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Abstract

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Physical Chemistry

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Temperature and Concentration Dependence of the Frequencies and Intensities of Raman Scattering Lines of Mixtures of Ketones with Chloroform

The study of IR absorption spectra and Raman scattering spectra of the acetone–chloroform system showed that the frequencies of the stretching vibrations of the carbonyl group and of the C–H group of chloroform do not change in comparison with their values in the individual substances. Meanwhile, the intensity of the corresponding bands increases significantly ([1–4]). The increase in intensity in this case is the result of the formation of a molecular compound. This example shows that the formation of a hydrogen bond may be reflected to a considerable extent in the intensities and to a lesser extent in the vibration frequencies.

To clarify the nature of the interaction, we investigated the temperature dependence of the frequencies and intensities of Raman scattering lines in the nonpolar solvent hexane, and also in ketone–chloroform mixtures. Upon lowering the temperature, the interaction manifests itself more distinctly, since the thermal disorientation that hinders the formation of molecular compounds decreases. Below we present experimental data on the concentration and temperature dependence of the Raman scattering lines corresponding to the stretching vibrations of the C=O bonds of ketones and of the C–H, C–Cl bonds of chloroform in the systems, as well as in the corresponding individual substances.

In Tables 1 and 2 the integral intensities $I = \int I_\nu d\nu$ are given, expressed on an arbitrary scale, where the intensity of the Raman scattering line of an individual substance at $t = +30^\circ$C, referred to one mole, is taken as 100.

The measurements were performed on an ISP-51 spectrograph with photoelectric recording of the spectrum. The optical part of the temperature apparatus consisted of a thermostated cuvette. The required temperature was attained by

evaporation of liquid nitrogen. When measuring intensities at different temperatures it is necessary to take into account the change in the ratio n^2/d, where n is the refractive index and d the density. In our experiments the greatest change in this quantity over the temperature interval from $+30^\circ$ to -90° is about 4%. The error in measuring intensities is 10%, and in measuring frequencies ± 2 cm^{-1}. The temperature from $+30$ to -30° was measured with an accuracy of up to 1°. The errors in measuring lower temperatures did not exceed 3°.

The experiments show that the intensity of the C=O and C–H lines increases in the ketone + chloroform system and decreases in solutions of these substances in hexane. The intensity of the C–Cl line in both cases changes practically not at all (Fig. 1). The constancy of the frequency and intensity of the C–Cl line indicates that the intermolecular interaction affects mainly the C=O bonds of the ketone and the C–H bond of chloroform. The picture of hydrogen-bond formation is complicated by the fact that ketones at room temperature are strongly associated and, apparently, partially dimerized. This con–

Table 1

Concentration dependence of frequencies and intensities

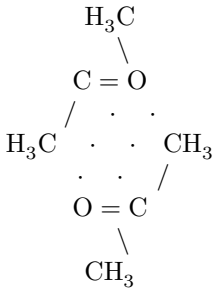
Acetone + chloroform + hexane			Acetone + hexane		Acetone + chloroform			Acetophenone + hexane		Acetophenone + chloroform			Chloroform + hexane						
Acetone conc. [C], mol/l	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	$I_{C=O}$	Acetone conc. [C], mol/l	$\Delta\nu_{C=O}$	$I_{C=O}$	Acetophenone conc. [C], mol/l	$\Delta\nu_{C=O}$	$I_{C=O}$	Chloroform conc. [C], mol/l	$\Delta\nu_{C-H}$	I_{C-H}	$\Delta\nu_{C-Cl}$	I_{C-Cl}	$\Delta\nu_{C-H}$	I_{C-H}	$\Delta\nu_{C-Cl}$	I_{C-Cl}
13.6	1708	100	1708	100	8.5	1682	100	1682	100	12.5	3019	100	667	100	3019	100	667	100	
6.8	1709	131	1712	91	4.3	1682	116			6.7					3019	87	668	95	
5.5	1711	137	1714	85	4.0			1686	106	6.2	3018	127	667	97					
4.2	1712	155			2.0	1681	139			4.0	3018	140	667	104					
2.3	1713	158			1.3			1691	115	3.8									
2.1			1716	74	1.1	1681	149			3.6					3019	78			
					0.7			1693	118	2.7	3017	148	667	103			669	99	
					0.3	1680	170			1.9									
										1.8	3016	158	667	101			669	101	

Table 2

Temperature dependence of frequencies and intensities

	Acetone + chloroform, 7 mol/L		Acetone + chloroform, 7 mol/L		Acetone + hexane, 6.2 mol/L		Acetone + hexane, 6.2 mol/L		Diethyl ketone + chloroform, 7.5 mol/L		Diethyl ketone + chloroform, 7.5 mol/L		Acetone, 13.6 mol/L		Acetophenone, 4.8 mol/L		Acetophenone + chloroform, 2.5 mol/L		Acetophenone + hexane, 2.5 mol/L		Acetophenone + chloroform, 9 mol/L		Acetophenone + hexane, 9 mol/L		Benzophenone, 0.7 mol/L		Benzophenone + chloroform, 3.2 mol/L		Benzophenone + chloroform, 12.5 mol/L	
t, °C	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	I_{CH}	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	I_{CH}	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	$I_{C=O}$	$\Delta\nu_{C=O}$	I_{CH}
+30	1708	133	3019	108	1712	94	1708	100	1711	123	1681	133	3019	120	1693	118	1656	131	3019	100								
0		151														123												
−10				123				119				156				128	1655	170	3019	117								
−20	1705	172	3016		1709	109	1705	128			1677	157			1691	129												
−30				138				134			1675	166	3015	145			1653	173	3019	123								
−40											1674	168																
−50	1703	188	3014	145	1705	125	1703	143	1707	146	1672	185	3013	163			1652	203	3019	130								
−60																			3019	140								
−70	1702	206	3012	165	1703		1700	154		160							1650	226										
−90	1698	222	3010				1699	167	1703	196																		

is confirmed by the increase in the vibration frequency of the carbonyl group of ketones in hexane when ketone dimers, associated probably in the form of quadrupoles, dissociate:



Such an assumption agrees with experiments on the dielectric polarization of acetone solutions, which changes from 160 cm^3 in extremely dilute solutions in nonpolar solvents to $\simeq$ 40 cm^3 in pure liquid acetone ([5]). In the presence of $CHCl_3$, the vibration frequency of the carbonyl group does not change, despite

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

the fact that chloroform causes dissociation of the dimers. This is explained, possibly, by the fact that simultaneously with the dissociation of the dimers there occurs the formation of a molecular compound with chloroform, and moreover

Fig. 1. Concentration dependence of the intensities of chloroform lines:
1 –intensity of the C–H line (3019 cm^{-1}) in acetone solution;
2 –intensity of the C–Cl line (667 cm^{-1}) in acetone and hexane solutions;
3 –intensity of the C–H line (3019 cm^{-1}) in hexane solution

Fig. 2. Temperature dependence of the intensity of the acetone line (1708 cm^{-1}):
1 –in chloroform solution (6.5 mol/l);
2 –pure acetone;
3 –in hexane solution (7.5 mol/l)

the vibration frequencies of the carbonyl group in dimers and in the molecular compound are very close. Another reason for the constancy of the frequencies is the relatively low concentration of complexes at room temperature. Thus, when the temperature is lowered to -90°, the vibration frequency of the C–H bond of chloroform, $\Delta\nu = 3019$ cm^{-1}, in the acetone–chloroform system decreases to 3010 cm^{-1}, whereas in pure chloroform it remains unchanged down to its melting temperature.

The change in the intensity of the carbonyl-group line in liquid acetone, in a solution of acetone in hexane, and in a mixture of acetone with chloroform as a function of temperature is shown in Fig. 2.

The intensity of the lines of the carbonyl bond and of the C–H bond of chloroform is composed of the intensity of the lines of isolated molecules (I_m) and of molecules associated in the complex (I_k), where $I_k > I_m$. The enthalpy of formation (ΔH) of the acetone + chloroform molecular compound can be estimated from the temperature course of the change in the integral intensity of the line with frequency 3019 cm^{-1} of chloroform. If it is assumed that the intensity of the 3019 cm^{-1} line of chloroform at a given temperature is composed of the intensities of the lines of monomeric molecules and of molecules associated into a complex, which are not resolved, then

$$I_T = \left[I_m + (I_k - I_m)\frac{C_k}{C_0^{\mathrm{chl}}} \right] \left(\frac{1}{1 - e^{-h\nu/kT}} \right),$$

where I_τ is the intensity of the line at the given temperature; I_m is the intensity of the 3019 cm^{-1} line in hexane, extrapolated to infinite dilution; I_k is the intensity of the 3019 cm^{-1} line in acetone, extrapolated to infinite dilution; C_k

is the concentration of the molecular compound; C_0^{chl} is the initial concentration of chloroform.

The factor $\frac{1}{1-e^{-h\nu/kT}}$ for $\Delta\nu = 3019$ cm^{-1} remains practically constant in the temperature interval studied. Therefore one may take

$$I_\tau = I_m + (I_k - I_m)\frac{C_k}{C_0^{\text{chl}}}.$$

From the experimental data we calculated the equilibrium constants for the reaction

$$\begin{array}{ccc} & H_3C & H_3C \\ CO + HCCl_3 & \rightleftarrows & C=O\ldots H-CCl_3 \\ & H_3C & H_3C \end{array}$$

at temperatures of 301, 263, and 243°K, and obtained the values 0.2, 0.44, and 0.75 l/mole. From these quantities we found the enthalpy and entropy of the reaction: $\Delta H \simeq -3350$ cal/mole, and $\Delta S = -14.3$ entropy units. According to the data of Melvin-Hughes from vapor elasticities ([6]), $\Delta H = -4070$ cal/mole, while according to Pimentel' s data, obtained from proton magnetic resonance, $\Delta H = -2500$ cal/mole ([7]). The values we found lie in between. The standard free energy of formation of the molecular compound is 910 cal/mole. This explains its instability at elevated temperature.

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Note: Figure translations are in progress. See original paper for figures.