Molecular Interaction in the Ternary Mixture of Acetylacetone with (Carbon Tetrachloride and Heptane) – Linear Correlation Factor, Excess Molar Polarization, and Excess Gibbs Energy of Mixing

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The relative permittivity in the ternary mixtures of acetylacetone with (carbon tetrachloride and heptane) has been measured at 303.16 K and 455 kHz. The Kirkwood—Fröhlich linear correlation factor g, excess molar polarization, and the excess Gibbs energy of mixing in these mixtures are calculated using the experimental value of relative permittivity on the basis of the Winkelmann—Quitzsch equation.

These parameters are found to be mole fraction-dependent indicating the existence of angular correlation between the polar molecules in the nonpolar solvent. The study reveals that the nonpolar solvent carbon tetrachloride is dominant over heptane in the mixtures.

In earlier papers [1—5] we have investigated the molecular interaction of the two nuclear extractants, namely acetylacetone (HAA) and diisobutyl ketone (DIBK) in binary mixtures with various polar and nonpolar solvents and also in the ternary mixtures of DIBK with two nonpolar solvents with a view to identify an efficient modifier to be used in the solvent extraction process in the nuclear energy industry.

The mechanism associated with the solvent extraction process is one of the simple complex formations. There appear two distinct phases in the product – an organic phase which contains the metal (nuclear) and an aqueous phase which contains the rest of the product of the reaction. The organic phase could be separated from this aqueous phase for the separation of metal. It is however observed that when the concentration of the extracted species exceeds the solubility of solvent in the organic system, a third phase appears at the interface of the organic and aqueous phase [6]. This third phase being a mixture of both organic and aqueous phases complicates the separation of the organic phase which contains the nuclear metal. Thus these extractants in the pure form have low extraction efficiency. Mixing the extractants with suitable diluents alters their physical properties and helps to improve phase separations with consequent enhanced extraction efficiency [6]. When the extractant is blended with diluent, the relative permittivity of organic phase changes and therefore we aim to undertake dielectric studies of acetylacetone with binary mixture of carbon tetrachloride and heptane as the solvents. Acetylacetone is not only a flexible molecule but exhibits moreover keto-enol tautomerism making it an interesting candidate for investigation of molecular interaction.

The relative permittivity ε_m of various mole fractions in the mixture is measured at the fixed temperature 303.16 K and fixed frequency 455 kHz. The data are used to compute the linear correlation factor (g), excess molar polarization (ΔP), and excess Gibbs energy of mixing (ΔG) to elucidate the picture of liquid structure.

The Kirkwood—Fröhlich linear correlation factor (g) is a shape-dependent parameter indicative of short-range intermolecular force leading to dipole—dipole interaction [7, 8]. Furthermore, the nature of variation of g with mole fraction of HAA reflects upon the dipolar alignment and hence nature of multimerization of HAA molecules. Besides g, other parameters like ΔP and ΔG also contribute to corroborate the liquid structure.

THEORETICAL

The Kirkwood—Fröhlich relation for linear correlation factor extended to the solutions can be written as

$$g = \frac{9\varepsilon_0 k_B T}{N_A \mu^2 x_2} \frac{(2\varepsilon_m + \varepsilon_\infty)^2}{(\varepsilon_\infty + 2)^2 (2\varepsilon_m + 1)}.$$

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$$\cdot \left[V \frac{\varepsilon_{\mathrm{m}} - 1}{\varepsilon_{\mathrm{m}}} - \frac{3x_1 V_1 (\varepsilon_1 - 1)}{(2\varepsilon_{\mathrm{m}} + \varepsilon_1)} - \frac{3x_2 V_2 (\varepsilon_\infty - 1)}{(2\varepsilon_{\mathrm{m}} + \varepsilon_\infty)} \right] \quad (1)$$

The excess molar polarization of mixing ΔP is calculated taking into account both long-range and short-range interactions between identical molecules. According to this, the molar polarization of the mixtures utilizing the separation of total correlation (Nienhuis and Deutch) and incorporating Onsager's reaction field factor is given by [9]

$$P_{\mathrm{M}} = \frac{\varepsilon_{\mathrm{m}}}{\varepsilon_{\mathrm{m}} + 2)} \left[\frac{3x_1 V_1 (\varepsilon_1 - 1)}{(2\varepsilon_{\mathrm{m}} + \varepsilon_1)} + \frac{3x_2 V_2 (\varepsilon_\infty - 1)}{(2\varepsilon_{\mathrm{m}} + \varepsilon_\infty)} + \right.$$
$$\left. + g' \frac{N_{\mathrm{A}}}{9\varepsilon_0 k_{\mathrm{B}} T} \mu^2 x_2 \frac{(\varepsilon_\infty + 2)^2 (2\varepsilon_{\mathrm{m}} + 1)}{(2\varepsilon_{\mathrm{m}} + \varepsilon_\infty)^2} \right] \quad (2)$$

The excess molar polarization is

$$\Delta P = P_{\mathrm{M}} - (x_1 P_1 + x_2 P_2) \quad (3)$$

The expression for excess Gibbs energy ΔG for a matter in condensed phase is given [10] as follows

$$\Delta G = -\frac{N_{\mathrm{A}}}{2} [R_{\mathrm{f2}} - R_{\mathrm{f2}}^0] \cdot [x_2 \mu^2 \{x_2 (g' - 1) + 1\}] \quad (4)$$

where

$$R_{\mathrm{f2}}^0 = \frac{2N_{\mathrm{A}}}{9\varepsilon_0 V_2} \frac{(\varepsilon_2 - 1)(\varepsilon_\infty + 2)}{(2\varepsilon_2 + \varepsilon_\infty)} \quad (5)$$

$$R_{\mathrm{f2}} = \frac{2N_{\mathrm{A}}}{9\varepsilon_0 V_2} \frac{(\varepsilon_{\mathrm{m}} - 1)(\varepsilon_\infty + 2)}{(2\varepsilon_{\mathrm{m}} + \varepsilon_\infty)} \quad (6)$$

where ε_{m} is the relative permittivity of the ternary mixtures, $\varepsilon_\infty = n^2$ square of refractive index of the pure solute, ε_0 permittivity of the vacuum, ε_1 relative permittivity of (carbon tetrachloride and heptane), ε_2 relative permittivity of pure solute, x_1, x_2 mole fraction of the solvents (carbon tetrachloride and heptane) and solute (HAA), respectively, x_1', x_1'' mole fraction of heptane and carbon tetrachloride, respectively, V_1 molar volume of (heptane and carbon tetrachloride) (cm^3), respectively, V_2 molar volume of pure solute (cm^3), P_1 molar polarization of heptane and carbon tetrachloride, respectively, P_2 molar polarization of solute, P_{M} molar polarization of ternary mixtures, ΔP excess molar polarization of ternary mixture (cm^3 mol^{-1}), g' linear correlation factor for pure solute, g linear correlation factor for ternary mixture, N_{A} Avogadro's constant, k_{B} Boltzmann constant, T absolute temperature, μ gas phase dipole moment of pure solute, ΔG Gibbs energy of ternary mixture (J mol^{-1}), R_{f2}^0, R_{f2} reaction field parameters in the pure liquid and in the mixture.

EXPERIMENTAL

The chemicals used were of anal. grade purified by standard procedure [11, 12] and redistilled before use.

The experimental arrangement used for the measurement of relative permittivity, *etc.* is the same as used by the author of [13] earlier. The relative permittivity measurement for pure liquids as well as for mixtures was carried out by wavemeter—oscillator combination at 455 kHz [2]. The device was standardized with the help of standard liquid of known relative permittivity [14]. The cell temperature was controlled with the electronically regulated thermostatic arrangement with temperature variation of $\pm$ 0.1 °C. The refractive index was measured at the regulated temperature by Pulfrich refractometer at the sodium D-line. The density was measured using pycnometer of 25 cm^3 capacity. The reproducibility of relative permittivity is $\pm$ 0.003 and those of refractive index and density measurements are $\pm$ 0.00002 and $\pm$ 0.00002 g cm^{-3}, respectively, at the temperature 303.16 K.

RESULTS AND DISCUSSION

The relevant data are presented in Table 1, some representative ones are displayed graphically in Figs. 1—4.

Prior to discussion on the ternary mixtures, it is worthwhile to include a brief resume of the response in binary mixtures involving the polar solute with both the nonpolar solvents separately.

The value of g for undiluted HAA is 1.56. This indicates the predominance of parallel orientation leading to the formation of α-multimers in HAA. Short-range specific interaction between polar molecules leads to preferential dipolar alignment. Reinforcement of angular correlation results in parallel dipolar alignment leading to the formation of α-multimers where $g > 1$. On the other hand, antiparallel dipolar alignment results in β-multimers where $g < 1$.
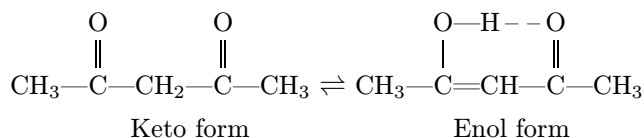
When acetylacetone is blended with carbon tetrachloride (solvent), it is observed that the value of g is less than unity but it increases with increasing acetylacetone mole fraction, the rate of increase being rather high in the lower mole fraction region. This indicates that α-multimers predominate in solute-rich region, while β-multimers are in excess in acetylacetone-deficient region.

Also, in heptane medium the value of g is relatively low in acetylacetone-deficient region and with the increase of solute content in the mixture, the value of g increases steadily and approaches the value of pure solvent. In this mixture in acetylacetone-deficient region, the proportion of β-multimers to α-multimers is significantly greater. Acetylacetone molecules exhibit tautomerism, *i.e.* they exist in both keto and enol forms [2].

Table 1. Variation of ε_m, g, ΔP, and ΔG in Ternary Mixtures of Acetylacetone with (Carbon Tetrachloride and Heptane)

x_2	ε_m	g	ΔP cm^3 mol^{-1}	ΔG J mol^{-1}
		$x_1'' = 0.107,\ x_1' = 0.893$		
0.040	2.18	0.560	10.10	350.00
0.126	2.70	0.600	35.00	800.00
0.200	3.50	0.774	55.25	1200.00
0.250	4.40	0.946	65.25	1340.00
0.350	6.00	1.060	80.00	1540.00
0.418	7.40	1.130	80.25	1560.00
0.500	9.20	1.200	80.25	1510.00
0.600	11.70	1.270	75.25	1400.00
0.800	17.00	1.380	55.25	1100.00
0.900	21.00	1.450	35.00	760.00
		$x_1'' = 0.207,\ x_1' = 0793$		
0.050	2.20	0.760	7.50	400.10
0.150	3.20	0.806	40.00	820.20
0.210	4.00	0.850	65.00	1000.00
0.300	5.50	1.050	65.12	1150.00
0.410	7.70	1.070	72.15	1300.00
0.500	10.48	1.130	72.17	1350.00
0.650	13.40	1.250	65.00	1240.00
0.700	14.50	1.320	60.00	1150.15
0.800	17.50	1.410	40.00	950.00
0.900	21.00	1.470	28.00	600.00
		$x_1'' = 0.306,\ x_1' = 0.694$		
0.080	2.50	0.780	8.50	450.52
0.150	3.30	0.900	38.10	830.12
0.200	4.30	1.020	53.00	1100.00
0.330	6.50	1.140	63.14	1280.32
0.440	8.50	1.230	75.20	1320.00
0.550	10.80	1.300	75.10	1240.10
0.600	12.00	1.336	62.00	1110.00
0.770	16.20	1.436	55.00	920.32
0.850	19.00	1.470	40.00	800.12
0.960	22.00	1.530	25.10	550.32
		$x_1'' = 0.410,\ x_1' = 0.590$		
0.080	2.60	0.664	10.00	280.13
0.150	3.40	0.850	40.30	1000.00
0.200	4.20	0.987	58.20	1220.30
0.330	6.80	1.140	58.10	1400.10
0.450	8.60	1.230	83.30	1560.50
0.500	9.40	1.320	83.10	1300.12
0.600	11.40	1.420	75.00	1110.30
0.770	15.50	1.460	65.10	920.12
0.580	18.00	1.520	42.30	800.12
0.950	21.50	1.540	20.30	600.00
		$x_1'' = 0.506,\ x_1' = 0.494$		
0.050	2.58	0.760	15.00	300.00
0.160	3.80	0.989	50.00	1100.23
0.250	5.20	1.140	65.12	1410.00
0.350	7.00	1.230	80.00	1550.00
0.450	8.70	1.310	82.15	1520.00
0.630	12.20	1.400	75.00	1340.00
0.750	15.20	1.460	62.10	1150.00
0.850	18.50	1.500	45.00	860.00
0.720	20.20	1.530	35.00	700.30
		$x_1'' = 0.606,\ x_1' = 0.394$		
0.078	2.70	0.800	14.30	400.42
0.150	4.00	1.180	45.16	1200.00
0.260	5.50	1.280	68.00	1550.00
0.360	7.50	1.340	75.00	1560.12
0.450	9.00	1.370	80.12	1200.30
0.550	11.00	1.400	80.32	1100.00
0.650	13.00	1.430	55.12	900.32
0.780	16.00	1.460	40.00	800.12
0.950	22.00	1.520	32.12	600.00
		$x_1'' = 0.707,\ x_1' = 0.293$		
0.060	2.60	0.728	9.12	280.12
0.140	3.90	1.090	39.00	950.32
0.260	6.00	1.190	59.00	1110.34
0.370	7.70	1.290	68.12	1250.00
0.460	9.50	1.340	78.00	1320.10
0.550	11.10	1.380	65.13	1120.00
0.650	13.50	1.420	50.12	1050.12
0.850	19.00	1.470	43.00	920.15
0.950	21.50	1.530	18.12	600.10
		$x_1'' = 0.800,\ x_1' = 0.200$		
0.050	2.65	0.893	12.30	270.00
0.140	4.00	1.098	52.10	870.10
0.230	5.30	1.210	68.00	1000.13
0.350	7.60	1.320	78.12	1220.00
0.450	9.50	1.370	85.30	1320.14
0.560	11.50	1.420	80.10	1210.20
0.650	13.50	1.450	75.00	1170.00
0.820	18.00	1.470	60.10	900.00
0.960	22.50	1.520	30.30	500.13
		$x_1'' = 0.900,\ x_1' = 0.100$		
0.050	2.50	0.750	10.00	250.00
0.150	3.70	0.834	45.00	900.00
0.250	5.30	0.961	57.10	1110.20
0.350	7.20	1.120	62.50	1250.20
0.450	9.30	1.300	67.50	1330.30
0.550	11.30	1.350	70.00	1290.00
0.650	13.60	1.470	65.20	1200.00
0.850	19.50	1.530	40.00	800.00
0.960	22.50	1.540	18.00	400.14

$$CH_3-\underset{\underset{\text{O}}{\|}}{C}-CH_2-\underset{\underset{\text{O}}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\underset{\underset{\text{O}-\text{H}--\text{O}}{|}}{C}=CH-\underset{\|}{C}-CH_3$$

Keto form   Enol form

In the keto form they have wood-pile structure due to intramolecular association between $C^{\delta+}$ of one carbonyl group and $O^{\delta-}$ of other carbonyl group resulting in α-multimers

α-multimers
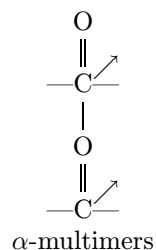
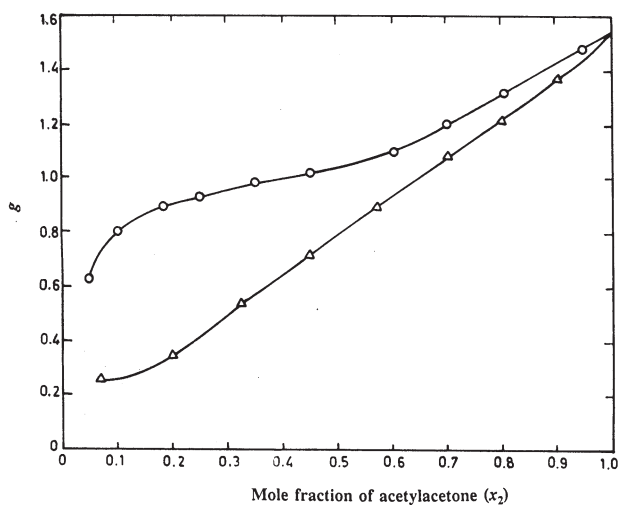**Fig. 1.** Variation of g with mole fraction of acetylacetone in binary mixtures at temperature 303.16 K. ○ Carbon tetrachloride, △ heptane.

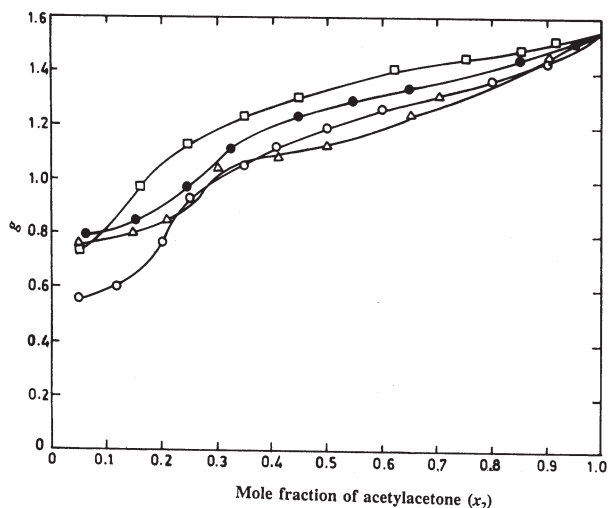**Fig. 3.** Variation of ΔP with mole fraction of acetylacetone in ternary mixtures at temperature 303.16 K. x_1'' (Carbon tetrachloride), x_1' (heptane): ○ 0.107, 0.893; △ 0.207, 0.793; □ 0.506, 0.494; ● 0.900, 0.100.

Fig. 2. Variation of g with mole fraction of acetylacetone in ternary mixtures at temperature 303.16 K. x_1'' (Carbon tetrachloride), x_1' (heptane): ○ 0.107, 0.893; △ 0.207, 0.793; □ 0.506, 0.494; ● 0.900, 0.100.

Fig. 4. Variation of ΔG with mole fraction of acetylacetone in ternary mixtures at temperature 303.16 K. x_1'' (Carbon tetrachloride), x_1' (heptane): ○ 0.107, 0.893; △ 0.207, 0.793; □ 0.506, 0.494; ● 0.900, 0.100.

In the enol form, there is internal hydrogen bonding between $H^{\delta+}$ and $O^{\delta-}$ in the monomeric species. In nonpolar medium, some of these internal bonds break and bifunctional groups are free to form intramolecular hydrogen bonding, which leads to alteration of the multimerization of the polar liquid. This is reflected in the change in the linear correlation factor g of the polar solute when diluted by nonpolar solvent [2].

The carbon tetrachloride molecule is relatively small in size and nearly spherical in shape and its abundance in solute-deficient region effectively screens the scarce solute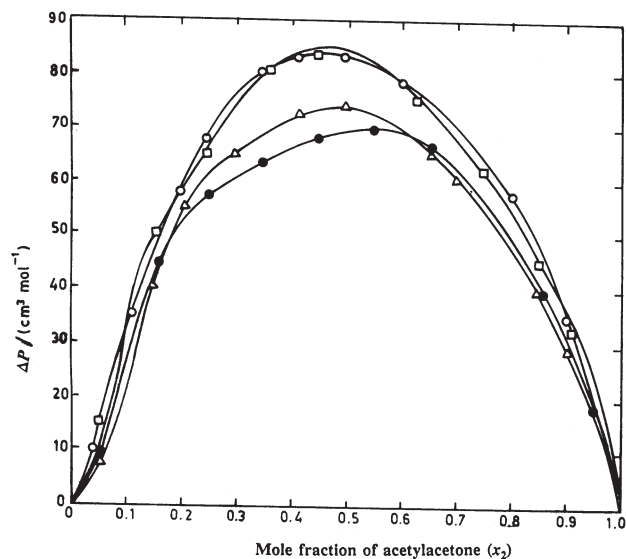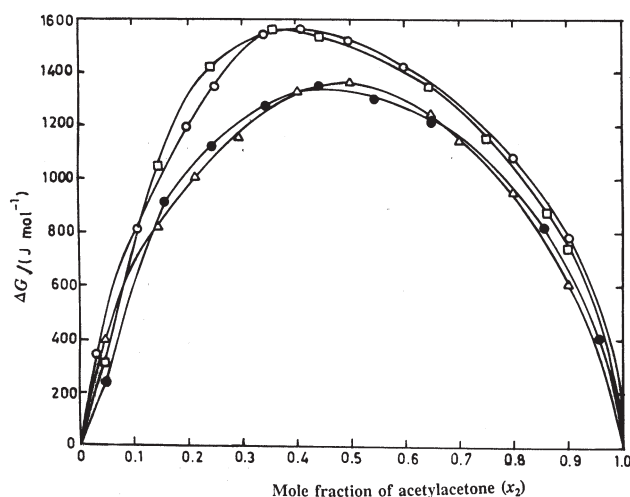 molecules thereby reducing correla- tion among them. However, because of small size the screening effect reduces considerably with decreasing mole fraction of carbon tetrachloride molecules. As a result the interaction gradually lapses into that corresponding to pure solute.

On the other hand, heptane being a long-chain molecule with relatively big size, the screening effect is more due to steric hindrance in solute-deficient region. As such, in heptane-rich region the scarce solute molecules are effectively isolated and fail to establish correlation among themselves. Whereas with reduction of nonpolar molecules, the polar molecules

could establish correlation among themselves resulting in rapid increase of g value.

The responses of ternary mixtures are mostly identical in HAA-rich region in as much as the value of g attains a value close to that of pure solute around mole fraction 0.4 of acetylacetone.

In the mixed solvent when carbon tetrachloride mole fraction is 0.1 and heptane mole fraction is 0.9, in low HAA mole fraction region, the value of g drops to 0.600 for solute-deficient region and steadily increases to attain the pure value of solute with the increase of HAA mole fraction. It is identical to that in the carbon tetrachloride system.

The response is identical, when carbon tetrachloride mole fraction in the mixture is increased from 0.2 to 0.9 where the value of g increases but remains below unity. In all cases β-multimers result in low acetylacetone mole fraction range. The β-multimers in all cases are expected to be open-chain ones. Taking into account the individual responses of acetylacetone in carbon tetrachloride and heptane, it is apparent that the effect of carbon tetrachloride masks the effect of heptane in the ternary mixture. Even in the mixtures when carbon tetrachloride content in the mixed solvent is around mole fraction of 0.1—0.2, α-multimers continue to be in excess over large range of acetylacetone mole fraction. Even for acetylacetone-deficient region, the value g (< 1) is rather close to unity, though in the binary mixture of acetylacetone—heptane, it is appreciably low.

In acetylacetone-deficient region, the response appears to be influenced by relative proportion of two nonpolar components in the mixed solvent. It is the steric effect of heptane on one hand and the easy mobility of carbon tetrachloride molecules on the other, they seem to be affecting the intramolecular association of polar liquid, the heptane molecules are effectively screened by mobile carbon tetrachloride molecules. Hence with the increase of carbon tetrachloride content, the intramolecular association of HAA molecules is influenced by carbon tetrachloride molecules.

The trend of variation of excess molar polarization (ΔP) is nearly identical for all mole fractions of carbon tetrachloride and heptane and it is found to be positive in all cases of ternary mixtures. This corroborates our results from evaluation of g, *i.e.* α-multimers are in excess in all the system. The maximum value of ΔP is observed around 0.5 mole fraction of HAA indicating reinforcement of alignment due to the increased multimerization. In ternary mixture, ΔP_{max} is observed when heptane mole fraction is around 0.9 and carbon tetrachloride mole fraction is around 0.1. This response of ternary mixtures is identical to bi-

nary mixtures [2]. The lowering in value of ΔP in acetylacetone-deficient region coincides with lowering in value of g of ternary mixture. Reduction of ΔP value for acetylacetone-rich region is probably due to depolymerization of HAA multimers.

The trend of variation of excess Gibbs energy ΔG in ternary mixture seems to be identical in all mole fractions of carbon tetrachloride and heptane and remains positive throughout. It is found that the excess Gibbs energy increases with the increase in mole fraction of solute, attains maximum at around 0.5 mole fraction of solute and finally drops to zero. In ternary mixture ΔG_{max} is observed when carbon tetrachloride mole fraction is around 0.1 and heptane mole fraction is around 0.9. The positive value of ΔG is due to conversion of some α-multimers in pure HAA to β-multimers in ternary mixtures. The β-multimers are characterized by reduced internal energy making excess energy positive. The fact that ΔG is higher when heptane mole fraction is 0.9 and carbon tetrachloride mole fraction is 0.1 corroborates our conclusion from the study of g and ΔP that interaction in that system is the strongest.

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