Optical Spectra and Densities of Molten Chloride Salts Having Large Nickel Chloride Concentrations. Nickel Chloride–Tri-*n*-butylbenzylphosphonium Chloride Systems up to 33.3 Mole % Nickel Chloride[1a]

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Abstract: The optical absorption spectra of nickel chloride–tri-*n*-butylbenzylphosphonium chloride melts and glasses were measured over the wavelength range of 350–1650 mμ, at compositions of 0.1–33.3 mole % $NiCl_2$, at temperatures of 22–174°, and with path lengths of 0.007–1.00 cm. It was concluded that the nickel in these melts was present almost exclusively as approximately tetrahedral $NiCl_4^{2-}$ anions under all conditions studied. The internal absorbance, A, at all wavelengths was found to be proportional to the molar concentration of $NiCl_2$ to within a small error over the entire composition range at 174°. Furthermore, A was a linear function of temperature over the range 22–172° at a fixed composition of 33.3 mole % $NiCl_2$. In order to interpret absorption intensities in terms of volume concentrations, the densities of molten mixtures containing 5.03–33.44 mole % $NiCl_2$ were measured as functions of temperature. The molar volume at a fixed temperature was found to be a linear function of the mole per cent composition.

Extensive studies have been made of the absorption spectra of dilute solutions of transiton metal halides in molten halide salts.[2] These studies provide information on the coordination geometry of the transition metal ions. At this laboratory we are extending such measurements to melts that contain large concentrations of transition metal ions including concentrations large enough to represent molten compounds. In such studies one is able to deal with important questions that cannot very well be answered from measurements on dilute solutions. For example, one may inquire as to what extent the coordination geometry in a crystal is preserved or destroyed upon melting.

In the present paper we describe work on the system nickel chloride–tri-*n*-butylbenzylphosphonium chloride. The measurements show that in melts ranging in composition from dilute solutions of $NiCl_2$ in $[(C_4H_9)_3PCH_2C_6H_5]Cl$ up to the composition of the compound $[(C_4H_9)_3PCH_2C_6H_5]_2NiCl_4$ the nickel is present exclusively as the approximately tetrahedral complex anion $NiCl_4^{2-}$ to within a small error. The internal absorbance of melts was found to be proportional to the molar concentration of nickel (Bouguer–Beer law) to within a small uncertainty at all wavelengths over the entire concentration range. This quantitative result permits one to exclude all but a trace of other coordination geometries at all concentrations, and shows that changes in the environment of $NiCl_4^{2-}$ due to changes in composition are sufficiently small as to have no consequential effects on the intraconfigurational states of Ni^{2+}. Studies of the effect of temperature on the spectral profile showed a quantitatively simple behavior like that reported by Morrey[3] for other molten salt systems. These results indicate that there was no significant change in coordination geometry on cooling.

In order to perform a Bouguer–Beer's law study it was necessary to know the molar volumes of the melt. Hence, we measured the density of various mixtures and report the results here.

Experimental Section

Chemicals. Anhydrous nickel(II) chloride was prepared from $NiCl_2 \cdot 6H_2O$. Water was driven from the hydrated salt by heating slowly up to 450° under a flowing atmosphere of dry hydrogen chloride. Then the dehydrated material was purified by sublimation under hydrogen chloride at 800 to 900°.

Tri-*n*-butylbenzylphosphonium chloride ($[(C_4H_9)_3PCH_2C_6H_5]Cl$, designated Bu_3BzPCl in this paper) was prepared from the reaction between tri-*n*-butylphosphine and excess benzyl chloride in an anhydrous ethanol medium under 1 atm of dry nitrogen. When the reaction was completed, the solvent and excess benzyl chloride were removed by vacuum distillation at successively higher temperatures up to 150°. The phosphonium chloride product was further purified by recrystallization from anhydrous ethanol–diethyl ether mixtures followed immediately by prolonged vacuum drying while slowly heating to 80°. Melting point of the product was 163.0–163.5°.

Anal. Calcd: C, 69.3; H, 10.0; Cl, 10.3. Found: C, 69.4; H, 10.4; Cl, 10.8.

Previous work indicates that Bu_3BzPCl is stable in the molten state at temperatures not far above the melting point so long as the liquid is kept under an inert atmosphere.[4] We performed the following additional test which supports this conclusion. A sample of molten phosphonium salt at 180° was kept under an atmosphere of purified nitrogen for about 240 hr in an optical absorption cell with a 1-cm path length. At 12-hr intervals measurements were made of the light absorption in the region of a minimum in the ultraviolet spectrum. During this 240-hr test there was no observable change in the absorbance of the minimum.

In all of the measurements reported here molten Bu_3BzPCl and molten $NiCl_2$–Bu_3BzPCl mixtures were protected from oxidation by 1 atm of purified nitrogen. The composition of mixtures was determined by weighing the components prior to mixing.

Nickel chloride dissolved very slowly in melts that already contained more than a few per cent of this material. At 175° about 24 hr of continuous agitation was required to dissolve 5 mole % nickel chloride in Bu_3BzPCl, and about 72 hr was required to dissolve 33 mole %. Nickel chloride rich mixtures readily supercooled to form glassy materials at room temperature.

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[2] See, for example, G. P. Smith in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers Inc., New York, N. Y., 1964, pp 427–505.

[3] J. R. Morrey, *J. Phys. Chem.*, **66**, 2169 (1962).

[4] T. R. Griffiths, *J. Chem. Eng. Data*, **8**, 568 (1963).

Density Measurements. The density of melts was measured by the buoyancy method. A platinum bob, suspended from a balance beam by a fine platinum wire, was weighed both in air and in a melt. The density of the melt was calculated from the weight difference. The apparatus of Smith and Petersen,[5] as modified by Griffiths,[4] was used for these measurements.

Spectrophotometric Measurements. Absorption spectra were measured with a Cary Model 14-H spectrophotometer. The melts were contained under nitrogen in silica absorption cells with a 1-cm path length that was reduced to as little as 0.007 cm by means of silica inserts. Descriptions have been published of the cells,[6] the method of calibrating short path lengths,[7] and the spectrophotometer furnace.[8] The furnace was designed for measurements at very high temperatures, and the uncertainty in temperature determination was probably 2° at the relatively low temperatures reported here.

Spectra were measured against dry nitrogen as reference so that the quantity measured was the apparent absorbance, log (P_i/P_t), where P_i is the radiant power incident on the cell and P_t is the power transmitted through the cell and its contents. The spectra were chart recorded.

The quantity which we wished to glean from the spectra was the internal absorbance, $A = \log (P_0/P)$, where P is the radiant power rectilinearly transmitted through some specified distance (the path length) in the molten mixture when a power P_0 enters the melt over a flat plane at normal incidence. Values of A for a liquid $NiCl_2$–Bu_3BzPCl mixture were estimated by subtracting the apparent absorbance of a cell and insert containing pure liquid Bu_3BzPCl at a specified temperature from the apparent absorbance of the same cell and insert containing the liquid mixture at the same temperature. For the wavelengths reported here the internal absorbance of silica in the cell and insert and of pure liquid Bu_3BzPCl at a path length of 0.013 cm was small at most wavelengths so that this method of estimating A amounted largely to correcting for interface reflections. We estimate that the error made in this method of correction was usually less than 0.01 absorbance unit.

We define the molar extinction coefficient, ϵ, to be A/bM, where A is the internal absorbance, b the path length in centimeters, and M the concentration of nickel in moles/liter.

Wavenumbers are reported here in kilokaysers (kK), where 1 kK equals 10^3 cm^{-1}.

Results

Density. The density of molten $NiCl_2$–Bu_3BzPCl mixtures was measured at four to six temperatures at each of four melt compositions, and the data at each composition were fitted to the empirical relation $\rho = \alpha - \beta t$ by the method of least squares. In this relation ρ is the density in g/cc, t is the temperature in °C, and α and β are empirical parameters. The results are listed in Table I together with Griffiths' parameters[4] for pure Bu_3BzPCl. We also redetermined the density of pure Bu_3BzPCl at five temperatures over the range of 171–185°, and our results are represented by Griffiths' parameters to within a standard deviation of 0.0005 g/cc.

Table I. Density Equations for Nickel Chloride–Tri-*n*-butylbenzylphosphonium Chloride Mixtures

	$\rho = \alpha - \beta t$			
Mole % $NiCl_2$	α, g/cc	$\beta \times 10^4$, g/cc deg	Std dev $\times 10^3$, g/cc	Temp range, °C
0	1.021	5.48	0.2	178–240[a]
5.03	1.028	5.1	1.0	161–183
10.10	1.048	5.4	0.7	157–178
20.76	1.081	5.3	0.6	134–183
33.44	1.180	7.8	1.1	120–164

[a] From ref 4.

At temperatures on the order of 160–180°, the molar volume was found to be a linear function of the mole fraction of the constituents.

Spectra. The absorption spectra of $NiCl_2$–Bu_3BzCl_2 mixtures were measured over the wavelength range of 350–1650 mμ at $NiCl_2$ concentrations from about 0.1 to 33.3 mole %. At the lowest concentration, measurements were made at the single temperature of 174°, while at successively higher concentrations measurements were made over a successively wider range of temperatures that extended downward from 174°. At 33.3 mole % $NiCl_2$ spectra were measured over the range of 22–174°. Various path lengths were used from 1 to 0.007 cm.

At all concentrations and temperatures the spectra were very similar. When the temperature was lowered at a fixed composition, bands shifted slightly in position and narrowed in width. In a few instances bands which overlapped at high temperatures to such an extent that they could hardly be identified as separate absorptions became clearly resolved at low temperatures. Nevertheless, at all temperatures there was every indication that the same set of optical transitions was involved under all experimental conditions.

Smith, Liu, and Griffiths[9] previously measured the spectra of $NiCl_2$–Bu_3BzPCl melts in the dilute solution range of 0.001–0.03 M at 134°. The upper end of this range, 0.03 M, corresponds approximately to 1 mole % so that the measurements reported here overlap the previous determinations with which they are in excellent agreement. Inasmuch as Smith, Liu, and Griffiths described the spectrum in considerable detail, we shall not pictorially present it here. The princial features of the spectrum as measured here at 174° were the following. The most intense absorption consisted of a group of three overlapping bands with two maxima at 14.13 kK (707 mμ) and 15.34 kK (652 mμ), and a shoulder near 16.2 kK (~617 mμ). A band of intermediate intensity occurred at 7.41 kK (1350 mμ), and weak bands were found at 11.59 kK (peak, 863 mμ), ~12.5 (shoulder, ~800), ~20.5 (shoulder, ~488), and ~22.2 (shoulder, ~450). The last two bands were not reported by Smith, Liu, and Griffiths for $NiCl_2$–Bu_3BzPCl melts although these authors found similar bands in other solvent systems which contained the same light-absorbing entity.

Effect of Concentration. A quantitative survey of concentration dependence was conducted in the following way. At 174° seven successive additions of $NiCl_2$ were made to molten Bu_3BzPCl contained in a cell with insert to give a measured path length of about 0.013 cm. Determinations were made of the spectrum of pure Bu_3BzPCl and of the mixtures formed by each addition of $NiCl_2$. The compositions produced by these additions were 1.65, 5.75, 9.69, 15.04, 20.04, 24.55, and 33.30 mole % $NiCl_2$. Because of the slow rate of dissolution of $NiCl_2$ in the more concentrated mixtures, long equilibration times were allowed following each addition, and the melts were stirred by vertical motion of the insert. The experiment required 2 weeks. The progress of dissolution was followed by visual inspection of the melt under intense illumination.

A single path length was used for all measurements because the largest source of error in the work de-

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[5] G. P. Smith and G. F. Petersen, *J. Chem. Eng. Data*, **6**, 493 (1961).
[6] C. R. Boston and G. P. Smith, *J. Phys. Chem.*, **62**, 409 (1958).
[7] G. P. Smith and C. R. Boston, *J. Chem. Phys.*, **34**, 1396 (1961).
[8] C. R. Boston and G. P. Smith, *Rev. Sci. Instr.*, **36**, 206 (1965).
[9] G. P. Smith, C. H. Liu, and T. R. Griffiths, *J. Am. Chem. Soc.*, **86**, 4796 (1964).

scribed here is the determination of short path lengths. At a path length of 0.013 cm, the most strongly absorbing band maximum had an absorbance of about unity at a composition of 15.04 mole % $NiCl_2$. At all concentrations the highest absorbance value that was measured was a little above 2 absorbance units. Consequently, the absorbance of the most intense bands at their maxima (652 and 707 mμ) was determined at 24.55 mole % $NiCl_2$ but not at 33.30 mole %. However, the absorbance of the sides of these bands was measured at all compositions.

For this series of measurements the internal absorbance was obtained at many wavelengths over the entire wavelength range and a selection of representative results is presented in Figure 1, where the ratio of absorbance to path length, A/b, is plotted against the molar concentration of $NiCl_2$. Each straight line in this figure is labeled with the wavelength in mμ at which the experimental points were measured. These lines pass through the origin and best represent the data at intermediate concentrations.

Data for the three most intense maxima, 1350, 707, and 652 mμ, are shown in Figure 1. The latter two had the same absorbance to within experimental error. The data at 877 mμ correspond to a position on the low-energy side of the weak band that had a maximum at 863 mμ. The remaining data shown in Figure 1 are for wavelengths on the sides of the broad absorption formed by overlap of the most intense bands. Only three points are shown in Figure 1 for absorption at compositions of 1.65 and 5.75 mole % $NiCl_2$ (concentrations below 0.2 M) because these data are poorly represented by the scale of the figure. However, all data in this low concentration range fit the indicated straight lines in a satisfactory way.

The precision of the data varied substantially with wavelength because many of the data were measured at positions where the absorbance changed rapidly as a function of wavelength and, hence, were sensitive to small wavelength errors. For those wavelengths at which A was most sensitive to wavelength errors, 725 mμ, for example, we estimate that the error in the relative value of A due to this source could be as great as 1.5%. On the other hand, there are no significant errors of this type in the data at 1350, 707, and 652 mμ. Percentagewise, the error made in estimating internal absorbance from apparent absorbance could be significant for weak absorptions such as that at 877 mμ but is inconsequential at the relatively intense 652- and 707-mμ maxima.

It will be seen from Figure 1 that the data at each wavelength are well represented by a straight line that passes through the origin. Taking all of the data into account, the only uniform deviation from straight-line behavior of any consequence occurred at 24.55 mole % $NiCl_2$ (0.880 M) where the experimental points lay about 2–3% below the indicated straight lines. Some of the data at 33.30 mole % (1.323 M) deviated by this much, but some hardly deviated at all. At compositions below 24.55 mole % $NiCl_2$, the data fitted the appropriate straight lines to within experimental error. For example, at 652 and 707 mμ, absorbance values at compositions of 1.65–20.04 mole % $NiCl_2$ fitted a straight line that passed through the origin to withstand a standard deviation of 0.007 absorbance unit, which is about 0.7% of A at 15 mole %. Likewise, the standard deviation at 600 mμ was 0.002 absorbance unit (~0.4% of A at 15 mole %), and at 1350 mμ was 0.005 absorbance unit (~4.5% of A at 15 mole %). Similar statements of precision apply at all wavelengths investigated.

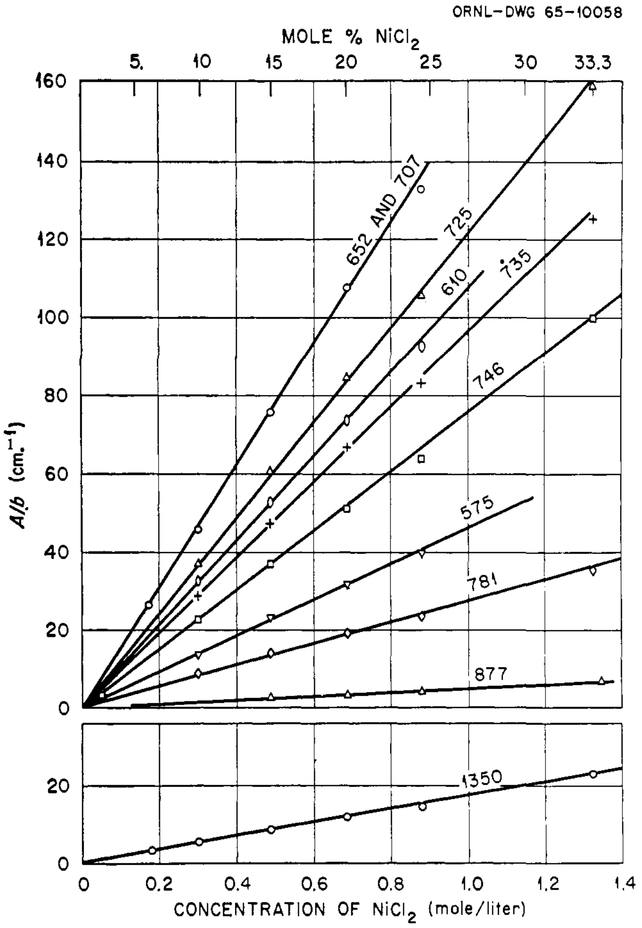

Figure 1. Absorbance per unit path length as a function of the molar concentration of $NiCl_2$ at representative wavelengths. Each set of data is labeled with the wavelength in mμ. All measurements were made at 174° with the same cell and insert at a path length of 0.013 cm. Most of the available absorbance data below 0.2 M are not plotted but lie close to the appropriate straight lines as discussed in the text.

The molar extinction coefficient, computed as the slope of the best straight line on an A/b *vs.* M plot, was 156 l./mole cm at the 652- and 707-mμ band maxima with an uncertainty on the order of 5% because of the uncertainty in the path length. The molar extinction coefficient of the 1350-mμ band was about 18 ± 2 l./mole cm.

In order to obtain more reliable estimates of molar extinction coefficients, measurements were made with a 1.00-cm cell at 0.112, 0.119, and 0.336 mole % $NiCl_2$ and 174°. The value of A was found to be 162 l./mole cm at the 652-mμ maximum and 161 l./mole cm at the 707-mμ maximum. These values are satisfactorily close to those reported above and are in agreement with the values of Smith, Liu, and Griffiths[9] at 165° (161 l./mole cm for the 652-mμ band and 159 l./mole cm for the 707-mμ band). Additional measurements with a 0.0236-cm path length and concentrations of 5.11, 10.00, 13.96, and 18.00 mole % at 174° confirmed the linear dependence of A on M and gave a value of 160 l./mole cm for the 652-mμ band maximum.

Temperature Effects. The spectrum of a mixture containing 33.3 mole % $NiCl_2$ in a cell of 0.007-cm path length was measured at 22, 31, 42, 67, 119, and 172° over the visible range. These measurements gave data on the thermal behavior of the relatively broad and intense absorption composed of two peaks and a high-energy shoulder. With increasing temperature over the full range (22–172°), the band maximum near 707 mμ (14.13 kK) shifted slightly toward higher energies (blue shift) by roughly 0.04 kK and decreased in A by about 24%. At the same time the other maximum shifted from about 660 mμ (15.15 kK) to about 652 mμ (15.34 kK) for a blue shift of 0.19 kK and decreased in A by about 21%. Both maxima had the same A value at 172°.

As the band maxima decreased in intensity on heating, the composite absorption broadened by a small amount and points of thermally invariant A (isosbestic points) were formed on either side of the absorption at about 616 and 732 mμ. The change in A with increasing temperature was measured at several fixed wavelengths (mμ), namely, 580 (on the lower part of the high-energy band edge), 660 (near a band maximum), 680 (near the minimum between the two bands), and 710 (near the other band maximum). At each of these four wavelengths A was a linear function of temperature. At 680 mμ, for example, dA/dt was -0.00172 absorbance unit/deg and the standard deviation from a straight line of the form $A = (dA/dt)t + A_0$, where A_0 is the intercept, was 0.005 absorbance unit or about 2% of the change in A in going from 22 to 172°. The set of deviations appeared to be random and was consistent with the uncertainty in A due to a combination of noise and the uncertainty in temperature. With increasing temperature A increased at 580 mμ and decreased at the other wavelengths.

It was noted that two very weak bands may be observed at 174° on the high-energy side of the region of relatively intense absorption in the visible. When the temperature was lowered substantially below 174°, the decrease in intensity of the high-energy foot of this intense absorption exposed a third weak band. In particular, at 29° weak bands (mμ) were observed at 434 (23.0 kK, peak), ~500 (20.0 kK, well-formed shoulder), and 517 (19.34 kK, peak) for a mixture containing 33.3 mole % $NiCl_2$ in a cell with a 1-cm path length.

Discussion

Band Assignments. It was established previously[9] that the spectrum of dilute solutions of $NiCl_2$ in liquid Bu_3BzPCl is that of the approximately tetrahedral $NiCl_4^{2-}$ anion. The spectrum that we measured in the same composition range agreed in a quantitatively detailed way with that of $NiCl_4^{2-}$. The assertions made here regarding band assignments presuppose a familiarity with the previous analysis.[9]

Orbital assignments of the spin-allowed absorptions are as follows: 7.41 kK to $^3T_1(F) \rightarrow {}^3A_2(F)$; and 14.12, 15.34, and 16.2 kK to $^3T_1(F) \rightarrow {}^3T_1(P)$. The weak band at 11.59 kK is a component of the spin-forbidden $^3T_1(F) \rightarrow ({}^1D)$ transition; possibly it is $^3T_1(F) \rightarrow {}^1E(D)$. The assignment of the faint shoulder at 12.5 kK is quite uncertain.

The very weak bands at 19.34, 20.0, and 23.0 kK lie in the general region where the various components of $^3T_1(F) \rightarrow ({}^1G)$ are expected. These bands were not reported by Smith, Liu, and Griffiths for $NiCl_4^{2-}$ in another medium. Using parameters appropriate for $NiCl_4^{2-}$, the following transitions were predicted by the four-parameter point-charge model: $^3T_1(F) \rightarrow {}^1T_2(G)$ at 17.05 kK, $^1T_1(G)$ at 18.46 kK, $^1A_1(G)$ at 18.60 kK, and $^1E(G)$ at 19.99 kK. These band-energy estimates are expected to be too low by roughly 1 to 2 kK because the $^1G_4$ term of free Ni^{2+} is incorrectly predicted by the Slater–Condon–Shortly theory to lie about 1.4 kK below its measured position. Furthermore, the bands estimated to occur at 18.46 and 18.60 kK lie too close together to be resolved under the conditions of the present investigation unless they proved to be unexpectedly sharp. Therefore, the simple four-parameter point-charge model of cubic complexes leads us to expect three weak (because they are spin forbidden) bands at about 18.5, 20.0, and 21.5 kK. Considering the deficiencies of the point-charge model we regard this as a reasonable agreement with our measurements and make the tentative assignments of 19.34 kK to $^3T_1(F) \rightarrow {}^1T_2(G)$, 20.0 kK to $^3T_1(F) \rightarrow {}^1T_1(G)$, $^1A_1(G)$, and 23.0 kK to $^3T_1(F) \rightarrow {}^1E(G)$.

We can fairly well exclude the possibility that these weak bands are due to trace Co^{2+} contaminations because this ion in molten Bu_3BzPCl has intense bands at 18.8, 19.3, 22.1, and 22.4 kK.[10]

Effect of Composition. The measurements showed that at 174° A was proportional to the molar concentration of nickel to within a small uncertainty over almost the entire composition range. That is, the Bouger–Beer law was obeyed at all wavelengths at which the absorption intensity was sufficiently great to provide meaningful measurements.

There seems to be no plausible accounting for this proportionality other than to conclude that all of the nickel ions formed a single entity, the $NiCl_4^{2-}$ anion, to within a small uncertainty. Strictly speaking, obeyance of the Bouguer–Beer law of itself only assures that if more than one entity is formed, the concentrations of all entities are in fixed proportions at all concentrations. However, all bands except very weak ones could be unambiguously attributed to $NiCl_4^{2-}$, and any other chloronickel(II) complexes of virtually any coordination geometry should have absorbed somewhere within the wavelength range investigated had they been present. The combination of these facts limits nickel-containing entities other than $NiCl_4^{2-}$ to very small concentrations.

The systematic deviation from proportionality of 2–3% at 24.55 mole % $NiCl_2$ was not wavelength dependent and, hence, was not the sort of effect which one would expect if a portion of the nickel were tied up in a complex other than $NiCl_4^{2-}$. This deviation is most plausibly attributed to a weighing error.

The deviations at 33.30 mole % $NiCl_2$ differed from those at 24.55 mole % in that they were wavelength dependent. These deviations were somewhat larger than we expected from experimental errors but not a great deal larger. Therefore, it is possible that at 33.30

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(10) G. P. Smith and S. von Winbush, unpublished measurements.

mole % a second complex is making its appearance although still at a low concentration.

We have one reservation to make with regard to these deductions. It is possible although not likely that the spectrum of a polynuclear anion, such as $Ni_2Cl_6^{2-}$ or $Ni_2Cl_7^{3-}$ in which each nickel retains a tetrahedral coordination geometry, might be indistinguishable from that of the mononuclear $NiCl_4^{2-}$ anion.

Temperature Effects. The results presented here for the effect of temperature on the $^3T_1(F) \rightarrow {}^3T_1(P)$ absorption of a 33.3 mole % mixture are in agreement with Morrey's rule[3] for the behavior of a one-entity system; namely, A varied linearly with temperature at every wavelength.

Although we do not believe that Morrey's rule has general validity,[11] we propose that the small changes in spectral profile observed in the present case are reasonably consistent with the view that absorption was due to a single species of molecule ion. The most conspicuous changes were a small band broadening accompanied by a decrease in the intensity of maximum absorption. The band energies changed very little, but the direction of this small change—a blue shift with increasing temperature—was contrary to that expected from elementary considerations in terms of a Franck–Condon model.

Concluding Remarks. In summary we conclude that over the range 0.1–33.3 mole % $NiCl_2$ all of the nickel in $NiCl_2$–Bu_3BzPCl melts was present as $NiCl_4^{2-}$ to within a small uncertainty.

We are led to the following point of view. Upon dissolution of $NiCl_2$ in molten Bu_3BzPCl virtually every mole of $NiCl_2$ reacts with 2 moles of chloride ions from Bu_3BzPCl to form 1 mole of $NiCl_4^{2-}$ molecule anions. At 33.3 mole % $NiCl_2$ the free chloride ions are consumed and the melt may be regarded as the liquid compound $(Bu_3BzPCl)_2NiCl_4$. For homogeneous mixtures containing somewhat more than 33.33 mole % $NiCl_2$, a second nickel-containing entity must be present in addition to $NiCl_4^{2-}$. Undoubtedly this second entity is present in equilibrium with $NiCl_4^{2-}$ at all concentrations, but the equilibrium must strongly favor $NiCl_4^{2-}$ except at very small free chloride ion concentrations.

The fact that the Bouguer–Beer law is obeyed at all compositions not only implies that the coordination sphere of nickel remains unchanged over the entire composition range, it also implies that the surroundings of the chloronickel complex do not change sufficiently to perturb the intraconfigurational states of nickel in any different way at high concentrations than at low concentrations. This invariance of the effect of the surroundings, one might suppose, may be associated with the large size of the phosphonium cations so that the $NiCl_4^{2-}$ anions are primarily in contact with phosphonium cations at all compositions. Only the anionic composition is altered by changing the nickel content, and anion–anion contacts are presumably infrequent. The latter pictorial details cannot, however, be formulated quantitatively because there is very little systematic information on the effect which changes in the surroundings have on the states of halonickel complexes.

Acknowledgments. We gratefully record our thanks to C. R. Boston and W. M. Ewing for generous aid during this investigation, and to H. L. Holsopple for preparing the phosphonium salt.

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[11] An analysis of Morrey's rule will be published by J. Brynestad and G. P. Smith.

Relation of the Relaxation Time of Electric Dipoles in Condensed Phase to Molecular Structure

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Abstract: The relaxation rate of polar molecules in the condensed phase is treated as proportional to the frequency of a torsional oscillator in the periodic force field of its neighbors. Hence a reduced relaxation time $\tau_i^* \equiv \tau(E^\circ/I_i)^{1/2}$ can be defined, where E° is the appropriate lattice energy and I_i is the applicable principal moment of inertia of the dipole molecule. A corresponding states plot of log τ_i^* *vs.* the inverse of the common reduced temperature T^* leads to bands characteristic of structurally related "families" of compounds rather than a universal correlation. A simple geometrical structure parameter (characterizing the surface roughness of molecules) is proposed as a third correlating parameter. Typical of the correlation within a given band is the wide range of normal haloalkanes for which log τ^* *vs.* $(T^*)^{-1}$ falls on a single curve, regardless whether as pure liquid or admixed with solvents including solution in viscous paraffin oil. It appears that replacement of E° by the geometric mean lattice energy, etc., suffices to correlate relaxation times of solutions. Reference to the solvent viscosity (or any other viscosity), long recognized as unsatisfactory, is thereby obviated.

The present work has been undertaken as part of an effort to develop correlations of rotational and mass diffusion in the condensed phase without reference to viscosity. Macroscopic viscosity has been a moderately successful descriptor of liquids for predicting rotational and mass diffusion in simple systems but has become increasingly unsatisfactory for systems where small solute molecules diffuse in liquids com-