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Abstract

Full Text

PHYSICS

M. I. SHAKHPARONOV and D. K. BERIDZE

RAYLEIGH SCATTERING OF LIGHT IN SOLUTIONS OF ACETONE IN CARBON TETRACHLORIDE

(Presented by Academician V. V. Shuleikin, 26 X 1960)

Despite the fact that acetone molecules have a large dipole moment ($\mu_{(\text{CH}_3)_2\text{CO}} = 3.0D$), in liquid acetone at temperatures above 20° orientational ordering of the molecules apparently is practically absent ⁽¹⁾. One may expect that in solutions $(\text{CH}_3)_2\text{CO}-\text{CCl}_4$ orientational ordering of the molecules also does not arise. Verification of this assumption is of interest for the molecular theory of concentrated nonideal solutions in view of the fact that in solutions $(\text{CH}_3)_2\text{CO}-\text{CCl}_4$ rather considerable positive deviations from Raoult's law are observed. We have investigated the intensity I and the degree of depolarization Δ of monochromatic unpolarized light scattered at an angle of 90° by solutions of acetone in carbon tetrachloride at $0, 25, \text{ and } 40^\circ$.

After chemical purification and distillation the individual liquids had the following properties: acetone $T_k = 56.4^\circ$ at 760 mm Hg, $n_D^{20} = 1.35823$, $\rho_4^{20} = 0.7908$; carbon tetrachloride $T_k = 76.7$ at 760 mm Hg, $n_D^{20} = 1.4598$, $\rho_4^{25} = 1.5840$.

The method of investigation was the same as in ⁽²⁾. As the unit for measuring I , the intensity of scattering of unpolarized light in benzene at 25° was adopted. The results of measurements of I and Δ for wavelengths 4358, 5460, and 5780 Å are given in Table 1. For the pure components our data basically

Table 1

Intensity I , degree of depolarization Δ , and refractive index of light scattered by carbon tetrachloride (1)—acetone (2) solutions

x_2	0°			25°			40°			
	C	C	C	C	C	C	C	C	C	
	4358Å	5460Å	5780Å	4358Å	5460Å	5780Å	4358Å	5460Å	5780Å	
	I	Δ	I	I	Δ	I	I	Δ	I	
0,0	1,4607	0,305,0	0,284,8	0,271,45	0,364,9	0,334,9	0,321,45	0,3405,0	0,364,9	0,36
0,2	1,4505	0,385,8	0,366,1	0,351,44	0,445,2	0,405,4	0,391,43	0,445,0	0,435,0	0,42
0,4	1,4383	0,426,9	0,426,9	0,391,42	0,486,3	0,486,1	0,421,41	0,535,4	0,505,4	0,48

		0°			25°			40°		
		0°	0°	0°	25°	25°	25°	40°	40°	40°
		C	C	C	C	C	C	C	C	C
		4358C	5460C	5780C	4358C	5460C	5780C	4358C	5460C	5780C
		Å	Å	Å	Å	Å	Å	Å	Å	Å
x_2	n_D	I	I	I	I	I	I	I	I	I
0,5	1,425	1,427,2	0,417,3	0,371,41	0,376,4	0,456,1	0,411,40	0,652,9	0,506,0	0,48
0,511	1,418	1,427,3	0,417,4	0,391,40	0,446,7	0,446,8	0,401,39	0,750,3	0,476,3	0,46
0,7	1,405	1,391,0	0,381,0	0,351,39	0,374,8,4	0,398,3	0,391,38	0,616,7,2	0,447,2	0,41
0,861	1,386	1,332,13,30	0,301,3,0	0,291,3,40	0,291,3,70	0,351,1,10	0,331,1,00	0,321,3,68	0,391,0,00	0,369,9
1,0	1,368	1,232,0,30	0,222,0,00	0,221,3,55	0,251,6,60	0,231,6,60	0,231,3,40	0,229,15,20	0,271,5,40	0,27

agree with the data of M. F. Vuks and M. N. Dadenkova (3). The small difference in the values of I for acetone is possibly explained by the fact that we took into account the correction for the refractive index of the liquid. The decrease in the values of I with increasing λ in Table 1 is apparently caused by disper-

of the refractive index n . Using the values of I and Δ given in Table 1, the intensities of light scattering due to fluctuations of anisotropy I_a , density I_{pl} , and concentration I_k were calculated. The method of calculation is described in (4).

Table 2

Intensity of light scattering due to anisotropy fluctuations and density fluctuations in acetone and carbon tetrachloride

$t, \text{ }^\circ\text{C}$	(CH ₃) ₂ CO				CCl ₄ :		CCl ₄ :	
	$I_{pl},$ exp.	$I_{pl},$ equa- tion (1)	$I_{pl},$ equa- tion (2)	I_a	$I_{pl},$ exp.	$I_{pl},$ equa- tion (1)	$I_{pl},$ equa- tion (2)	I_a
0.0	0.15	0.16	0.14	0.08	0.27	0.25	0.20	0.03
25.0	0.17	0.19	0.15	0.08	0.32	0.31	0.24	0.03
40.0	0.21	0.21	0.20	0.08	0.36	0.36	0.28	0.04

Table 2 gives the values of I_{pl} and I_a for (CH₃)₂CO and CCl₄. Figure 1 shows the results of calculating I_a , I_{pl} , and I_k in solutions at 25° and λ 4360 Å. Calculations for the other temperatures and wavelengths we investigated lead to the same dependences as in Fig. 1.

Fig. 1. Dependence of the intensity of light scattering due to density fluctuations I_{pl} , anisotropy fluctuations I_a , and concentration fluctuations I_k on the composition of solutions of acetone in carbon tetrachloride at 25° and λ 4358 Å (the scattering intensity in benzene at λ 4358 Å is taken as equal to 1). Points are

Fig. 1. Dependence of the intensity of light scattering due to density fluctuations I_{pl} , anisotropy fluctuations I_a , and concentration fluctuations I_k on the composition of solutions of acetone in carbon tetrachloride at 25° and $\lambda 4358 \text{ \AA}$ (the scattering intensity in benzene at $\lambda 4358 \text{ \AA}$ is taken as equal to 1). Points are the results of theoretical calculations of I_k and I_a ; solid lines are experimental results; x_2 is the mole fraction of acetone.

Figure 1: Fig. 1. Dependence of the intensity of light scattering due to density fluctuations I_{pl} , anisotropy fluctuations I_a , and concentration fluctuations I_k on the composition of solutions of acetone in carbon tetrachloride at 25° and $\lambda 4358 \text{ \AA}$ (the scattering intensity in benzene at $\lambda 4358 \text{ \AA}$ is taken as equal to 1). Points are the results of theoretical calculations of I_k and I_a ; solid lines are experimental results; x_2 is the mole fraction of acetone.

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In Table 2 the theoretical values of I_{pl} were calculated from the formulas

$$I_{pl} = \frac{\pi^2 kT}{2\lambda^4 R_{C_6H_6}} \beta_t (n^2 - 1)^2 \left(\frac{n^2 + 2}{3} \right)^2; \quad (1)$$

$$I_{pl} = \frac{\pi^2 kT}{2\lambda^4 R_{C_6H_6}} \beta_t (n^2 - 1)^2, \quad (2)$$

where $R_{C_6H_6}$ is the scattering coefficient of benzene at 25° and 4358 \AA ; n is the refractive index; β_t is the isothermal compressibility⁽⁵⁾. We took the “high” value $R_{C_6H_6} = 48.5 \cdot 10^{-6}$ in the calculation by equation (1) and the “low” value $R_{C_6H_6} = 33.0 \cdot 10^{-6}$ in the calculation by equation (2). The calculation results confirm the conclusion that equation (1) and the “high” values of $R_{C_6H_6}$ are correct^(1,6).

If the molecules in the solution have no orientational ordering, then the anisotropic scattering should obey the equation

$$I_a = \frac{13}{45} \frac{8\pi^4}{\lambda^4 R_{C_6H_6}} N \left(\frac{n^2 + 2}{3} \right)^4 \sum x_i \gamma_i^2; \quad (3)$$

where N is the number of molecules in 1 cm^3 of solution, x_i is the mole fraction of component i , and γ_i^2 is the optical anisotropy of the polarizability of molecule i , calculated from the formula

$$\gamma_i^2 = 1/2 [(a_{1i} - a_{2i})^2 + (a_{1i} - a_{3i})^2 + (a_{2i} - a_{3i})^2];$$

a_{1i}, a_{2i}, a_{3i} are the principal semiaxes of the polarizability ellipsoid of molecule i .

Since $\gamma_{\text{CCl}_4}^2 = 0$, for liquid CCl_4 the theory leads to the value $I_a = 0$. Experiment shows, however (see Table 2), that CCl_4 has a small anisotropic scattering. This contradiction has been discussed many times in the literature (see the review ⁽⁷⁾, as well as ⁽⁸⁾), but has not received a satisfactory explanation. It follows from Table 2 that in CCl_4 the anisotropic scattering increases with increasing temperature in proportion to the scattering by density fluctuations. One may suppose that, under the influence of density fluctuations, a local anisotropy of the field acting on the molecules arises in CCl_4 . This causes the appearance of anisotropy in the polarization state of the CCl_4 molecules and, consequently, of anisotropy fluctuations, which produce additional depolarized scattering of light. In other words, the anisotropic scattering of light in CCl_4 is apparently caused by the correlation between density fluctuations and anisotropy, $\Delta\rho\Delta a$, which is not taken into account in deriving equation (3).

The effective values of γ_i^2 for acetone and carbon tetrachloride molecules can be calculated from the data on I_a for these liquids. For liquid acetone the calculation gives a value of γ^2 which, within the experimental errors, coincides with the value of the optical anisotropy of acetone molecules in the gas phase. Substituting the effective values of γ_i^2 into equation (3), one can calculate I_a for the solutions. The obtained values of I_a for the solutions, as Fig. 1 shows, agree well with the values of I_a calculated from the experimental data on I and Δ of the light scattered by the solutions. This confirms the assumption that there is no orientational ordering of molecules in acetone-carbon tetrachloride solutions.

Fig. 1 shows that the concentration scattering passes through a maximum at $x \simeq 0.5$. As is known:

$$I_k = \frac{I_0 V}{r^2} \frac{\pi^2}{2\lambda^4 N_A} \frac{M_2 (\partial n^2 / \partial c)^2}{m_1 \partial \ln P_2 / \partial c}, \quad (4)$$

where N_A is Avogadro's number, M_2 is the molecular weight of component 2; $c = m_2/m_1$; r is the distance from the point of observation to the center of the scattering volume; P_2 is the partial pressure of the saturated vapor of component 2; m_1 and m_2 are the masses of components 1 and 2 in 1 cm³ of solution.

Since

$$\frac{\partial}{\partial c} = -\frac{M_1}{M_2} x_1^2 \frac{\partial}{\partial x_2}$$

and, according to ⁽⁹⁾,

$$\frac{\partial \ln P_2}{\partial x_2} = \frac{1}{x_2} - \frac{\tau z x_1}{kT},$$

then

$$I_k = \frac{I_0 \pi^2 V}{2r^2 N \lambda^4} \left(\frac{\partial n^2}{\partial x_2} \right)^2 x_1 x_2 \left(1 - \frac{\tau z x_1 x_2}{kT} \right)^{-1}, \quad (5)$$

where N is the number of molecules in 1 cm^3 of solution; z is the mean coordination number of molecules in the solution; $\tau = \text{const}_1(\varepsilon_1 - \varepsilon_2)^2 \approx \text{const}_2 \left(\frac{\mu_1^2}{v_1} - \frac{\mu_2^2}{v_2} \right)^2$; μ_1 and μ_2 are the dipole moments of the molecules; v_1 and v_2 are the molecular volumes; ε_1 and ε_2 are the static dielectric constants of components 1 and 2.

The quantity τz depends on the molecular structure of the solution, on the sizes of the molecules, and on the forces acting between the molecules. It may be assumed that in various solutions of acetone in nonpolar low-molecular-weight substances Y , where v_1 and v_2 do not differ very greatly, the values of τz are approximately the same and do not depend on concentration. Using the value of I_k at any one concentration of the solution $(\text{CH}_3)_2\text{CO}-Y$, one can, by means of equation (5), calculate the values of I_k at all concentrations.

using equation (5) to calculate $\tau z/kT$, and then to calculate I_k for other concentrations or other Y . According to the experimental data ⁽⁴⁾ for an acetone-benzene solution at concentration $x = 0.5$, $I_k = 0.22$ and $\partial n/\partial x = 0.39$. Substituting these values into equation (5), we find $\tau z/kT = 0.5$. For acetone-carbon tetrachloride solutions, $\partial n/\partial x = 0.12$ and is almost independent of x . Using these values of $\partial n/\partial x$ and $\tau z/kT$ and the values of n from Table 1, we obtain, for $x_{\text{ac}} = 0.25$, $I_k = 0.124$; for $x_{\text{ac}} = 0.5$, $I_k = 0.170$; and for $x_{\text{ac}} = 0.75$, $I_k = 0.120$. Experiment (see Fig. 1) gives values of I_k equal, respectively, to 0.124, 0.164, and 0.120. Consequently, equation (5) apparently correctly expresses the dependence of the intensity of light scattering by concentration fluctuations on the composition of acetone solutions in nonpolar low-molecular-weight substances.

Moscow State University
named after M. V. Lomonosov

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