

STUDY BY GAS-LIQUID CHROMATOGRAPHY OF THE THERMODYNAMICS OF THE INTERACTION OF POLY(VINYL ACETATE) WITH VARIOUS SOLVENTS

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(Received 23 August 1982)

Abstract—The solubility parameter of poly(vinyl acetate) at various temperatures has been obtained by using the method developed by DiPaola-Baranyi and Guillet, *Macromolecules* **11**, 228 (1978). The solubility parameter of polymer at 25°C was found to be $10.1 \text{ (cal/cm}^3)^{1/2}$ by linear extrapolation from higher temperatures (70–140°C). The interaction parameter χ of polymer in various solvents, at temperatures below the melting point T_m , has been determined by means of the solubility parameters of the polymer and solvents at this temperature, deduced from their values obtained chromatographically at higher temperatures. The value of the interaction parameter so obtained is in good agreement not only with values calculated by other techniques but also is independent of the temperature range used for the chromatographic measurements. Moreover, using the equation-of-state theory formulation, we have determined the values of the interaction parameter χ^* for various systems poly(vinyl acetate)/probes and from it the contact interaction energy, X_{12} , in the temperature range 70–140°C.

INTRODUCTION

According to the Flory–Huggins (FH) theory [1], the partial molar free energy is given thus:

$$\mu_1 - \mu_1^0 = RT[\ln(1 - \phi_2) + (1 - 1/x)\phi_2 + \chi\phi_2^2] \quad (1)$$

where ϕ_2 is the volume fraction of the polymer in the mixture, x the number of polymer segments and χ the interaction parameter defined by FH. The two first terms on the right represent the configurational or entropic partial molar free energy and the last term includes enthalpic changes produced during mixing and other entropic factors not included in the configurational term. Therefore, χ is a free energy with two contributions:

$$\chi = \chi_H + \chi_S \quad (2)$$

where χ_H has an enthalpic nature and χ_S is the entropic component. According to the original idea of the FH theory, χ is independent on the concentration but this is in disagreement with a later publication [2]. χ is usually taken to have a temperature dependence of the form:

$$\chi = \alpha + \beta/T \quad (3)$$

As shown in previous publications [3,4], the validity of this expression is restricted to a relatively narrow temperature range. In general, the variation of χ with reciprocal of temperature shows a minimum and consequently, as has been proved [4], the use of Eqn (3) is inadequate for determining the interaction

parameter by extrapolation from its values at higher temperatures.

The Flory treatment can be combined with the Hildebrand–Scatchard theory to give [5]:

$$\chi = V_1(\delta_1 - \delta_2)^2/RT \quad (4)$$

where V_1 is the molar volume of the solvent and δ_1 and δ_2 are the solubility parameters of solvent and polymer respectively. Here χ has only an enthalpic character in contradiction to its definition.

Evidently, as has been shown by DiPaola-Baranyi and Guillet [6], Eqn (4) can be rewritten as:

$$(\delta_1^2/RT - \chi/V_1) = (2\delta_2/RT)\delta_1 - \delta_2^2/RT \quad (5)$$

Therefore, a plot of $\delta_1^2/RT - \chi/V_1$ vs δ_1 of the probe should yield a straight line with slope $2\delta_2/RT$ and intercept $-\delta_2^2/RT$. The δ_2 values so obtained are slightly different [4, 6] depending on whether they have been obtained from the intercept or the slope.

From a refinement of the lattice model, Huggins [7] deduced that χ should be expressed approximately by:

$$\chi = V_1(\delta_1 - \delta_2)^2/RT + \chi_S \quad (6)$$

with $\chi_S = (1 - 1/m)/z$ where z is a coordination number and m is the chain length of the polymer.

As for Eqn (4), Eqn (6) can be rewritten, thus:

$$\delta_1^2/RT - \chi/V_1 = (2\delta_2/RT)\delta_1 (\delta_2^2/RT + \chi_S/V_1) \quad (7)$$

A plot of $\delta_1^2/RT - \chi/V_1$ vs δ_1 allows calculation of δ_2 from the slope and, using this value with the intercept, to estimate the entropic component χ_S .

As we will show later, both δ_i and χ_s are parameters linearly dependent on temperature over the whole range considered. Therefore, we can extrapolate to 25°C to obtain the value of the interaction parameter at that temperature, using Eqn (6).

According to the equation-of-state theory [8], the residual partial molar free energy, given by $RT\chi\phi_2^2$ in the FH theory, can be expressed by means of the following equation:

$$(\mu_1 - \mu_1^0)^R = P_1^* V_1^* \{3T_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\} V_1^* X_{12} \theta_2^2 / \tilde{v} \quad (8)$$

where P_1^* and V_1^* are the characteristic pressure and molar volume of the solvent, T_1 and \tilde{v}_1 are the reduced temperature and volume of the solvent, \tilde{v} the reduced volume of the mixture and X_{12} the specific interaction energy. θ_2 or site fraction is defined by the expression:

$$\theta_2 = s_2 x N_2 / (s_1 N_1 + s_2 N_2 x) \quad (9)$$

where N_i is the number of molecules, x the number of segments of the polymer having the same volume as the solvent molecule and s_1 and s_2 the number of contact sites in the solvent molecule and polymer segment respectively.

In inverse gas chromatography, at infinite dilution $\theta_2 = 1$ and the reduced volume of the mixture matches that of the polymer.

Equation (8) allows us to obtain the specific interaction energy X_{12} at the desired temperature, if the residual partial molar free energy can be determined chromatographically. In the equation-of-state theory, the residual partial molar free energy can be rewritten as:

$$(\mu_1 - \mu_1^0)^R = RT\chi^* \phi_2^2 \quad (10)$$

where the only difference is that ϕ_2 is now calculated using characteristic specific volumes of both components providing a χ^* value slightly different from χ .

EXPERIMENTAL

Materials

Solvents were reagent grade and were used without further purification. The following solvents of very different characteristics were used: *n*-octane, cyclohexane, methanol, ethanol, 1-propanol, 1-butanol, acetone, benzene, toluene, chlorobenzene, ethyl acetate, diethylene glycol diethyl ether and dioxane. An effort was made to use solvent and non-solvent compounds for polymer, both of polar and non-polar nature, to extend the validity of the method to more types of solvents. The samples of poly(vinyl acetate) were obtained from Union Explosivos Rio Tinto ($\bar{M}_w = 257,000$).

Columns

The polymers were first dissolved in a suitable solvent (chloroform) and deposited on an inert chromatographic support by slow evaporation of the solvent with gentle stirring and heating. After vacuum drying for *ca.* 48 h with slight heating, the chromatographic support was packed with the aid of a mechanical vibrator into 0.25 in. o.d. stainless-steel columns. The weight and percentage of the stationary phase were determined by direct weighing. Column parameters are described in Table 1.

Table 1. Column parameters

Polymer	Coating solvent	Loading	Polymer (mass, g)	Length (cm)	o.d. (in.)
PVA	Chloroform	4.02	0.6213	100	0.25
PVA	Chloroform	7.13	0.9620	100	0.25

Instrumentation

Measurements were carried out on a Perkin-Elmer 3920 B gas chromatograph, equipped with a dual flame ionization detector. N_2 was used as the carrier gas. CH_4 , as a non-interacting marker, was used to correct the dead volume in the column and the retention time was directly measured with a chronometer between the highest points of the peaks for CH_4 and the solute. At least 4 measurements were made for every molecular probe and for each temperature in both columns. Pressures at inlet and outlet of the column read from a Hg manometer (<0.05 mm Hg), were used to compute corrected retention volumes by the usual procedures. Flow rates were measured from the end of the column with a soap bubble flow meter. Three distinct gas flows, between 20 and 60 ml/min at 70°C, were used to verify the independence of the volume retention on the flow. Throughout the experiment the flow rate was fixed at 30 ml/min. The oven was modified to accommodate a water bath at $90 \pm 0.1^\circ\text{C}$ and an oil bath at $140 \pm 0.5^\circ\text{C}$. The solute molecules, including a small amount of CH_4 marker, were injected manually with a 10 μl Hamilton syringe (<0.01 μl). The precision of the retention data from the Perkin-Elmer 3920 B gas chromatograph was previously checked [4].

DATA REDUCTION

Specific retention volumes, V_g , were calculated from the relation:

$$V_g = (t_r F / w_L) J_2^3 (P_0 - P_w) / 760 \quad (11)$$

where t_r is the net retention time, F is the flow rate at 273.16 K, w_L is the mass of polymer and J_2^3 is given by the relation:

$$J_n^m = (m/n) [(P_i/P_0)^n - 1] / [P_i - P_0]^m - 1 \quad (12)$$

where $m = 3$, $n = 2$ and P_i and P_0 are the inlet and outlet pressures.

Solute vapour pressures were computed from the Antoine equation:

$$\ln P_1^0 = A - B/(T + C) \quad (13)$$

where P_1^0 is the solute vapour pressure in mm Hg, T is the temperature (K) and A , B and C are constants taken from standard sources [9].

Solute densities were obtained from Timmermans compilation [10]. Second virial coefficients (B_{11}) were computed from [11]:

$$B_{11}/\bar{V}_c = 0.430 = 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (14)$$

for *n*-octane, benzene, chlorobenzene, cyclohexane and diethylene glycol diethyl ether, where \bar{V}_c and T_c are critical volume and temperature, T is the temperature (K) and n is the number of carbon atoms of the *n*-alkane, or alternatively an effective number of carbon atoms, n_A , was estimated and replaced n

in Eqn (14) [12]. n_A takes on the value of n of the normal alkane having the same value for the vapour pressure parameter A , in the equation:

$$\ln(P_c/P) = A(T_c - T)/T \quad (15)$$

where P_c and T_c are the critical pressure (mm Hg) and temperature (K) of the solute.

Second virial coefficients for acetone, methanol, ethanol, 1-propanol, 1-butanol, toluene, ethyl acetate and dioxane were determined by Kreglewski Eqn [13]. The vapour pressures for diethylene glycol diethyl ether were literature values [24]. The critical constants P_c , T_c and V_c were evaluated by the Lydersen method [14]. The densities were measured experimentally. The critical constants and the deduced constants have been given [4].

Weight fraction activity coefficients $(a_1/w_1)^x$ at infinite dilution were then calculated from the following relationship [15]:

$$\ln(a_1/w_1)^x = \ln(273.16R/P_1^0 V_g M_1) - P_1^0(B_{11} - V_1)/RT \quad (16)$$

where V_1 and M_1 are the molar volume and molecular weight of the probe molecule, and R is the gas constant. χ parameters were calculated from:

$$\chi = \ln(273.16Rv_2/P_1^0 V_g V_1) - 1 - P_1^0(B_{11} - V_1)/RT \quad (17)$$

where v_2 is the specific volume of polymer, known from the literature [16].

State-equation χ^* parameters were calculated using:

$$\chi^* = \ln(273.16Rv_2^*/P_1^0 V_g V_1^*) - 1 - P_1^0(B_{11} - V_1)/RT \quad (18)$$

where v_2^* is the characteristic specific volume of the polymer and V_1^* the characteristic molar volume of the probe.

From Eqns (18), (10) and (8), the state-equation contact energy parameter X_{12} can be obtained by the following expression:

$$V_1^* X_{12}/\tilde{v}_2 = RT\chi^* - P_1^* V_1^* \{3T_1 \ln[(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\} \quad (19)$$

where P_1^* has been calculated from published data [17].

RESULTS AND DISCUSSION

The experimental retention volumes, activity coefficients (weight fraction) and χ parameter for 13 solutes between 70 and 140°C were tabulated. Retention volumes were obtained for at least 8 temperatures, over each temperature range of 20°C.

Weight fraction activity coefficients (corrected for vapour phase non-ideality) of solutes in PVA at several temperatures are given in Table 2. In all the cases, the activity coefficient at infinite dilution decreases with the temperature, showing a miscibility increase of the system when T increases. Relatively high values for the non-solvent probes (*n*-octane, cyclohexane) have been found. The high values for the 1-alcohols, usually good solvents for

Table 2. Weight fraction activity coefficients of solutes in PVA at several temperatures

Solute	80°C	100°C	120°C
<i>n</i> -Octane	14.9	13.5	12.6
Cyclohexane	15.5	11.5	8.97
Methanol	10.05	8.63	7.74
Ethanol	9.05	7.34	6.30
1-Propanol	7.56	6.10	5.25
1-Butanol	7.19	5.66	4.79
Acetone	4.78	4.29	3.95
Benzene	3.95	3.56	3.30
Toluene	4.50	4.05	3.75
Chlorobenzene	2.84	2.61	2.46
Ethyl acetate	3.91	3.63	3.47
Diethylene glycol diethyl ether	3.72	3.73	3.71
Dioxane	2.86	2.59	2.41

the polymer, can be explained by the possibility of hydrogen-bonding in the pure liquid state. Low values for the other probes indicate good miscibility between probe and polymer. Interaction parameters χ and χ^* of the Flory-Huggins and equation-of-state theories respectively vary similarly with temperature. Table 3 summarizes the χ and χ^* values at three temperatures (80, 100 and 120°C) for all the studied systems.

The solubility parameters δ_1 for the solutes were calculated from the relationship

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{1/2} \quad (20)$$

where R is the gas constant and V_1 is the solute molar volume corresponding to temperature T (K), which was chosen as the midpoint of the temperature range investigated. The units of δ_1 are (cal/cm³)^{1/2}.

The molar enthalpies of vaporization were calculated from the relationship

$$\Delta \bar{H}_v^x = \Delta \bar{H}_1^x - \Delta \bar{H}_{\phi_s} \quad (21)$$

where $\Delta \bar{H}_1^x$ is the partial molar heat of mixing of the solute at infinite dilution in the polymer, calculated from

$$\Delta \bar{H}_1^x = R\partial \ln(a_1/w_1)/\partial(1/T) \quad (22)$$

Therefore, $\Delta \bar{H}_1^x$ was obtained from the slope of the best straight line through a plot of $\ln(\text{activity coefficient})$ vs $(\text{absolute temperature})^{-1}$, as determined by a linear leastsquares analysis.

The corresponding heats of solutions were obtained similarly from:

$$\Delta H_{\phi_s}^x = -R\partial(\ln V_g)/\partial(1/T) \quad (23)$$

Values of the solubility parameter δ_1 of the various solutes so obtained have been given previously [4]. Values at 25°C in Table 4 have been obtained by linear extrapolation of the values at higher temperatures. Following the Ito and Guillet method [18] and by means of Eqn (7), the polymer solubility parameter δ_2 and the entropic component of the interaction parameter χ_s may be obtained from the slope and the intercept respectively. Figures 1 and 2 show plots of $\delta_1/RT - \chi/V_1$ vs δ_1 at 80 and 120°C respectively. The correlation is excellent.

The δ_2 variation with temperature is shown in

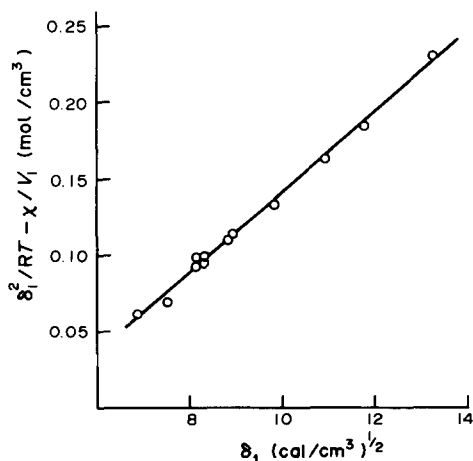
Table 3. Flory–Huggins and equation-of-state theories interaction parameters for all the studied systems at several temperatures

Systems	80°C		100°C		120°C	
	χ	χ^*	χ	χ^*	χ	χ^*
PVA						
<i>n</i> -Octane	1.14	1.25	1.03	1.15	0.943	1.07
Cyclohexane	1.28	1.38	0.971	1.08	0.706	0.826
Methanol	0.863	0.960	0.700	0.807	0.578	0.695
Ethanol	0.759	0.893	0.533	0.679	0.362	0.519
1-Propanol	0.604	0.719	0.482	0.602	0.211	0.348
1-Butanol	0.568	0.614	0.324	0.377	0.151	0.211
Acetone	0.104	0.240	−0.0227	0.125	−0.123	0.0364
Benzene	0.0326	0.134	−0.0829	−0.173	−0.173	−0.0514
Toluene	0.158	0.233	0.0458	0.129	−0.0408	0.0515
Chlorobenzene	−0.0526	0.0136	−0.144	−0.0693	−0.212	−0.129
Ethyl acetate	0.0352	0.191	−0.0598	0.1089	−0.128	0.0540
Diethylene glycol diethyl ether	0.0161	0.0822	0.0113	0.0855	0.00115	0.0833
Dioxane	−0.118	−0.0415	−0.229	−0.144	−0.311	−0.216

Fig. 3. From this plot, the solubility parameter at 25°C was found to be 10.1 (cal/cm³)^{1/2}, in good agreement with published values (9.36–11.1 (cal/cm³)^{1/2}) [19]. Figures 4 and 5 show plots of χ_s vs temperature

Table 4. Solutes solubility parameter at 25°C obtained by linear extrapolation from values at higher temperatures

Solutes	δ (cal/cm ³) ^{1/2}
<i>n</i> -Octane	7.57
Cyclohexane	8.14
Methanol	14.9
Ethanol	13.3
1-Propanol	12.5
1-Butanol	11.4
Acetone	9.98
Benzene	9.17
Toluene	8.88
Chlorobenzene	9.52
Ethyl acetate	9.16
Diethylene glycol diethyl ether	7.71
Dioxane	10.1

Fig. 1. Plot of $\delta_1^2/RT - \chi/V_1$ vs δ_1 for all the studied systems at 80°C.

over the whole investigated range. The good linearity enables us to extrapolate to lower temperatures. The published value of 0.30 [20] as a fixed value for all the systems and temperatures is in complete disagreement with our experimental values, since they are strongly dependent either on thermodynamic system as on temperature.

Table 5 summarizes values of δ_1 , δ_2 , V_1 and χ_s at 30, 40 and 50°C obtained by linear extrapolation along with χ values obtained from Eqn (6),

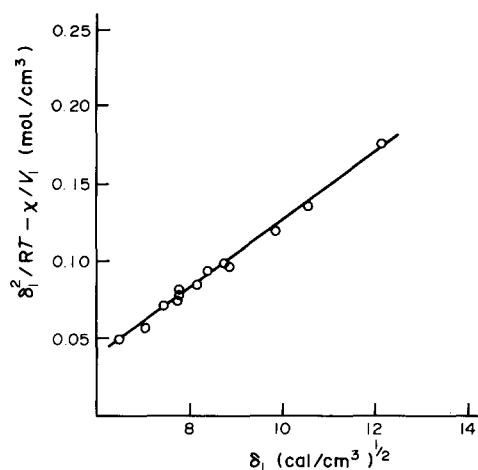
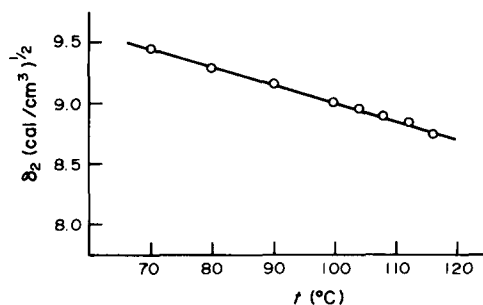
Fig. 2. Plot of $\delta_1^2/RT - \chi/V_1$ vs δ_1 for all the studied systems at 120°C.Fig. 3. Plot of polymer solubility parameter, δ_2 , vs temperature (°C) for poly(vinyl acetate).

Table 5. Solubility parameters $\delta_i(\text{cal/cm}^3)^{1/2}$ of solutes and polymer, entropic component of the interaction parameter, χ_s , for several polymer/solute systems and molar volume, $V_1(\text{cm}^3/\text{mol})$ of solutes

Solutes	t (°C)	δ_1	δ_2	χ_s	χ^*	χ^\dagger	V_1
Acetone	30	9.88	10.0	0.41	0.41	0.31	74.54
Acetone	40	9.68	9.88	0.34	0.34	0.35	75.65
Acetone	50	9.48	9.74	0.29	0.30	0.39	76.79
Benzene	30	9.10	10.03	0.17	0.30	0.30	89.96
Benzene	40	8.96	9.88	0.12	0.24	0.36	91.10
Benzene	50	8.81	9.74	0.070	0.19	0.26	92.27
1-Propanol	30	12.31	10.03	0.53	1.2	1.3	74.47
1-Propanol	40	12.03	9.88	0.48	1.04	1.1	75.47
1-Propanol	50	11.75	9.74	0.43	0.91	1.0	76.51

* Our data.

† R. J. Kokes, D. R. Pietro and F. A. Long, *J. Am. chem. Soc.* **75**, 6319 (1953).

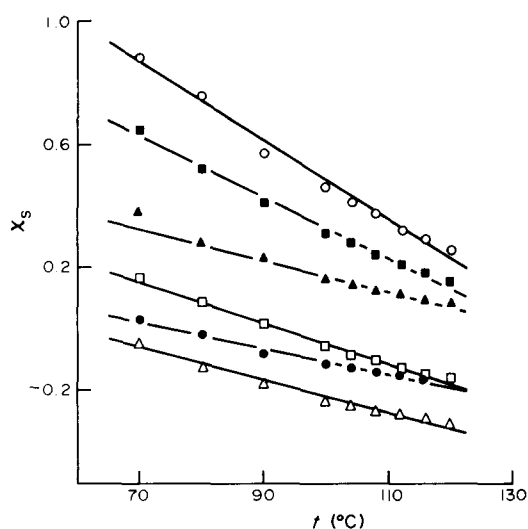


Fig. 4. Plot of entropic component of interaction parameter, χ_s , vs temperature for: PVA-cyclohexane (O—O); PVA-butanol (■—■); PVA-propanol (▲—▲); PVA-acetone (□—□); PVA-dioxane (Δ—Δ); PVA-toluene (●—●).

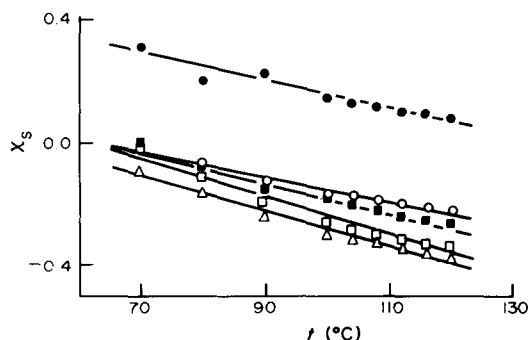


Fig. 5. Plot of entropic component of interaction parameter, χ_s , vs temperature for: PVA-ethanol (●—●); PVA-benzene (□—□); PVA-DEGDEE (■—■); PVA-ethyl acetate (Δ—Δ); PVA-chlorobenzene (O—O).

Table 6. Interaction energy, $X_{12}(\text{J/cm}^3)$, values for all the studied systems at several temperatures

Systems	80(°C)	100(°C)	120(°C)
PVA-octane	28.0	26.0	25.5
PVA-cyclohexane	51.1	35.9	22.6
PVA-methanol	100	82.2	71.5
PVA-ethanol	57.7	36.0	22.2
PVA-propanol	33.2	14.7	2.61
PVA-benzene	-1.08	-9.28	-15.3
PVA-toluene	5.39	-1.24	-6.28
PVA-chlorobenzene	-3.39	-9.38	-13.6
PVA-dioxane	-8.40	-18.1	-25.4

for the following systems: PVA/acetone, PVA/benzene, and PVA/1-propanol. Published values are also given for comparison. Chromatographic values are in good agreement with those obtained by other techniques.

The more representative magnitude for measuring, specifically, the interaction energy between the components of the mixture is the specific contact of interaction energy X_{12} . This parameter of the equation-of-state theory has been computed from Eqn (19) in which all the components are known.

Table 6 collects the values of X_{12} for nine solutes between 70 and 140°C.

For the other solutes P^* characteristic values were not found in the literature. X_{12} values decrease markedly with temperature, showing that it cannot be used as a parameter independent of temperature. High values for alcohols, decreasing with increase in the number of carbon atoms in the chain, can be explained on the basis of hydrogen bonding in the pure liquid state. Fairly high values for hydrocarbons show unfavourable interaction between polymer and solvent. Values obtained for aromatic compounds can be interpreted on the basis of dispersion forces, since these values are similar to those recognized as characteristic of this type of interaction [23].

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