

INVESTIGATION OF PARTICULARTIES FOUND IN INTERMOLECULAR INTERACTION FOR GLYCERINE ETHERS AND ESTERS BY ACOUSTIC METHODS¹⁾

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Investigation results of the structure of glycerine ethers such as 1-monomethyl ether, glycidol, triacetate, tributinate and tristyrate performed by acoustic methods are presented in the paper. The existence of volumetric and shear relaxation has been found for the studied liquids. Molecular mechanisms of structure rebuilding of glycerine ethers and esters are proposed on the base of certain relaxation and thermodynamical parameters determining the found regions of acoustic dispersion and also the analysis of complex dielectric permeability and infrared absorption spectra.

ИССЛЕДОВАНИЕ ОСОБЕННОСТЕЙ МЕЖМОЛЕКУЛЯРНОГО ВЗАМОДЕЙСТВИЯ В ПРОСТЫХ И СЛОЖНЫХ ЭФИРАХ ГЛИЦЕРИНА ПРИ ПОМОЩИ АКУСТИЧЕСКИХ МЕТОДОВ

В работе представлены результаты исследования структуры различных эфиров глицерина (1-монометилловый эфир, глицидол, триацетат, трибутират и тристеарин) при помощи акустических методов. В изучаемых жидкостях обнаружено существование объемной и сдвиговой релаксации. На основе определенных релаксационных и термодинамических параметров, характеризующих обнаруженные области акустической дисперсии, а также на основе анализа комплексной диэлектрической проницаемости и инфракрасных спектров поглощения предложены механизмы перестройки структуры простых и сложных эфиров глицерина.

1. INTRODUCTION

Considerable interest in the investigation of the structure of glycerine ethers and esters has been stimulated because of their participation in biophysical processes occurring in cells and the use in technological processes in the production of polyurethane, alkylid resins, etc. These facts and also the possibility of studying intermolecular interaction during the change of the hydroxyl group number and

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molecular mass motivated the present investigation of molecular process mechanisms of glycerine ethers in the liquid phase.

Glycerine 1-monomethyl ether and glycidol and glycerine esters such as triacetate, tributerine and tristyrarine were chosen as objects of the study. Out of the mentioned liquids there are data on acoustic properties only for triacetate obtained for several fixed frequencies [1]. Taking into account the above mentioned facts we believe expedient to: 1. carry out systematic investigations of acoustic spectra of glycerine ethers and esters in the liquid phase on longitudinal and shear waves in a wide range of frequencies; 2. study dielectric properties and infrared spectra of ether absorption; 3. elucidate the mechanisms of molecular processes responsible for acoustic relaxation in the investigated objects and define their thermodynamic and kinetic characteristics.

Experimental data presented here have been obtained in the Laboratory of acoustic spectroscopy of the Thermophysics Department of the Uzbek Academy of Sciences.

II. EXPERIMENTAL METHODS

For the measurement of acoustic parameters of liquid systems on longitudinal and shear waves in the frequency range f from 0.02 to 6000 MHz and from 6 to 1000 MHz in the temperature range of $T = 260 + 430$ K, respectively, the following methods were used: the method of statistic reverberation, the Mandelstam-Brillouine heat loss, the resonance, impulsive and impedance methods [2]. An average relative error in the determination of V propagation velocity values and the amplitude coefficient of absorption α of longitudinal acoustic waves were $\sim 0.6\%$ and $\sim 15\%$ and for dynamic shear viscosity η_s and elastic module shear σ' they did not exceed 8 and 15% respectively.

Measurement of dielectric permeability ϵ' and dielectric losses ϵ'' of liquids at $f = 40$ Hz \div 17 GHz was performed in the indicated temperature range with the relative error of 0.5 \div 1.5% and 1 \div 3%, respectively. In this case four devices designed on the base of a bridge network, a meter for the transmission of complex parameters, the method of "head seas" and the meter of a standing wave coefficient were used [3, 4].

Infrared spectra of absorption were taken in the range of wave numbers $\nu = 700 \div 4000$ cm^{-1} at 293 K with the error of estimation of ν and transmittance being not more than 1%.

Besides, the coefficient of surface tension σ , refraction index n_D , density ρ and coefficient of static shear viscosity η_{st} were measured by the method of "blister most pressure", by a refractometer, a pycnometer and a viscometer, respectively. The error in the determination of ρ and n_D is 0.02%, $\sigma \sim 0.4\%$ and $\eta_{st} \sim 2\%$.

The investigated compounds, i.e. 1-monomethyl ether, glycidol, triacetate; tributerine and tristyrarine were subjected to vacuum distillation and degassing. The impurity content determined by gas-liquid chromatography did not exceed 0.5 wt. %.

III. RESULTS AND DISCUSSION

During the investigation of the physico-chemical properties of glycerine ethers it was found that with the increase of molecular mass μ_m viscosity drops practically by one order, ρ , n_D and σ values also decrease. The reduction of viscous flow activation enthalpy ΔH_n^\ddagger is also observed. Thus, if for 1-monomethyl ether $\Delta H_n^\ddagger = 45$ kJ/mol, then for tristyrarine $\Delta H_n^\ddagger = 25$ kJ/mol. These facts are connected with the decrease of the hydroxylic group number and the increase of the hydrocarbon radical during the μ_m growth.

The frequency dependence of the values of V , α/f^2 , η_s , σ' , the dynamic volumetric viscosity η_0 and the elastic module under uniform compression K' ($\eta_0 = \frac{4}{3}\eta_s$; $\eta_s = \frac{\rho V_0^2}{2\pi^2} \left(\frac{\alpha}{f^2}\right)_{exp}$; $K' = M' - \frac{4}{3}\sigma'$; $M' \approx \rho V^2$) for glycerine ethers within the experiment error are described by the following ratios [2]:

$$\left(\frac{V_0}{V}\right)^2 = 1 - \sum_{i=1}^n \frac{b_{ai}\omega^2\tau_{ai}^2}{1 + \omega^2\tau_{ai}^2}; \quad \frac{\alpha}{f^2} = \sum_{i=1}^n \frac{A_i}{1 + \omega^2\tau_{ai}^2} + B; \quad (1)$$

$$\eta_s = \sum_{i=1}^n \frac{\eta_{si}}{1 + \omega^2\tau_{si}^2} + \eta_{s\infty}; \quad \sigma' = \sigma'_0 + \sum_{i=1}^n \frac{\sigma'_{ai}\omega^2\tau_{ai}^2}{1 + \omega^2\tau_{ai}^2}; \quad (2)$$

$$\eta_0 = \sum_{i=1}^n \frac{\eta_{0i}}{1 + \omega^2\tau_{0i}^2} + \eta_{0\infty}; \quad K' = K'_0 + \sum_{i=1}^n \frac{K'_{0i}\omega^2\tau_{0i}^2}{1 + \omega^2\tau_{0i}^2}; \quad (3)$$

where b_{ai} and τ_{ai} are relaxation force and relaxation time of the i -relaxation process, respectively; A_i , B , η_{si} , σ'_0 and η_{0i} , K'_0 are constants; $K'_{0i} = K_{0i} - K_{0i}$; K_{0i} and σ'_{ai} are the maximum high frequency values of K' and σ' for the i -process; K'_{0i} is a low frequency value of K' for the i -area of volumetric relaxation; τ_{si} and τ_{0i} are the times of shear and volumetric relaxation of the i -relaxation process; $\eta_{s\infty}$ and $\eta_{0\infty}$ are values of η_s and η_0 at $\omega = 2\pi f \rightarrow \infty$.

Computer calculation results according to (1) show that for glycidol, 1-monomethyl ether and triacetate the relaxation times are $\tau_{a1} \sim 10^{-6}$ s; $\tau_{a2} \sim 10^{-9}$ s and $\tau_{a3} \sim 10^{-10}$ s and for tributerine and tristyrarine they are $\tau_{a1} \sim 10^{-7}$ s and $\tau_{a2} \sim 10^{-10}$ s. For all the liquids there is a sonic speed dispersion, whose maximum value is $\sim 30\%$ for glycidol and 1-monomethyl ether at 260 K. Shear viscosity relaxation is observed for triacetate in the whole frequency range and $\tau_{s1} \sim 10^{-6}$ s, $\tau_{s2} \sim 10^{-9}$ s and $\tau_{s3} \sim 10^{-10}$ s, for the remaining ethers the dependence of η_s and σ' on f follows (2) the ratios with one and the same time of $\tau_{2i} \sim 10^{-9}$ s. K' and η_0 relaxation for

glycerine ethers is described by ration (3) with three times, i.e. $\tau_{n1} \sim 10^{-6}$ s, $\tau_{n2} \sim 10^{-9}$ s and $\tau_{n3} \sim 10^{-10}$ s.

Fig. 1 presents frequency dependences of values α/f^2 and V for triacetate (a) and η_H , η_s and η_v for glycidol (b) illustrating acoustic relaxation in esters and its manifestation in viscosity change in glycerine ethers. It should be noted that low-frequency areas of acoustic dispersion in glycerine ethers are mostly connected

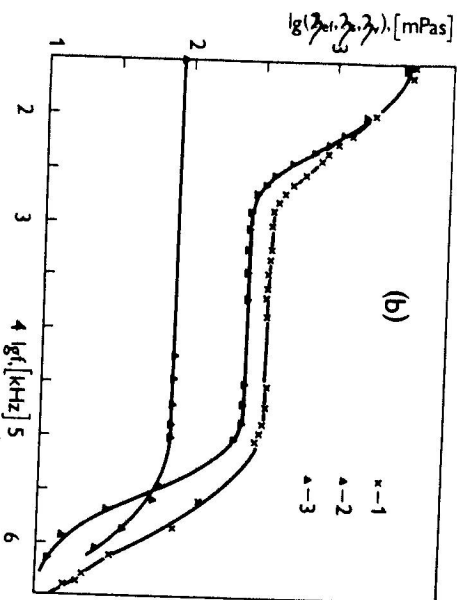
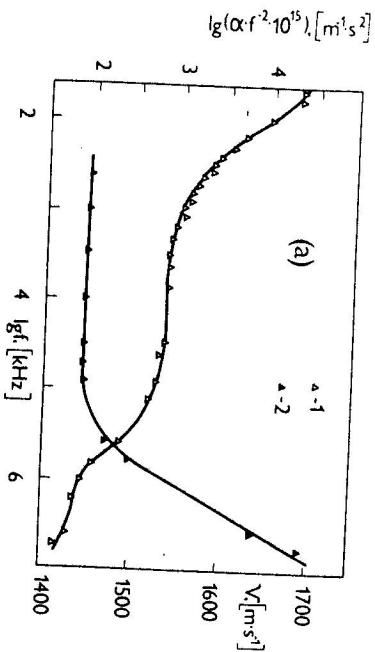


Fig. 1. a) Frequency dependence of α/f^2 (1) and V (2) sound values for triacetate at 283 K. b) Frequency dependence of η_H (1), η_s (2) and η_v (3) values for glycidol at 283 K. (Calculation curves are according to the ratios (1—3)).

with the volumetric relaxation and high-frequency ones are connected with both volumetric and shear relaxation. When the temperature increases, relaxation parameters A_i , τ_{ai} , b_{ai} , η_{Hi} , τ_{Hi} , η_{vi} and τ_{vi} for all the liquids as a whole decrease.

Using the idea of irreversible process thermodynamics the effective values of ΔH_{ai}^- enthalpy, $\Delta \Phi_{ai}^-$ free enthalpy and ΔS_{ai}^- entropy of the activation of relaxation processes were calculated according to the acoustic data. Within the error of their estimation, which is 20—30 % these parameters for volumetric and shear relaxation and for ethers are as follows: $\Delta H_{a2}^- \sim 24$ kJ/mol, $\Delta H_{a2}^- \sim 20$ kJ/mol and $\Delta H_{a3}^- \sim 11$ kJ/mol. The obtained data show that with the increase of μ_m the acoustic and relaxation parameters V and α/f^2 ; η_s and σ' , η_n and K' , τ_{ai} , τ_{Hi} and τ_{vi} decrease and for thermodynamic parameters within the error of their estimation changes are not observed.

It should be stressed that the comparison of experimental data with the ratios of non-local-diffusion theory [6] gives a good agreement for the rate of acoustic wave propagation, and for the amplitude absorption coefficient a marked discrepancy is observed.

Measurement of ϵ' dielectric permeability and ϵ'' dielectric losses in glycerine ethers in the wide frequency range allows to compare the experiment with the formulae, taking into account the final number of dielectric relaxation times τ_{di} , characterizing the i -relaxation process [7]:

$$\epsilon' = \sum_{i=1}^n \frac{(\epsilon_{di} - \epsilon_{oi}) b_{di}}{1 + \omega^2 \tau_{di}^2} + \epsilon_{oi}; \quad (4)$$

$$\epsilon'' = \sum_{i=1}^n \frac{(\epsilon_{di} - \epsilon_{oi}) b_{di}}{1 + \omega^2 \tau_{di}^2} \quad (5)$$

where b_{di} is a relative relaxation force of the i -region of dielectric relaxation; ϵ_{di} and ϵ_{oi} are low- and high-frequency values of ϵ' for the i -relaxation process; ϵ_{oi} is a constant.

The results of the ϵ' and ϵ'' calculations in the liquids under investigation showed that within the errors of their estimation there is a good agreement of the experiment with the Eqs. (4), (5) with three times $\tau_{d1} \approx \tau_{d1}$ for 1-monomethyl ether, glycidol and triacetate and for tributeryne and tristyryne $\tau_{d1} \approx \tau_{d1}$ and $\tau_{d2} \approx \tau_{d2}$. Besides, on account of a larger frequency range in dielectric property measurement than in acoustic property measurement a third high-frequency relaxation process with $\tau_{d3} \sim 10^{-11}$ s was found in tributeryne and tristyryne. To show the changes of ϵ' and ϵ'' values with μ_m Fig. 2 presents ϵ''/f for glycerine esters. The segments correspond to the area of dielectric dispersion. With the temperature growth for the investigated substances relaxation decrease and with the μ_m increase a ϵ' and ϵ'' decrease occurs. The calculation of thermodynamical parameters describing the found relaxation processes shows that they are equal to the corresponding value obtained from acoustic data.

Infrared absorption spectra point to the existence of bands in the wide range of wave numbers. Fig. 3 shows absorption spectra of 1-monomethyl ether and tributeryne to illustrate the main bands in glycerine ethers. In ethers the $\nu_{OH} =$

3150 cm^{-1} band is conditioned by the valent vibration of the hydroxylic group and in esters $\nu_{\text{C=O}} \sim 1700 \text{ cm}^{-1}$ results from the valent vibration of the carbonyl group. With an μ_m increase ν_{OH} and $\nu_{\text{C=O}}$ bands are shifted to the range of large wave numbers, in which case their intensity drops. The bands caused by vibrational deformation of methylene and metine groups are also shifted to the same side. Valence variations of C—H, C—C and C—O groups are shifted to the area of lower frequencies with an μ_m growth and their intensity is increased.

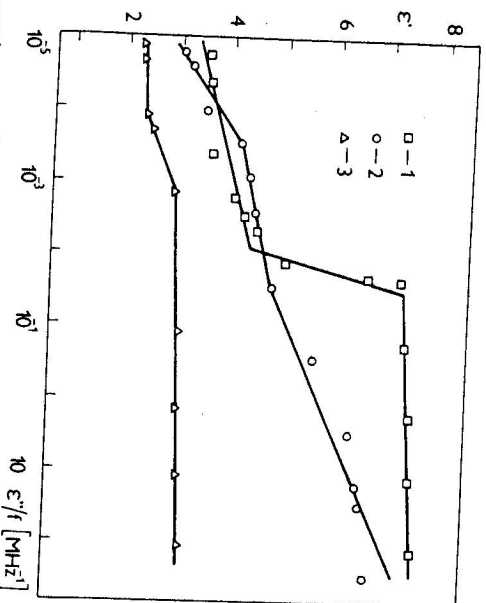


Fig. 2. ϵ' value dependence on ϵ''/f for triacetine (1) and tributurine (2) at 283 K and trisyrarine (3) at 353 K.

Considering these peculiarities in the change of infrared spectra and also the found regularity, i.e. in an ether solution in weakly polar liquids (tetrachlorated carbon) ν_{OH} and $\nu_{\text{C=O}}$ absorption bands are shifted to the area of smaller wave lengths, it is possible to say that in the compounds under investigation there are intermolecular hydrogen bonds (IHB). In ethers intramolecular hydrogen bonds are also formed. It should be noted that in the ethers IHB of the O—H...O type are found and in esters they are of the C—H...O=C type. Peculiarities in the change of band position and form of absorption of valence vibrational C—C and C—O groups point to the existence of turning-isomeric transformations of ether molecules around main methylene and metine groups.

The calculations of the IHB effective enthalpy were performed on the basis of empiric ratios for liquids with hydroxylic group, obtained from dependences of the ν_{OH} band position change of the concentration of a weakly polar solvent [8]:

$$-\Delta H_{\text{r}} = 1.38 (\Delta\nu - 40)^{1/2} \text{ kJ/mol}; \quad (6)$$

where $\Delta\nu$ is a ν_{OH} change under IHB formation.

It should be stressed that the formula does not take into account the contribution to the change of the ν_{OH} band position made by intramolecular hydrogen bonds. $-\Delta H_{\text{r}} = 29 \text{ J/mol}$ for 1-monomethyl ether and glycidol. According to the structure analysis of glycerine ether associated with the use of the data obtained by spectroscopic methods and Stewart models it is possible to show that in ester dimers, which can be fragments of more complicated formations, the molecules are bound by one or two IHB.

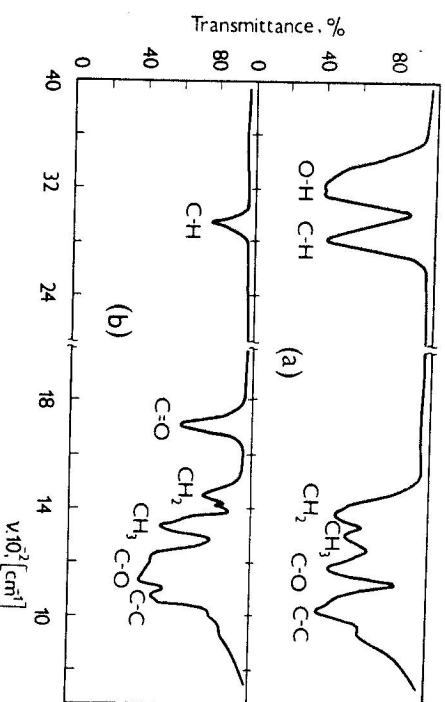
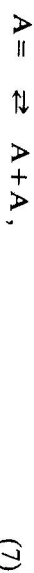


Fig. 3. Infrared spectra for 1-monomethyl ether of glycerine (a) and tributurine (b) at 293 K (transmittance is given relative units).

Natural reactions, occurring with breakage and formation of IHB are as follows:



where A is an ether molecule presentation, the horizontal line of IHB of the O—H...O type for ethers and the C—H...O=C type for esters of glycerine. Reactions with intramolecular hydrogen bonds, the existence of which is shown by the data of infrared and dielectric spectra of glycerine ethers are neglected as their main contribution is revealed in the frequency range above $\sim 10 \text{ GHz}$ which at present is not accessible to acoustic investigations.

The analysis of data obtained by the methods of acoustic, dielectric and infrared spectroscopy permits to correlate the regions of acoustic dispersion observed experimentally with the reactions of IHB breakage and formation. Thus, the first low-frequency relaxation process is mostly conditioned by a normal reaction

representing linear combination of natural reactions of two IHB breakages and formations of the corresponding type in associates of glycerine ethers and esters (7). The second relaxation process is apparently caused by the normal reaction representing the reaction of one IHB breakage and formation (8). The third reaction frequency process is probably connected with a normal reaction expressed by natural reactions of one IHB breakage and formation (9), which occurs without the change of molecular number in ether associates. It should be noted that turning-*isomeric* transformations of ether molecules around the C—C bond can make a contribution of a lowfrequency region of acoustic dispersion from main methylene and methine groups. It should be stressed that the indicated mechanisms of molecular processes responsible for the found regions of volumetric and shear relaxation are more probable and agree with the obtained independent methods, dependences of relaxation thermodynamics and physico-chemical parameters of temperature and molecular mass of glycerine ether series being considered.

IV. CONCLUSIONS

Molecular mechanisms of glycerine ether and ester rebuilding are proposed on the basis of investigations into acoustic, dielectric and infrared spectra and some physico-chemical properties. The regions of volumetric and shear relaxation revealed in the experiment are conditioned by normal reactions representing a linear combination of natural reactions occurring both with and without changes in the number of molecules in bound intermolecular hydrogen bonds of the corresponding type of associates of glycerine ethers and esters. Conformation transformations of molecules are also found in the investigated liquids and the existence of intramolecular hydrogen bonds is established in glycerine ethers.

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