PHYSICOCHEMICAL PROPERTIES OF ALKYL N-ACYLTHIOCARBAMATES

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The molecular weights, dipole moments, and infrared spectra of alkyl N-acylthiocarbamates in the range 3500–80 cm^{-1} (in the crystalline state and in solution in CCl_4) have been measured. In the solid state and partly in solution, the RSCONHCOR' molecules are associated by hydrogen bonding NH... O═C. In dilute solutions, the nonassociated molecules are apparently present in two conformations: the planar cis-trans form and an isomer with a nonplanar structure for the CONHCO group.

RESULTS AND DISCUSSION

We previously proposed [1, 2] methods for the synthesis of alkyl N-acylthiocarbamates and prepared the compounds RSCONHCOR', where R = C_2H_5, C_3H_7, C_6H_{13}, or $C_6H_5CH_2$, and R' = $CH_3-C_6H_{13}$. There is no published information on the physicochemical properties of these compounds.

Alkyl N-acylthiocarbamates are colorless crystalline compounds having an odor of onion or garlic, readily soluble in water and in polar and nonpolar organic solvents.

Table 1 gives the melting points, molecular weights, and dipole moments of RSCONHCOR'. The melting points decrease with increase in the size of the group R' (Nos. 1-6); the compounds with R' = CH_3 (Nos. 1, 9, and 11) or $CH_2C_6H_5$ (No. 12) melt at higher temperatures than the other analogs. The experimentally determined values of the molecular weights of the alkyl N-acylthiocarbamates in benzene (concentration range 0.020-0.230 mole in 1000 g) are greater than the formula values even at low concentrations. With increase in the concentration of RSCONHCOR' in the solution, the molecular weight approaches the value for the dimer. This indicates that the equilibrium dimer ⇌ 2 monomer is established in the solution.

The dipole moments of the alkyl N-acylthiocarbamates, measured in benzene at 20°, lie in the range 1.93-2.26 D according to Srivastava [3] or 2.05-2.34 D according to Halverstadt [4]. It can be seen from Table 1 that the dependence of the dipole moments on the length of the groups R and R' does not show any regular features.

TABLE 1. Melting Points, Molecular Weights, and Dipole Moments of RSCONHCOR'

No.	R	R'	MP, °C	M		Formula M of monomer	μ, D	
				conc. limits, mole/1000 g	limits of change in M		from [3]	from [4]
1	C_2H_5	CH_3	102	0,028—0,130	192—235	147	2,25	2,34
2	C_2H_5	C_2H_5	84	0,020—0,230	180—260	161	2,07	2,17
3	C_2H_5	C_3H_7	69	0,045—0,213	257—290	175	2,13	2,25
4	C_2H_5	iso-C_4H_9	54	0,031—0,190	218—284	189	1,99	2,05
5	C_2H_5	C_5H_{11}	51	0,023—0,098	263—303	203	2,21	2,33
6	C_2H_5	C_6H_{13}	51	—	—	217	2,10	2,19
7	C_3H_7	C_2H_5	66	0,029—0,130	227—266	175	2,00	2,10
8	C_3H_7	C_3H_7	66	0,024—0,170	215—290	189	2,12	2,21
9	C_6H_{13}	CH_3	91	0,025—0,130	278—318	203	2,11	2,21
10	C_6H_{13}	C_2H_5	65	0,020—0,130	250—335	217	2,00	2,11
11	$C_6H_5CH_2$	CH_3	146	—	—	211	1,93	2,05
12	$C_6H_5CH_2$	C_3H_7	109	—	—	225	2,00	2,11

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TABLE 2. Characteristic Frequencies (cm^{-1}) in the Infrared Spectra of RSCONHCOR' in the Crystalline State (for each compound, the group R is indicated first, and the group R', second)*

C_2H_5	CH_3	C_2H_5; C_2H_5	C_2H_5; C_3H_7	C_2H_5; C_4H_9	C_2H_5; C_5H_{11}	C_2H_5; C_6H_{13}	C_3H_7; C_2H_5	C_3H_7; C_3H_7	C_6H_{13}; CH_3
	3420 w.								
	3390 med.								
3250 s.	3280—	3260 s.	3260 s.	3260 s.	3280—	3270—	3250 s.	3265 s.	3250 s.
3200 s.	3180 br.s.				3250 br.s.	3260 s.br.			3200 s.
3160 s.	3120 med.	3180 s.	3160 s.	3170 s.	3220 s.sh.	3180 s.	3170 s.	3180 s.	3160 s.
	2980 med.								
	2940 med.								
	2880 w.								
1720	1730 v.s.	1740 v.s.	1740 v.s.	1730 v.s.	1730 v.s.	1730 v.s.	1730 v.s.	1740 v.s.	1730 v.s.
	1707								1710 s.
1700 med.	1680	1685 s.	1690 s.	1680 v.s.	1685 v.s.	1680 v.s.	1695 s.	1695 s.	
1660 v.s.	1667	—	1660 med.	1650 v.s.	1660 v.s.	1650 v.s.	1655 med.sh	1660 med.sh	1675 v.s.
	1640								
1530—		1540—	1540—	1520—	1500—	1520—	1530—	1540—	1510 s.
1510 s.	1490 med.	1530 s.	1520 s.	1510 v.s.	1490 s.	1500 s.	1510 s.	1520 s.	—
—	1455 s.								
1420 med.	1420 med.	1420 med.	1420 med.	1420 med.	1420 med.	1420 med.	1420 med.	1420 s.	1420 s.
—	1380 s.								
1330 v.w.		1330 w.	—	1350 med.sh	1330 med.	1340 w.	—	1320 w.	1330 med.
	1300 s.	—	—	1300 med.	—	—	—	1285 w.	—
1260 v.s.	1260 s.	1280 w.	1280 med.	1280 w.	—	1270 w.	1270 w.	1240 med.	1270 v.s.
	1240 s.	1220 med.sh	1210 s.sh.	1250 w.	1220—	1210 v.s.	1220 s.	1220 s.sh.	—
1190 s.	1210 med.	1180 v.s.	1180 v.s.	1210 v.s.	1200 v.s.br.	—	1180 v.s.	1180 v.s.	1200 v.s.
	1130 s.	1150 v.s.	1150 v.s.	1170 v.s.		1170 v.s.	1150 v.s.	1150 v.s.	—
	1120 s.	—	—	1140 v.s.	1140 v.s.	1135 v.s.	—		1120 w.
1070 w.	1070 w.	1075 med.	1080 med.	1090 med.	1070 med.	1070 w.	1090 w.	1095 med.	1090 med.
1050 w.	1050 w.	—	1060 med.	1070 med.	—	—	—	1060 w.	1050 w.
1000 med.	1030 med.	1010 med.					1010 med.	980 w.	1000 med.
	1000 w.	980 w.	975 med.	969 med.	980 w.	980 w.	970 w.	910 v.s.	—
820 med.	890 med.	900 w.	910 w.	855 med.	840 s.	840 w.	910 w.	840 med.	820 med.
770 w.	—	800 med.	700 med.	760 s.	770 med.	760 w.	810 med.	770 med.	
710 s.med.	700 w.	710 med.	730 med.	725 med.	740 med.	710 w.	730 med.	730 med.	730 med.
690 s.	675 s.	667 med.	680 med.	590 med.	700 med.	665 med.	670 med.	670 med.	690 s.
670 med.	665 med.	640 med.	665 med.s.						
655 med.s.	645 med.		640 med.	665 med.	665 med.	—	640 med.	645 med.	655 med.
								600 w.	
595 w.	590 w.					590 w.		570 w.	595 med.
—	560 med.		565 med.	575 med.	570 w.				
530 w.	530 w.	—	510 w.	500 w.	530 w.				520 med.
					455 w.	440 med.			460 w.
						420 med.			

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* The second column for the first compound gives the infrared spectroscopic data for the solution in CCl_4. The infrared spectra of the solutions of the other RSCONHCOR' in CCl_4 are analogous.

TABLE 2 (continued)

C_6H_{11}; C_2H_5	$C_6H_5CH_2$; CH_3	$C_6H_5CH_2$; C_3H_7	Assignment	Lit. cited
			νNH free	19—21
3270 v.s.	3270 m.sh.	3320 w.	νNH combined	5—9
	3220 med.	3240 s.		
3180 s.	3140 s.	3150 s.	Combination	5—9
			$\nu_{as}CH_3$	15
			$\nu_{as}CH_2$	15
			ν_sCH_2	15
1740 v.s.	1720 s.	1720 s.		
—	1700 s.	—	Imide I free	5—18
1690 s.	1675 v.s.	1680 v.s.	Imide I combined	
—	—	—		
1540—	1540 w.	1520 s.		
1520 s.	1510 s.	—	Imide II	5—12
			$\delta_{as}CH_3$	
1420 m.	1420 w.	1420 m.	$\delta_{as}CH_2$	15
			δ_sCH_3	
1330 w.	—	1320 m.	δCH_2 rock.	
—	1305 v.s.	—	ν_sC—N—C	5—9
	1250 w.	1260 w.	δCH_2	13—22
1230 m.	—	1240 v.s.		
1170 v.s	—	1190 v.s.	Imide III	
1140 v.s	1145 v.s.	1170 v.s.	ρCH_3 rock.	
1090 w.	1110 w.	1100 m.	νC—C rock.	5—9,15
1080 w.	1080 w.	1080 m.	νC—C+ρCH_3	
—	1055 w.	1050 m.	ρCH_3,ρCH_2	
1010 w.	1035 s.	1000 m.	νC—C+ρCH_3	15
950 w.	895 s.	910 m.		
800 s.	830 med.	800 m.	Imide V+δCH_2	5—9
740 m.	790 w.	770 m.	δCH_2+δCH_3	
710 m.	720 v.s.	720 s.	Imide V+δCH_2	5—9
665 s.	700 med.	700 m.		13, 14
	665 med.	680 s.	νC—S	
650 m.		630 w.	Imide IV	5—9
—	570 med.	570 w.	Imide VI	5—9
	490 w.	520 m.	δC—C=0+δN—C=0	
—	430 w.	480 m.	δC=0+δC—C—C	13—15
		450 w.	δ C—C—N	

TABLE 3. Wavenumbers (cm^{-1}) in the Infrared Spectra of RSCONHCOR' in the Range 400-80 cm^{-1}

No.	R	R	Frequencies and their assignment					
			δ C—C—S δ C—C=O δC—C—N	δ C—C—N δC—C=O	δS—C—N	δC—C_α—C_β+δC=0 δ C—S—C	τ C—N	τ—C—N, δC—N—C + lattice vib.
1	C_2H_5	CH_3	368 w.	342 med.	315 s.	280 m, 270 sh.	211 m,171 med.	140—80 br.
2	C_2H_5	C_2H_5	391 s.	347 w.	310 s.	270 s.	205 w.	150—80 br.
3	C_2H_5	C_3H_7	400 med.	368 w. 338 w.	312 s.	268 s.	196 w.	130—80 br.
4	C_2H_5	iso-C_4H_9	402 s.	355 m.s.	320 m, 292 s.	260 sh.	190 m,170 sh.	120 br.
5	C_2H_5	C_5H_{11}	—	362 med.	312 s.	258 w.	215 w.	130—80 br.
6	C_3H_7	C_2H_5	401 s.	365 med.	320 s.	280 s, 240 w.		140—80 br.
7	C_3H_7	C_3H_7	407 med.	355 med.	320 s.	275 s.	200 w.	125—80 br.

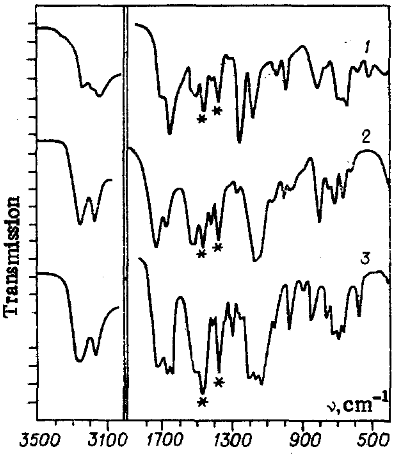


Fig. 1

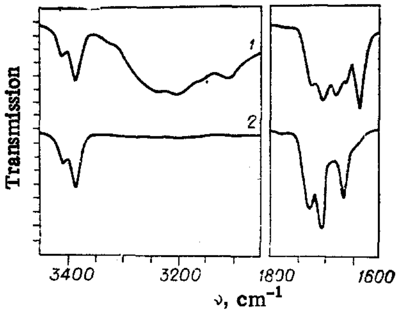


Fig. 2

Fig. 1. Infrared absorption spectra (400-3500 cm^{-1}) in liquid paraffin (the absorption bands due to liquid paraffin are marked with asterisks): 1) $C_2H_5SCONHCOOCH_3$; 2) $C_2H_5SCONHCOC_2H_5$; 3) C_2H_5-$SCONHCOC_4H_9$ (iso).

Fig. 2. Infrared absorption spectra of $C_2H_5SCONHCOC_2H_5$in CCl_4 in the range 3500-3100 cm^{-1} and 1800-1600 cm^{-1}: 1) C = 0.05 M, 2) C = 0.001 M.

We studied the infrared spectra of the alkyl N-acylthiocarbamates in the crystalline state and in solution (in CCl_4) in the range 3600-400 cm^{-1}, and for some compounds in the low-frequency range (400-80 cm^{-1}). Tables 2 and 3 give the characteristic frequencies for all the compounds, and Fig. 1 gives as an illustration the spectra of $C_2H_5SCONHCOCH_3$, $C_2H_5SCONHCOC_2H_5$, and $C_2H_5SCONHCOC_4H_9$-iso (in liquid paraffin). Since the infrared spectra of RSCONHCOR', for which there are no published data, are in many respects similar to the spectra of aliphatic N-acyl-substituted amides RCONHCOR', we used the assignment published for the latter [5-13]. The bands belonging to the C–S bond were assigned from [13-16].

The spectra of the solutions of all the compounds in CCl_4 in the range corresponding to the stretching vibrations of the N–H and C=O bonds are similar to one another. Several absorption bands are observed in the range 3500-3000 cm^{-1} (Fig. 2). The range 3420-3390 cm^{-1} contains two bands, the relative intensity of which increases with decrease in the concentration of the alkyl N-acylthiocarbamate in the solution. The range 3300-3110 cm^{-1} contains broad bands with poorly resolved peaks (3280, 3240, 3200, 3160, 3110 cm^{-1}), the relative intensity of which decreases with dilution of the solutions. The spectra of very dilute solutions ($C \approx 1 \cdot 10^{-3}$ M) do not contain the broad bands, and show only the two high-frequency bands at 3420-3410 cm^{-1} and 3400-3390 cm^{-1}, which we assigned to stretching vibrations of NH groups not involved in hydrogen bond formation, and the bands in the range 3300-3110 cm^{-1}, assigned to the ν_{NH} vibration of associated molecules and combination vibrations. In the range corresponding to the stretching vibrations of the C=O bond there are five intense absorption bands, at 1730, 1707, 1680, 1667, and 1640 cm^{-1}. With decrease in the concentration of the solutions, the relative intensity of the bands at 1640 and 1680 cm^{-1} decreases, and that of the bands at 1730, 1707, and 1667 cm^{-1} increases. The spectra of the solution with $C = 1 \cdot 10^{-3}$ M contain only three intense Imide I bands at 1730, 1707, and 1667 cm^{-1}. We therefore interpret these bands as ν_{CO} vibrations in the monomeric molecules, and the low-frequency bands at 1680 and 1640 cm^{-1} as due to the associates.

Thus the infrared spectra of the solutions in the νNH and νC=O range indicate the formation of a hydrogen bond CO...NH and agree with the cryoscopic measurements, which indicate that an equilibrium is established in the solution between associated and monomeric molecules of the alkyl N-acylthiocarbamates.

The compounds containing the CONHCO group are characterized by the presence in the spectrum of two Imide I absorption bands, due to the symmetric and antisymmetric vibrations of the bonds of two C=O groups undergoing resonance interaction [15, 17, 18]. The presence in the spectra of very dilute solutions of alkyl N-acylthiocarbamates of three intense absorption bands in the ν(C=O) range, together with two bands due to the νNH vibrations of free NH groups (the ratio of their intensities remains approximately constant for solutions of different concentrations) is probably due to the presence in solution of not only associates but also mono-

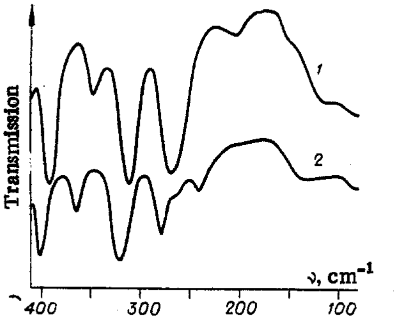
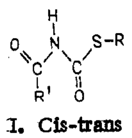


Fig. 3. Infrared absorption spectra in the range 80-400 cm^{-1} in liquid paraffin: 1) $C_2H_5SCONHCOC_2H_5$; 2) $C_3H_7SCONHCOC_2H_5$.

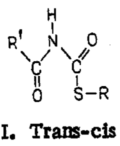
meric molecules, in the form of two rotational isomers. Other authors [19-21] observed the appearance of two νNH (free) bands and an increase in the number of Amide I bands, due to the rotational isomerism of trialkyl-substituted derivatives of urea, and secondary amides and thioamides.

The infrared spectra of the alkyl N-acylthiocarbamates in the solid state show only two or three fairly intense absorption bands in the range 3280-3160 cm^{-1}. In the range corresponding to the stretching vibrations of the C=O bonds we observed not only a decrease in the number of absorption bands but also a change in their intensity.

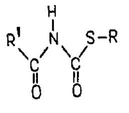
The spectra of compounds 1 and 9 show an intense band at 1660 cm^{-1}, and two bands of medium intensity at about 1720 and 1700 cm^{-1}. In the spectra of compounds 2, 3, 7, 8, and 10, the band of higher frequency at 1730 cm^{-1} is very intense, the band at 1685 cm^{-1} is less intense, and the absorption at 1660-1650 cm^{-1} either is nonexistent or appears as a shoulder of medium intensity. For the other substances, all three bands are intense. The long-wave displacement of the νNH band to 3280-3160 cm^{-1} relative to the band for the free NH group, and also the position, intensity, and number of νC=O bands, indicate that in the crystalline state the molecules of alkyl N-acylthiocarbamates are joined by a hydrogen bond NH... O=C and are present as various conformers, which will be discussed later. The spectra of all the crystalline alkyl N-acylthiocarbamates show a fairly intense broad band at 1540-1500 cm^{-1} (Imide II – ν_{as}C–N–O and δNH), which is displaced by 20-50 cm^{-1} towards lower frequencies in the spectra of the solutions. The presence of this band shows that in the molecules RSCONHCOR', at least one of the CO–NH groups has the trans configuration [5-12]. In the range 1300-1100 cm^{-1} the spectra of the solid substances and their solutions show a number of intense bands, due to the symmetric and antisymmetric stretching vibrations of the C–N bonds in the C–N–C group, δNH, and νC–C (Imide III), and also the bending vibrations of the CH_2 groups adjoining the sulfur atom [13]. The intensity of these bands is greater, and they are displaced by 30-40 cm^{-1} towards longer wavelengths compared with the same bands in the spectra of aliphatic diacylamines RCONHCOR' [22], and this can be attributed to the influence of the sulfur atom on the C–N and C–C bonds [13, 23]. The stretching vibrations of the C–S bond for RSCONHCOR' appear in the form of bands of medium intensity in the range 700-640 cm^{-1}; their positions remain unchanged in the spectra of the solutions. The low-frequency range of the spectra (400-80 cm^{-1}) contains intense absorption bands, which must be assigned to the bending vibrations of the groups C–C=O, C–C–S, C–C–N, S–C–N and the rotational vibrations of the groups C–N–C, C–C, C–S–C [15, 24] (Table 3 and Fig. 3). The accumulated data obtained indicate the analogy and at the same time certain differences in the structures of RSCONHCOR' and acyclic diacylamines. Alkyl N-acylthiocarbamates, like the diacylamines RCONHCOR', can exist in the form of several conformers, differing in the spatial arrangement of the N–H and C=O bonds in the CONHCO group*:



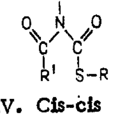
I. Cis-trans form A μ = 2.04D



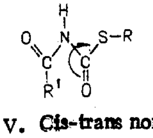
II. Trans-cis form A' μ = 3.90D



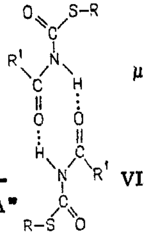
III. Trans-trans form B μ = 4.75D



IV. Cis-cis form C μ = 2.16D



V. Cis-trans nonplanar form A* μ = 2.37D



VI. Dimer of form A μ = 0D

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*For structures I-VI, the values of the dipole moments, calculated by the vector additive scheme, are given.

Examination of the geometry of the molecules shows that the steric hindrance should be least in structures I, III, and V, so that the alkyl N-acylthiocarbamates probably have one of these structures.* In fact, the infrared spectra of compounds 1, 9, and 11 in the solid state are similar (particularly in the νNH and νC=O range) to the spectrum of diacetamide in the cis-trans configuration (form A) and the spectra of the other compounds resemble the spectrum of diacetamide molecules having the trans-trans structure (form B) [5-9].

The spectra of solutions of RSCONHCOR' in CCl_4 are similar to one another and in many respects resemble the spectrum of diacetamide, which in solution adopts the stable configuration A, present in equilibrium with cyclic dimers [22, 25].

The spectra of very dilute solutions of the alkyl N-acylthiocarbamates, however, in addition to the νCO and νNH bands of form A (1730, 1707 cm^{-1} and 3400-3390 cm^{-1}, respectively), contain additional absorption bands at 1667 cm^{-1} (νC=O) and 3420 cm^{-1} (νNH free), which are not observed in the spectrum of solutions of diacetamide with the same concentration. The presence of thse bands probably indicates that the solution of RSCONHCOR' in CCl_4 contains a second conformer in addition to isomer I. This may be the nonplanar cis-trans form A" (structure V), since the νC=O band at 1667 cm^{-1} lies at lower frequencies than the Imide I band for structures having a planar imido group [5, 17, 18]. Rotation of the COSR group through 90° relative to the plane of the CO–NH group should lead to breakdown of the configuration in the imido group and a displacement of the Imide I bands towards lower frequencies, and a displacement of the νNH bands towards shorter wavelengths. The ratio of the intensities of the νNH bands at 3420 and 3400-3390 cm^{-1} remains constant for different solution concentrations (~1:2) and evidently indicates that molecules with the planar structure I predominate in the solutions.

The experimental values of the dipole moments of the alkyl N-acrylthiocarbamates in benzene (Table 1) agree with the calculated values for structure I and V, and apparently confirm the above conclusion regarding the structures of these compounds.

Thus we assume that unlike RCONHCOR', the alkyl N-acylthiocarbamates can exist not only in the form of conformers I and III but also in the form of conformer V.

EXPERIMENTAL

The alkyl N-acylthiocarbamates were synthesized by the method developed earlier [1, 2] by the action of the carboxylic acids on the complexes of tin(IV) chloride with the alkyl thiocyanate $SnCl_4 \cdot 2RSCN$.

Compounds 1, 2, 7, 9, 10, 11, and 12 were purified by recrystallization from a mixture of CCl_4 and petroleum ether, and compounds 3, 6, and 8 from petroleum ether.

The molecular weights and dipole moments were determined by the published methods [22], and the infrared spectra were recorded on a UR-20 spectrometer in the range 3600-400 cm^{-1} and on an FIS-3 spectrometer in the range 400-80 cm^{-1}. The specimens were prepared in the form of suspensions in liquid paraffin and in solution in CCl_4. The spectra of the solids were recorded between KRS plates, and the spectra of the solutions, with concentrations of 0.1-0.001 M, were recorded in NaCl and LiF cells with path length 0.1-10 mm (6 nm range) and 0.5-20 mm (3 nm range).

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DIELECTRIC PROPERTIES OF HYDRAZINE AND ITS AQUEOUS SOLUTIONS

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The complex dielectric constant of aqueous solutions of hydrazine in the centimeter range of wavelengths in the temperature range 5-50°C has been measured by the wave guide method. The complex dielectric constant of the mixtures studied is described by the Debye equation. The concentration dependence of the relaxation time has a maximum corresponding to the composition $N_2H_4 \cdot H_2O$. The static dielectric constant of aqueous solutions of hydrazine has been determined; its concentration dependence shows a negative deviation from additivity. the energy characteristics of the dielectric relaxation processes have been calculated. On the basis of the experimental data obtained, suggestions have been put forward regarding the nature of the molecular motion in hydrazine–water mixtures.

The electrical properties of pure hydrazine and its aqueous solutions have been insufficiently studied, since "at a platinum electrode, hydrazine decomposes rapidly as a result of the catalytic activity of platinum" [1]. It was of interest to study hydrazine and its aqueous solutions by electrical methods, particularly since many physical constants of hydrazine (particularly those characterizing the dielectric properties) are close to the corresponding values for water:

	Water	Hydrazine
Static DC	80.1(20°C)	52.9(20°C)
Dipole moment	1.84 D	1.83-1.90 D

The present paper gives the results of a study of the dielectric properties (the complex dielectric constant $(DC)\varepsilon^*$) of hydrazine and its solutions, obtained by the wave guide method [2] at frequencies of 3, 9.4, and 14 GHz in the temperature range 5-50°C. The uncertainties in the measurement of the real (ε') and imaginary (ε'') parts of the complex dielectric constant were 1.5-2 for ε' and 2.5-3% for ε''. The apparatus was calibrated

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