Thermodynamic Interactions and the Properties of PVC–Plasticizer Systems*

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Synopsis

Gas–liquid chromatography (GLC) has been applied to the study of thermodynamic interactions in poly(vinyl chloride) (PVC) plasticized by di-*n*-octyl phthalate (D*n*OP). A number of vapor-phase "probes" were used to evaluate the Flory-Huggins thermodynamic parameter for the PVC–D*n*OP interaction in stationary phase mixtures of the components which covered the entire composition range. Experiments were carried out in the temperature span of 100–130°C. The interaction parameter was strongly negative, indicating high PVC–D*n*OP compatibility, up to 0.25 volume fraction of plasticizer. It then became less negative and finally positive at 0.55 volume fraction of D*n*OP, suggesting a lower compatibility limit. The composition dependence of the interaction parameter and its apparent variation with the chemical nature of the vapor-phase probe may reflect a nonrandom solution of the probe in the stationary phase and/or nonrandom mixing of PVC–D*n*OP, particularly at D*n*OP contents in the limited compatibility range. Evaluations of the influence of D*n*OP on zero-shear melt viscosity and T_g of compounds indicate that both thermodynamic interactions and volume-of-dilution effects must be taken into account in assessing the effectiveness of the plasticizer.

INTRODUCTION

It is intuitively probable that the processing behavior and certain end-product properties of complex polymer systems depend upon the thermodynamic interaction among the components of such systems. Correlations among thermodynamic interaction parameters and selected processing and use properties might therefore represent a valuable fundamental basis for predicting behavior characteristics in new formulations of polymer systems. The value of such correlations has long been recognized, but it has been difficult to measure the thermodynamic properties in relevant composition and temperature ranges. It is an overall objective of our work to help overcome this difficulty.

The motivation for our present work originates in studies[1-4] which have demonstrated the usefulness of gas–liquid chromatography (GLC) as a means of evaluating the thermodynamic interactions between a wide range of very dilute volatile phases and a polymer in the stationary phase. More recently,[5] we have extended the applicability of the GLC experiment to stationary phases consisting of two nonvolatile components, thereby making it possible

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to determine thermodynamic interaction values for polymer mixtures, polymer–plasticizer combinations, etc. The flexibility and speed of the GLC approach makes it possible to obtain thermodynamic data over a wide range of compositions and temperatures, so that a relatively convenient means is at hand for subjecting to experimental test the principle of correlating component interaction with performance characteristics.

In this paper we report on thermodynamic interactions for the system PVC/di-n-octyl phthalate (DnOP). The recognized importance of plasticized PVC compositions has led to various earlier attempts[6,7] to determine thermodynamic interaction parameters for similar compounds. The methods used, however, restricted observations to very high concentrations of plasticizer and/or to a narrow range of temperatures centered upon room temperature or the reduced melting temperature of the polymer–plasticizer combination.[7] Our purpose is to extend the thermodynamic data into ranges of composition and temperature more consistent with use conditions, and to make a preliminary examination of the interdependence between thermodynamic interaction parameters and the effectiveness of DnOP as a modifier of polymer melt viscosity (processing behavior) and of the polymer's glass transition temperature (use characteristic).

THEORY

In earlier work,[1-5] the link between the basic datum of GLC, the specific retention volume V^0_g of a very dilute volatile phase by a stationary phase (in this case, the polymer) and the activity coefficient of the volatile phase, has been fully developed. Applying the GLC equation to the case of a polymeric stationary phase, it has been shown that the well-known χ parameter, representing the free energy of interaction between the polymer and the volatile diluent, is given by

$$\chi_{12} = \ln\left[\frac{273.2Rv_2}{V^0_g \cdot V_1 \cdot P^0_1}\right] - \left[1 - \frac{V_1}{M_2 v_2}\right] - \frac{P^0_1}{RT}(B_{11} - V_1) \qquad (1)$$

where the gas and polymer phases are identified by subscripts 1 and 2, V_1 is the molar volume of volatile in the liquid state at TK, P^0_1 is the saturation vapor pressure at T, v_2 is the specific volume of the polymer, M_2 is the polymer molecular weight, and B_{11} is the gas-phase second virial coefficient correcting for nonideality.

In many practical cases, it is the interaction between components of polymer mixtures which is of concern, where an interpretation of the properties of such mixtures is sought. Consequently an extension of polymer solution theory is needed to relate the GLC datum to the interaction of a polymer-polymer pair. Using Scott's extension[8] of the Flory-Huggins lattice theory, it has been shown[5] that the overall interaction parameter between the volatile probe and the binary stationary phase (2–3) is given by

$$\chi_{1(23)} = \left[\left(\frac{\chi_{12}}{V_1}\right)\varphi_2 + \left(\frac{\chi_{13}}{V_1}\right)\varphi_3 - \left(\frac{\chi_{23}}{V_2}\right)\varphi_2\varphi_3\right]V_1 = \ln\frac{273.2R(w_2v_2 + w_3v_3)}{P^0_1 \cdot V^0_g \cdot V_1}$$

$$- \left(1 - \frac{V_1}{V_2}\right)\varphi_2 - \left(1 - \frac{V_1}{V_3}\right)\varphi_3 - \frac{P^0_1}{RT}(B_{11} - V_1) \qquad (2)$$

where the φ's are volume fractions of the components, w is the weight fraction, and all other symbols are as defined previously.

The equation shows that the affinity of the stationary phase for the probe depends not only on interactions with the separate polymers (χ_{12} and χ_{13}) but also on the interaction between the polymers themselves (χ_{23}). Thus, with suitable calibration using the simple systems (1–2) and (1–3), the GLC experiment and eq. (2) lead to an explicit evaluation of the polymer–polymer interaction. Reference 5 indicates that the most convenient parameter to report is not χ_{23} itself, which refers to a number of intermolecular contacts in a mole of the polymer 2; rather, it is $V_1\chi_{23}/V_2$ which is normalized, as in reference 5, to correspond to a number of polymer–polymer contacts equal to that in a mole of the probe species (V_1). This is the same normalization as used for the quantities χ_{12} and χ_{13}. An alternative normalization would be to a mole of some reference probe species of volume V_r. This would correspond to a value of the polymer–polymer interaction parameter equal to $V_r\chi_{23}/V_2$. This parameter should be independent of the probe. Because of the relatively small variation of V_1 among the probes used here, this further departure from the direct experimental quantity $\chi^{\dagger}_{23}$ does not seem warranted.

Here, for brevity, we will use the notation

$$\chi^{\dagger}_{23} \equiv V_1\chi_{23}/V_2 \qquad (3)$$

Values of $\chi^{\dagger}_{23}$ may be obtained conveniently over the entire composition range and over a wide temperature span with a precision of about 10%. It is in this regard that the GLC approach appears to hold particular promise for the generation of thermodynamic data directly relevant to application. Other theoretical and experimental routes[9,10] are available for the evaluation of thermodynamic interactions in polymer systems. The experimental techniques, however, do not have the simplicity of the GLC approach, and in such cases as the solubility parameter theory, assumptions are involved in estimating polar and nonpolar contributions.

EXPERIMENTAL

Materials

The poly(vinyl chloride) used was a commercial sample with an intrinsic viscosity in THF at 25°C = 1.16 dl/g and a density of 1.392 g/ml. In all cases, it was used in combination with 1% of a liquid organotin thermal stabilizer. Plasticizer grade DnOP was used as received, without further purification.

Chromatography

The chromatographic apparatus used in this work has been fully described elsewhere.[2] Columns were constructed of $\frac{1}{4}$-in. O.D. copper tubing, methanol washed before use. To prepare columns, the polymer and plasticizer were dissolved in THF (30°C) and coated onto Chromosorb W support (60/80 mesh, AW-DMCS treated). Following removal of excess THF, all columns were oven dried at 60°C. The composition of the supported phase* (not nec-

* See *Note Added in Proof.*

TABLE I
Column Composition

Column	PVC, wt-%	$\varphi_2{}^a$	$\varphi_2{}'^b$
A	0	0	0.0
B	38	0.28	0.24
C	62	0.51	0.46
D	74	0.645	0.59
E	82	0.745	0.70
F	88	0.82	0.79
G	94.5	0.92	0.90
H	100	1.00	1.00

a Assuming amorphous polymer.
b Assuming 20% crystallinity in polymer phase.

essarily identical with that of the starting solutions) was determined by elut-ing a sample of coated support with a fixed volume of THF, measuring the specific viscosity of the ensuing solution and comparing this against calibration results prepared at the reference overall concentration for the entire PVC/DnOP composition range. Details of column composition are shown in Table I. Two entries are made for the polymer volume fraction; φ_2 is based on the assumption that the PVC is noncrystalline. Considering the micro-crystallinity attributed to PVC, φ'_2 assumes that the polymer is 20% crystal-line under the specified experimental conditions. As in earlier work,[2] the total weight per cent of stationary phase was in the range of 4–7%, in order to avoid interfering effects due to sorption at a probe/support interface.

Columns were thermostatted in the range of 90–130°C (±0.5°C in all cases), and the retention times of six volatile materials ("probes") were mea-sured from three to five times. The probes are identified in Table II. In all cases, symmetric peaks were obtained, indicating the existence of equilibrium sorption conditions.[11] Peak maxima were used to calculate values of $V^0{}_g$, using the expression of Littlewood and co-workers.[11] The peaks were found to be independent of the flow rate of helium carrier gas. Procedures for the computation of $V^0{}_g$ data have been elaborated in previous reports.[1,2,5] Typi-cal $V^0{}_g$ results are entered in Table II for an experimental temperature of 110°C.

TABLE II
Specific Retention Volumes for PVC^a—DnOP at 110° C

Probe	Column A φPVC 0	B 0.28	C 0.51	D 0.645	E 0.745	F 0.82	G 0.92	H 1.00
n-Heptane	33.97	21.25	13.95	9.57	6.47	6.26	5.60	5.11
n-Octane	68.60	42.86	27.44	18.41	12.04	11.74	10.46	9.34
n-Nonane	137.0	87.51	53.37	34.65	24.13	21.53	18.84	17.77
n-Decane	274.0	—	104.1	64.86	41.27	39.60	34.32	33.40
Toluene	93.41	69.60	58.72	44.29	36.95	38.91	34.73	33.02
Chlorobenzene	194.1	144.70	111.6	89.17	74.64	78.08	68.85	62.11

a Assumes zero crystallinity of PVC. All values are means of at least three deter-minations with maximum error of 1%.

Viscometry

Melt viscosities of PVC compounds were determined by capillary viscometer methods described in a preceding publication.[12]   The apparent zero-shear melt viscosity at 150°C was used to seek a relationship between flow behavior of plasticized compounds and the interaction thermodynamics between the components.

T_g Properties

The glass transition behavior of polymer samples was established by differential scanning calorimetry (Perkin-Elmer, DSC 1-B) at heating and cooling rates of 2.5°C/min.   Only relative values of T_g were obtained for present purposes.   Supplementary T_g values for very similar systems were kindly supplied by Braun and Guillet.[13]

RESULTS AND DISCUSSION

Pure Component Systems

Tables III and IV present values of the interaction parameters χ_{13} (probe–DnOP) and χ_{12} (probe–PVC), respectively.   The DnOP–probe interaction extends previously available data[5] to a temperature range more consistent with the processing of plasticized PVC.   The values of χ_{13} are essentially independent of temperature, however, so that the available results may be considered as valid calibrations for more extended temperature ranges of application.   The chain-length dependence of n-alkane–DnOP interactions is negligible, but markedly lower values of χ_{13} are obtained for the aromatic probe molecules.   The higher affinity of these for the plasticizer molecule is consistent with expectations.

The χ_{12} results display various points of interest.   The first is that a significant reduction in χ_{12} occurs when it is assumed that the polymer retains 20% residual crystallinity.   This portion of the polymer would of course not interact with the probe.   The V^0_g value in eq. (1), corresponding to retention volume per gram of amorphous polymer, is thereby increased accounting for the decreased χ.   However, the relative sequence of interactions with the various probes remains unaltered.   The series of n-alkane probes is highly incompatible with PVC, the incompatibility becoming more pronounced with increas-

TABLE III
Interaction in DnOP—Probe (χ_{13})(Col. A) as Function of Temperature

Probe	χ_{13} at 75° C[a]	90° C[a]	100° C[a]	110° C	120° C	130° C
n-Heptane	0.67	0.64	0.63	0.62	0.63	0.60
n-Octane	0.68	0.64	0.63	0.61	0.59	0.58
n-Nonane	—	0.66	0.64	0.63	0.61	0.60
n-Decane	—	0.67	0.65	0.63	0.62	0.62
Toluene	0.16	0.13	0.13	0.16	0.14	0.14
Chlorobenzene	—	0.02	0.03	0.06	0.05	0.06

[a] From ref. 7.

TABLE IV
Interaction in PVC–Probe (χ_{13}) [Col. H] as Function of Temperature.
Effect of Crystallinity on χ_{12}

Probe	χ_{12} at 110° C	120° C	130° C	$\chi_{12}^{\dagger a}$ at 130° C
n-Heptane	1.68	1.62	1.55	1.32
n-Octane	1.74	1.65	1.55	1.33
n-Nonane	1.77	1.70	1.61	1.38
n-Decane	1.79	1.73	1.64	1.42
Toluene	0.47	0.46	0.44	0.21
Chlorobenzene	0.41	0.40	0.37	0.15

^{a} $\chi_{12}^{\dagger}$ based on assumption of 20% crystallinity in PVC.

ing chain length, though slightly modified as temperature increases. Finally, the aromatic probes here produce a drastic lowering in χ_{12}; these are, in a sense, plasticizing molecules in their own right.

It should be noted that, as shown by Braun and Guillet,[14] thermodynamic interaction values for a pure polymer should be sought at temperatures some 50° above T_g. In the case of PVC, this would entail the risk of thermal instability. Thus, for the present purpose, the somewhat lower temperature range of 30–50° above T_g was selected. The mild temperature dependence observed for χ_{12} suggests that this procedure does not significantly compromise the validity of the thermodynamic values.

PVC–DnOP Interaction

An explicit illustration of $\chi_{23}^{\dagger}$ values is given in Table V for column E (see Table I). Normally, the interaction between components is characterized by positive (unfavorable) χ values, increasingly positive values indicating increasing incompatibilities. Thus, the strikingly large negative values of $\chi_{23}^{\dagger}$ indicate a high degree of compatibility between the components. This is entirely consistent with practical experience, which would rank DnOP as a very effective plasticizer for PVC.

In principle, the polymer–polymer interaction should be independent of the probe. Reference 5 has already noted that this expectation is apparently not met in all cases, and here Table V shows a considerable variation of $\chi_{23}^{\dagger}$ with the probe. Part of the variation may be due to the change of V_1, the

TABLE V
Typical $\chi_{23}^{\dagger}$ Results for PVC–DnOP at 82% PVC and 18% DnOP:
Effect of Temperature

Probe	$\chi_{23}^{\dagger a}$ at 110° C	120° C	130° C
n-Heptane	−1.20	−1.04	−0.81
n-Octane	−1.17	−1.07	−0.94
n-Nonane	−1.24	−0.89	−0.43
n-Decane	−1.63	−0.66	−0.14
Toluene	−0.72	−0.66	−0.60
Chlorobenzene	−0.78	−0.68	−0.56

^{a} Assumes no crystallinity in PVC. All data based on use of column E, Table I.

normalizing quantity in $\chi^{\dagger}_{23}$, see eq. (3). However, these results and those on other columns do show a difference between aromatic and aliphatic probes, and this would seem to correspond to the difference in compatibility of the aromatic and aliphatic probes with the individual components.

A number of reasons for the probe dependence of $\chi^{\dagger}_{23}$ may be put forward. First, we might speculate that the (2–3) interaction indeed depends on the nature of the probe. This, however, is difficult to reconcile with solution thermodynamic theory which usually considers a contact between a pair of molecules as being independent of the nature of a neighboring molecule. Secondly, we should point out that eq. (2) follows the usual Flory-Huggins approach where the total interaction of a molecule with its surroundings increases with the *volume* of the molecule. As reference 5 points out, a more modern approach involves the molecular *surface area*, but we do not believe that very different results would be obtained by making this change in the present case. It is probably more important that the validity of eq. (2) rests on the assumptions that (a) components 2 and 3 are randomly mixed in the stationary phase, and (b) that the probe 1 senses the (2–2), (3–3), and (2–3) contacts in a random manner. It is improbable that perfectly random mixing occurs for components such as DnOP and PVC which interact in a specific fashion. Furthermore, the n-alkane probes will tend to selectively avoid contacts involving PVC with which they are extremely incompatible (see Table IV). On the other hand, the aromatic probes may be expected to have a more random view of their stationary phase environment. We cannot associate the probe dependence of $\chi^{\dagger}_{23}$ with any one factor and merely note for present purposes that the dependence is not surprising.

Composition Dependence of PVC–Plasticizer Interaction

Of particular interest to the present study is the apparent variation of $\chi^{\dagger}_{23}$ with composition of the polymer–plasticizer system. In order to represent this concisely, $\chi^{\dagger}_{23}$ results for the eight compositions at each temperature were averaged for the four n-alkane probes, and the resulting function of $\chi^{\dagger}_{23}$ versus PVC volume fraction was plotted in Fig 1. The bars indicate maximum probe-to-probe variations of $\chi^{\dagger}_{23}$ at each of the column compositions. It was assumed throughout that no residual crystallinity existed in the PVC phase. The implications of the results in Figure 1 are interesting. The compatibility of the PVC/DnOP system is uniformly high, i.e., $\chi^{\dagger}_{23}$ is negative up to plasticizer volume loadings of about 25%. From 25% to about 60% (by volume) of DnOP, $\chi^{\dagger}_{23}$ rises and becomes positive at about 60%. It is reasonable to suppose that at these large concentrations of DnOP, much of the plasticizer is "mobile," i.e., in contact with other DnOP molecules rather than "bound," in contact with PVC molecules. Using the interaction parameters already obtained, it is clear that when the probe enters the stationary phase, the DnOP–DnOP contacts are much more easily broken than the DnOP–PVC and PVC–PVC contacts, and this is especially so for the alkane probes. This, of course, corresponds to the greater compatibility of the probes with DnOP than with PVC and also to the strong attractive PVC–DnOP interaction. By selectively breaking the DnOP–DnOP contacts, the value of $\chi_{1(23)}$ is lowered below what it would be for a completely random attack by the
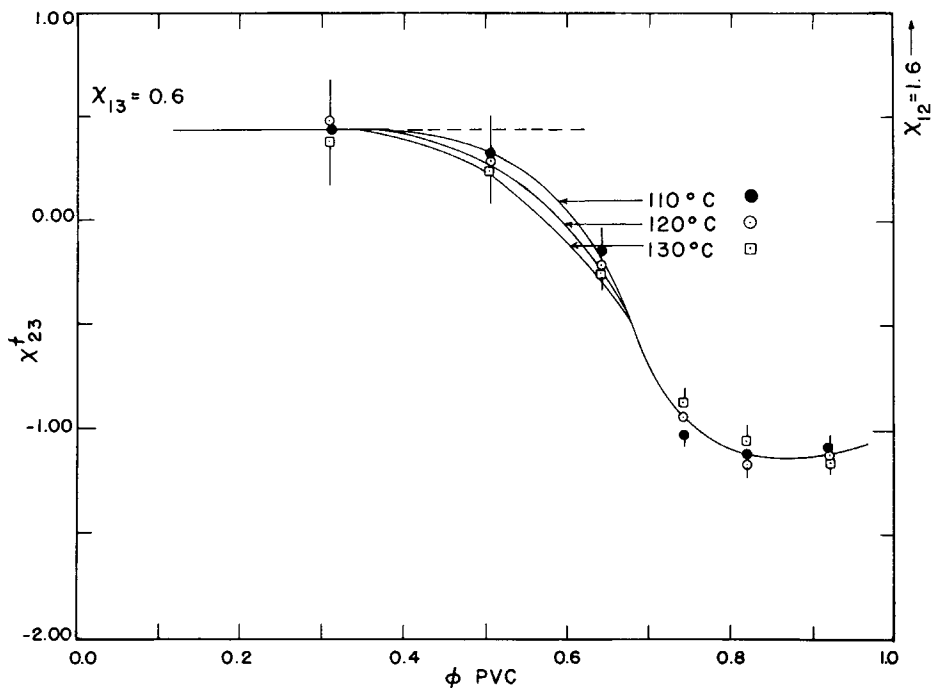
Fig. 1. Concentration dependence of $\chi^{\dagger}_{23}$ for PVC/DnOP.

probe. Equation (2) evaluates $\chi^{\dagger}_{23}$ by obtaining the difference between $\chi_{1(23)}$ and $\varphi_2\chi_{12} + \varphi_3\chi_{13}$. Hence, a lowering of $\chi_{1(23)}$ can have the effect of giving a positive apparent value to $\chi^{\dagger}_{23}$, and this will occur in the region of high DnOP concentration where the nonrandom sensing of the stationary phase by the probe is facilitated.

Plasticizer Effectiveness

In the present work, we have attempted to seek, in a largely empirical manner, the existence of interrelationships between the thermodynamic interaction parameters of the PVC/DnOP system and the effectiveness of the plasticizer as a modifier of solid-state and processing characteristics. An empirical normalization procedure was adopted both for melt viscosity and glass transition temperature data in order to study the point.

(i) The reduction in apparent zero-shear melt viscosity (η_0) of the polymer, due to an increase in the plasticizer volume fraction from φ'_3 to some greater value φ''_3, was normalized by the expression

$$[\log (\eta_0)_{\varphi'_3} - \log (\eta_0)_{\varphi''_3}]/(\varphi''_3 - \varphi'_3) \tag{4}$$

the quotient defining a dimensionless viscosity reduction number.

(ii) In similar manner, a T_g reduction number was calculated from the expression

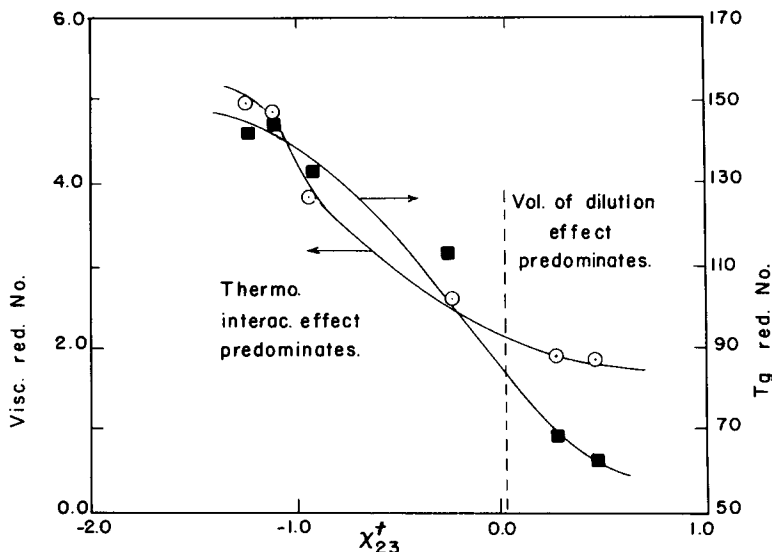$$[(T_g)_{\varphi'_3} - (T_g)_{\varphi''_3}]/(\varphi''_3 - \varphi'_3) \ (°C). \tag{5}$$

Fig. 2. Apparent dependence of glass transition and melt viscosity lowering by DnOP on thermodynamic interaction with polymer.

The reduction numbers were calculated for pairs of compounds with increasing plasticizer content and plotted in each case against the $\chi^{\dagger}_{23}$ value for the more highly plasticized system. The results of this procedure are shown in Figure 2. For convenience of presentation, a single plot has been used, placing $\chi^{\dagger}_{23}$ on the abscissa. This procedure illustrates the type of interrelationship which may exist between thermodynamic and processing properties of the systems, but is not meant to imply that the absolute value of $\chi^{\dagger}_{23}$ is the best independent variable.

The curves for both η_0 and T_g reduction effectiveness of DnOP suggest that both thermodynamic interaction and volume-of-dilution effects are operative in the reduction of η_0 and T_g. The importance of the thermodynamic interaction contribution may be inferred if it is assumed that for negative values of $\chi^{\dagger}_{23}$, it is this effect which is primarily responsible for the observed reductions, while for $\chi^{\dagger}_{23} > 0$ (i.e., $\varphi_3 \gtrsim 0.5$), additional reductions in the chosen parameters are due largely to the dilution of the polymer rather than to any significant loosening of its state of association or entanglement. A separation of these contributions to η_0 and T_g lowering should be possible upon the examination of systems utilizing a variety of plasticizers, and this is the subject of continuing studies in these laboratories.

CONCLUSIONS

The GLC method has proved useful in evaluating interaction parameters for a PVC–plasticizer system over a composition and temperature range of practical significance. The PVC–DnOP interaction parameter $\chi^{\dagger}_{23}$ is negative, indicating a specific attraction. At a DnOP volume fraction about 0.5, the value of $\chi^{\dagger}_{23}$ shifts to positive indicating, we believe, a preferential sensing by the probe of weak contacts between DnOP molecules. This coincides

with a "compatibility limit" of the PVC for the DnOP at about 0.5 volume fraction. A preliminary study of plasticizer effectiveness suggests that the degree of thermodynamic interaction has a strong influence on the lowering of melt viscosity and glass transition temperature of the plasticized compounds. The results encourage more detailed studies of polymer/diluent interaction thermodynamics as a route to the rationalization of behavior characteristics in polymer-containing systems.

Note Added in Proof

A forthcoming publication by Braun and Guillet will discuss fully the extent to which errors in evaluating composition can affect interaction parameter data. For certain simple polymer-gas systems the effects can be significant, but they have little influence on the data of the present study, the accuracy of which remains as given.

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