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Molecular Polarizability of Organic Compounds and Their Complexes: LII.[1] Molar Volumes of Polymeric Compounds in Solutions, Extrapolated to Infinite Dilution, and Steric Structure of Their Molecules

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Abstract — The molar volumes in solutions at infinite dilution were determined for a series of vinyl, glycol, isoprene, and cyclopentadiene polymers and oligomers with various degrees of polymerization. An additive analysis of the molar volumes showed that molecules of vinyl, ethylene glycol, and isoprene polymers exist in solutions in elongated helical conformations. In the majority of polymer molecules, except polystyrenes, polyisoprenes, and polycyclopentadienes, there are randomly disordered regions creating additional volumes inaccessible to solvation with solvent molecules. Cyclopentadiene oligomers formed by the Diels–Alder reaction have in solution the conformation of corrugated bands. The additive scheme for calculating the molar volumes considerably simplifies the determination of the dipole moments and Kerr constants of the compounds for which this scheme has been constructed.
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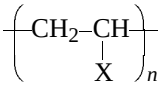
Our previous studies [1–5] concerned the molar volumes of low-molecular-weight compounds. In this study we examined by the method of molar volumes a series of macromolecular structurally nonrigid systems in solutions.

We chose polymeric compounds for which reliable experimental data on the concentration dependences of the solution densities (obtained in the course of detemining the dipole moments and Kerr constants) are available [6–13]. At the same time, final conclusions about the structure of the majority of the examined polymers in solutions were not made in [6–13]. As objects of this study we chose series of vinyl polymers, ethylene glycol polymers, cis and trans polymers and oligomers of isoprene, and cyclopentadiene oligomers (for all the compounds, samples of different molecular weights were taken). The formulas of these compounds are given below.

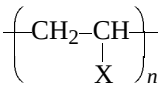
Polyvinyl compounds:



I–XXIV

n is degree of polymerization.

Poly(vinyl chlorides),
X = Cl: *n* = 538 (**I**), 688 (**II**), 852 (**III**), 966 (**IV**), 1586 (**V**), 2023 (**VI**);
Poly(vinyl bromides),
X = Br: *n* = 100 (**VII**), 128 (**VIII**), 187 (**IX**), 216 (**X**), 268 (**XI**), 350 (**XII**);
Poly(methyl acrylates),



I–XXIV

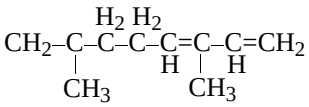
X = $COOCH_3$: *n* = 232 (**XIII**), 438 (**XIV**), 1367 (**XV**), 3016 (**XVI**), 21173 (**XVII**);

[1] For communication LI, see [1].

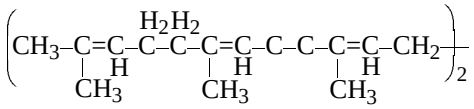
Poly(vinyl acetates),
X = $OCOCH_3$: n = 116 (**XVIII**), 209 (**XIX**), 523 (**XX**);
Polystyrenes,
X = C_6H_5: n = 9 (**XXI**), 24 (**XXII**), 77 (**XXIII**), 2402 (**XXIV**);

Poly(ethylene glycols),

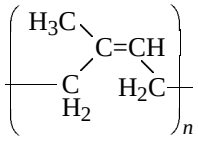
n = 4 (**XXV**), 6 (**XXVI**), 18 (**XXVII**), 34 (**XXVIII**), 78 (**XXVIX**), 153 (**XXX**);
Isoprene oligomers and polymers:



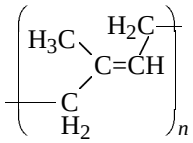
XXXI,
ocimene



XXXII,
squalene

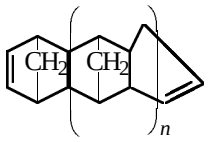


XXXIII,
cis-polyisoprene
n 13742

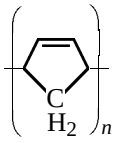


XXXIV
trans-polyisoprene
n 3120

Suggested alternative structures of cyclopentadiene oligomers:



A



B

n = 3 (**XXXV**), n = 4 (**XXXVI**), n = 9 (**XXXVII**), n = 22 (**XXXVIII**), n = 31 (**XXXIX**)
(**A**) Diels–Alder polymerization; (**B**) Diene polymerization.

The results of determination of the molar volumes of these compounds, extrapolated to infinite dilution ($_\infty V_2$), are listed in Table 1.

An additive analysis of the experimental values of $_\infty V_2$ of **I**–**XXIV** was performed by additive calculation of the molar volumes [V_{ad}, Eq. (1)]:

$$V_{ad} = nV(CH_2–CHX) + (n - 1)\Delta V_{C–C}, \qquad (1)$$

where n is the degree of polymerization; $V(CH_2–CHX)$ is the increment of the molar volume of the monomeric unit of the polymer in which X = Cl for **I**–**VI**, Br for **VII**–**XII**, $COOCH_3$ for **XIII**–**XVII**, $OCOCH_3$ for **XVIII**–**XX**, and C_6H_5 for **XXI**–**XXIV**; and $\Delta V_{C–C}$ is the increment of the molar volume of the C–C link between the monomeric units.

The increment of the molar volume of a monomeric unit was found by formula (2):

$$V(CH_2–CHX) = \Delta V_2(C_2H_5X) - 2\Delta V_{CH}, \qquad (2)$$

where $_\infty V(C_2H_5X)$ is the molar volume of a compound simulating the monomeric unit (Table 2);

Table 1. Molar volumes at infinite dilution in solutions of polymeric systems, additive calculation of these quantities, and determination of dipole moments and Kerr constants of molecules in solutions using the additivity of the molar volumes[a]

Comp. no.	Solvent	β	${}_{\infty}V_2$, $cm^3\,mol^{-1}$ (25°C)	V_{ad}, $cm^3\,mol^{-1}$	ε_V, %	Data obtained in this study by simplified method		Experimental data		Reference
						μ, D	${}_{\infty}(_mK_2)\times 10^{12}$, esu	μ, D	${}_{\infty}(_mK_2)\times 10^{12}$, esu	
				Poly(vinyl chlorides)						
I	Dioxane	0.268	24000±800	19162	20	36.5	1350	37.4	1433	[6]
II	Dioxane	0.270	30600±200	24502	20	41.5	6460	42.5	6722	[6]
III	Dioxane	0.267	37900±400	30340	20	46.4	11020	47.4	11434	[6]
IV	Dioxane	0.274	42600±200	34399	20	49.6	16000	50.7	16549	[6]
V	Dioxane	0.278	69600±900	56471	19	63.2	46600	64.6	48170	[6]
VI	Dioxane	0.284	88000±2000	72028	18	74.1	70000	75.4	72147	[6]
				Poly(vinyl bromides)						
VII	Dioxane	0.498	5230±200	4009	23	13.5	207	14.1	228	[7]
VIII	Dioxane	0.502	6620±200	5129	22	15.8	410	16.4	440	[7]
IX	Dioxane	0.450	9730±100	7489	23	20.4	1106	21.2	1165	[7]
X	Dioxane	0.522	10800±900	8649	20	22.8	1402	23.4	1469	[7]
XI	Dioxane	0.528	13100±700	10729	18	26.8	2103	27.4	2193	[7]
XII	Dioxane	0.520	17500±500	14008	20	32.8	3350	33.5	3489	[7]
				Poly(methyl acrylates)						
XIII	C_6H_6	0.264	16800±100	14116	16	21	5990	22	6160	[8]
XIV	C_6H_6	0.276	31300±900	26641	15	28	8340	29	8566	[8]
XV	C_6H_6	0.274	97800±1000	83124	15	50	24300	52	25494	[8]
XVI	C_6H_6	0.278	215000±900	183383	15	75	50100	78	52407	[8]
XVII	C_6H_6	0.285	1490000±10000	1287329	14	199	233000	205	247618	[8]
				Poly(vinyl acetates)						
XVIII	CCl_4	–0.326	8370±50	7456	11	17.8	1066	18.3	1070	[9]
	C_6H_6	0.268	8382±30		11	17.9	–17.6	18.4	70	
XIX	CCl_4	–0.315	14900±50	13426	10	23.9	1990	24.5	1998	[9]
	C_6H_6	0.265	15100±70		11	23.4	142	24.0	252	
XX	CCl_4	–0.357	38500±1000	33585	13	–	–	–	–	[9]
	C_6H_6	0.275	37300±300		10	35.9	633	36.9	900	
				Polystyrenes						
XXI	CCl_4	–0.489	846±8	811	4	0.5	104	0.9	104.4	[10]
XXII	CCl_4	–0.425	2250±50	2150	4	1.4	284	1.9	285.0	[10]
XXIII	CCl_4	–0.341	6770±200	6883	2	2.4	715	2.0	720.0	[10]
XXIV	CCl_4	–0.363	215000±8000	214506	0.2	10.4	21800	10.0	21750	[10]
				Poly(ethylene glycols)						
XXV	C_6H_6	0.222	178±1	129	30	3.53	85.7	3.64	89	[11]
XXVI	C_6H_6	0.223	267	190	30	3.95	60.9	4.10	66	[11]
XXVII	C_6H_6	0.237	699±2	561	20	5.24	138.0	5.46	149.6	[11]
XXVIII	C_6H_6	0.240	1300±20	1056	19	6.66	43.3	6.97	60	[11]
XXIX	C_6H_6	0.245	2980±30	2415	19	9.6	–241	10.1	–203.6	[11]
XXX	C_6H_6	0.238	5880±40	4733	20	13.3	–808	14.0	–729	[11]
				Isoprene oligomers, *cis*- and *trans*-polyisoprenes						
XXXI	C_6H_6	–0.109	173±1	169	2	0.48	42.1	0.54	42.4	[12]
XXXII	C_6H_6	–0.036	490±1	459	6	–	36.2	0.68	38.4	[12]

Table 1. (Contd.)

Comp. no.	Solvent	β	${}_\infty V_2$, $cm^3\,mol^{-1}$ (25°C)	V_{ad}, $cm^3\,mol^{-1}$	ε_V, %	Data obtained in this study by simplified method		Experimental data		Reference
						μ, D	${}_\infty(_mK_2)\times 10^{12}$, esu	μ, D	${}_\infty(_mK_2)\times 10^{12}$, esu	
Isoprene oligomers, *cis*- and *trans*-polyisoprenes										
XXXIII	C_6H_6	0.043	1020000 ± 2000	970194	5	18.4	–335000	33.3	–331900	[12]
XXXIV	C_6H_6	0.032	235000 ± 400	220634	6	9.2	–91200	17.2	90290	[12]
Cyclopentadiene oligomers										
XXXV [b]	C_6H_6	0.251	170 ± 0.4	187	10	0.74	10.8	0.51	9.7	[13]
				174	2	0.60	10.0			
XXXVI	C_6H_6	0.255	225 ± 4	239	6	0.70	12.0	0.55	11.2	[13]
				217	4	0.42	10.6			
XXXVII	C_6H_6	0.261	506 ± 0.2	500	1	0.45	19.3	0.55	19.8	[13]
				431	15	–	14.8			
XXXVIII	C_6H_6	0.263	1240 ± 3	989	20	–	–2.5	0.58	14.3	[13]
				1180	5	–	10.1			
XXXIX	C_6H_6	0.263	1710 ± 10	1651	3	–	4.9	0.56	8.5	[13]
				1375	20	–	–13.3			

[a] (β) Concentration coefficient, (${}_\infty V_2$) molar volume extrapolated to infinite dilution, (ε_V) relative deviation of experimental values of ${}_\infty V_2$ from the additively calculated values (V_{ad}), (μ) dipole moment, and ${}_\infty(_mK_2)$ Kerr constant. [b] For **XXXV**–**XXXIX**, V_{ad} was calculated assuming structures **A** (first figure in the column) and **B** (second figure).

Table 2. Molar volumes at infinite dilution in solutions of model compounds

Compound	Solvent	β	${}_\infty V_2$, $cm^3\,mol^{-1}$	Reference
Methyl chloride	CCl_4	–0.680	53.6 ± 2.0	[14]
Ethyl chloride	CCl_4	–0.734	70.6 ± 0.6	[15]
Methyl bromide	CCl_4	0.046	57.2 ± 0.4	[14]
Ethyl bromide	CCl_4	–0.085	74.6 ± 0.1	[16]
Methyl iodide	CCl_4	0.290	63.6 ± 0.2	[14]
Ethyl iodide	CCl_4	0.180	80.8 ± 0.2	[17]
Methyl acetate	C_6H_6	0.064	79.4 ± 0.5	[18]
Methyl propionate	C_6H_6	0.036	97.2 ± 0.3	[18]
Ethyl acetate	CCl_4	–0.705	98.9	[18]
Ethylbenzene	Neat liquid	–	122.5	[19]
Diethyl ether	CCl_4	–1.093	97.9 ± 4.9	[20]
Isoprene	C_6H_6	–0.265	98.6 ± 0.4	[12]
2-Methyl-2-butene	C_6H_6	–0.316	105.6 ± 0.9	[12]
Cyclopentadiene	CCl_4	–0.9677	82.1	[13]
Dicyclopentadiene	CCl_4	–0.611	134.4 ± 2.2	[13]
Cyclopentene	Neat liquid	–	88.2	[19]
2,2,3,3-Tetramethylbutane	Neat liquid	–	165.5	[19]
Isobutane	Neat liquid	–	105.4	[19]

Table 3. Increments of the molar volumes V(X) of bonds

X	V(X), $cm^3\,mol^{-1}$
C–C [a]	–9.0
C–C [b]	–8.6
C–C [c]	–10.4
C–C [d]	–8.7
C–C [e]	–7.2
C–C [f]	–19.3
C–O [g]	–5.1
C–Cl h	14.6
C–Br	18.2
C–I	24.6
C–H	13.0

[a] Determined for ethyl chloride. [b] Determined for ethyl bromide. [c] Determined for methyl propionate. [d] Determined for ethyl acetate. [e] Determined for ethylbenzene. [f] Determined by the formula $V(X) = V[(CH_3)_3C - C(CH_3)_3] - 2\{V[(CH_3)_3CH] - \Delta V_{CH}$. [g] Determined for diethyl ether. [h] Determined by the formula $V(X) = {}_\infty V_2(CH_3X) - 3\Delta V_{CH}$, where X = Cl, Br, I.

ΔV_{CH}, increment of the molar volume of the CH bond, equal to 13.0 $cm^3\,mol^{-1}$ and calculated previously [3] (Table 3). The increment of the molar volume of the C–C link (Table 3) was calculated by formula (3):

$$\Delta V_{C-C} = \Delta V2(C_2H_5X) - \Delta V2(CH_3X) - 2\Delta V_{CH}, \quad (3)$$

where ${}_\infty V_2(C_2H_5X)$ and ${}_\infty V_2(CH_3X)$ are the molar volumes of model compounds with the corresponding substituent X (Table 2).

The molar volumes of terminal groups of polymers **I**–**XXIV** were neglected because of relatively high degrees of polymerization of these compounds.

The additive molar volumes V_{ad} of poly(ethylene glycols) **XXV**–**XXX** were determined by formula (4):

$$V_{ad} = nV(CH_2–CH_2–O) + (n - 1)\Delta V_{CO}, \quad (4)$$

where $V(CH_2–CH_2–O) = \{{}_\infty V_2[(C_2H_5)_2O]\}/2 - \Delta V_{CH}$ is the additive molar volume of the monomeric unit found by us from data for the diethyl ether molecule (Table 2); $\Delta V_{CO} = 1/2\{{}_\infty V_2[(C_2H_5)_2O] - 2V(C_2H_5)\}$ is the increment of the molar volume of the C–O bond; the increment of the ethyl group, $V(C_2H_5) = 54\ cm^3\,mol^{-1}$, was found previously [1].

Since the degrees of polymerization of poly(ethylene glycols) were also relatively high, the contributions of the terminal groups were also neglected.

The results of an additive calculation of V_{ad} of vinyl polymers and poly(ethylene glycols) are compared in Table 1 with the experimental values of ${}_\infty V_2$.

The comparison shows that the relative deviation ε_V of the additively calculated values, V_{ad}, from the experimental values, ${}_\infty V_2$, are appreciable for the majority of vinyl polymers and poly(ethylene glycols): ε_V 18–20% for poly(vinyl chlorides) **I**–**VI**, 18–23% for poly(vinyl bromides) **VII**–**XII**, 14–16% for poly(methyl acrylates) **XIII**–**XVIII**, 10–13% for poly(vinyl acetates) **XVIII**–**XX**, and 19–30% for poly(ethylene glycols) **XXV**–**XXX**. Only for polystyrenes **XXI**–**XXIV** the relative deviation ε_V between the calculated and experimental values is as low as 0.2–4%, which is within the error of experimental determination of the molar volumes ${}_\infty V_2$. Good agreement between the experimental and additive values of molar volumes, as we noted in our previous papers [3, 5], indicates that all the fragments of solute molecules are well solvated with solvent molecules from all the sides and that there are no additional cavities inaccessible to solvent molecules between fragments of solute molecules. Among the vinyl polymers examined in this study, this is probably the case only for polystyrenes **XXI**–**XXIV**; in the chains of other polymers, apparently, there are areas inaccessible to the solvent. To confirm these assumptions, we determined the molar volumes and performed an additive calculation for a series of unsubstituted alkanes as neat liquids and of mono- and dihalo-substituted saturated hydrocarbons in solutions (Tables 4, 5). We chose compounds with an even number of carbon atoms in molecular chains, to have a closer analogy with vinyl polymers [formula (1)].

The additive molar volumes V_{ad} of alkanes were determined by formula (5):

$$V_{ad} = nV(CH_2–CH_2) + (n - 1)\Delta V_{C-C} + 2V_{CH}, \quad (5)$$

where n is the number of "monomeric units" in a molecule of the compound; $V(CH_2–CH_2)$, molar volume of a "monomeric unit" [by analogy with the molar volume of a monomeric unit of a vinyl polymer $V(CH_2–CHX)$]; ΔV_{C-C}, increment of the molar volume of the C–C bond [we chose the value for poly(vinyl chlorides) **I**–**VI**, see above, Table 3]; and ΔV_{CH}, increment of the molar volume of the CH bond (Table 3).

The additive molar volumes V_{ad} of mono- and dihaloalkanes were determined by formulas (6) and (7), respectively:

$$V_{ad} = nV(CH_2–CH_2) + (n - 1)\Delta V_{C-C} + \Delta V_{CH} + V(X), \quad (6)$$

$$V_{ad} = nV(CH_2–CH_2) + (n - 1)\Delta V_{C-C} + 2V(X), \quad (7)$$

where V(X) is the increment of the molar volume of substituent C–X (Table 3); the other designations and values are the same as above.

The attained agreement between the additive calculation and the experiment indicates that the molecules of alkanes and their halo derivatives exist in the form of elongated helices. The pitch and radius of these helices in solutions are favorable for efficient solvation with solvent molecules; therefore, the additivity of the molar volume of these compounds is preserved. It should be noted here that *n*-paraffin molecules of various molecular weights in the liquid state have the same molecular structure and are packed in a liquid similarly to cylinders of revolution (helices), with approximately six nearest neighbors [22]. However, for the majority of vinyl polymers and poly(ethylene glycols) examined in this study, no definite conclusions can be made on the molecular structure in solutions. Since the deviation between the additive and experimental molar volumes of polymers **I**–**XX** and **XXV**–**XXX** is moderate (10–30%), we believe that their molecules also have helical conformations. There are, however, areas in which the helical conformation is disturbed and the mutual arrangement of units of polymer chains is randomly disordered. The internal volumes of the disordered segments of molecules may be inaccessible to a solvent, which leads to higher values of ${}_{\infty}V_2$ compared to the additive estimates V_{ad}.

Table 4. Molar volumes of alkanes as neat liquids and additive calculation of these quantities[a]

Compound	V, $cm^3\,mol^{-1}$ (20°C)	V_{ad}, $cm^3\,mol^{-1}$	ε_V, %
CC_4H_{10}	100.4	99	1.4
C_6H_{14}	130.5	131	0.4
C_8H_{18}	162.6	163	0.2
$C_{10}H_{22}$	194.9	195	0.1
$C_{12}H_{26}$	227.5	227	0.2
$C_{14}H_{30}$	260.1	259	0.4
$C_{16}H_{34}$	294.0	291	1.0
$C_{18}H_{38}$	327.6	323	1.4
$C_{20}H_{42}$	358.4	355	0.9
$C_{22}H_{46}$	391.0	387	1.0
$C_{26}H_{54}$	471.2	451	4.3

[a] Determined from the density of the neat liquid [19]; (V) molar volume of the neat liquid.

An additional information can be derived from the dipole moments of the compounds. The dipole moment $\vec{\mu}$ of a polymeric molecule can be represented as a vector sum of the dipole moments of the monomeric units $\vec{\mu}_i$:

$$\vec{\mu} = \sum_i^n \vec{\mu}_i, \qquad (8)$$

Table 5. Molar volumes at infinite filution in CCl_4 of mono- and dihaloalkanes and additive calculation of these quantities

Compound	β	${}_{\infty}V_2$, $cm^3\,mol^{-1}$	V_{ad}, $cm^3\,mol^{-1}$	ε_V, %	Reference
C_4H_9Cl	–0.781	104 ± 0.5	105	1	[15]
$C_6H_{13}Cl$	–0.794	136 ± 0.2	139	2	[15]
C_4H_9Br	–0.245	108 ± 1	109	1	[16]
$C_6H_{13}Br$	–0.346	140 ± 0.2	144	3	[16]
$C_8H_{17}Br$	–0.411	172 ± 1	179	4	[16]
$C_{10}H_{21}Br$	–0.488	208 ± 0.5	213	2	[16]
$C_{12}H_{25}Br$	–0.527	240 ± 10	248	3	[16]
$C_{14}H_{29}Br$	–0.539	269 ± 4	282	5	[16]
$C_{16}H_{33}Br$	–0.591	307 ± 1	317	3	[16]
$C_{18}H_{37}Br$	–0.595	336 ± 1	352	5	[16]
C_4H_9I	0.025	113 ± 2	115	2	[17]
$C_6H_{13}I$	–0.109	148 ± 1	149	1	[17]
$C_8H_{17}I$	–0.210	183 ± 0.3	183	0	[17]
$C_{10}H_{21}I$	–0.267	214 ± 1	218	2	[17]
$Cl[CH_2]_2Cl$	–0.286	80.4 ± 0.3	72.2	10	[21]
$Cl[CH_2]_4Cl$	–0.385	111 ± 0.2	106	4	[21]
$Cl[CH_2]_{10}Cl$	–0.601	213 ± 2	208	2	[21]
$Br[CH_2]_2Br$	0.265	87.1	80	8	[21]
$Br[CH_2]_4Br$	0.141	117 ± 0.2	115	2	[21]
$Br[CH_2]_{10}Br$	–0.163	220 ± 2	218	1	[21]

where n is the degree of polymerization. Raising (8) to the scalar second power and averaging over all the possible conformations of macromolecules, we obtain

$$\mu^2 = n\mu_{unit}^2 + \Sigma\langle\vec{\mu_i}\vec{\mu_j}\rangle, \quad (9)$$

where μ_{unit} is the dipole moment of the monomeric unit (all units are identical); the sum in the right part of (9) is the correlation term reflecting the correlations in the mutual orientation of the polymeric units of the macromolecules. For a freely articulated chain with independent orientation of units, only the first term $n\mu_{unit}^2$ remains in the right side of (9) [23]. The squares of the experimental dipole moments of polymers **I**–**XX** and **XXV**–**XXX** are compared in Table 6 with the calculated squares of the dipole moments for the freely articulated polymer chain. The experimental dipole moments of these polymers are listed in Table 1. We used the following dipole moments of molecules simulating monomeric units: 1.89 D for ethyl chloride [unit of poly(vinyl chlorides)] [15]; 1.93 D for ethyl bromide [unit of poly(vinyl bro-

Table 6. Comparison of squared experimental dipole moments of polymer molecules with those calculated for the model of a freely articulated polymer chain

Comp. no.	n [a]	$n\mu_{unit}^2$, D	μ_{exp}^2, D	ε_V, %	References
			Poly(vinyl chlorides)		
I	538	1920	1400	37	[6]
II	688	2460	1810	36	[6]
III	852	3040	2250	35	[6]
IV	966	3450	2570	34	[6]
V	1586	5660	4170	36	[6]
VI	2023	7220	5680	27	[6]
			Poly(vinyl bromides)		
VII	100	372	199	87	[7]
VIII	128	476	269	77	[7]
IX	187	696	449	55	[7]
X	216	804	548	47	[7]
XI	268	997	751	33	[7]
XII	350	1300	1120	16	[7]
			Poly(methyl acrylates)		
XIII	232	710	484	47	[8]
XIV	438	1340	841	59	[8]
XV	1367	4180	2700	55	[8]
XVI	3016	9230	6080	52	[8]
XVII	21173	64800	42000	54	[8]
			Poly(vinyl acetates)		
XVIII	116	392	335 [b]	17	[9]
			338	16	
XIX	209	706	600	18	[9]
			576	22	
XX	523	1770	–	–	[9]
			1360	30	
			Poly(ethylene glycols)		
XXV	4	3.48	13.2	74	[11]
XXVI	6	5.22	16.8	70	[11]
XXVII	18	15.70	29.8	47	[11]
XXVIII	34	29.60	48.6	39	[11]
XXIX	78	67.90	102	33	[11]
XXX	153	133	196	32	[11]

[a] (n) Degree of polymerization, (μ_{unit}) dipole moments of molecules simulating the monomeric units, (μ_{exp}) experimental dipole moments of polymers **I**–**XX** and **XXV**–**XXX**, and (ε_V) relative deviation of the experimental values (μ_{exp}^2) from those calculated ($n\mu_{unit}^2$). [b] For **XVIII**–**XX**, the first figure in the column is for solutions in CCl_4, and the second figure, for solutions in C_6H_6.

mides)] [16]; 1.76 D for methyl propionate [unit of poly(methyl acrylates)] [18]; 1.84 D for ethyl acetate [unit of poly(vinyl acetates)] [18]; and 1.32 D for diethyl ether [unit of poly(ethylene glycols)] [20]. As seen from this table, the squared dipole moments calculated for the model of a freely articulated chain significantly deviate from the experimental squared dipole moments of the polymers. This fact indicates that polymer molecules in solution do not form fully random molecular coils. The monomeric units are ordered in a certain way in their orientation relative to each other. The structure of macromolecules, as already noted, is closer to a molecular helix, but for the majority of macromolecules there are areas of random disorder in the mutual arrangement of the monomeric unit, which gives rise to an excess volume inaccessible to solvent molecules. It should be noted that Le Fevre et al. [6–11] whose data were used for determining the molar volumes of the polymers made no conclusions on whether the macromolecules have a structure of a molecular helix or a random coil.

The additive molar volume of isoprene oligomers and polymers **XXXI**–**XXXIV** was calculated by formulas (10)–(13).

Ocimene **XXXI**: In accordance with its structural formula, V_{ad} can be represented as follows:

$$V_{ad} = {}_{\infty}V_2(\text{2-methylbut-2-ene}) + {}_{\infty}V_2(\text{isoprene}) + \Delta V_{C-C} - 2\Delta V_{CH}, \quad (10)$$

where ${}_{\infty}V_2$(2-methylbut-2-ene) and ${}_{\infty}V_2$(isoprene) are the molar volumes of model compounds (Table 2); ΔV_{C-C} is the increment of the molar volume of the C–C bond [we used the same value as for poly(vinyl chlorides) **I**–**VI**, Table 3; this value was also used in calculations of the other isoprene oligomers and polymers **XXXI**–**XXXIV**].

Squalene **XXXII**: The molar volume V_{ad} was calculated by formula (11):

$$V_{ad} = 2[3{}_{\infty}V_2(\text{2-methylbut-2-ene}) + 2\Delta V_{C-C} - 5\Delta V_{CH}] + \Delta V_{C-C}. \quad (11)$$

The additive molar volumes of *cis*-polyisoprene **XXXIII** and *trans*-polyisoprene **XXXIV** were calculated by formula (12):

$$V_{ad} = n[{}_{\infty}V_2(\text{2-methylbut-2-ene}) - 2\Delta V_{CH}] + (n - 1)\Delta V_{C-C}. \quad (12)$$

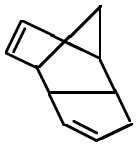
The results of the additive calculation are compared with the experimental data in Table 1. It is seen that agreement between V_{ad} and ${}_{\infty}V_2$ is very good. Apparently, the molecules of both oligomers and polymers of isoprene are well solvated with solvent molecules from all the sides, which ensures the additivity of the molar volumes. The molecules of *cis*- and *trans*-polyisoprenes, apparently, form helices with the pitch and radius that do not prevent solvation.

In the case of cyclopentadiene oligomers **XXXV**–**XXXIX**, it was interesting to determine whether they are formed by the Diels–Alder reaction (diene synthesis [24], structure **A**) or by common diene polymerization typical, e.g., for isoprene (structure **B**).

The additive molar volumes for structure **A** were calculated by formula (13):

$$V_{ad} = n_{\infty}V_2(\text{cyclopentadiene}) + (n - 1)\Delta V, \quad (13)$$

where ${}_{\infty}V_2$(cyclopentadiene) is the molar volume of cyclopentadiene (Table 2); $\Delta V = {}_{\infty}V_2(\text{dimer}) - 2{}_{\infty}V_2(\text{cyclopentadiene})$ is the negative increment of the molar volume at Diels–Alder coupling of two cyclopentadiene molecules; and ${}_{\infty}V_2$(dimer) is the molar volume of cyclopentadiene (Table 2). According to [13], dicyclopentadiene is indeed formed by the diene synthesis.



dicyclopentadiene,
endo form

The additive molar volumes of oligomers of structure **B** were calculated by formula (14):

$$V_{ad} = nV(\text{unit}) + (n - 1)\Delta V_{C-C} + 2\Delta V_{CH}, \quad (14)$$

where V(unit) is the molar volume of the monomeric unit, simulated by the molar volume of cyclopentene (Table 2) minus increments of the molar volumes of two C–H bonds. The term $2\Delta_{CH}$ in formula (14) takes into account the terminal units. For structure B, it is necessary to take into account the increment ΔV_{C-C} as accurately as possible, because this increment corresponds to the C–C bond strongly shielded by other bonds of the adjacent fragments. The increment of this bond was found using as model compound 2,2,3,3-tetramethylbutane $(CH_3)_3C–C(CH_3)_3$ (Table 2) in which the central C–C bond is shielded to approximately the same extent as the C–C bonds between five-membered rings in oligomers of structure **B** (Table 3).

The results of the additive calculation of V_{ad} of oligomers **XXXV**–**XXXIX** are compared with the experimental values, ${}_{\infty}V_2$, in Table 1. It is seen that structure **A** ensures the best agreement between the experimental and calculated data. If the oligomer molecules have a band shape in solutions, their twisting with the formation of additional molecular volumes inaccessible to solvent molecules can hardly be expected. Therefore, if structure **A** is actually realized, agreement between V_{ad} and ${}_{\infty}V_2$ should be good. For structure **B**, the discrepancy between the calculated and experimental values is more significant, despite the fact that here the shielding of the C–C bond was taken into account. Furthermore, the relatively low molecular weight of the oligomers gives no grounds to expect formation of noticeable additional molecular volumes inaccessible to solvent molecules. Hence we conclude that cyclopentadiene oligomers most probably have structure **A** and their molecules are formed by diene synthesis. This conclusion coincides with the conclusions made by the methods of Kerr effect and dipole moments [13].

Then we demonstrated the possibility of substantial simplification of methods for determining the dipole moments and Kerr constants for compounds for which we constructed an additive scheme for calculating the molar volumes. We calculated the Kerr constants ${}_{\infty}({}_mK_2)$ and dipole moments μ of the compounds by a new simplified procedure [2] using additive quantities V_{ad}. We used the concentration coefficients α, γ, and δ from the papers cited above, with which the quantities ${}_{\infty}V_2$ were determined. The transformed Le Fevre and Fujita's formulas for calculating the dipole moments and Kerr constants are given elsewhere [2]. The results of the simplified calculation and the experimental data are given in Table 1. In most cases, the values obtained by the simplified calculation well agree with the published data. However, for squalene **XXXII**, cyclopentadiene oligomers of structure **B** (**XXXVII**), and compounds **XXXVIII** and **XXXIX** of structures **A** and **B** we failed to obtain reasonable values of the dipole moments, because the published experimental refraction and the polarizability calculated by the simplified procedure appeared to be very close. Similarly, for poly(vinyl acetates) **XVIII**–**XX** in benzene solutions we failed to bring the Kerr constants calculated by the simplified procedure to agreement with the published experimental data. This is caused by the fact that the major contribution to the molar Kerr constant of these compounds is made by the concentration coefficients β and α, rather than by the quantity δ associated with the Kerr effect. However, here specifically β was estimated through the molar volume V_{ad} with the lowest accuracy. In the other cases the agreement between the experimental and calculated values is fairly good. Thus, in most cases the procedures for determining μ and ${}_{\infty}({}_mK_2)$ can be considerably simplified by replacing the experimental determination of solution densities with calculation of the additive molar volumes of the compounds and use of the modified Le Fevre and Fujita's formulas. This simplification is the more accurate, the closer V_{ad} and ${}_{\infty}V_2$.

EXPERIMENTAL

The experimental dependences of the solution densities on their concentrations, required for the determination of the molar volumes at infinite dilution ${}_{\infty}V_2$, were taken from [6–18, 20, 21]. We chose systems for which the available data set included no less than five concentrations with the corresponding densities and other properties of solutions. The linear correlations $\rho_{12} = \rho_1(1 + \beta\omega)$ were treated by the least-squares method to determine β; the correlation coefficients were no less than 0.99. The experimental molar volumes of the solutes ${}_{\infty}V_2$ were calculated by extrapolation formula (15) derived previously [2]:

$$ {}_{\infty}V_2 = \frac{M_2(1-\beta)}{\rho_1}. \qquad (15) $$

In calculation of the dipole moments and Kerr constants of compounds using the additive molar volumes V_{ad}, the required parameters α, γ, and δ were taken from the same above-cited papers.

It is difficult to refine by statistical treatment the published [11, 13, 18, 21] concentration dependences of the solution densities for poly(ethylene glycol) **XXVI** (Table 1), cyclopentadiene, ethyl acetate (Table 2), and 1,2-dibromoethane (Table 4); therefore, we took authors' values of β for these compounds.

When determining the experimental molar volumes of compounds, we used for solvents the following data. Carbon tetrachloride: ρ_1 1.58454 g cm^{-3}, ε_1 2.2270 at 25°C [16, 20, 21]; ρ_1 1.5845 g cm^{-3}, ε_1 2.2270 at 25°C [10, 13, 14]. Dioxane: ρ_1 1.02800 g cm^{-3}, ρ_1 2.209 at 25°C [6, 7]. Benzene: ρ_1 0.87378 g cm^{-3}, ε_1 2.2725 at 25°C [8, 11, 12]; ρ_1 0.87380 g cm^{-3}, ε_1 2.2725 at 25°C [9, 13]. The other solvent properties required for calculating the Kerr constants are given in [25]. In [15, 17, 18], the solvent properties are not given; when determining the experimental molar volumes of compounds examined in these studies, we used the following data. Carbon tetrachloride: ρ_1 1.58454 g cm^{-3}, ε_1 2.2270 at 25°C. Benzene: ρ_1 0.87378 g cm^{-3}, ε_1 2.2725 at 25°C.

The dipole moments of the compounds are given in debyes (D), and the Kerr constants, in CGSE units

(esu). The conversion factors are as follows: 1 C m = 0.2998×10^{30} D, 1 $m^5 V^{-2} mol^{-1}$ = 0.8988×10^{15} esu mol^{-1}.

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