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Vapor Pressure Measurements and Gas Chromatographic Studies of the Solution Thermodynamics of Metal β -Diketonates¹

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The vapor pressures and heats of vaporization of the tris(hexafluoroacetylacetonates) (hfa) of Cr(III) and Rh(III) and the heptafluorodimethyloctanedionates (fod) of Al(III), Cr(III), Fe(III), Cu(II), and Pd(II) have been measured. These results show the hfa chelates to be more volatile than the fod chelates and the fod chelates to exhibit similar volatility to trifluoroacetylacetonate (tfa) chelates. Gas-liquid chromatography retention data over a range of temperatures were gathered for ten different chelates in three liquid phases and the heats of solution were calculated for each system. The chelates studied were Al(hfa)₃, Cr(hfa)₃, Rh(hfa)₃, Al(tfa)₃, Cr(tfa)₃, Al(fod)₃, Cr(fod)₃, Fe(fod)₃, Cu(fod)₂, and Pd(fod)₂. Liquid phases were squalane, Apiezon L (a high molecular weight hydrocarbon), and QF-1 (a partially fluorinated siloxane polymer). Specific retention volumes as a function of temperature are reported for each of the systems studied and activity coefficients and excess enthalpies of mixing were determined for each system. These results indicate that the solution behavior of the tris octahedral complexes is determined solely by nonspecific van der Waals type forces and that there is no evidence in these systems for specific types of intermolecular forces such as hydrogen bonding. Square-planar bis chelates, however, do exhibit an apparent specific interaction, which can be attributed to possible solvation at the vacant coordination sites in these molecules and a possible large entropy contribution from nonrandom orientation in solution.

Introduction

Although the gas-liquid chromatography (glc) of volatile metal β -diketonates has been studied for over a decade, knowledge of the physical parameters necessary to understand and predict the chromatographic behavior of these compounds has been noticeably scarce. The purpose of this study was to gain information about those parameters which would give some insight into the magnitude and types of interactions that affect the retention behavior of these metal chelates in various glc systems. Since the relative volatility of a mixture of compounds in a chromatographic column depends upon the relative vapor pressures of the pure compounds and upon the relative interactions of the compounds with the stationary phase, physical data about each of these factors are required.

Several authors have reported measurements, taken by either the isoteniscope or Knudsen effusion method, of the vapor pressures of several metal β -diketonates.³⁻⁵ However, serious discrepancies were observed between the results obtained in the previous work and several inherent problems in the use of these two methods for metal chelates have been pointed out.⁶ A recent study in which a sensitive quartz spiral Bourdon gauge was used for some precise measurements of the vapor pressures of the Al(III) and Cr(III) complexes of the ligands acetylacetonone [H(acac)], trifluoroacetylacetonone

[H(tfa)], and hexafluoroacetylacetonone [H(hfa)] has resolved some of the earlier discrepancies and a critical review of the earlier work was made.⁹ The precise measurements of the vapor pressures of a series of lanthanide chelates with the ligand 2,2,6,6-tetramethyl-3,5-heptanedione, H(thd), have also recently been reported.¹⁰

Since the amount of reliable vapor pressure data on metal β -diketonates was limited to these few recent reports, precise measurements of the vapor pressures of an extended series of compounds were made and are reported herein.

A considerable amount of information related to the interaction of the solute within the column is available from a study of the solution thermodynamics. The use of glc for the determination of activity coefficients and thermodynamic properties has been the subject of several recent reviews.¹¹⁻¹³

Only a few studies of the solution thermodynamics of metal chelates by glc have been reported. The heats of solution of the Al(III), Cr(III), and Rh(III) chelates of acetylacetonone and hexafluoroacetylacetonone were measured in several liquid phases.¹⁴ However, reliable values for vapor pressure data and heats of vaporization were not available at that time and the conclusions that could be drawn from these data were limited. This work will be discussed more fully later in this paper. Gere and Moshier¹⁵ in a study of the chelate Yb(thd)₃ in several liquid phases showed the feasibility of obtaining solution thermodynamic data for metal chelates by glc and showed some of the information that can be gained by a treatment of this type.

(1) (a) Presented in part at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970. (b) Presented in part at the 37th Annual Chemical Engineering Symposium, Tulane University, New Orleans, La., Dec 1970. (c) Taken in part from the Ph.D. dissertation of W. R. Wolf, Kent State University, 1969; *Diss. Abstr. B*, **31**, 1142 (1970). (d) This work was done at the Aerospace Research Laboratories.

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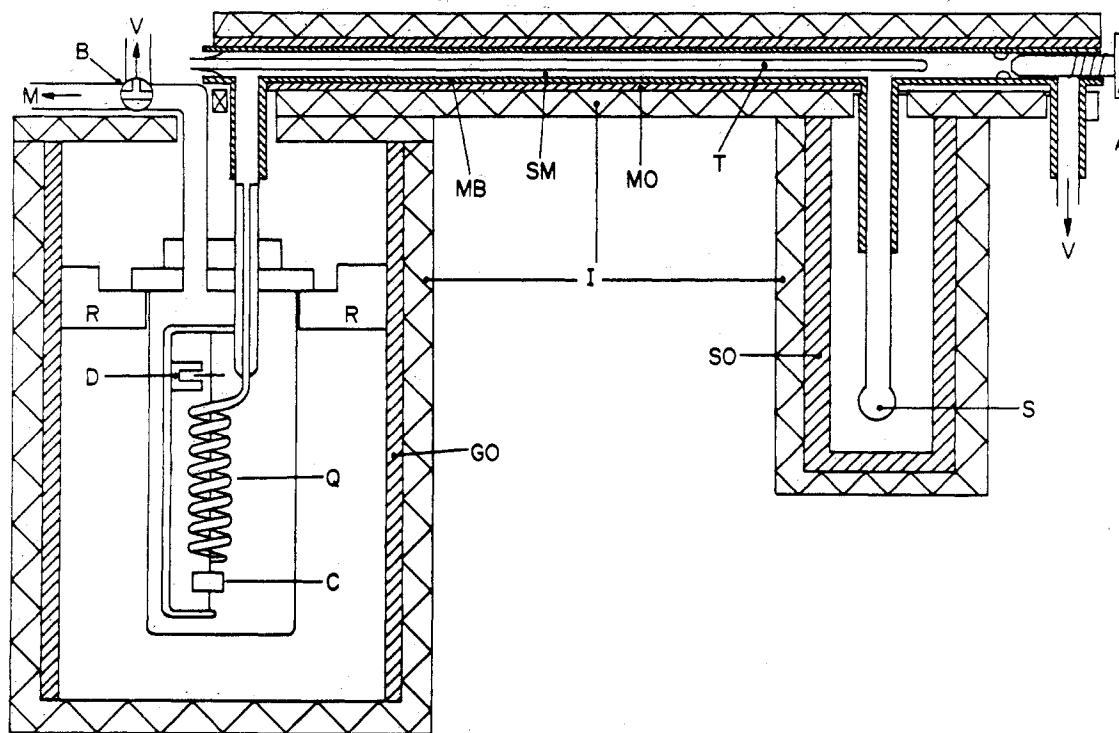


Figure 1.—Vapor pressure apparatus: (Q) quartz spiral Bourdon gauge, (C) mirror, (D) magnetic damping device, (R) support ring, (SM) sample manifold, (T) thermocouple well, (S) chelate sample, (A) Pyrex glass stopcock with Teflon valve, (B) three-way valve, (V) vacuum system, (M) manometers and McLeod gauge, (MB) manifold bushing, (MO) manifold oven, (SO) sample oven, (GO) gauge oven, (I) insulation.

Experimental Section

Samples.—All metal chelates studied in this work were synthesized by published methods or obtained from previous investigations in our laboratory.^{16–18} Chelates were purified by recrystallization from dichloromethane or carbon tetrachloride and/or by vacuum sublimation. Physical properties (melting points, ir, tga) and elemental analysis of the purified samples were in agreement with published values.

Vapor Pressure Measurements.—In order to overcome the inherent problems of decomposition and/or dissolution of these chelates in various manometric fluids used in the isotenoscopic vapor pressure methods, a system was constructed in which the chelate vapors came in contact only with fused quartz, borosilicate glass, and Teflon. The apparatus is similar to one used by Sicre, *et al.*,¹⁰ except the Pyrex spoon gauge is replaced by a quartz spiral Bourdon gauge (Texas Instruments, Inc.). The assembled apparatus is shown in Figure 1.

The deflections of the mirror caused by pressure differentials in the quartz spiral cell were monitored by a light beam from a fixed source reflected from the mirror onto a photosensitive cell whose output was measured with a digital voltmeter (Weston Electric Model 1423). The manifold and capsule oven temperatures were held at 10–20° higher than the sample oven in order to prevent condensation of the sample anywhere in the system except under equilibrium conditions in the sample tube. A small amount of silicone oil was placed in the bottom of the sample oven to distribute the heat uniformly to the end of the sample tube S shown in Figure 1. The temperature of the sample was measured to $\pm 0.1^\circ$ by placing a thermocouple directly on the bottom of the sample tube.

In this system the quartz spiral was utilized as a null device to measure the vapor pressure using the following procedure. (a) The purified chelate was placed in the sample tube and de-

gassed by repeatedly subliming and condensing the sample and then pumping out occluded vapors. (b) The sample was frozen, both sides of the gauge were evacuated to zero pressure (<0.005 Torr), and the zero point was recorded. (c) The sample was then heated and allowed to reach thermal equilibrium, and air was bled into the reference side of the gauge to bring the mirror back to the zero point. Under this condition the pressure in the reference side was equal to the vapor pressure of the chelate, and the pressure in the reference side was then measured by a sensitive McLeod gauge (Consolidated Vacuum Corp., Type GM-100A) in the range 0.1–10 mm and by an oil manometer, calibrated against the McLeod gauge, for pressures above 10 mm. (d) The sample oven was then lowered and the sample cooled in ice water. Since the chelates studied are condensable and have negligible vapor pressure at 0°, the pressure in the sample tube should then be reduced to zero. The reference side of the system was then evacuated to zero pressure and the reading on the voltmeter recorded, providing a check on the zero reference point. Any change in this reference point would indicate either incomplete outgassing or decomposition and the measurement at that temperature was repeated.

The accuracy of the system was checked by determining the vapor pressure of benzoic acid as a standard. Agreement with literature values was excellent (*e.g.*, 1.16 mm at 100°).

Gas-Liquid Chromatography Measurements.—The chromatograph used in this study was an F & M Model 810 research chromatograph equipped with a thermal conductivity detector. Columns made of Teflon tubing and glass liners in the injection port were used to minimize the amount of metal surface in the system. Peak retention times from the air peak were measured to ± 0.005 min with a stopwatch. The helium carrier gas flow rate was measured at the detector outlet by a soap bubble flowmeter. The inlet pressure was measured to ± 1.0 mm by connecting a differential manometer (Manostat Corp.) with a Swagelok Quick-Connect valve to the carrier gas stream just prior to entry into the injection port. The outlet pressure was assumed to be atmospheric.

The column temperature was measured by placing four thermocouples on various points on the column and taking the average value. The thermocouples were placed in various parts of the oven to check for temperature variations. The maximum variance found was 0.2° at 50° increasing to 2.0° at 200°. The variations were horizontal with the temperature being constant

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in the area above the oven fan. In order to minimize any thermal gradient effects, the columns were coiled so that the majority of the column length was directly over the oven fan and the variance was 0.5° at 200° . Once the oven had reached equilibrium, average column temperature was $\pm 0.1^\circ$ over the time of a particular run and $\pm 0.3^\circ$ over the course of several hours. The thermocouples were monitored continuously on a digital voltmeter and readings taken before and after each injection. If the average column temperature fluctuated more than $\pm 0.1^\circ$ the injection was repeated. A deviation in temperature of this magnitude would account for the observed deviation of 2–3% in peak retention times.

Saturated solutions of the chelates in toluene, *n*-heptane, or *n*-pentane were used and sample volume was chosen so that a symmetrical peak of 30–50% full-scale deflection was observed at the lowest attenuation available. This corresponded to approximately 0.01–0.1 μmol of chelate. Sample sizes 10 times as great as this showed no change in peak retention times. A slight tailing of the peaks was noticed for several systems at larger sample sizes. This was attributed to incomplete volatilization in the injection port as noted by Veening and Huber.¹⁹

It was observed that at flow rates of carrier gas above 60 cm^3/min the error in reproducibility of peak retention times increased to about 5%. This may be due to nonequilibrium conditions arising from the low solubility of these chelates in the liquid phases studied.

Previous experience has shown that hydrocarbon and siloxane phases have some utility in the gas chromatography of metal chelates. The liquid phase squalane (2,6,10,15,19,23-hexamethyltetracosane, Matheson) was chosen for study since it is a nonpolar pure hydrocarbon that should have no specific interactions with the metal chelates. This phase is useful only to about 110° before excessive bleeding makes the amount of phase in the column uncertain. The chelates containing the hexafluoroacetylacetone ligand can be successfully chromatographed below 100° but the chelates containing other ligands require somewhat higher temperatures (*ca.* 150°) for reasonably rapid elution.

The liquid phase chosen for use at these higher temperatures was Apiezon L (James G. Biddle Co.), a narrow boiling range mixture of high molecular weight hydrocarbons which may contain some cyclic and branched chains. The molecular weight of the sample of Apiezon L used in this study as determined by vapor-phase osmometry²⁰ is 1472. A molecular weight of 1488 was obtained by use of the gas chromatography method of Martire and Purnell.²¹

The third phase chosen was QF-1 (Applied Science), which is a trifluoropropylmethylsiloxane polymer whose molecular weight is approximately 7285 by vapor-phase osmometry.²⁰ This phase has a slight permanent dipole due to the CF_3 group and is a slightly more "polar" phase than Apiezon L.

The solid support used was Chromosorb W-HP, acid washed, DMCS treated (Johns-Manville). The silanizing of the solid support to remove active sites and reduce possible adsorption is very important in this type of study since metal fluoroacetylacetonates have been found to undergo a very severe interaction with unsilanized supports.¹⁹

Another source of adsorption in gas chromatographic systems is at the gas-liquid surface interface.²² Since polymeric liquids tend to have high viscosities and higher resistance to solute diffusion compared with lower molecular weight liquid phases, this mode of interaction for the glc of metal chelates may be an important factor. The amount of surface adsorption *vs.* partition in the solvent is dependent upon the surface to volume ratio and its effect can be minimized by using columns with a high percentage of liquid phase (>15%).

The stationary phases were prepared by the following standard procedure. The solid support was sieved and then coated by dissolving the liquid phase in an appropriate solvent, pouring this onto a slurry of the solid support, and removing the excess solvent in a rotary evaporator. The coated support was dried for about 4 hr in a vacuum oven at 110° to remove any excess water. Finally, the phase was resieved and the per cent loading of liquid phase determined before packing the columns. For the hydrocarbon liquid phases, it was found that low-temperature ashing

in an oxygen plasma (Tracerlab Low Temperature Dry Asher, LTA-600) quantitatively removed the liquid phase without changing the solid support. The weight loss upon ashing the coated support then gave a direct measurement of the amount of liquid phase present. For the silicone phase (QF-1) which gives a residue to nonvolatile silicon oxides upon low-temperature ashing, it was found that the liquid phase is completely volatilized upon heating in a helium atmosphere. For this phase, the total weight loss of the stationary phase measured by thermogravimetric analysis (Du Pont Model 950 tga instrument) gave a measurement of the amount of liquid phase present.

The following columns were used to obtain the gas chromatography data listed in Table II: (a) 24.9% squalane (1.353 g), length 33 in.; (b) 23.4% Apiezon L (0.793 g), 46 in.; (c) 23.4% Apiezon L (0.387 g), 24 in.; (d) 19.1% QF-1 (0.301 g), 24 in.; (e) 19.1% QF-1 (0.291 g), 24 in.; (f) 16.6% Apiezon L (0.665 g), 60 in.; columns (a) and (f) were $3/16$ -in. i.d. Teflon tubing; the others were $1/8$ in.; column (a) was 80/100 mesh Chromasorb W-HP; the others were 60/80 mesh.

Results

Vapor Pressure.—Equilibrium vapor pressure measurements for a series of metal β -diketonates were made over a range of temperatures. For the samples where it was possible to measure both the liquid and solid equilibrium vapor pressures, a sharp break in the plot of $\ln p$ *vs.* $1/T$ was observed which corresponded to the experimentally measured melting point. The remaining samples, which all contained the 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate (fod) ligand, exhibited values of about 0.2–0.4 mm for the vapor pressure at the observed melting points. Since the maximum sensitivity of this system was ± 0.02 mm, it was felt that measurements of the sublimation vapor pressures of these compounds were not warranted due to the resulting large experimental errors.

The vapor pressure plots of the raw data showed no observable curvature over the temperature ranges studied. Therefore, the heats of vaporization and sublimation can be assumed constant over these ranges and a simplified form of the Clausius-Clapeyron equation can be used adequately to represent the data

$$P = Ae^{-\Delta H/RT} \quad (1)$$

The raw data were processed using a nonlinear least-squares program^{23,24} which minimizes the sum of the squares of the pressure residuals in the form of eq 1. In order to obtain an idea of the error involved in the value of the heats of vaporization (ΔH_v) or sublimation (ΔH_{subl}), it was necessary to do a multiple regression analysis of the data in the logarithmic form of eq 1

$$\log P = A' - \Delta H/2.3RT \quad (2)$$

After proper weighting of the $\log P$ values, the results for ΔH by the regression analysis were in good agreement with the nonlinear fit. The constants and ΔH values listed in Table I are from the nonlinear fit. The error limits for ΔH represent the standard deviation obtained in the multiple regression fit.

Figure 2 shows the Clausius-Clapeyron plots for the chelates studied. Included in Figure 2 are the vapor pressure results obtained for similar metal β -diketonates studied by Shulstad.⁹ These results are included for comparison in order to show several trends in volatility

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TABLE I
CONSTANTS FOR VAPOR PRESSURE EQUATIONS^b AND MOLAR
HEATS OF VAPORIZATION AND SUBLIMATION

Liquid			
Chelate	A'	ΔH_v , kcal	Temp range, °C
Cr(hfa) ₃	10.26 (10.17) ^a	15.5 ± 0.7 (15.4 ± 0.2) ^a	85-103
Rh(hfa) ₃	9.91	15.4 ± 0.7	115-136
Al(hfa) ₃	9.82 ^a	14.3 ± 0.2 ^a	75-111
Al(tfa) ₃	10.24 ^a	17.8 ± 0.3 ^a	121-148
Cr(tfa) ₃	9.62 ^a	17.3 ± 1.0 ^a	155-183
Al(fod) ₃	9.56	17.5 ± 0.3	132-185
Cr(fod) ₃	9.44	17.6 ± 0.1	117-183
Fe(fod) ₃	10.46	19.5 ± 0.5	118-171
Cu(fod) ₃	9.09	16.2 ± 0.3	104-141
Pd(fod) ₃	8.69	15.9 ± 0.5	106-149
Solid			
		ΔH_{sub} , kcal	
Rh(hfa) ₃	14.65	23.8 ± 0.5	88-114
Al(fod) ₃	11.40	21.0 ± 1.2	96-125

^a Data from ref 9. ^b Equation 2 where pressure is mm.

tures studied. The Fe(fod)₃ chelate showed slight decomposition above 175°, and the Pd(fod)₂ and Cu(fod)₂ chelates showed decomposition above 160°. The Hf(fod)₄ compound exhibited the lowest thermal stability of those studied, slight decomposition was observed at the melting point, 174°, and decomposition became too severe to obtain even approximate values above 190°. The vapor pressure values for this compound over the narrow range of 175-185° are included in Figure 2 in order to show some idea of their approximate magnitude.

Gas-Liquid Chromatography.—The net retention volume at the column temperature is²⁶

$$V_n^T = F_c^T J (t_r - t_a) \quad (3)$$

where $(t_r - t_a)$ is the retention time in minutes of the solute peak minus the retention time of the air peak, J is the compressibility factor to correct for pressure drop across the column, and F_c^T is the corrected flow rate in cm³/min at the column temperature T . The

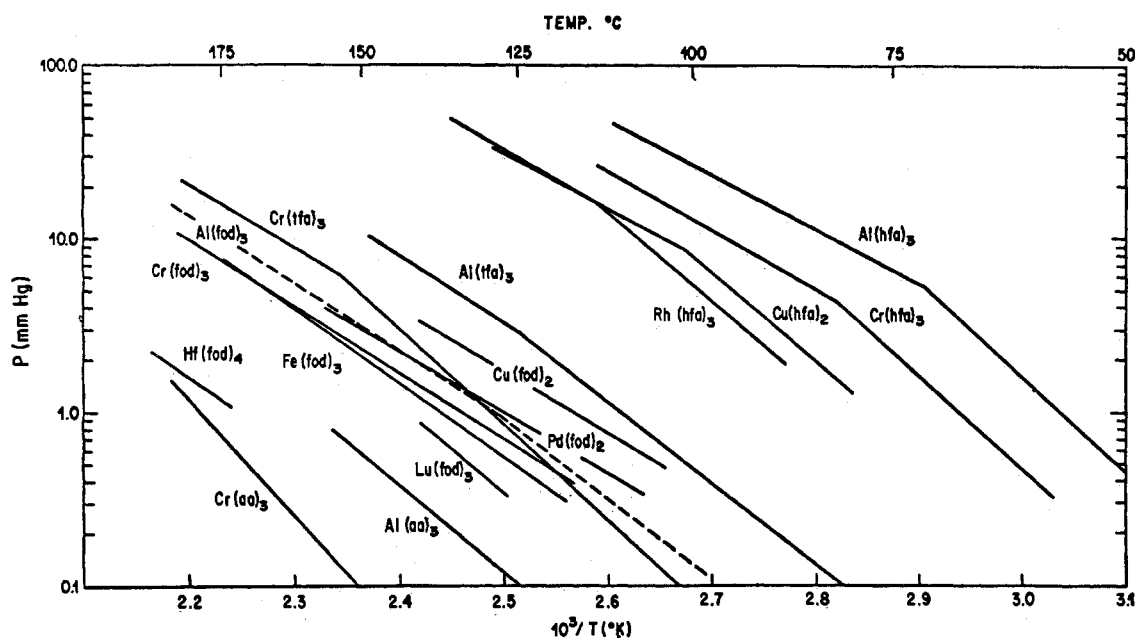


Figure 2.—Clausius-Clapeyron plots for metal β -diketonates.

in metal β -diketonate compounds. The results for Lu(fod)₃ are from the work of Koch.²⁵

It can be seen from Figure 2 that the volatility of these complexes is strongly dependent upon the ligand, with the more highly fluorinated ligands being more volatile in the order hfa \gg tfa $>$ fod \gg acac. It can also be seen that the bis square-planar fod complexes of Cu(II) and Pd(II) have vapor pressures greater than the tris fod complexes which are in turn more volatile than the tetrakis Hf(IV) complex.

The results for Cr(hfa)₃ are in agreement with Shulstad's⁹ values and serve to lend further support to that work in resolving some of the discrepancies in the earlier literature. A third independent measurement²⁵ of the vapor pressure of Cr(hfa)₃ has recently reconfirmed both Shulstad's and our values.

The Cr(hfa)₃, Rh(hfa)₃, and Al(fod)₃ chelates showed no thermal decomposition over the range of tempera-

specific retention volume as defined by Littlewood, *et al.*, is²⁷

$$V_g^0 = (273/T)(V_n^T/W_L) \quad (4)$$

where W_L is the weight in grams of liquid phase on the column. The specific retention volume is related to the heat of solution ΔH_s by²⁸

$$\ln V_g^0 = -\Delta H_s/RT + \text{const} = -M/T + A \quad (5)$$

Data for the experimental parameters necessary to calculate V_g^0 were collected for a series of chelates as described in the Experimental Section. Calculated values of $\ln V_g^0$ were then fitted to eq 5 by a multiple regression analysis and values for ΔH_s and the con-

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TABLE II
CONSTANTS FOR SPECIFIC RETENTION VOLUME EQUATION^a AND HEATS OF SOLUTION

Chelate	Column ^b	A	ΔH_s , kcal/mol	Temp range, °C
Squalane				
Al(hfa) ₃	a	10.34	-9.6 ± 0.1	69-98
Cr(hfa) ₃	a	11.74	-11.2 ± 0.1	69-98
Rh(hfa) ₃	a	12.28	-12.0 ± 0.1	69-98
Apiezon L				
Al(hfa) ₃	f	14.31	-11.4 ± 0.2	52-72
Cr(hfa) ₃	f	14.43	-12.0 ± 0.4	52-77
Rh(hfa) ₃	f	15.45	-13.1 ± 0.1	52-87
Al(tfa) ₃	c	11.52	-13.3 ± 0.1	127-152
Cr(tfa) ₃	b	11.54	-14.1 ± 0.1	167-202
Al(fod) ₃	c	13.36	-15.7 ± 0.2	132-162
Cr(fod) ₃	b	12.14	-14.9 ± 0.1	167-202
Fe(fod) ₃	c	13.14	-15.9 ± 0.2	132-192
Cu(fod) ₂	c	12.34	-16.0 ± 0.3	162-192
Pd(fod) ₂	c	13.64	-17.6 ± 0.2	162-192
QF-1				
Al(hfa) ₃	d	14.34	-14.0 ± 0.2	67-92
Cr(hfa) ₃	d	15.11	-15.1 ± 0.1	67-107
Rh(hfa) ₃	d	15.44	-15.6 ± 0.1	67-107
Al(tfa) ₃	d	13.71	-16.1 ± 0.3	147-167
Cr(tfa) ₃	d	12.41	-15.5 ± 0.1	147-172
Al(fod) ₃	d	14.02	-17.3 ± 0.1	147-172
Cr(fod) ₃	d	13.31	-16.8 ± 0.1	147-172
Cu(fod) ₂	e	13.90	-17.3 ± 0.1	147-164
Pd(fod) ₂	e	13.93	-17.5 ± 0.2	147-164

^a Equation 5. ^b See Experimental Section.

stant A obtained from this fit are listed in Table II.

The excess heat of mixing, ΔH_m , can be calculated from the relationship²⁸

$$\Delta H_m = \Delta H_s + \Delta H_v \quad (6)$$

Calculated values of ΔH_m for the systems studied are presented in Table III.

TABLE III
EXCESS HEATS OF MIXING (KCAL/MOL)

Chelate	Apiezon L	QF-1	Squalane
Al(hfa) ₃	2.9	0.3	4.7
Cr(hfa) ₃	3.5	0.5	4.3
Rh(hfa) ₃	2.3	-0.2	3.4
Al(tfa) ₃	4.5	1.7	
Cr(tfa) ₃	3.2	1.8	
Al(fod) ₃	1.8	0.2	
Cr(fod) ₃	2.7	0.7	
Fe(fod) ₃	3.6		
Cu(fod) ₂	0.2	-1.1	
Pd(fod) ₂	-1.7	-1.6	

Figure 3 shows the variation of V_g^0 with reciprocal temperature for the hexafluoroacetylacetonate (hfa) chelates. Values for V_g^0 were calculated from the constants in Table II over the range 65–85°. Figure 3 shows that the order of retention volumes of the hfa chelates is Al < Cr < Rh for the three phases studied and that the retention volumes are significantly different for the three chelates in each of the phases, leading to good separations for these chelates.

Since the chelates containing ligands other than hfa were out of experimental necessity studied at a higher temperature range, the magnitude and temperature dependence of both the vapor pressures and specific retention volumes at 140, 150, and 160° for these systems are listed in Table IV.

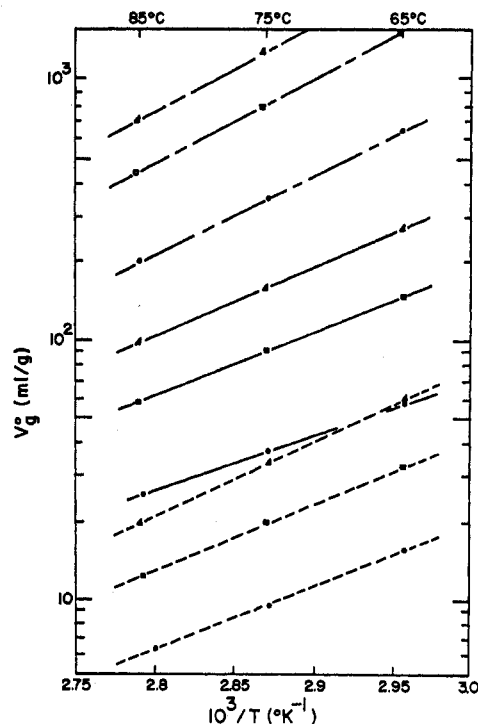


Figure 3.—Temperature dependence of specific retention volumes for $M(\text{hfa})_3$ chelates. Metal ions: Al(III), O; Cr(III), □; Rh(III), Δ. Liquid phases: squalane, —; Apiezon L, ---; QF-1, -·-·-.

Values for the activity coefficients, γ_2 , at 140, 150, and 160° for these systems were calculated from²⁸

$$\gamma_2 = 273R/V_g^0 P_2^0 M_2 \quad (7)$$

where P_2^0 is the vapor pressure of the chelate and M_2 the molecular weight of the liquid phase. These results are listed in Table V. Table V shows very large values of γ_2 for all the chelates in the hydrocarbon phase, thus indicating very low solubility. The activity coefficients are nearer to unity in the QF-1 phase indicating better solubility of these slightly polar, fluorinated chelates in this phase. The square-planar chelates $\text{Cu}(\text{fod})_2$ and $\text{Pd}(\text{fod})_2$ are seen to have significantly lower activity coefficients in both phases; this corresponds to their experimentally observed increased solubility relative to the tris octahedral chelates.

Estimation of Solubility Parameters.—Hildebrand's²⁹ treatment of solutions of nonelectrolytes makes use of the solubility parameter or cohesive energy density of the separate components of a mixture. This parameter is related to the intermolecular forces of the pure component in the liquid state (which is the standard state taken for discussion of thermodynamic studies by glc). This parameter is defined as²⁹

$$\delta_2 = [(\Delta H_v - RT)/V_2^0]^{1/2} (\text{cal/ml})^{1/2} \quad (8)$$

Where ΔH_v is the heat of vaporization and V_2^0 is the molar volume of the pure component.

There are no density data available for the compounds studied. Molar volumes were estimated from

(29) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," 3rd ed, Dover Publications, New York, N. Y., 1964.

TABLE IV
 VALUES OF P_2^0 AND V_g^0 FOR METAL β -DIKETONATES

Chelate	P_2^0 , mm			V_g^0 , cm ³ /g					
	140°	150°	160°	Apiezon L			QF-1		
	140°	150°	160°	140°	150°	160°	140°	150°	160°
Al(tfa) ₃ ^a	6.7	11.1	18.1	107	73	50	340	216	141
Cr(tfa) ₃ ^a	3.0	4.9	7.9	263	176	120	606	390	256
Al(fod) ₃	1.9	3.1	5.1	318	203	132	1150	702	437
Cr(fod) ₃	1.4	2.3	3.8	387	254	170	1330	820	516
Fe(fod) ₃	1.2	2.1	3.7	507	323	210			
Cu(fod) ₂	3.0	4.8	7.4	1280	794	505	1290	782	487
Pd(fod) ₂	1.9	3.0	4.6	2370	1430	880	1640	996	618

^a Vapor pressure data from ref. 9.

 TABLE V
 VALUES OF ACTIVITY COEFFICIENTS

Chelate	Apiezon L			QF-1		
	140°	150°	160°	140°	150°	160°
Al(hfa) ₃ ^a	92	84	78	0.86	0.85	0.83
Cr(hfa) ₃ ^a	87	78	70	0.89	0.86	0.84
Rh(hfa) ₃ ^a	112	105	99	0.99	0.99	0.99
Al(tfa) ₃	16.2	14.3	12.6	1.04	0.98	0.92
Cr(tfa) ₃	14.7	13.4	12.2	1.29	1.20	1.16
Al(fod) ₃	19.1	18.1	17.1	1.07	1.06	1.05
Cr(fod) ₃	21.1	19.4	17.9	1.25	1.22	1.20
Fe(fod) ₃	18.8	16.7	15.0			
Cu(fod) ₂	3.02	3.04	3.06	0.61	0.63	0.65
Pd(fod) ₂	2.56	2.70	2.83	0.75	0.79	0.82

^a Extrapolated from 60–80° range.

literature values for the molar volume³⁰ and parachor³¹ of Al(acac)₃ used as the reference chelate. Volume increments for other ligands derived from H(acac) were estimated from Quayle's³² parachor values. Since no parachor values were available for each of the different metal ions, and the size of the metal ion has only a small effect on the molar volume, they were assumed to be nearly identical. Estimated molar volumes at 150° for tris octahedral metal chelates are M(hfa)₃ 448 cm³/mol for M = Al, Cr, Rh; M(tfa)₃ 379 cm³/mol for M = Al, Cr; and M(fod)₃ 730 cm³/mol for M = Al, Cr, Fe. Experimental data on the density of these chelates are required before these estimates can be further refined. Calculation of the solubility parameters at 150° using eq 8 and values of heats of vaporization from Table I gave the following results in (cal/ml)^{1/2}: Al(hfa)₃, 5.48; Cr(hfa)₃, 5.47; Rh(hfa)₃, 5.70; Al(tfa)₃, 6.69; Cr(tfa)₃, 6.59; Al(fod)₃, 4.78; Cr(fod)₃, 4.79; Fe(fod)₃, 5.07.

Values for the solubility parameters of the liquid phases also are not known, but reasonable estimates can be made by extrapolating from similar compounds of lower molecular weight. Values for δ_2 of the liquid phases were obtained as follows.

Squalane ($\delta_2 = 8.0$).—Values for the heat of vaporization and molar volume of n -C₃₀H₆₂ were estimated by extrapolating values for the n -C₈ to n -C₂₀ hydrocarbons taken from API Project 44.³³ A solubility parameter of 8.2 was calculated for n -C₃₀H₆₂, which would be slightly lowered in squalane due to the branching.

Apiezon L ($\delta_2 = 7.8$).—This liquid phase was judged to be similar to other polymeric hydrocarbons, *i.e.*, polyethylene or polyisobutylene, which have solubility parameters of approximately 7.7–7.9.³⁴

QF-1 ($\delta_2 = 5.4$).—By analyzing a large number of compounds, Small³⁵ has reported additive group contributions to the cohesive energy density. Replacing one CH₃ group by CH₂CH₂CF₃ in the monomer unit of SE-30 (polydimethylsiloxane) constitutes the monomer of QF-1. Utilizing the series of compounds used to determine the solubility parameter of SE-30 and Small's group constants, one can see that the solubility parameter approaches a constant value of 5.4 for a high polymerization number.

SE-30 ($\delta_2 = 5.0$).—Values for the solubility parameters of a series of [(CH₃)₂SiO]_{*n*} compounds were calculated from heat of vaporization and molar volume data from the literature.^{36,37} The solubility parameter tended toward a constant value of 5.0 for large values of *n*.

Kel F-200 ($\delta_2 = 5.9$).—The solubility parameters of a wide series of fluorocarbons have been reported by Scott.³⁸ These fall in the range 5.7–6.1. Scott also reported an estimate of 6.0 for the solubility parameter of "Teflon," (CF₂)_{*n*}. Since Kel F is (CF₂CFCl)_{*n*}, its solubility parameter should be very close to those of the fluorocarbons.

Discussion

Evidence can be presented that these systems may possibly be explained within the framework of Hildebrand's²⁹ nonelectrolyte solution theory. An examination of solutions of several metal chelates in a variety of solvents has led Jones, *et al.*,^{39,40} to conclude that these solutions are "regular" in the sense proposed by Hildebrand and that no interactions exist which would render them nonregular. Irving and Smith⁴¹ have applied the theory of "regular" solutions to the study of Cr(acac)₃ in organic solvents.⁴²

For "regular" solutions with no strong specific interactions, such as hydrogen bonding, the heat of mixing, ΔH_m , has been shown to be approximated by the difference between the cohesive energy densities of the two components by²⁹

$$\Delta H_m = V_2^0(\delta_1 - \delta_2)^2 \quad (9)$$

(34) F. W. Billmeyer, Jr., "Textbook of Polymer Science," Interscience, New York, N. Y., 1962, p 26.

(35) P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).

(36) D. F. Wilcock, *J. Amer. Chem. Soc.*, **68**, 691 (1946).

(37) C. B. Hurd, *ibid.*, **68**, 364 (1946).

(38) R. L. Scott, *ibid.*, **70**, 4090 (1948).

(39) M. M. Jones, J. L. Wood, and W. R. May, *J. Inorg. Nucl. Chem.*, **23**, 305 (1961).

(40) M. M. Jones, A. T. Davilla, J. E. Hix, Jr., and R. V. Dilts, *ibid.*, **25**, 369 (1963).

(41) H. M. N. H. Irving and J. S. Smith, *ibid.*, **30**, 1873 (1968).

(42) The work of Irving and Smith⁴¹ reports a value of the solubility parameter δ_2 for Cr(acac)₃ of 9.04 ± 0.07. Combining this with the molar volume of Cr(acac)₃, the calculated value for the heat of vaporization from $\delta_2 = [(\Delta H_v^0 - RT)/V_2^0]^{1/2}$ is 22.1 kcal/mol.

(30) R. A. Robinson and D. A. Peak, *J. Phys. Chem.*, **39**, 1125 (1935).

(31) S. Sugden, *J. Chem. Soc.*, 316 (1929); *Chem. Abstr.*, **23**, 2423 (1929).

(32) O. R. Quayle, *Chem. Rev.*, **53**, 439 (1953).

(33) API Research Project 44, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, Pa., 1953.

This gives estimates for ΔH_m which are positive values. The fact that the observed values for ΔH_m are positive in all cases for the tris chelates suggests that the interactions in these systems are predominantly of the nonspecific or van der Waals types.

For the tris β -diketonate chelates, the general trend of a significant lowering of the activity coefficient in the QF-1 phase compared to Apiezon L (Table V) and a significant drop in ΔH_m (Table III) are observed. This can be explained by a better matching of solubility parameters (see above) and dipole moments of the chelates in the slightly polar, fluorinated QF-1 ($\delta_2 = 5.4$) phase compared with the nonpolar Apiezon L hydrocarbon phase ($\delta_2 = 7.8$). Thus, the contribution of $(\delta_1 - \delta_2)^2$ to ΔH_m would be less in QF-1 than in Apiezon L, and one might indeed expect the observed lowering of ΔH_m .

Chelates with three unsymmetrical bidentate ligands, such as H(tfa) and H(fod), can exist in both the cis and trans forms. Both of these isomers have a permanent dipole. This dipole has not been measured for the compounds studied in this work; however, Palmer, *et al.*,⁴³ have measured the dipole moments for the related *cis*- and *trans*-Co(tfa)₃ compounds and found 6.48 and 3.80 D, respectively.

The contribution of dipole-dipole interactions to the internal energy can be handled in a method similar to the solubility parameter. If ω_1 and ω_2 are the dipole "solubility parameters" for dipole interactions of the pure solute and solvent, respectively, than eq 9 can be modified to⁴⁴

$$\Delta H_m = V_2^0[(\delta_1 - \delta_2)^2 + (\omega_1 - \omega_2)^2] \quad (10)$$

The permanent dipole in these chelates ($\omega_1 > 0$) will lead to a positive contribution to ΔH_m in the hydrocarbon liquid phase ($\omega_2 = 0$) due to the $(\omega_1 - \omega_2)^2$ term being nonzero. In the QF-1 phase, which has a slight dipole ($\omega_2 > 0$), the contribution of the $(\omega_1 - \omega_2)^2$ term will be less.

A rigorous calculation of the predicted values of ΔH_m for these systems is not possible at the present time because of the lack of the physical data needed to obtain accurate values for δ_1 and δ_2 of the pure substances. Estimates of the molar volumes and solubility parameters of these compounds can be made (see above) and attempts to calculate ΔH_m from these properties, while not showing good agreement, at least show some of the trends noted experimentally. This suggests that agreement might be much better with refined values for molar volumes and solubility parameters of the chelates.

Durbin¹⁴ studied several of these chelates in the liquid phases SE-30 and Kel F-200 (trifluorochloroethane polymer). His results for the aluminum, chromium, and rhodium hexafluoroacetylacetonate chelates are shown in Table VI, along with the results for these chelates in the phases studied in this work.

It is interesting to note that the phases QF-1 and Kel F-200 have nearly identical solubility parameters (5.4 and 5.9, respectively) and molecular weights (7300 and 7500, respectively). Therefore, the retention behavior of the chelates in the two phases should be similar. Indeed, the values of ΔH_s (and correspondingly ΔH_m) are identical within experimental error.

TABLE VI
HEATS OF SOLUTION FOR H(hfa) CHELATES IN
SEVERAL LIQUID PHASES, ΔH_s (KCAL/MOL)

Chelate	SE-30 ^a	Kel F ^a	Apiezon L	QF-1	Squalane
Al(hfa) ₃	-11.8	-13.6	-11.4	-14.0	-9.6
Cr(hfa) ₃	-12.4	-14.9	-12.0	-15.1	-11.2
Rh(hfa) ₃	-12.9	-15.3	-13.1	-15.6	-12.0

^a See ref 14.

The heats of solution in the phases SE-30 and Apiezon L also show close agreement, suggesting in this case that even though their estimated solubility parameters differ greatly, the dimethylsiloxane phase interacts in a manner similar to that of a hydrocarbon phase with these chelates. This is not entirely unexpected since the solubility behavior depends upon the peripheral groups, as in the case of *c*-Si₄O₄(CH₃)₈ which acts superficially as a paraffin.⁴⁵

Durbin,¹⁴ in discussing his results, assumed that the interaction of SE-30 liquid phase with the chelates was negligible and that values for the ΔH_s in this phase should closely approximate ΔH_v (*i.e.*, $H_m = 0$). He then attributed the decrease in ΔH_s for the Kel F-200 phase to weak hydrogen bonding between the hydrogen on the chelate ring and fluorines in the liquid phase. According to this reasoning, the values for ΔH_m for the Kel F-200 phase should be negative. However, if we compare the values for ΔH_s with the recently measured values of the heats of vaporization for these chelates, we notice that exactly the opposite is true. The values of ΔH_m are positive in all five phases, and indeed the values for ΔH_s in the Kel F and QF-1 phases are a much closer approximation to the heat of vaporization.

The fact that ΔH_m is positive for these systems shows that nonspecific intermolecular forces predominate and suggests that hydrogen bonding of the type suggested by Durbin does not occur for the tris β -diketonates in these systems. Linck and Sievers⁴⁶ in studying the solvent effects on the nmr spectra of aluminum β -diketonates postulated that the solvent-induced chemical shifts of the chelate ring hydrogen were due to solvation of the metal chelates along their C₃ axes, rather than H bonding to the chelate ring hydrogen.

The Cu(fod)₂ and Pd(fod)₂ chelates do show evidence of some specific interaction in the liquid phase. This is shown by the negative values for ΔH_m and the low value of the activity coefficient. It is not possible at the present time to say what form the specific interaction takes. Possibly it is merely a specific orientation of these planar chelates on the surface of the liquid phase, or it may be some interaction of the liquid phase at the two vacant coordination sites in these molecules. Water is known to coordinate at these axial sites fairly readily in copper(II) β -diketonates and possible active sites on the support could conceivably form weak donor complexes with this chelate.

The values for the activity coefficients listed in Table V represent the total excess free energy of mixing of these systems and take into account both the enthalpy and entropy contributions to the deviations from Raoult's law. Ashworth and Everett⁴⁷ have suggested

(45) J. H. Hildebrand and R. L. Scott, "Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962.

(46) R. G. Linck and R. E. Sievers, *Inorg. Chem.*, **5**, 807 (1966).

(47) A. J. Ashworth and D. H. Everett, *Trans. Faraday Soc.*, **56**, 1609 (1960).

(43) R. A. Palmer, R. C. Fay, and T. S. Piper, *Inorg. Chem.*, **3**, 875 (1964).

(44) D. E. Martire, *Anal. Chem.*, **33**, 1143 (1961).

that the deviations from Raoult's law exhibited by molecules of differing sizes may be expressed as the sum of a temperature-independent (athermal) and a temperature-dependent (thermal) contribution to the logarithm of the activity coefficient

$$\ln \gamma_2 = \ln \gamma_2^{\text{ath}} + \ln \gamma_2^{\text{th}} \quad (11)$$

where $\ln \gamma_2^{\text{ath}}$ arises from the statistical effects due to the size differences of the molecules, and $\ln \gamma_2^{\text{th}}$ is a term associated with the interaction energies between the molecules.

Following Martire's⁴⁸ treatment of the thermodynamics of dilute solutions, the athermal term can be calculated from

$$\ln \gamma_2^{\text{ath}} = \ln (1/r) + 6 \ln (6r/5r + 1) \quad (12)$$

where r is taken as the ratio of partial molar volumes of solvent to solute, V_1^0/V_2^0 . The evaluation of the thermal term is complicated by the fact that there are both enthalpy (h) and entropy (s) contributions to this interaction term

$$\ln \gamma_2^{\text{th}} = \ln \gamma_2^{\text{th,h}} + \ln \gamma_2^{\text{th,s}} \quad (13a)$$

where the first term represents the enthalpy of mixing, ΔH_m , and the second term is a consequence of the effect of a decrease in the excess orientational entropy, ΔS_m^{th} , of the solute molecules due to a lack of randomness in the solution.

$$\ln \gamma_2^{\text{th}} = \Delta H_m/RT - \Delta S_m^{\text{th}}/R \quad (13b)$$

In simplest forms of the theory $\Delta S_m^{\text{th}}/R$ is taken to be zero; however, Langer and Purnell⁴⁹ have noted that this term is sometimes an important contribution to the total excess entropy.

For the systems studied in this work, the size differences between the solute and solvent molecules are large enough to give significant values to the athermal term. Estimates of these effects for several representative systems are given in Table VII. Values for γ_2^{th} in Table VII were calculated from eq 12. Values of V_2^0 for the metal chelates were estimated above and values for V_1^0 of the liquid phase were for the molar volumes representing the number-average molecular weight.¹⁵ A more realistic value for the effective molar volume of the liquid phase would represent some contact segment of the molecule as discussed by Huggins.^{50,51} Thus the values for r listed in Table VII would represent maximum values and actual effects on γ_2^{ath} would be somewhat less than this. A great deal of work is needed to refine the estimates in Table VII further and would

(48) D. E. Martire in "Gas Chromatography—Rome 1966," A. B. Littlewood, Ed., The Institute of Petroleum, London, 1966.

(49) S. H. Langer and J. H. Purnell, *J. Phys. Chem.*, **67**, 263 (1963).

(50) M. L. Huggins, *ibid.*, **74**, 371 (1970).

(51) M. L. Huggins, *ibid.*, **75**, 1255 (1971).

TABLE VII
ESTIMATED SIZE EFFECTS OF ACTIVITY COEFFICIENTS
FOR METAL β -DIKETONATES

Chelate	Liquid phase	$r(V_1^0/V_2^0)$	γ_2^{ath}
M(hfa) ₃	Squalane	1.17	0.99
M(hfa) ₃	Apiezon L	3.91	0.57
M(hfa) ₃	QF-1	12.70	0.21
M(tfa) ₃	Apiezon L	4.62	0.50
M(tfa) ₃	QF-1	15.00	0.18
M(fod) ₃	Apiezon L	2.40	0.77
M(fod) ₃	QF-1	7.80	0.33

be of great help in the further understanding of these systems.

It should be noted in Table VII that there is a definite decrease in the activity coefficient in going from the Apiezon L to the QF-1 liquid phase, but this is not the entire contribution to the decrease in γ_2 shown in Table V above. A large portion of the decrease in activity coefficient between the two phases is due to the $\ln \gamma_2^{\text{th,h}}$ term in eq 13 as represented by the values for the excess heats of mixing shown in Table VI. Attempts to calculate γ_2 by combining eq 12 and 13 above, with the assumption that the contribution from $\gamma_2^{\text{th,s}}$ is negligible, led to poor quantitative agreement with experimental values. However, most of the major trends predicted from these calculations were observed in the experimental results. The poor quantitative agreement can be explained by several factors: (1) the extreme sensitivity of excess enthalpies to experimental error⁴⁸ with resultant error in calculation of the $\ln \gamma_2^{\text{th,h}}$ term, (2) the estimates involved in the partial molar volumes in the $\ln \gamma_2^{\text{ath}}$ term, and (3) the assumption that the $\ln \gamma_2^{\text{th,s}}$ term is negligible for these systems which is probably very poor (the liquid phases are polymer solutions with long-chain molecules and orientational and conformational randomness may not exist).

In the case of the square-planar chelates, the significant drop in activity coefficients relative to the octahedral chelates (which have approximately spherical shape) may have a very large contribution from the $\gamma_2^{\text{th,s}}$ term. It would not be unreasonable to postulate that the long-chain molecules of the liquid phase could solvate the chelate in such a manner as to prevent complete randomness of orientation, leading to a significant contribution to the excess free energy of mixing from the entropy terms.

It is felt that a more rigorous examination of these systems in the framework of the most recent theories of dilute solutions of nonelectrolytes will give valuable insight into their further understanding and also serve as a challenging test of these theories.

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