing the free volume dissimilarity, and the enthalpies of the solutes with polyethylene reveal four distinguishable patterns.

Activity Coefficients Greater than Unity and Large Positive Enthalpies—This pattern is typical of solute-solvent interactions unfavorable to mixing because of the greater interaction energy among the solute molecules. The entropy containing the free volume

dissimilarity is positive because the solute-solvent interactions are not strong enough to be conducive to volume shrinkage. In this category are *n*-butanol, 2-nitropropane, *tert*-butanol, and chlorobutanol. The *n*-butanol molecules associated by means of hydrogen bonds exhibit the largest activity coefficients since this type of interaction between the "like" molecules is energetically superior to the others in this work. The 2-nitropropane molecules are strong permanent dipoles (14) due to resonance in the nitro group; therefore, the size-corrected activity coefficient is also large but not as large as that for the *n*-butanol. The *tert*-butanol exhibits a considerably smaller coefficient compared to *n*-butanol due to steric shielding of the hydroxyl group. Since this value and the positive enthalpy are smaller than the respective ones for 2-nitropropane, it appears that the interactions between the like molecules may be attributed to dipole forces rather than hydrogen bonding. The dipoles seem to be "buried" in the molecule and the interactions are, therefore, weaker than those for 2-nitropropane. Chlorobutanol appears to behave in a similar manner.

Activity Coefficients Smaller than Unity, Negative Enthalpies and Negative Entropies with Free Volume Dissimilarity—This pattern is characteristic of solute-solvent interactions favorable to mixing. It is observed with hexane and octane. The behavior of this system conforms with the observations of Desmyer and Van Der Waals (15) concerning negative volume changes during mixing of alkanes that were proportional to the chain length difference.

Activity Coefficients Greater than Unity but Negative Entropies Containing Free Volume Dissimilarity—This pattern is observed with methylparaben, propylparaben, phenol, and methyl isobutyl ketone. The parabens appear to behave as low number molecular aggregates, most probably dimers, where a hydroxyl group of one molecule participates in hydrogen bonding with the carboxyl group of the other. The hydrogen bonding and polar forces are thus balanced within the molecular pairs which then participate predominantly in dispersion-type interactions. In agreement with this, the excess enthalpy for the methylparaben is a small positive value; for propylparaben, it is negative approaching those for the alkanes. If a polymeric self-associated structure had been assumed for these compounds, the enthalpies would have been large positive values as observed for *n*-butanol. The size-corrected coefficients for the parabens are large; therefore, the condition unfavorable to mixing arises from the large free volume dissimilarity between the aggregates and the polymer chains as evidenced by the large negative entropies resulting from it. The participation of molecular aggregates in the solute-solvent interactions of phenol and methyl isobutyl ketone with polyethylene rationalizes the thermodynamic quantities observed with these compounds. To a lesser degree, the same appears to be true for benzyl alcohol and butyl acetate, which may be considered as borderline cases. For these, the hydrogen bonding and polar energy are balanced within the aggregates to a lesser degree; therefore, some energy is required to break the bonding with a polymeric structure, as evidenced by the enthalpies.

Activity Coefficients Approaching Unity—This is a special case and is observed with toluene. The enthalpy indicates an almost athermal mixing; thus the main factor favoring miscibility is the configurational entropy. The volume change for this system appears

Table II—Size-Corrected Activity Coefficient^a, γ_s , at 25° and Entropies Containing the Free Volume Dissimilarity, $\Delta\bar{S}_v^E$

Solute	On Polyethylene		Solute	On Polyvinyl Chloride	
	γ_s	$\Delta\bar{S}_v^E$ ^b		γ_s	$\Delta\bar{S}_v^E$
<i>n</i> -Butanol	146.0	8.9	<i>tert</i> -Butanol	112.2	13.1
2-Nitropropane	49.8	11.3	Octane	67.7	6.6
<i>tert</i> -Butanol	25.0	8.9	Hexane	36.3	4.2
Butyl acetate	4.35	3.9	<i>n</i> -Butanol	29.4	6.3
Methyl isobutyl ketone	1.98	-0.8	Methyl isobutyl ketone	5.55	3.0
Toluene	0.98	0.3	2-Nitropropane	5.41	2.3
Hexane	0.49	-5.3	Toluene	2.74	-1.1
Octane	0.39	-4.3	Butyl acetate	2.55	-2.6
Methylparaben	53.0	-4.9	Propylparaben	251.0	6.4
Propylparaben	30.6	-7.7	Methylparaben	92.5	4.6
Chlorobutanol	17.4	11.6	Chlorobutanol	17.3	6.8
Benzyl alcohol	5.27	0.5	Phenol	5.96	0.9
Phenol	2.47	-1.4	Benzyl alcohol	4.19	-1.0

^a Computed from Reference 10. ^b $\Delta\bar{S}_v^E$ in calories per mole degree.

Table III—Partial Molar Heats of Solution, $\overline{\Delta H^s}$, and Heats of Vaporization, $\overline{\Delta H^v}$

Solute	$\overline{\Delta H^s}$ ^a		Experimental ^b	$\overline{\Delta H^v}$ ^a		Reference
	Polyethylene	Polyvinyl Chloride		Literature		
<i>n</i> -Butanol	4.5	6.8	10.4	10.3	21	
<i>tert</i> -Butanol	4.1	2.5	8.9	10.0	3	
2-Nitropropane	6.7	8.2	11.2	9.3	21	
Methyl isobutyl ketone	8.0	6.6	8.4	—		
Butyl acetate	7.3	8.0	8.6	—		
Hexane	8.8	3.6	6.9	6.9	21	
				6.4	3	
Octane	10.3	4.3	8.6	8.6	3	
				8.2	21	
Toluene	7.9	7.9	8.1	8.1	2	
				8.1	3	
				7.9	21	
Chlorobutanol	9.6	9.1	13.8	—		
Phenol	11.2	11.4	10.9	10.9	21	
Benzyl alcohol	11.8	12.0	12.7	—		
Methylparaben	13.1	10.3	14.2	—		
Propylparaben	14.5	10.6	15.2	—		

^a In kilocalories per mole. ^b Means of values obtained on polyethylene and on polyvinyl chloride.

to be negligible, as evidenced by the entropy containing the free volume dissimilarity.

The interactions with polyvinyl chloride were shown to involve hydrogen bonding and polar forces (16, 17). Adelman and Klein (18) observed that compounds exhibiting only dispersion forces and those with strong self-associative capacity showed poor interaction affinity for this polymer. Among the compounds capable of hydrogen bonding, the interaction affinity increased with the electron donor capacity, provided steric hindrance did not interfere. This finding is substantiated by the size-corrected activity coefficients and enthalpies in this work. Hexane, octane, and *n*-butanol exhibited a

poor interaction affinity, while methyl isobutyl ketone and butyl acetate exhibited a considerably stronger one because of their electron donor capacity. Crowley *et al.* (19) and Hansen and Skaarup (20) assigned higher hydrogen-bonding values to butyl acetate (8.8 and 3.1) than for methyl isobutyl ketone (7.7 and 2.0), and this relative grading of the hydrogen-bonding capacity is substantiated by their enthalpies and size-corrected coefficients in this work. Benzyl alcohol and phenol appear to participate in strong hydrogen bonding with polyvinyl chloride. Most probably, these compounds exhibit less self-association compared to *n*-butanol and thus participate more readily in hydrogen bonding. The large activity coeffi-

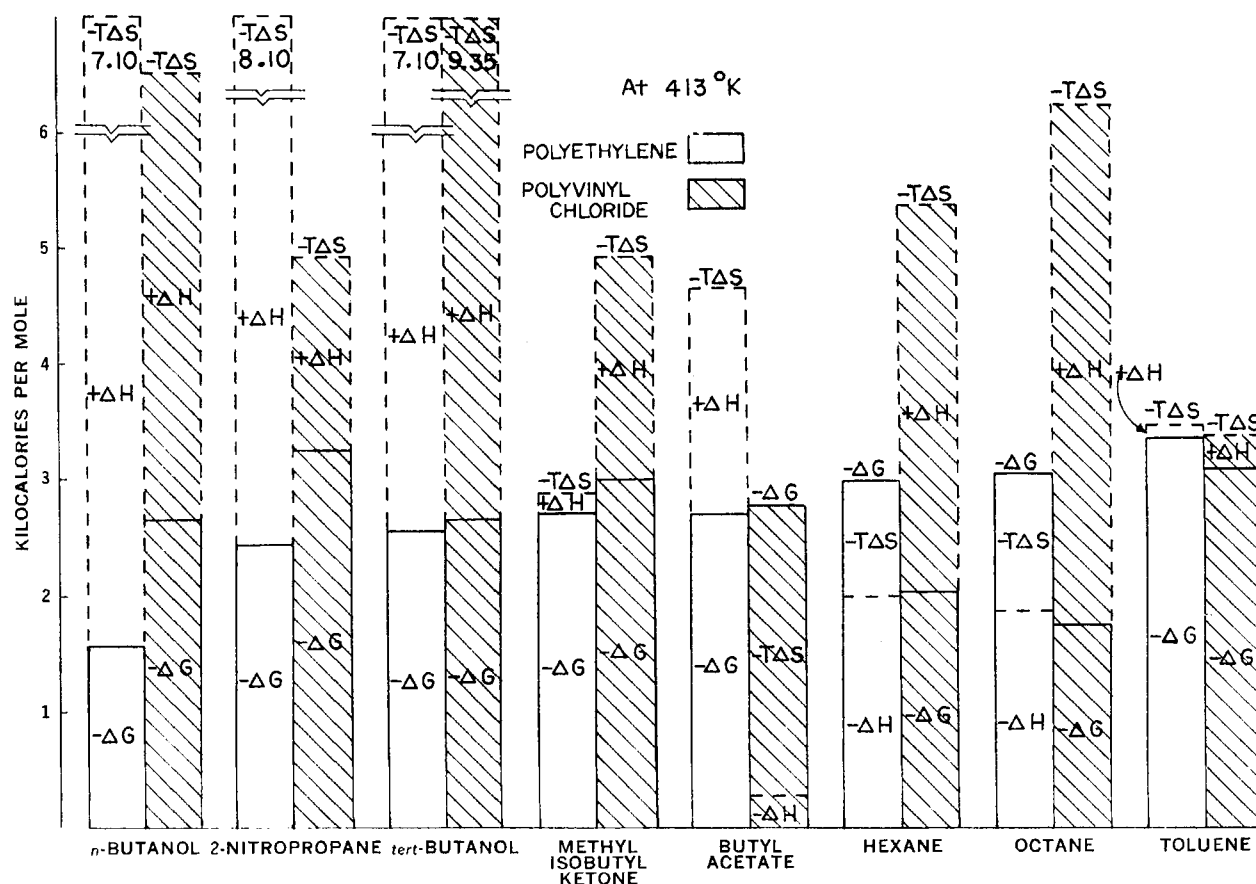


Figure 1—Enthalpy and entropy contributions to the Gibbs free energy of mixing for the organic solvents group.

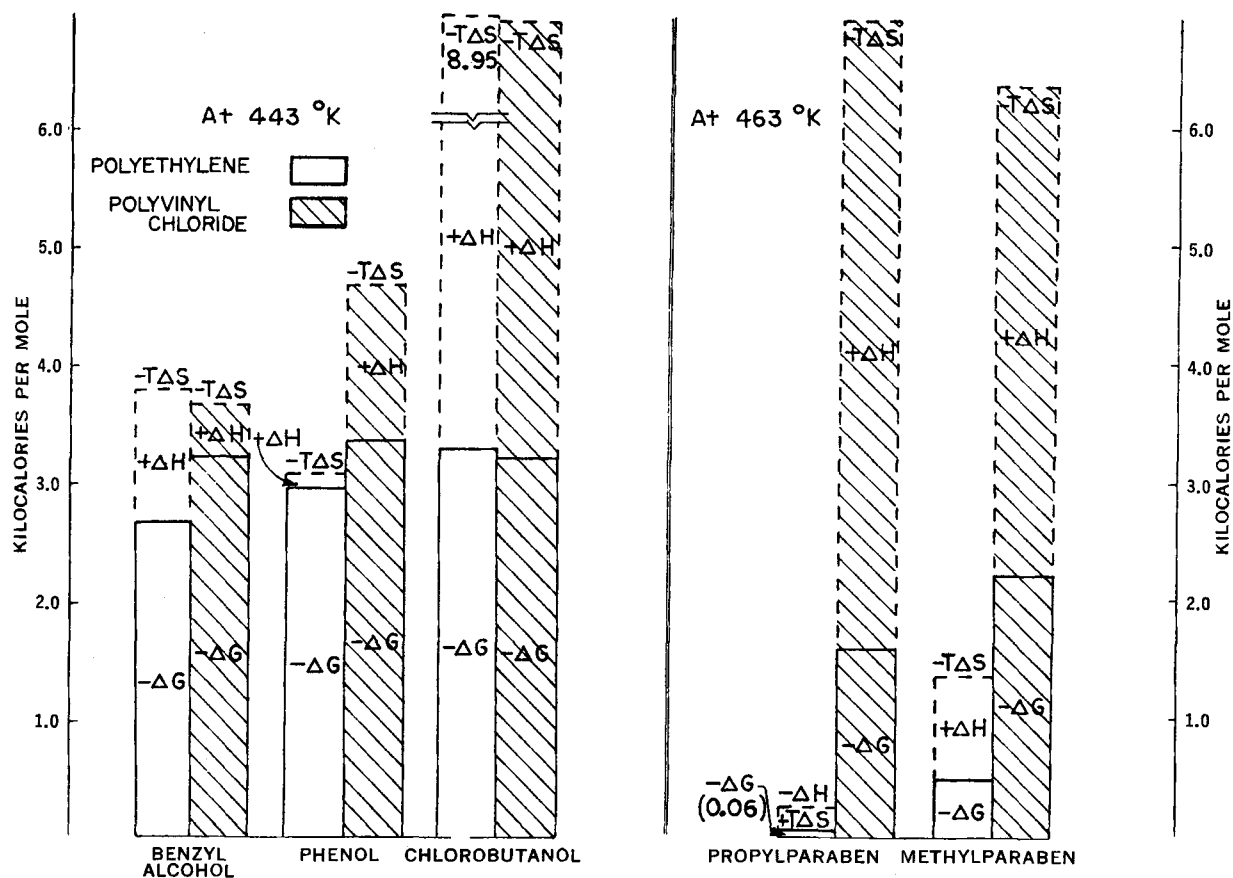


Figure 2—Enthalpy and entropy contributions to the Gibbs free energy of mixing for the bacteriostatic agents.

agents and large positive enthalpies for *tert*-butanol are most probably due to steric factors. The interaction affinity for chlorobutanol is considerably greater than for *tert*-butanol, indicating that hydrogen bonding involving a chlorine atom of the solute may be occurring. The parabens show large positive enthalpies, which approach those of octane and hexane, and also large size-corrected activity coefficients. These quantities indicate contact interactions considerably more resistant to mixing of the parabens with polyethylene than the respective values with polyvinyl chloride. The rationalization that the parabens interact as aggregates exhibiting predominantly dispersion forces is, therefore, further substantiated. The interaction affinity of toluene with polyvinyl chloride is strong, as may be seen from the small positive enthalpy and the small activity coefficient, although these values are somewhat less favorable to mixing than the respective ones for polyethylene. Crowley *et al.* (19) and Hansen and Skaarup (20) assigned smaller hydrogen-bonding values for toluene (4.5 and 1.0) than those for methyl isobutyl ketone and butyl acetate; therefore, the hydrogen-bonding capacity of toluene does not completely rationalize the observed interaction affinity. The behavior of this system supports the observation (18) that cyclic or bulky molecules exhibit enhanced interaction affinity compared to flexible straight-chain aliphatic molecules because they act to separate the polymer chains and thus reduce the interchain forces.

Supplementary Data Obtained by GLC—In addition to serving the main objectives of this work, the methodology employed provides a means for obtaining data that are closely related to the main purpose or are of general interest.

Heats of Solution (Sorption) and Heats of Vaporization—Littlewood *et al.* (2) demonstrated that the partial molar heat of solution, $\overline{\Delta H}^s$, for a solute may be obtained from the slope of the $\log V_0^0$ versus $1/T$ plots and sign inversion. This quantity is identical to the heat of sorption. The heat of vaporization, $\overline{\Delta H}^v$, may be derived from the excess heat of mixing and the heat of solution through (4):

$$\overline{\Delta H}^v = \overline{\Delta H}^E - \overline{\Delta H}^s \quad (\text{Eq. 4})$$

Table III presents the values obtained in this manner. The comparison with data from other sources is reasonably good.

Partition Coefficients—The partition coefficients, K , of the solutes at the experimental temperatures were derived using the specific retention volumes from (22):

$$K = \frac{V_0^0 \rho_1 T \text{ weight/milliliter of liquid phase}}{273 \text{ weight/milliliter of gaseous phase}} \quad (\text{Eq. 5})$$

where ρ_1 is the density of the solvent at the column temperature. The heats of solution were applied to compute the partition coefficients at varying temperatures from (22):

$$\log \frac{K}{T \rho_1} = \frac{\overline{\Delta H}^s}{2.303RT} + C \quad (\text{Eq. 6})$$

where C is a constant. The values computed from Eq. 6 for the experimental temperatures and those found experimentally coincided, indicating that the heats of solution employed in the computations were valid within that temperature range. The partition coefficients are meaningful for comparing the sorption propensities of a solute in respect to different polymers at identical temperature and concentration of the solute in the surrounding medium, since they depend both on the vapor pressure of the solute and the solute-solvent interaction energy. The comparison is in weight of solute per volume of polymer rather than in energy quantities or activity coefficients and may thus be more directly pertinent to applied sorption-desorption considerations. Further convenience in comparing the partitioning of a solute with respect to the two polymers may be gained by means of the ratios of the partition coefficients (Table IV)². It may be noted that a unit volume of polyethylene contained almost twice the mole quantity compared to polyvinyl chloride; consequently, the partition coefficients do not always follow the

² The partition coefficients at 25, 30, 40, 60, and 140° are presented in the dissertation.

Table IV—Ratios of Partition Coefficients

	$K_{\text{polyethylene}}/K_{\text{polyvinyl chloride}}$		
	25°	40°	60°
<i>n</i> -Butanol	0.154	0.185	0.230
2-Nitropropane	0.328	0.367	0.426
<i>tert</i> -Butanol	3.50	3.07	2.62
Butyl acetate	1.20	1.27	1.36
Methyl isobutyl ketone	2.32	2.08	1.82
Toluene	2.48	2.49	2.50
Hexane	69.0	45.1	27.2
Octane	149	102	51.6
Methylparaben	1.40	1.11	0.845
Propylparaben	3.18	2.39	1.65
Chlorobutanol	2.60	2.51	2.49
Benzyl alcohol	0.096	0.980	0.995
Phenol	1.08	1.10	1.12

relative grading obtained from the activity coefficients presented in Part I (1).

Comparison with Data from Other Sources—The results obtained in this work concerning the organic solvents correlate with the general knowledge of solvent-polymer miscibility; however, there is a scarcity of values available for direct comparison. Therefore, some additional evidence is presented which has a bearing in substantiating these results.

Martire (12) determined the activity coefficients of several hydrocarbons on *n*-eicosane which is expected to exhibit interaction characteristics similar to polyethylene. To make the analogy more valid, the values from this work used for comparison are the size-corrected activity coefficients:

hexane/ <i>n</i> -eicosane:	$\gamma = 0.877$ from Reference 12
hexane/polyethylene:	$\gamma = 0.643$ from this work
toluene/ <i>n</i> -eicosane:	$\gamma = 0.888$ from Reference 12
toluene/polyethylene:	$\gamma = 0.982$ from this work

It may be seen that, considering the assumptions made, the activity coefficients are in good agreement.

It was shown that the activity coefficients for the toluene-polyethylene system may be attributed predominantly to configurational entropy and could, therefore, be computed from theory. The comparison is presented below:

experimental	0.0167
calculated from Reference 11	0.0172
calculated from Reference 12	0.0188

The observed agreement substantiates the results in this work and its theoretical premises. For this system Reference 11 yielded better agreement with experimental values than Reference 12.

The pharmaceutical literature offers very few possibilities for comparison. Autian (23) reported sorption of bacteriostatic agents by polyethylene determined by static methodology at 50°. The grading of sorption propensities appears to be phenol > benzyl alcohol > propylparaben > methylparaben, and it coincides with the grading of the activity coefficients in Part I (1).

CONCLUSIONS

The thermodynamic quantities obtained from GLC were meaningful toward revealing the nature of the interactions in the investigated systems. The values obtained from theory are approximations which should be regarded as indicators for elucidating the interactions—not as rigorous quantities. This, however, does not detract

from the value of the presented approach. Its utility for evaluation and elucidation of polymer-sorbent interactions is substantiated by the evidence from other sources and the consistency with solution theory.

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