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Enthalpic and volume effects in the interaction of D-glucose with crown ethers in water

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Abstract

The enthalpies of solution of 12-crown-4, 15-crown-5, 18-crown-6 and 1,10-diaza-18-crown-6 in aqueous D-glucose, were determined experimentally. The cross coefficients of the virial expansion of the excess enthalpies were calculated. On the basis of experimental density data, the limiting partial molar volumes of transfer of crown ethers from water to 1 m aqueous D-glucose solution were also evaluated. It is shown that the interactions between crown ethers and D-glucose are weak, but that the endothermic effect of these interactions decreases with an increase in the size of the crown ether macrocycle.

Keywords: Crown ethers; Glucose; Enthalpic cross coefficient; Volumes

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1. Introduction

Saccharides are one of the main sources of energy in living organisms. Their application, biosynthesis and transport are controlled and provided by different enzymes. Specific mechanisms of action of enzymes can be investigated on the basis of model systems. Some artificial and natural ligands may be considered as appropriate enzyme models. The interactions, similar to a saccharide-macrocyclic compound, play an essential role in the transport processes of saccharides through cell membrane.

In the present work, the enthalpy and volume effects of the interactions of D-glucose with 12-crown-4, 15-crown-5, 18-crown-6 and 1,10-diaza-18-crown-6 have been studied.

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2. Experimental

2.1. Materials

12-Crown-4, 15-crown-5, 18-crown-6 and 1,10-diaza-18-crown-6 were synthesized in the Institute of Chemical Regents and Pure Chemical Substances (Moscow). The purity of these compounds was above 99 mol %. D-Glucose was purified by recrystallization from ethanol and dried under vacuum over several days at 333 K before use. The solutions were prepared by weight using doubly-distilled, degassed water.

2.2. Calorimetry

The enthalpies of solution were determined by means of an isothermal calorimeter at 298.15 K controlled to ± 0.005 K. The solute molality in all cases was estimated to be lower than 2×10^{-3} mol kg^{-1}, which in this connection can be considered as infinitely dilute. No concentration dependence was observed and mean values were taken as the enthalpy of solution at infinite dilution. The errors in the heat effect measurements was not greater then 0.08 J.

2.3. Densimetry

Solution densities were measured with the help of bicapillary picnometers ($V \sim 10$ cm^3). The picnometers were calibrated with water [1] and aqueous NaCl solutions [2]. The error in the density measurements was not greater then 2×10^{-5} g cm^{-3}. All the measurements were carried out at 298.15 K controlled to ± 0.005 K and the solutions were made up by weight. The solute concentration was varied from 0.05 to 0.7 mol kg^{-1}. The concentration of D-glucose was constant at 1 mol kg^{-1}.

3. Results

The samples of crown ethers were dissolved in aqueous solutions of D-glucose of different concentrations in order to obtain the enthalpic heterotactic coefficients to the pair and triplet interactions [3]

$$\Delta_{tr}H_x(w \rightarrow w + y)/m_y = 2h_{xy} + 3m_y h_{xyy} + 3m_x h_{xxy} \qquad (1)$$

where $\Delta_{tr}H_x(w \rightarrow w + y)$ is the enthalpy of transfer of crown ether (x) from water to aqueous solutions of D-glucose (y); m_x and m_y are the molalities of x and y solutes in ternary solutions respectively; h_{xy}, h_{xxy} and h_{xxy} are the enthalpic heterotactic coefficients of pair and triplet interactions. This equation is based on the McMillan–Mayer virial expansion [4] for the excess enthalpies of solution. Since we used very low m_x, i.e. $m_x \rightarrow 0$, the respective term in Eq. (1) may be neglected. The values of the h_{xy} and h_{xyy} coefficients were determined by a least-square method. The results are listed in Tables 1 and 2.

Table 1
Enthalpies of transfer of crown ethers (x) from water to aqueous solutions of D-glucose (y) at 298.15 K

m_y/ (mol kg^{-1})	$\Delta_{tr}H_x(w \rightarrow w + y)$/ (J mol^{-1})	m_y/ (mol kg^{-1})	$\Delta_{tr}H_x(w \rightarrow w + y)$/ (J mol^{-1})
12-Crown-4		15-Crown-5	
0.0995	807.1	0.0496	268.0
0.1434	1160.0	0.0999	544.7
0.2001	1596.4	0.1997	1085.0
0.2488	1987.7	0.2995	1618.3
0.3006	2301.2	0.3999	2171.2
0.4005	3065.5	0.4999	2626.8
0.4993	3796.6	0.5999	3176.4
0.5993	4266.6	0.7001	3675.5
18-Crown-6		1,10-Diaza-18-Crown-6	
0.1011	219.1	0.0505	2200.0
0.2004	494.0	0.0992	2318.5
0.2501	658.2	0.1502	4224.9
0.2998	898.2	0.1997	5683.5
0.3899	1215.0	0.2997	6795.7
0.4500	1570.0	0.3502	8606.5
0.5005	1826.1	0.3997	8581.4
		0.4492	8401.6
		0.5003	10243.9

Table 2
Enthalpic cross interaction coefficients of crown ethers (x) and D-glucose (y) in water at 298.15 K

Solutes (x + y)	h_{xy}/ (J kg mol^{-2})	h_{xyy}/ (J kg^2 mol^{-3})
12-Crown-4 + D-glucose	4167 (270)	− 601 (35)
15-Crown-5 + D-glucose	2736 (120)	− 100 (43)
18-Crown-6 + D-glucose	876 (22)	1245 (108)
1,10-Diaza-18-Crown-6 + D-glucose	904 (34)	5193 (202)

On the basis of experimental density data, the apparent molar volume (Φ_v) and limiting partial molar volumes ($\bar{V}_x^0$) of 12-crown-4 and 15-crown-5 in 1 m aqueous D-glucose solution were evaluated using equations [5]

$$\Phi_v = M/d - (d - d_0)1000/m_x d d_0 \tag{2}$$

$$\Phi_v = \bar{V}_x^0 + S_v m_x \tag{3}$$

where M is the molar mass of the crown ether, d and d_0 are the densities of the ternary solution and 1 m aqueous D-glucose respectively and S_v is the experimental slope. The limiting partial molar volumes of transfer ($\bar{V}_{tr}^0$) of crown ethers from water to 1 m aqueous D-glucose solution were also calculated [5]

$$\bar{V}^0_{tr}(w \rightarrow y + w) = \bar{V}^0_x(y + w) - \bar{V}^0_x(w) \qquad (4)$$

The results are listed in Tables 3 and 4.

4. Discussion

The enthalpic pair interaction coefficients are the sum of the processes occurring in the systems discussed here. The types of processes can be classified as: (i) partial dehydration of two solute particles (endothermic effect); (ii) hydrophobic interactions (endothermic effect); (iii) intermolecular interactions between solutes due to specific forces (H-bonding, dipole–dipole interactions, etc.) (exothermic effect). The h_{xy} values between crown ethers and D-glucose are positive. This suggests that the partial dehydration effect and, perhaps, the hydrophobic interactions dominate over specific forces. However, the positive values of h_{xy} decrease linearly with the increase in the number of O-atoms of the crown ether macrocycle (Fig. 1 and Table 2). As concluded

Table 3

Densities and apparent molar volumes of 12-crown-4 (x) and 15-crown-5 (x) in 1 m aqueous D-glucose solution at 298.15 K

m_x/ (mol kg^{-1})	d/ (g cm^{-3})	Φ_v/ (cm^3 mol^{-1})	m_x/ (mol kg^{-1})	d/ (g cm^{-3})	Φ_v/ (cm^3 mol^{-1})
12-Crown-4			15-Crown-5		
0.0000	1.05820	–	0.1209	1.0651	186.02
0.2054	1.06210	149.28	0.1726	1.06225	185.97
0.2309	1.06257	149.26	0.2070	1.06305	185.95
0.3353	1.06449	149.20	0.2887	1.06487	185.82
0.3375	1.06448	149.18	0.3670	1.06670	185.72
0.4150	1.06583	149.16	0.4140	1.06719	185.65
0.5339	1.06775	149.13	0.5250	1.07015	185.57
0.5608	1.06833	149.07	0.5986	1.07120	185.52
0.7212	1.07097	149.99			

Table 4

Parameters of Eq. (3) and limiting partial molar volumes of transfer of 12-crown-4 and 15-crown-5 from water to 1 m aqueous D-glucose solution at 298.15 K

Crown ether	$\bar{V}^0_x$/ (cm^3 mol^{-1})	S_v/ (cm^3 mol^{-2} kg^{-1})	$\Delta_{tr}\bar{V}^{0\,a}_x$ (cm^3 mol^{-1})
12-Crown-4	149.38 ± 0.02	−0.53 ± 0.04	−0.77
15-Crown-5	186.15 ± 0.02	−1.11 ± 0.06	−0.31

[a] The data needed for the calculation of $\Delta_{tr}\bar{V}^0_x$ values were taken from ref. [7].

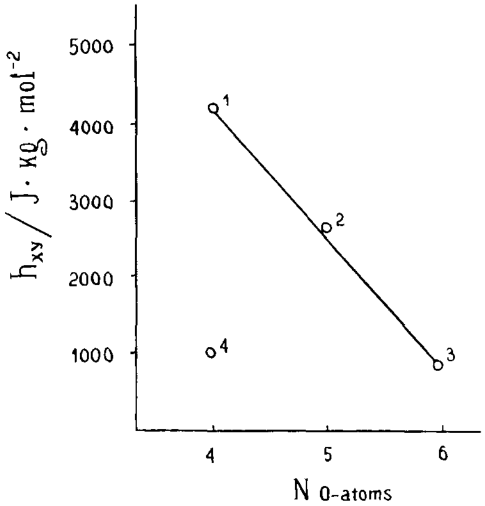

Fig. 1. The heterotactic enthalpic coefficients for the pair interactions of crown ethers with D-glucose versus the number of O-atoms in the crown ether macrocycle: 1,12-crown-4; 2,15-crown-5; 3,18-crown-6; 4, 1,10-diaza-18-crown-6.

earlier [6,7], the increase in the positive values of the enthalpic coefficients of intermolecular interactions and limiting partial molar capacity with increasing ring size of crown ethers are caused by the strengthing of the hydrophobic effect. The opposite tendency as shown in Fig. 1 could probably be attributed to the increase in the number of centres of specific interactions of crown ethers with D-glucose molecules and/or to the steric accordance between solutes favouring these interactions. Therefore the exothermic contribution becomes greater in this direction.

It is interesting to note that the h_{xy} values for 18-crown-6 and 1,10-diaza-18-crown-6 are practically equal. The presence of the two amino groups in 1,10-diaza-18-crown-6 does not affect the solute–solute interactions. This can be explained assuming that the amino groups do not take part in the glucose–crown ether interaction. The favourable orientations of the solute molecules enable interaction only through the oxygen atoms of the crown ethers.

As can be seen from Table 4, the volume changes when crown ethers transfer from water to 1 m aqueous D-glucose solution are small. But the negative values of S_v decrease essentially from 12-crown-4 to 15-crown-5. This suggests that the interactions between crown ether molecules becomes weaker than in aqueous D-glucose solution.

Acknowledgments

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