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Abstract

Full Text

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ON THE RELATION OF THE VISCOSITY COEFFICIENT TO THE STRUCTURE OF A SUBSTANCE IN THE LIQUID STATE

(Presented by Academician G. V. Kurdyumov, 12 XI 1956)

The relation of the viscosity coefficient to other physical properties and, above all, to the structure of a substance in the liquid state is of great interest both for the development of the theory of the liquid state and of viscosity in particular, and for the practice of physicochemical analysis. However, this relation has not yet been established, on the one hand because of the lack of the necessary information on the structure of liquids, and on the other because their physical properties have not been sufficiently studied.

The difficulties arising in the search for a relation between viscosity and the structure and other physical properties of liquids we attempted to overcome by a rational choice of the objects of investigation and by studying, simultaneously with viscosity, other structure-sensitive properties. We chose the objects of investigation on the basis of the similarity of their molecular structure. Over a wide temperature interval we studied density, viscosity, heat of vaporization, molecular scattering of light, and critical temperature. It was shown that the curves of the temperature dependence of viscosity and of the heat of vaporization are situated the higher, and the compressibility curves the lower, the higher the critical temperature of the given substance is ([1]).

Fig. 1. Temperature dependence of the viscosity of solutions of Zn and Cd in Hg.
1–30.8% Cd and 21% Zn; 2–16% Zn; 3–22% Cd; 4–18% Cd and 12% Zn; 5–13.9% Cd and 8.7% Zn; 6–7.3% Cd; 7–6.1% Cd; 8–Hg.

It was shown that the relation of viscosity and other structure-sensitive prop-

Fig. 2

Figure 2: Fig. 2

erties to the critical temperature is a consequence of the periodic law of D. I. Mendeleev ([2]).

The density, viscosity, heat of vaporization, and critical temperature were also studied for molecularly mixing solutions whose components possess similar molecular structure. It was shown that the curves of the temperature dependence of the viscosity of these solutions are situated between

with the curves of the components, and the higher the greater the critical temperature of the given solution. When the critical temperatures of two or several solutions of this group were equal, complete coincidence of the viscosity–temperature curves was observed. We called such liquids isoviscous. We decided to use isoviscous liquids to establish the relation between the viscosity coefficient and molecular structure.

Fig. 2. Intensity curves of scattered X-rays. Isoviscous solutions in Hg: 1—30.8% Cd and 21% Zn; 2—18% Cd, 12% Zn; 3—13.9% Cd and 8.7% Zn

As the object of investigation we took solutions of zinc and cadmium in mercury, whose structure, viscosity, and density we had studied earlier ([3–5]). These solutions belong to the molecularly mixing type, and their components have a similar structure; Fig. 1 gives the dependence of viscosity on temperature for some of them.

The following solutions are isoviscous: 13.9% cadmium in mercury and 8.7% zinc in mercury; 18% cadmium in mercury and 12% zinc in mercury; 30.8% cadmium in mercury and 21% zinc in mercury (percentages are atomic throughout). The structure of these solutions was studied.

As the source of X-rays, a BSV-4 tube with a copper anticathode was used. Monochromatization of the X-rays was achieved by reflection of the rays from a bent quartz crystal. The intensity distribution of the scattered X-rays was studied by the photographic method. The temperature of the metal was determined with a chromel–alumel thermocouple. Photometry was carried out on an MF-4 microphotometer. From each solution no fewer than three photographs suitable for calculation were obtained.

After exclusion of the polarization and absorption factors, the experimental intensity curves were reduced to electron units. The criterion for correct reduction was that the integral be equal to zero,

$$\int_0^{s_0} s^2[i'(s) - 1]\, ds = 0,$$

where

$$i'(s) = \frac{I}{n_1 f_1^2 + n_2 f_2^2}; \qquad s = 4\pi \frac{\sin \vartheta}{\lambda};$$

I is the intensity of the scattered radiation; f_1 and f_2 are the atomic factors, respectively, for atoms of the first and second kind; n_1 and n_2 are the concentrations of atoms of the first and second kinds.

Figure 2 presents the experimental intensity curves in electron units for the above-mentioned isoviscous solutions. As is seen from the figure, the curves of intensity versus $\sin \vartheta / \lambda$ for the isoviscous solutions are superposed on one another.

Table 1 gives data characterizing the positions of the intensity maxima on these curves.

The functions of atomic distribution were determined from equation (8)

$$4\pi r^2 \left[c_2^1 n_1 \rho_1(1) + c_1^2 n_2 \rho_2(2) + 2 n_1 \rho_2(1)\right] =$$

$$= 4\pi r^2 \left[c_2^1 n_1 \rho_1^0 + c_1^2 n_2 \rho_2^0 + 2 n_1 \rho_2^0\right] + \frac{2r}{\pi} \int_0^\infty i(s) \sin sr \, ds, \qquad (1)$$

where

$$c_2^1 = [f_1/f_2]_{\text{cp}}^2; \qquad c_1^2 = [f_2/f_1]_{\text{cp}}^2; \qquad n_1 = N_1/N; \quad n_2 = N_2/N; \quad N = N_1 + N_2$$

$\rho_1(1) = N_1 W_1(1)/V$ is the radial density function of atoms of the first kind, when an atom of the same kind is located at the origin of coordinates; $\rho_2(2) = N_2 W_2(2)/V$ is the radial density function of atoms of the second kind in the case when an atom of the first kind is located at the origin of coordinates;

$$i(s) = \frac{I/N - n_1 f_1^2 - n_2 f_2^2}{f_1 f_2} \, s;$$

N_1 and N_2 are the numbers of atoms of the corresponding kind; V is the scattering volume; $W_1(1)$ and $W_2(2)$ are the radial probability functions for atoms of the first and second kinds; ρ_1^0 and ρ_2^0 are the mean densities of atoms of the corresponding kind.

Table 1

Substance	Temp. in °C	Main max.	2nd max.	3rd max.
Hg [6]	20	0.190	0.360	0.525

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Substance	Temp. in °C	Main max.	2nd max.	3rd max.
13.9% Cd in Hg	70	0.195	0.367	0.530
18% Cd in Hg	70	0.200	0.370	0.538
30.8% Cd in Hg	110	0.202	0.373	0.540
Cd [7]	350	0.203	0.360	0.550
8.7% Zn in Hg	70	0.194	0.368	0.530
12% Zn in Hg	70	0.200	0.372	0.540
21% Zn in Hg	110	0.202	0.37[[unclear: last digit]]	0.540
Zn [7]	460	0.228	0.380	–

The integral in equation (1) was calculated by the method described in [9].

Fig. 3. Curves of the atomic distribution of solutions of Cd in Hg.
1–30.8% Cd; 2–18% Cd; 3–13.9% Cd

$$G(r) = 4\pi r^2 \left[c_2^1 n_1 \rho_1(1) + c_2^1 n_2 \rho_2(2) + 2 n_1 \rho_2(1)\right]$$

Fig. 4. Curves of the atomic distribution of solutions of Zn in Hg.
1–21% Zn; 2–12% Zn; 3–8.7% Zn.

Figures 3 and 4 present the atomic distribution curves of isoviscous solutions obtained by the method described.

Analysis of the atomic distribution curves of isoviscous solutions, like analysis of the intensity curves, reveals their complete similarity. Consequently, liquids possessing identical coefficients of viscosity (isoviscous liquids) possess the same short-range order, the same structure.

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