VOLUME PROPERTIES OF DILUTE AQUEOUS SOLUTIONS OF POLY(OXYETHYLENE) AND ITS LOW MOLECULAR MODELS

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Dedicated to Dr B. Sedláček on the occasion of his 60th birthday.

The densities were measured of pure liquid mono-, di-, tri-, and poly(oxyethylene) up to the molar mass 20 000, of 3-oxa-1-butanol and 3,6-dioxa-1-heptanol, 3-oxa-1-pentanol and 3,6-dioxa-1-octanol, 3,6-dioxa-1-decanol, 2,5-dioxahexane, 2,5,8,11-tetraoxadodecane and 2,5,8,11,14-pentaoxapentadecane, 3,6-dioxaoctane and 3,6,9-trioxaundecane and their aqueous solutions at the mass concentrations smaller than 0·02 in the temperature range 15—50°C. The experimental data thus obtained were used to calculate values of the apparent specific volume at infinite dilution, specific expansion at infinite dilution, excess limiting partial specific volume and excess limiting molar expansibility of the dissolved compound. The suitability of these values as criteria of hydrophobicity of the respective compounds was verified. The volume contributions of homologous and end groups were calculated.

The partial molar volumes, $\bar{V}_2^0$, or the apparent molar volumes, Φ_2^0, of compounds in aqueous solutions at infinite dilutions belong to the thermodynamic properties used in the investigation of interactions in aqueous solutions[1]. Important information on processes taking place during dissolution is provided not only by the values of $\bar{V}_2^0$ and Φ_2^0, but also by their changes with temperature and concentration[2-6].

In this study we measured the temperature dependences of the apparent specific volume at infinite dilution, ϕ_2^0, and of the specific volume, v_2, of pure liquid poly(oxyethylenes) and their monomethyl, ethyl, butyl, dimethyl, and diethyl ethers in aqueous solutions. The data were employed to verify the dependence of $\bar{V}_2^0$ $(= \Phi_2^0)$ on the van der Waals volume, V_w, using Terasawa's relation[7]

$$\bar{V}_2^0 = a + bV_w \qquad (1)$$

in the range of high molar masses, to interpret the constants a, b and to calculate the volume contributions of the individual groups. The effect was also investigated of the length of the poly(oxyethylene) chain on the excess limiting partial specific volume, $\bar{v}_2^{0E} = \phi_2^0 - v_2$, limiting specific expansibility of the dissolved compound, $\alpha_0 = (\partial\phi_2^0/\partial T)_P$, and excess limiting molar expansibility, $\bar{\alpha}_2^{0E} = M(\alpha_0 - \alpha)$, where M

is the molar mass of the dissolved compound and $\alpha = (\partial v_2/\partial T)_P$ is its specific expansibility. The applicability of these quantities as the measure of hydrophobicity of the dissolved compound was estimated.

EXPERIMENTAL

The mono-, di, and tri(oxyethylenes) (compounds G1, G2, and G3, respectively) were produced by Lachema, Czechoslovakia, and were analytical purity grade. The other compounds, namely, poly(oxyethylenes) designated as PEG 200, PEG 400, PEG 600, PEG 2 000, PEG 20 000, 3-oxa-1-butanol and 3,6-dioxa-1-heptanol (monomethyl ethers designated further as M1 and M2, respectively), 3-oxa-1-pentanol and 3,6-dioxa-1-octanol (monoethyl ethers E1 and E2), 3,6-dioxa-1-decanol (compound B2), 2,5-dioxahexane, 2,5,8,11-tetraoxadodecane and 2,5,8,11,14-pentaoxapentadecane (dimethyl ethers, designated as DM1, DM3 and DM4, respectively), and finally 3,6-dioxaoctane and 3,6,9-trioxaundecane (diethyl ethers DE1 and DE2) were produced by Fluka and were of the highest available purity. These compounds were used without further purification.

The densities of pure liquid compounds and aqueous solutions were measured by means of a vibrational densitometer DMA 02 C provided with a Setaram thermostat in the temperature range 15—50°C. The densitometer was calibrated using water and air densities.

The individual concentrations were obtained by weighing the sample and redistilled water into glass ampoules. The measurements were performed in two concentration ranges, for the mass fractions of the sample $w_2 < 0{\cdot}02$ and $w_2 < 0{\cdot}15$.

The values of the apparent specific volume of the sample in an aqueous solution, ϕ_2, were calculated from

$$\phi_2 = [d_1 - d(1 + w_2)]/dd_1 w_2\,, \qquad (2)$$

where d_1 is the water density calculated for the individual temperatures using a relation suggested by Kelle[8], d is the density of the sample solution at a given concentration and temperature, and w_2 is the mass fraction of the sample.

RESULTS AND DISCUSSION

As there are still some ambiguities regarding the limiting value $\partial \bar{v}_2/\partial w_2$, and thus also extrapolation of the concentration dependences of ϕ_2 to zero concentration[9-11], the ϕ_2 values were calculated from measurements of the density of solutions (d) at six concentrations ($w_2 < 0{\cdot}02$), and the $\phi_2^0 = \bar{v}_2^0$ values were obtained by linear extrapolation. It was found that in this range the ϕ_2 values of the samples are virtually independent of concentration. The extrapolated ϕ_2^0 values are given along with those of the specific volumes of liquid samples and of the specific expansibility of the dissolved compound at infinite dilution in Table I. These values were used in the further treatment. They are in fair agreement with the available reported data (Table II).

For some selected samples the densities were measured for six concentrations up to $w_2 \sim 0{\cdot}15$, when the concentration dependence of ϕ_2 became distinct. The constants k and ϕ_2^0 of the concentration dependence $\phi_2 = \phi_2^0 + kw_2$ are summarized in Table III. The slope k characterizes pair interactions between molecules of the dissolved compound in solution. In aqueous solutions it is directly related to the

TABLE I

Apparent limiting specific volumes, ϕ_2^0, and specific volumes, v_2, of poly(oxyethylene) and its low molecular models (mass fraction $w_2 < 0{\cdot}02$); α is specific expansibility and α_0 limiting specific expansibility of the dissolved compound

T °C	ϕ_2^0 $cm^3 g^{-1}$	T °C	v_2 $cm^3 g^{-1}$	T °C	ϕ_2^0 $cm^3 g^{-1}$	T °C	v_2 $cm^3 g^{-1}$
Ethylene glycol				3-Oxa-1,5-pentanediol			
15·0	0·8739	15·0	0·89531	14·6	0·8617	14·6	0·89191
25·0	0·8794	19·9	0·89818	24·7	0·8675	22·0	0·89622
35·0	0·8843	24·9	0·90092	34·8	0·8739	24·9	0·89789
40·1	0·8887	35·0	0·90688	35·0	0·8726	35·0	0·90378
50·1	0·8949	50·1	0·91586	42·0	0·8779	45·0	0·90974
				44·8	0·8809		
$\alpha_0 = 5{\cdot}97 \, . \, 10^{-4}$		$\alpha = 5{\cdot}85 \, . \, 10^{-4}$		49·8	0·8822		
				$\alpha_0 = 5{\cdot}97 \, . \, 10^{-4}$		$\alpha = 5{\cdot}87 \, . \, 10^{-4}$	
3,6-Dioxa-1,8-octanediol				PEG 200			
15·0	0·8525	15·0	0·88639	14·8	0·8489	15·0	0·88541
24·9	0·8600	25·0	0·89264	25·0	0·8918	20·0	0·88868
35·0	0·8654	35·0	0·89896	34·8	0·8620	25·0	0·89181
40·1	0·8685	50·1	0·90864	42·0	0·8664	35·0	0·89830
50·1	0·8750			49·8	0·8719	50·1	0·90811
$\alpha_0 = 6{\cdot}27 \, . \, 10^{-4}$		$\alpha = 6{\cdot}34 \, . \, 10^{-4}$		$\alpha_0 = 6{\cdot}55 \, . \, 10^{-4}$		$\alpha = 6{\cdot}44 \, . \, 10^{-4}$	
PEG 400				PEG 600			
14·6	0·8405	14·6	0·88384	15·0	0·8351	25·0	0·88972
24·7	0·8473	22·0	0·88884	25·0	0·8430	35·0	0·89650
34·8	0·8558	24·9	0·89078	35·0	0·8506	50·0	0·90663
42·0	0·8588	35·0	0·89750	40·1	0·8534		
49·8	0·8656	45·0	0·90420	50·0	0·8606		
$\alpha_0 = 7{\cdot}05 \, . \, 10^{-4}$		$\alpha = 6{\cdot}70 \, . \, 10^{-4}$		$\alpha_0 = 7{\cdot}26 \, . \, 10^{-4}$		$\alpha = 6{\cdot}76 \, . \, 10^{-4}$	
PEG 2 000				PEG 20 000			
15·0	0·8426			15·0	0·8282		
25·0	0·8404			25·0	0·8357		
35·2	0·8478			35·2	0·8429		
49·9	0·8617			49·9	0·8578		
$\alpha_0 = 8{\cdot}29 \, . \, 10^{-4}$				$\alpha_0 = 8{\cdot}44 \, . \, 10^{-4}$			

TABLE I
(*Continued*)

T °C	ϕ_2^0 cm^3 g^{-1}	T °C	v_2 cm^3 g^{-1}	T °C	ϕ_2^0 cm^3 g^{-1}	T °C	v_2 cm^3 g^{-1}
3-Oxa-1-butanol				3,6-Dioxa-1-heptanol			
15·0	0·9800	15·0	1·02930	15·2	0·9264	14·8	0·97387
25·0	0·9862	25·0	1·03941	25·0	0·9332	24·9	0·98276
35·0	0·9916	35·0	1·04894	35·0	0·9394	35·0	0·99147
40·1	0·9975	50·1	1·06469	42·3	0·9451	42·1	0·99763
50·1	1·0046			48·0	0·9499	48·0	1·00247
$\alpha_0 = 7{\cdot}04 \,.\, 10^{-4}$		$\alpha = 10{\cdot}01 \,.\, 10^{-4}$		$\alpha_0 = 7{\cdot}03 \,.\, 10^{-4}$		$\alpha = 8{\cdot}61 \,.\, 10^{-4}$	
3-Oxa-1-pentanol				3,6-Dioxa-1-octanol			
15·1	1·0060	15·1	1·07100	15·1	0·9487	15·1	1·00614
25·1	1·0099	25·0	1·08124	25·1	0·9552	25·0	1·01501
34·8	1·0167	34·8	1·09165	34·8	0·9612	34·8	1·02396
42·3	1·0234	42·2	1·09992	42·3	0·9674	42·2	1·03098
50·2	1·0310	50·2	1·10907	50·2	0·9744	50·2	1·03873
$\alpha_0 = 7{\cdot}21 \,.\, 10^{-4}$		$\alpha = 10{\cdot}84 \,.\, 10^{-4}$		$\alpha_0 = 7{\cdot}25 \,.\, 10^{-4}$		$\alpha = 9{\cdot}28 \,.\, 10^{-4}$	
3,6-Dioxa-1-decanol				2,5-Dioxahexane			
14·8	0·9756	14·8	1·04470	15·0	1·0542	15·0	1·14677
25·0	0·9860	25·0	1·05408	25·0	1·0607	25·0	1·16149
34·9	0·9926	34·8	1·06317	35·0	1·0663	35·0	1·17614
42·1	0·9999	42·1	1·07024	40·1	1·0723	50·1	1·19978
48·1	1·0068	48·1	1·07602	50·1	1·0836		
$\alpha_0 = 9{\cdot}06 \,.\, 10^{-4}$		$\alpha = 9{\cdot}40 \,.\, 10^{-4}$		$\alpha_0 = 8{\cdot}15 \,.\, 10^{-4}$		$\alpha = 15{\cdot}10 \,.\, 10^{-4}$	
2,5,8,11-Tetraoxadodecane				2,5,8,11,14-Pentaoxapentadecane			
15·0	0·9408	14·6	1·00584	14·8	0·9204	14·6	0·98378
25·0	0·9492	24·9	1·01594	25·1	0·9293	24·9	0·99315
35·1	0·9536	35·0	1·02580	35·2	0·9344	35·0	1·00240
41·9	0·9617	49·8	1·04078	42·0	0·9401	45·0	1·01168
50·1	0·9692			49·9	0·9490		
$\alpha_0 = 7{\cdot}89 \,.\, 10^{-4}$		$\alpha = 9{\cdot}93 \,.\, 10^{-4}$		$\alpha_0 = 7{\cdot}79 \,.\, 10^{-4}$		$\alpha = 9{\cdot}19 \,.\, 10^{-4}$	
3,6-Dioxaoctane				3,6,9-Trioxaundecane			
15·1	1·0627	15·1	1·17571	15·1	0·9982	15·1	1·08754
25·0	1·0691	25·0	1·18942	25·1	1·0039	25·0	1·09867
34·8	1·0766	34·8	1·20351	34·8	1·0125	34·8	1·10999
42·3	1·0842	42·2	1·21478	42·3	1·0198	42·2	1·11903
50·2	1·0919	50·2	1·22701	50·2	1·0282	50·2	1·12899
$\alpha_0 = 8{\cdot}35 \,.\, 10^{-4}$		$\alpha = 14{\cdot}63 \,.\, 10^{-4}$		$\alpha_0 = 8{\cdot}62 \,.\, 10^{-4}$		$\alpha = 11{\cdot}80 \,.\, 10^{-4}$	

so-called "Hydrophobic interactions", and therefore distinctly dependent on the size of the nonpolar part of the molecule; with increasing part of the nonpolar surface its value decreases[2], as documented by Table III and Fig. 1. A rise in temperature leads to gradual destruction of the water structure in the surroundings of nonpolar parts of the molecule, and at temperatures about 50°C the value of k approaches zero. A similar effect has been observed also for other compounds[3,4].

TABLE II

Reported data for the compounds investigated. The references are quoted as superscripts at respective values of the experimental quantities. The designation of compounds *cf.* Experimental

Compound	$\phi^0_{2,25}$ cm^3 g^{-1}	$(dv_2/dT) \,.\, 10^4$ cm^3 g^{-1} K^{-1}	$(d\phi_2/dT) \,.\, 10^4$ cm^3 g^{-1} K^{-1}	$\bar{v}^0_{2,25} \,.\, 10^2$ cm^3 g^{-1}	$\bar{\alpha}^{0E}_2 \,.\, 10^2$ cm^3 mol^{-1} K^{-1}
G1	$0{\cdot}8797^{2}$	$6{\cdot}26^{15}$	$7{\cdot}1-6{\cdot}3^{14}$	$-2{\cdot}17^{2}$	
	$0{\cdot}8806^{12}$		$1{\cdot}75^{12}$		
	$0{\cdot}8807^{13}$				
G2	$0{\cdot}8669^{6}$	$6{\cdot}97^{6}$	$6{\cdot}19^{6}$	$-3{\cdot}20^{2}$	
	$0{\cdot}8685^{2}$		$6{\cdot}2-5{\cdot}8^{14}$		
	$0{\cdot}8723^{12}$				
	$0{\cdot}8694^{13}$				
G3	$0{\cdot}8604^{6}$	$6{\cdot}97^{6}$	$7{\cdot}02^{6}$	$-3{\cdot}33^{2}$	
	$0{\cdot}8608^{2}$		$7{\cdot}1-6{\cdot}4^{14}$		
	$0{\cdot}8647^{12}$				
	$0{\cdot}8609^{13}$				
PEG 200	$0{\cdot}8566^{6}$	$6{\cdot}97^{6}$	$7{\cdot}19^{6}$		
	$0{\cdot}8559^{2}$		$7{\cdot}6-6{\cdot}5^{14}$		
	$0{\cdot}8647^{12}$				
	$0{\cdot}8568^{13}$				
PEG 600	$0{\cdot}8451^{6}$	$6{\cdot}97^{6}$	$8{\cdot}25^{6}$	$-4{\cdot}79^{2}$	
	$0{\cdot}8431^{2}$	$7{\cdot}23^{15}$			
PEG 2 000	$0{\cdot}8390^{2}$				
M1	$0{\cdot}9871^{16}$		$6{\cdot}3-7{\cdot}5^{14}$	$-5{\cdot}44^{16}$	
E1	$0{\cdot}9678^{16}$		$5{\cdot}6-7{\cdot}4^{16}$	$-6{\cdot}57^{16}$	$-3{\cdot}86^{16}$
					$-2{\cdot}93^{16}$
DM1	$1{\cdot}0640^{2}$	$11{\cdot}90^{15}$	$6{\cdot}3-8{\cdot}5^{14}$	$-9{\cdot}81^{2}$	
	$1{\cdot}0608^{17}$		$7{\cdot}5-9{\cdot}7^{17}$		
	$1{\cdot}0636^{13}$				
	$1{\cdot}0612^{7}$				
DM3	$0{\cdot}9517^{2}$	$9{\cdot}77^{15}$	$7{\cdot}9-8{\cdot}0^{14}$	$-6{\cdot}92^{2}$	
DM4	$0{\cdot}9297^{2}$	$9{\cdot}30^{15}$	$8{\cdot}3-7{\cdot}7^{14}$	$-6{\cdot}57^{2}$	
DE1	$1{\cdot}0433^{18}$			$-10{\cdot}33^{18}$	
DE2	$1{\cdot}0133^{3}$	$7{\cdot}78^{3}$		$-9{\cdot}52^{3}$	$-6{\cdot}0^{3}$

The volume of liquid compounds falls into the group of additive properties. The partial limiting molar volume is also assumed to be given by the sum of volume contributions of the individual groups of which the molecule is composed. Exner[19] has demonstrated that the calculation of these contributions is best based on the dependence of the volume on the reciprocal molar mass, $1/M$. This procedure was employed by Lepori and Mollica[2] in the determination of the volume contribution of the repeating unit $—CH_2—O—CH_2—$. As can be seen in Fig. 2, however, the dependence of ϕ_2^0 on $1/M$ is not linear in a wide range of M. Similar departures from linearity due to causes still not clear have also been observed with other polymers[20].

TABLE III

Constants of concentration dependences of the apparent specific volume, $\phi_2 = \phi_2^0 + kw_2$, and specific expansibility, α_0, of ethylene glycol, 3-oxa-1-butanol, and 2,5-dioxahexane in water for $w_2 < 0·15$ (w_2 is mass fraction)

T, °C	ϕ_2^0, cm^3 g^{-1}	k . 10^2, cm^3 g^{-1}
	Ethyleneglycol	
15·0	0·8742	−2·3
25·0	0·8810	−1·7
35·0	0·8863	−0·5
41·8	0·8893	−0·6
50·0	0·8960	−0·6
$\alpha_0 = 5·99 . 10^{-4}$		
	3-Oxa-1-butanol	
15·0	0·9798	−8·3
25·0	0·9869	−6·9
35·1	0·9925	−3·1
42·1	0·9996	−3·2
50·1	1·0045	−1·0
$\alpha_0 = 7·08 . 10^{-4}$		
	2,5-Dioxahexane	
15·0	1·0552	−16·8
25·0	1·0613	−12·3
35·0	1·0702	−9·7
41·8	1·0769	−8·9
50·0	1·0815	−2·8
$\alpha_0 = 7·83 . 10^4$		

It was found that the $\overline{V}_2^0/V_w$ *vs* $1/V_w$ plot (Fig. 3) (in which $\overline{V}_2^0 = \Phi_2^0 = M\phi_2^0$ and V_w is the van der Waals volume of the molecule calculated according to Bondi[21]) is linear within the whole range of measured molar masses. In order to interpret the intercept and slope of this dependence, we use a simple model in which the volume of the individual groups is expressed[22] by the sum of the van der Waals volume V_w

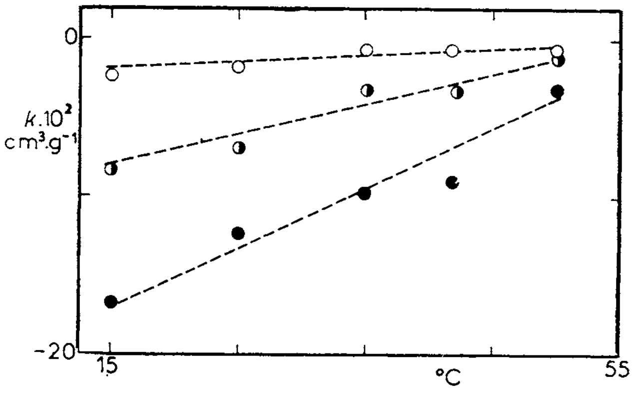

FIG. 1

Temperature dependence of the constant k from Eq. $\phi_2 = \phi_2^0 + kw_2$ for $w_2 < 0{\cdot}15$; ○ ethylene glycol, ◑ 3-oxa-1-butanol; ● 2,5-dioxahexane

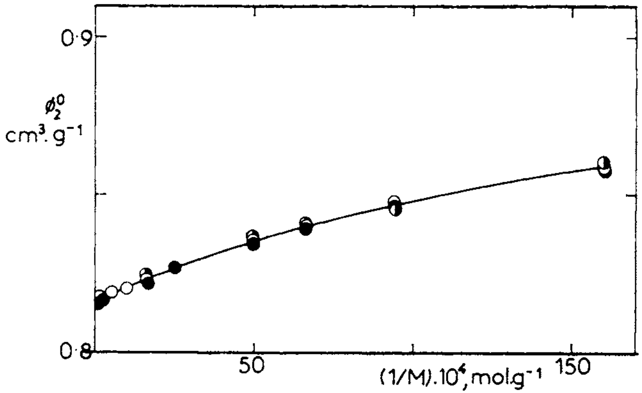

FIG. 2

Dependence of the apparent limiting specific volume of poly(oxyethylenes), ϕ_2^0, on the reciprocal molar mass value: ● this paper; ○ Ref.[2]; ◑ Ref.[6]

and the void volume Δ. The partial molar volume $\bar{V}_2^0$ may then be written as

$$\bar{V}_2^0 = n(V_{w,h} + \Delta_h) + (V_{w,c} + \Delta_c)\,, \tag{3}$$

where n is the number of homologous groups in the molecule, $V_{w,h}$, Δ_h are the van der Waals volume and the void volume of the repeating homologous group, respectively, and $V_{w,c}$, Δ_c are the respective quantities for groups, the number of which in molecules of the homologous series is constant (*e.g.* end groups). By dividing Eq. (*3*) with the van der Waals volume of the whole molecule $nV_{w,h} + V_{w,c}$ we obtain, then,

$$\bar{V}_2^0/V_w = (1 + \Delta_h/V_{w,h}) + (\Delta_c - \Delta_h V_{w,c}/V_{w,h})/V_w\,. \tag{4}$$

The first term on the right-hand side of Eq. (*4*) corresponds to the constant b of Terasawa's relation (*1*) and may be used to calculate the volume contribution of the homologous group. The coefficient at $1/V_w$ is the constant a which involves the volume contributions of not repeating groups. Table IV summarizes values of the volume contributions of the individual groups calculated using Eq. (*4*) from our own and

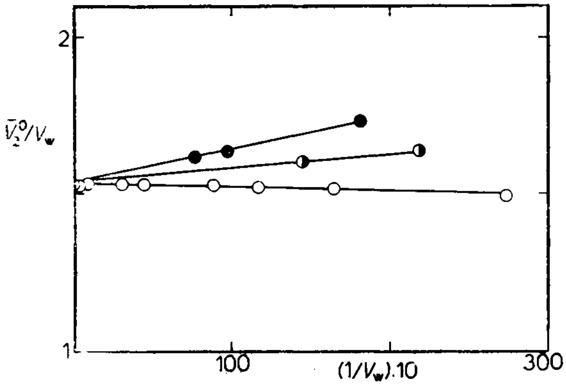

FIG. 3

Dependence of $\bar{V}_2^0/V_W$ on $1/V_W$ in water at 25°C ○ poly(oxyethylenes); ◑ 3-oxa-1-butanol, 3,6-dioxa-1-heptanol; ● 2,5-dioxahexane, 2,5,8,11-tetraoxadodecane, 2,5,8,11,14-pentaoxapentadecane

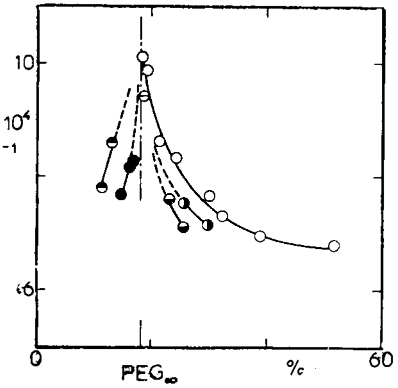

FIG. 4

Dependence of the limiting expansibility coefficient, $\alpha'_0 = (1/\phi_2^0)(\mathrm{d}\phi_2^0/\mathrm{d}T)_P$, on the percentage of the hydrophilic surface: ○ poly(oxyethylenes); ◑ 3-oxa-1-butanol, 3,6-dioxa-1-heptanol; ◒ 3-oxa-1-pentanol, 3,6-dioxa-1-octanol; ⊖ 3,6-dioxa-1-decanol; ● 2,5-dioxahexane, 2,5,8,11-tetraoxadodecane, 2,5,8,11,14-pentaoxapentadecane; ◓ 3,6-dioxaoctane, 3,6,9-trioxaundecane

TABLE IV

Volume contributions of groups in infinitely diluted aqueous solutions. References are given as superscripts at the respective values of experimental quantities

Group	$\bar{V}^0$, cm^3 mol^{-1}				Homologous series	Literature	
	15°C	25°C	35°C	45°C		$\bar{V}^0$, cm^3 mol^{-1}	T, °C
—CH_2—	15·7	15·9	16·1	16·3	3,6-dioxa-1-heptanol	16[23]	25
					3,6-dioxa-1-octanol		
					3,6-dioxa-1-decanol		
		15·8			ketones[22]	15·9[13]	25
		16·1			alcohols[22]	16·4[13]	45
		16·2			diols[22]		
		15·9			amides[24]		
		16·0			amines[24]		
		15·7			diamines[24]		
		15·9			secondary amines[24]		
—CH_2OH	27·3	27·4	27·6	27·8	α,ω-dihydroxypoly(oxyethylenes)	27·6[13]	25
		27·8			diols[22]	27·9[13]	45
—CH_2OCH_2—	36·6	36·9	37·3	37·6	α,ω-dihydroxypoly(oxyethylenes)	36·9[13]	25
	36·7	37·0	37·3	37·6	α-hydroxy-ω-methoxypoly(oxyethylenes)	37·6[13]	45
	36·5	36·8	37·1	37·5	α,ω-dimethoxypoly(oxyethylenes)		
	36·7	37·0	37·4	37·7	α-hydroxy-ω-ethoxypoly(oxyethylenes)		
	36·2	36·6	37·1	37·5	α,ω-diethoxypoly(oxyethylenes)		

—CH_2OCH_3	47·3	47·6	48·0	48·4	α-hydroxy-ω-methoxypoly(oxyethylenes)		
	47·4	47·8	48·2	48·5	α,ω-dimethoxypoly(oxyethylenes)		
—$CH_2OCH_2CH_3$	62·7	63·2	63·7	64·2	α,ω-diethoxypoly(oxyethylenes)		
	63·2	63·7	64·2	64·7	α-hydroxy-ω-ethoxypoly(oxyethylenes)		
—CH_3	26·4	26·6	26·7	26·9	(—$CH_2OCH_2CH_3$)—(—CH_2OCH_2—)	26·7[23]	25
		26·7			alcohols[22]		
		26·4			amines[22]		
—OH		11·7			diols[22]	12[23]	25
—NH_2		15·5			diamines[24]		
—NH—		6·6			secondary amines[24]	6·3[23]	25
—$CONH_2$		28·8			amides[24]	28·8[23]	25
—O—	5·1	5·1	5·0	4·9	(—CH_2OCH_2—)—2(—CH_2)—	4·1[23]	25
	5·2	5·2	5·2	5·3	(—CH_2OCH_3)—(—CH_2—)—(—CH_3)	5·2[2]	25
	5·1	5·1	5·0	4·9	(—$CH_2OCH_2CH_3$)—(—CH_3)—2(—CH_2)		

reported density data. The agreement between the values thus calculated and those obtained by employing other procedures is very good.

Differences in the behaviour of hydrophobic and hydrophilic compounds in aqueous solutions are distinctly reflected, among other things, in the volume properties such as $\bar{v}_2^{0E}$ – excess limiting partial specific volume, $\bar{\alpha}_2^{0E}$ – excess limiting molar expansibility, α_0 – specific limiting expansibility of the dissolved compound, and $\alpha_0' = (1/\phi_2^0)(\partial\phi_2^0/\partial T)_P$ – the limiting coefficient of expansibility[1,10,11].

Fig. 4 shows the dependence of α_0' on the fraction (%) of the hydrophilic (—O—, —OH) surface of the molecule calculated according to Bondi[21]. The value of α_0' depends on the type of the endgroup and on the size of the molecule. With increasing chain length α_0' approaches the value for an infinitely long poly(oxyethylene) chain independently of the type of the endgroup. The increase in α_0' with increasing chain length may be interpreted as a consequence of the cooperative destructive effect of ether oxygen atoms on the order of water molecules in the surroundings of the poly(oxyethylene) chain, similarly to the case of cyclic ethers in water[17].

No unequivocal conclusion as to the effect of the ether oxygen atom can be drawn from the dependence of $\bar{v}_2^{0E}$ on the fraction of the hydrophilic surface in % (Fig. 5),

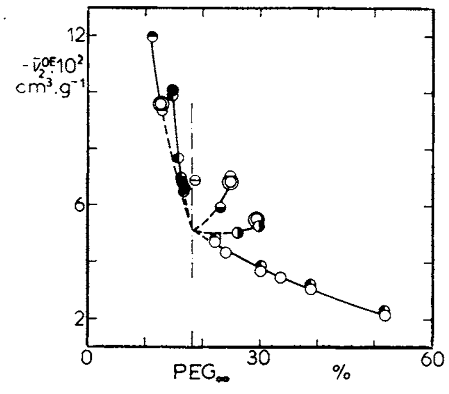

FIG. 5

Dependence of the excess limiting specific volume, $\bar{v}_2^{0E}$, on the percentage of the hydrophilic surface: ○ poly(oxyethylenes); ◑ 3-oxa-1-butanol, 3,6-dioxa-1-heptanol; ◒ 3-oxa-1-pentanol, 3,6-dioxa-1-octanol; ⊖ 3,6-dioxa-1-decanol; ● 2,5-dioxahexane, 2,5,8,11-tetraoxadodecane, 2,5,8,11,14-pentaoxapentadecane; ◓ 3,6-dioxaoctane, 3,6,9-trioxaundecane; ◐ Ref.[2]; ◎ Ref.[3]

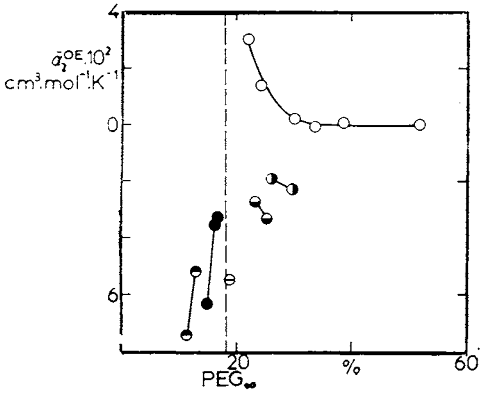

FIG. 6

Dependence of the excess limiting molar expansibility, $\bar{\alpha}_2^{0E}$, on the percentage of the hydrophilic surface: ○ poly(oxyethylenes); ◑ 3-oxa-1-butanol, 3,6-dioxa-1-heptanol; ◒ 3-oxa-1-pentanol, 3,6-dioxa-1-octanol; ⊖ 3,6-dioxa-1-decanol; ● 2,5-dioxahexane, 2,5,8,11-tetraoxadodecane, 2,5,8,11,14-pentaoxapentadecane; ◓ 3,6-dioxaoctane, 3,6,9-trioxaundecane because this dependence is influenced by several effects with different volume contributions. These effects comprise a decreasing effect of endgroups with increasing chain length, the destructive effect of ether oxygen atoms on the order of water molecules and the more difficult packing of long molecules in the free volume. Moreover, $\bar{v}_2^{0E}$, as any excess quantity, involves the effect of interactions in the reference state.

For "effectively hydrophobic" compounds, Franks[10] gives $\bar{v}_2^{0E}$ and $\bar{\alpha}_2^{0E}$ values lower than zero. For typically hydrophobic compounds, Chan[11] gives $\bar{V}_2^{0E} < -15$ cm^3 mol^{-1}. For poly(oxyethylene) and its low molecular models, $\bar{v}_2^{0E} < 0$ and its limiting value is $-5{\cdot}1 \,.\, 10^{-2}$ cm^3 g^{-1}, *i.e.* $-2{\cdot}2$ cm^3 mol^{-1} (related to one mole of repeating units). For α,ω-dihydroxypoly(oxyethylenes), $\bar{\alpha}_2^{0E} \geqq 0$, in agreement with the values calculated from the data given by Harada[14], while for monoethers and diethers, $\bar{\alpha}_2^{0E} < 0$ (Fig. 6). Hence, it may be said that the behaviour of poly(oxyethylene) in water is situated somewhere between that of hydrophobic and hydrophilic compounds, similarly to 1,4-dioxan[1]. The etherified derivatives behave as "effectively hydrophobic" compounds; at the same time, their behaviour depends markedly on the type of the substituent and on the length of the poly(oxyethylene) chain. When comparing the hydrophobicity of the individual compounds by using the volume properties, it may be assumed that the $\bar{v}_2^{0E}$, $\bar{\alpha}_2^{0E}$ values, the percentage of the hydrophilic surface, and α_0 will decrease with increasing hydrophobicity[1,5,6,10,11]. According to $\bar{v}_2^{0E}$, $\bar{\alpha}_2^{0E}$, and the percentage of the hydrophilic surface, hydrophobicity increases in the series ethylene glycol, 3-oxa-1-butanol, 2,5-dioxahexane (*i.e.* compounds G1, M1, and DM1); 3-oxa-1,5-pentanediol, 3,6-dioxa-1-heptanol, 2,5,8-trioxanonane (*i.e.* compounds G2, M2, and DM2); 3,6-dioxa-1-heptanol, 3,6-dioxa-1-octanol, 3,6-dioxa-1-decanol (*i.e.* compounds M2, E2 and B2) and 2,5,8,11,14-pentaoxapentadecane, 2,5,8,11-tetraoxadodecane, and 2,5-dioxahexane (*i.e.* compounds DM4, DM3, and DM1), while according to α_0 the order of hydrophobicity is an opposite one. It may be said, therefore, that of the volume properties, $\bar{v}_2^{0E}$ and $\bar{\alpha}_2^{0E}$ are suitable criteria of hydrophobicity, while α_0 is not.

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