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The vaporization enthalpies of some crown and polyethers by correlation gas chromatography

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Abstract

Podands and crown ethers are an important class of solvents and metal complexing agents. The vaporization enthalpies of a series of ethers that include 18-crown-6 (87.3±2.3), dibenzo-18-crown-6 (137±7.4), dicyclohexano-18-crown-6 (mixture of diastereomers 124.2±4.0), 1,2-bis-(2-methoxyethoxy)ethane (63.7±3.3), 2,5-dimethoxy-2,5-dihydrofuran (*cis*/*trans* mixture: 44.2±0.3) and 1,3,5-trimethoxybenzene (68.2±2.0) kJ mol^{-1} are evaluated by the technique of correlation gas chromatography. This technique utilizes gas chromatographic retention times measured as a function of temperature and the known vaporization enthalpies of a series of standards. Vaporization enthalpies are obtained for both liquids and solids. Sublimation enthalpies for benzo-12-crown-4 (104.3±2.6), 18-crown-6 (119.1±6.7), benzo-15-crown-5 (128.1±10.8), and dibenzo-18-crown-6 (178.8±6.9) kJ mol^{-1} are calculated by adding experimental fusion enthalpies to vaporization enthalpies and adjusting for temperature. Uncertainties represent two standard deviations. The results are compared to estimated values. Despite the fact that crown ethers are excellent complexing agents their thermodynamic properties associated with phase changes appear quite similar to their acyclic counterparts and similar to analogous hydrocarbons. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Crown ethers; Podands; Vaporization enthalpies; Sublimation enthalpies

1. Introduction

Podands and crown ethers are an important class of solvents and metal complexing agents in organic chemistry [1–3]. Despite their importance, relatively few thermochemical data have been reported on these materials. We now report the vaporization enthalpies of the podands and crown ethers shown in Fig. 1 using the technique of correlation-gas chromatography (c-gc).

Gas chromatography has previously been used to measure various thermodynamic properties of solutions [4–10]. This technique, as modified to measure vaporization enthalpies, can be applied to a large variety of simple organic molecules [11]. All that is required is the availability of suitable standards with

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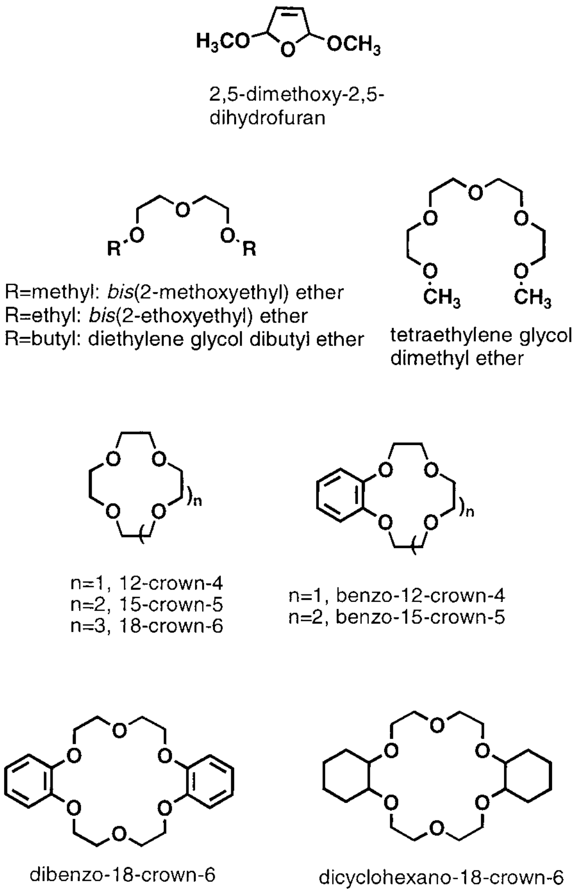

Fig. 1. Structures of the podands and crown ethers of this study.

reliable vaporization enthalpies. We would like to illustrate the use of this technique in evaluating the vaporization enthalpies of this class of compounds.

Vaporization enthalpies ($\Delta_{\mathrm{vap}}H_{\mathrm{m}}$) are measured by correlation gas chromatography by utilizing the observed correlation between a substances' enthalpy of transfer from solution to the vapor ($\Delta_{\mathrm{s}}^{v}H_{\mathrm{m}}$) and the vaporization enthalpy of that substance evaluated at some reference temperature, usually 298.15 K. The vaporization enthalpies of any additional components in the mixture can then be evaluated from the relationship established between the correlation equation and each respective enthalpy of transfer. $\Delta_{\mathrm{s}}^{v}H_{\mathrm{m}}$ values are measured by gas chromatography from the temperature dependence of retention time, once this time is corrected for the dead volume of the column. The corrected retention time, t_{r}, for each component is obtained from the difference in retention time between each solute and that of an unretained reference. The unretained reference, often the solvent, can usually be identified by its retention time-temperature profile. Unlike the other solutes, the retention time of an unretained sample is controlled by the temperature dependence of the He flow; it increases with temperature. The corrected retention time measures the time each component spends on the column and is inversely proportional to the compound's vapor pressure on the stationary phase of the column. Since each solute presumably dissolves in the stationary phase, $\Delta_{\mathrm{s}}^{v}H_{\mathrm{m}}$values can be measured for both solids and liquids. A plot of $\ln 1/t_{\mathrm{r}}$ versus $1/T$, similar to a Clausius Clapeyron plot of $\ln P$ versus $1/T$, results in a straight line whose slope by analogy is $-\Delta_{\mathrm{s}}^{v}H_{\mathrm{m}}/R$, where R is the gas constant.

The vaporization enthalpies determined by this method are entirely dependent on the compounds chosen as standards. The lack of reliable vaporization enthalpies for a set of suitable standards is a major limitation of the technique. For hydrocarbons, the vaporization enthalpies of the *n*-alkanes have served as useful standards [12]. Good correlations have been observed regardless of the structure of the hydrocarbon [11]. With other functional groups, good correlations between $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ and $\Delta_{\mathrm{s}}^{v}H_{\mathrm{m}}$ have been observed whenever the type and number of functional groups is kept constant. Correlations between compounds containing multiple functional groups cannot be assumed but must be demonstrated. In this study, good correlations between $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ and $\Delta_{\mathrm{s}}^{v}H_{\mathrm{m}}$of the *n*-alkanes and polyethers have been observed and both have been used as standards to obtain $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ for the podands and crown ethers having unknown vaporization enthalpies.

2. Experimental

All determinations described here were performed on a Hewlett-Packard Model 5890 Series II Gas Chromatograph equipped with a split/splitless capillary injection port and a flame ionization detector. Retention times were measure by way of a Hewlett-Packard Model 3396A integrator, and the column temperature was monitored independently using a Kluke 51 K/J thermometer.

Four different chromatographic columns were utilized: a 30 m×0.32 mm DB-5, a 60 m×0.32 mm DB-5, a 30 m×0.25 mm×0.25 µm SBP-5 and a 12 m×0.2 mm×0.33 µm HP-1 crosslinked methyl silicone capillary column. Helium was used as the carrier gas, with column head pressures of either 10 or 15 psi. Mixtures were analyzed isothermally over a range of at least 30 K, with chromatograms being acquired at every 5–10 K interval.

The retention times of all compounds, the exact column head pressure employed, and type of capillary column used for each specific mixture, are given in Table 1. An attempt was made to include each compound in more than one mixture, with a different

Table 1
Uncorrected retention times of the various alkanes, podands, and crown ethers in each mixture

Compound	Retention times (s)				
Mix CE1 (30 m DB-5/68 kPa)					
diethyl ether (unret. std.)	192.3	194.6	197.1	199.8	202.6
15-crown-5	237.9	233.1	229.7	228.1	–
octadecane	250.0	241.6	235.5	232.2	230.6
benzo-12-crown-4	271.2	260.0	251.6	246.4	242.8
18-crown-6	285.0	270.6	259.8	252.8	247.8
benzo-15-crown-5	368.1	225.6	311.2	293.9	282.1
tricosane	401.3	255.4	322.4	299.5	282.9
tetracosane	461.9	399.4	354.9	324.0	302.0
dicyclohexano-18-crown-6	792.2	652.5	551.1	478.6	427.4
octacosane	917.3	720.7	585.4	492.5	427.4
dibenzo-18-crown-6	1374.9	1073.8	857.6	704.9	596.4
Temperature (K)	543.2	553.2	563.2	573.2	583.2
Mix CE2 (12 m HP-1/68 kPa)					
CCl_4 (unret. std.)	45.7	46.3	46.6	46.9	47.6
12-crown-4	54.3	53.5	52.6	52.2	52.1
18-crown-6	75.3	70.7	66.8	64.1	62.0
tricosane	122.1	105.0	92.3	83.3	76.6
tetracosane	143.9	120.8	103.9	92.0	83.3
dicyclohexano-18-crown-6	231.0	188.2	156.8	134.1	117.2
octacosane	305.3	234.6	185.8	151.8	127.8
dibenzo-18-crown-6	383.8	299.2	237.3	193.8	162.2
triacontane	465.6	344.1	262.1	206.2	167.0
Temperature (K)	543.3	553.3	563.3	573.2	583.4
Mix CE3 (12 m HP-1/68 kPa)					
CCl_4 (unret. std.)	40.9	41.3	41.9	42.2	42.8
1,2-bis-(2-methoxyethoxy)ethane	68.8	63.0	58.9	55.9	53.9
12-crown-4	87.8	78.0	70.9	65.6	61.8
diethylene glycol dibutyl ether	117.1	97.8	84.6	75.2	68.5
tetraethylene glycol dimethyl ether	134.8	110.1	93.2	81.5	73.1
hexadecane	210.0	162.1	130.1	108.1	92.6
octadecane	431.7	309.4	230.4	177.9	142.1
18-crown-6	496.8	360.9	271.6	211.2	168.7
eicosane	941.9	633.9	442.9	320.4	239.5
Temperature (K)	443.6	453.3	463.3	373.1	382.9
Mix CE4 (12 m HP-1/68 kPa)					
CCl_4 (unret. std.)	34.7	35.1	35.5	36.1	36.5
1,2-bis-(2-methoxyethoxy)ethane	57.1	52.4	49.2	47.2	45.5
12-crown-4	72.6	64.7	59.0	55.1	52.0
tetradecane	91.8	77.6	67.9	61.4	56.3
diethylene glycol dibutyl ether	96.1	80.6	70.1	62.9	57.5
tetraethylene glycol dimethyl ether	109.9	90.0	76.9	67.9	61.1

Table 1 (*Continued*)

Compound	Retention times (s)				
15-crown-5	160.4	127.6	105.6	90.2	78.7
octadecane	350.7	252.1	188.6	146.7	117.8
18-crown-6	398.8	291.1	220.2	172.4	138.7
eicosane	763.6	515.4	361.1	263.0	197.5
Temperature (K)	443.5	454.5	464.4	473.3	483.3
Mix CE5 (30 m DB-5/101 kPa)					
CH_2Cl_2 (unret. std.)	185.3	187.6	189.4	191.9	193.7
12-crown-4	217.5	214.2	211.5	21.4	209.6
tetraethylene glycol dimethyl ether	229.7	223.6	219.1	216.5	214.6
tetradecane	265.1	252.7	243.2	236.6	231.6
18-crown-6	364.3	329.1	302.7	283.6	270.4
eicosane	394.0	346.6	312.5	288.4	270.4
pentacosane	1092.9	834.0	657.8	538.7	453.8
dicyclohexano 18-crown-6	1674.5	1271.3	990.0	794.2	653.8
Temperature (K)	513.3	523.5	533.3	543.3	553.2
Mix CE6 (30 m DB-5/68 kPa)					
CCl_4 (unret. std.)	358.0	360.8	364.7	369.7	
1,2-bis-(2-methoxyethoxy)ethane	401.2	396.1	392.9	392.7	
tetradecane	451.1	434.6	422.8	415.8	
diethylene glycol dibutyl ether	465.1	445.1	430.5	421.5	
tetraethylene glycol dimethyl ether	497.4	468.0	447.9	434.5	
15-crown-5	610.9	557.5	518.1	489.2	
octadecane	814.3	700.2	612.9	550.4	
Temperature (K)	483.6	493.5	503.6	513.6	
Mix CE7 (12 m HP-1/68 kPa)					
diethyl ether (unret. std.)	46.8	48.1	48.7	49.4	50.3
12-crown-4	56.2	55.6	55.1	54.8	54.7
tricosane	150.1	125.8	106.3	94.4	85.9
pentacosane	178.8	146.3	120.7	105.1	94.0
dicyclohexano-18-crown-6	241.7	196.1	159.5	136.3	119.8
octacosane	320.8	245.1	188.3	153.9	130.1
dibenzo-18-crown-6	403.4	311.4	239.9	195.6	164.3
triacontane	489.7	359.6	264.5	207.4	168.8
Temperature (K)	543.3	553.4	563.3	573.2	583.3
Mix CE8 (30 m DB-5/101 kPa)					
diethyl ether (unret. std.)	267.6	270.5	276.2	263.2	
dihexyl ether	310.5	305.9	305.5	–	
diethylene glycol dibutyl ether	349.1	336.5	328.8	325.5	
tetraethylene glycol dimethyl ether	371.8	351.8	339.9	334.4	
hexadecane	415.8	387.3	367.0	353.9	
15-crown-5	448.0	414.1	389.6	373.5	
octadecane	574.6	501.6	450.8	416.2	
18-crown-6	721.8	615.0	539.3	488.1	
eicosane	896.0	725.2	609.4	530.7	
Temperature (K)	483.1	492.8	502.8	512.8	
Mix CE9 (30 m DB-5/68 kPa)					
diethyl ether (unret. std.)	269.2	272.4	275.0	277.5	
dihexyl ether	315.3	307.4	306.2	304.0	
diethylene glycol dibutyl ether	352.9	336.4	327.9	321.0	
tetraethylene glycol dimethyl ether	373.9	351.9	337.2	330.0	
hexadecane	421.7	387.5	366.3	350.2	
octadecane	582.2	502.6	449.8	411.8	

Table 1 (*Continued*)

Compound	Retention times (s)				
18-crown-6	737.5	620.4	538.5	482.6	
eicosane	946.7	727.9	608.0	525.1	
Temperature (K)	482.9	492.8	502.8	512.8	
Mix CE10 (30 m DB-5/68 kPa)					
diethyl ether (unret. std.)	348.1	351.8	352.9	361.9	368.6
hexadecane	434.6	420.9	408.6	407.9	406.7
15-crown-5	459.6	441.9	429.1	424.2	420.6
benzo-12-crown-4	558.3	518.5	491.9	472.6	459.5
18-crown-6	5996	548.5	514.3	489.1	472.1
eicosane	653.1	582.5	534.4	500.6	478.4
benzo-15-crown-5	886.4	759.2	673.7	613.5	567.7
tricosane	1111.9	905.2	765.8	669.9	603.8
tetracosane	1379.9	1090.2	894.7	762.0	670.7
Temperature (K)	513.2	523.2	533.2	543.2	553.2
Mix CE11 (30 m DB-5/68 kPa)					
diethyl ether (unret. std.)	333.7	336.9	344.4	347.7	354.0
12-crown-4	412.0	400.7	397.3	391.8	391.6
diethylene glycol dibutyl ether	432.8	141.7	406.8	397.9	395.7
tetraethylene glycol dimethyl ether	458.5	434.4	421.3	409.2	404.7
hexadecane	517.6	477.8	454.5	434.4	424.3
octadecane	714.9	622.9	558.4	511.8	482.5
benzo-12-crown-4	784.5	684.1	611.6	557.7	522.1
18-crown-6	898.7	763.5	668.6	598.9	552.9
eicosane	1115.7	901.1	755.5	653.4	586.7
Temperature (K)	483.2	493.2	503.2	513.2	523.2
Mix CE12 (60 m DB-5/68 kPa)					
methane (unret. std.)	284.1	287.4	288.5	293.5	297.0
bis-(2-methoxyethyl)ether	343.1	334.3	324.7	321.4	320.0
bis-(2-ethoxyethyl)ether	404.0	378.6	357.1	345.9	338.6
1,2-bis-(2-methoxyethoxy)ethane	558.6	486.5	434.1	402.4	380.3
tetradecane	984.8	776.3	631.2	542.3	480.9
diethylene glycol dibutyl ether	1137.9	872.4	697.2	586.8	510.6
tetraethylene glycol dimethyl ether	1489.0	1096.1	850.0	691.5	581.2
hexadecane	2305.5	1611.1	1183.1	914.1	731.6
Temperature (K)	413.3	423.4	433.2	443.3	453.5
Mix CE13 (30 m DB-5/101 kPa)					
CCl_4 (unret. std.)	218.1	220.9	223.8	226.1	229.6
bis-(2-methoxyethyl)ether	242.0	239.9	239.2	238.5	–
bis-(2-ethoxyethyl)ether	266.0	258.2	253.7	249.3	–
dodecane	312.9	293.7	280.9	269.5	263.4
1,2-bis-(2-methoxyethoxy)ethane	323.5	301.6	286.0	272.2	267.2
diethylene glycol dibutyl ether	516.8	436.9	383.0	345.3	320.4
tetraethylene glycol dimethyl ether	626.8	510.0	439.1	380.1	345.4
hexadecane	868.7	673.9	539.8	459.7	402.6
15-crown-5	927.1	729.5	600.8	499.1	436.2
Temperature (K)	434.0	443.8	453.5	463.5	473.3
Mix CE14 (30 m DB-5/101 kPa)					
CCl_4 (unret. std.)	250.7	255.8	261.3	266.9	271.9
decane	301.1	295.4	292.8	292.3	–
dodecane	398.6	366.8	346.26	333.0	324.1
dihexyl ether	464.4	413.5	380.3	358.2	342.9
1,3,5-trimethoxybenzene	705.1	585.0	506.1	451.2	410.2

Table 1 (*Continued*)

Compound	Retention times (s)						
tetraethylene glycol dimethyl ether	932.6	729.9	601.6	516.12	453.6		
hexadecane	1366.8	1018.8	797.6	650.7	550.3		
Temperature (K)	423.8	433.6	443.5	453.2	463.1		
Mix CE15 (30 m DB-5/101 kPa)							
CCl_4 (unret. std.)	215.5	218.5	224.6	229.6	232.0		
decane	262.5	255.0	252.9	251.1	249.3		
dodecane	346.2	318.5	300.7	285.6	275.6		
dihexyl ether	402.6	358.5	329.9	306.9	291.4		
1,3,5-trimethoxybenzene	605.6	502.0	434.3	383.0	348.0		
tetraethylene glycol dimethyl ether	798.0	625.7	516.0	437.0	384.4		
hexadecane	–	873.6	685.3	553.1	465.8		
Temperature (K)	423.7	433.6	443.1	453.1	463.8		
Mix CE16 (30 m DB-5/101 kPa)							
CCl_4 (unret. std.)	221.7	225.0	229.0	231.6	233.8		
2,5-dimethoxy-2,5-dihydrofuran	265.9	259.3	256.4	253.2	251.2		
bis-(2-methoxyethyl)ether	274.5	265.3	260.6	256.2	253.2		
decane	298.9	283.5	274.3	266.7	261.4		
bis-(2-ethoxyethyl)ether	338.7	311.3	294.5	281.2	272.1		
dodecane	471.7	404.9	362.1	330.2	308.5		
1,2-bis-(2-methoxyethoxy)ethane	506.0	427.2	377.2	340.3	315.4		
Temperature (K)	383.4	393.2	403.5	413.3	423.5		
Mix CE17 (30 m DB-5/101 kPa)							
diethyl ether (unret. std.)	235.7	241.9	246.6	252.5	257.6		
2,5-dimethoxy-2,5-dihydrofuran	325.0	309.6	298.8	293.3	289.4		
bis-(2-methoxyethyl)ether	347.3	324.1	308.8	300.4	293.9		
decane	398.0	361.8	336.1	320.6	308.9		
bis-(2-ethoxyethyl)ether	497.2	427.7	381.7	352.8	331.8		
dodecane	818.3	647.1	532.4	458.9	408.5		
dihexyl ether	1145.5	860.4	673.8	555.2	475.7		
Temperature (K)	383.5	393.6	403.8	413.8	423.8		
Mix CE18 (30 m SPB-5/101 kPa)							
CH_2Cl_2 (unret. std.)	178.1	179.1	179.7	180.7	181.8	184.0	184.9
12-crown-4	207.9	206.5	204.7	203.8	203.1	202.4	202.0
15-crown-5	253.1	246.8	240.8	236.0	232.0	225.9	223.3
benzo-12-crown-4	315.8	302.0	289.4	279.4	270.5	256.6	251.0
18-crown-6	346.7	328.4	312	298.9	287.4	269.4	262.1
benzo-15-crown-5	525.0	482.3	445.3	414.9	388.3	347.0	330.6
Temperature (K)	514.8	519.9	524.6	534.8	534.8	545.1	550.1

combination of reference compounds in each separate mixture. This insured that our computed values were not dependent on one specific correlation equation or set of standards.

Fusion enthalpies were measured on a PE DSC-7 instrument using 6–10 mg sample sizes. Each crown ether was measured in triplicate. The instrument was standardized by using the fusion enthalpy of indium (fusion enthalpy: (3.286±0.013) kJ mol^{-1}) [13–15] and then checked using biphenyl (18.574±0.04) (for reference materials on calorimetry and differential thermal analysis see [15]), naphthalene (19.061±0.080) [15] and benzoic acid (18.063±0.042) kJ mol^{-1}) [15]. The results are reported in Table 4.

The uncertainties reported represent two standard deviations unless otherwise noted. Commercial samples were used for all measurements. While sample purity is not usually when using this technique, sample purity of the commercial samples generally were 99% as determined by gas chromatography. Crown ethers were purchased from Aldrich and the podands were obtained from Eastman or Aldrich.

3. Results and discussion

Using the retention time data listed in Table 1, $\Delta_s^v H_m$ was calculated by plotting ln $(1/t_r)$ versus $1/T$ for each compound in each of the 18 mixtures as illustrated in Figs. 2 and 3 and Table 2 for mixture CE3. The typical linear correlation obtained by plotting ln $(1/t_r)$ versus $1/T$ is illustrated in Fig. 2. All plots were characterized by correlation coefficients (r^2) of 0.99 or better. The slopes of the lines for mixture CE3 are given in the second column of Table 2. $\Delta_s^v H_m$ was obtained by multiplication by the gas constant. Correlation of the reported vaporization enthalpies ($\Delta_{vap}H_m$(298.15 K)) with $\Delta_s^v H_m$ results in Fig. 3. The equation obtained by a linear least squares treatment of the data is given at the bottom of Table 2.

A summary of the calculated vaporization enthalpies, resulting from correlations between $\Delta_{vap}H_m$ (298.15 K) and $\Delta_s^v H_m$ for all the mixtures studied, is given in Table 3. The $\Delta_{vap}H_m$ (298.15 K) values calculated from the correlation equations are in good agreement with the literature values. Calculated vaporization enthalpies also remained constant when the composition of the mixtures was changed. Tetraethylene glycol dimethyl ether provides an example of a compound used in 11 different mixtures. The mean value calculated was 76.9±1.3 kJ mol^{-1} and can be compared to the literature value of 76.2 kJ mol^{-1}. The uncertainties reported here and in Table 2 represent two standard deviations.

The observed correlation between ethers and hydrocarbons was vital to the success of this study. The correlation illustrated in Fig. 2 demonstrates this

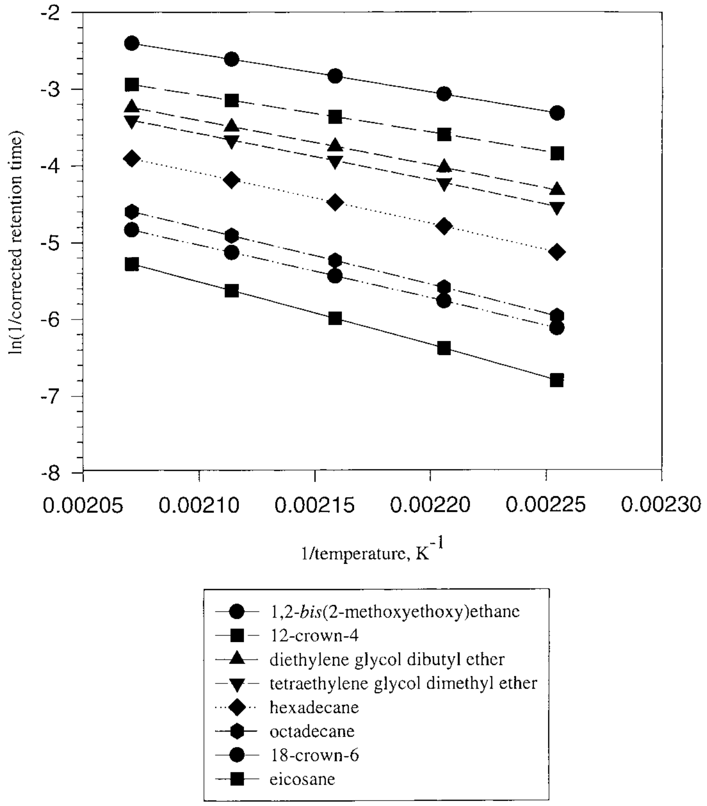

Fig. 2. ln$(1/t_r)$ vs $1/T$ plot for Mix CE3.

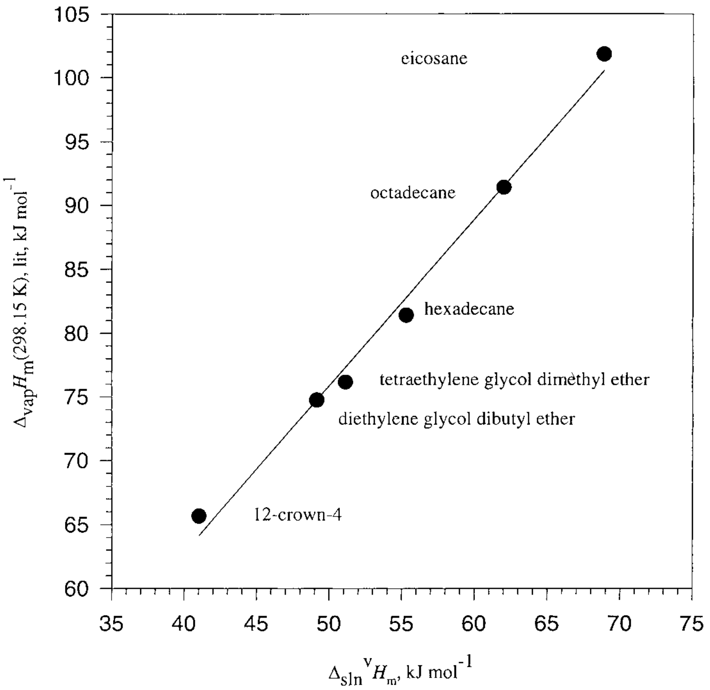

Fig. 3. Correlation of vaporization enthalpies at 298.15 K vs enthalpies of transfer for Mix CE3.

linear correlation as does the excellent agreement obtained between calculated and experimental vaporization enthalpies in Table 3 obtained for both ether and hydrocarbon standards used in the same mixture. This fact is extremely important in the analysis of the larger crown ethers. For these materials, standards with comparable thermochemical properties are required. Literature values for ethers of comparable size are not available. The vaporization enthalpies of the larger hydrocarbons served as standards in the evaluation of these compounds. An adequate analysis of the unknowns in each mixture can only be achieved if the volatility of each is bracketed by the standards in the mixture. This generally results in a bracketing of vaporization enthalpies as well. Standards were selected in these analyses with this in mind.

Table 2
Correlation data for mixture CE3 (enthalpies in kJ mol^{-1})[a]

Compound	Slope	$\Delta_s^v H_m$	$\Delta_{vap}H_m$(lit) (298.15 K)	$\Delta_{vap}H_m$(calc) (298.15 K)
1,2-bis-(2-methoxyethoxy)ethane	5020	41.7	–	65.07
12-crown-4	4935	41.0	65.65	64.15
diethylene glycol dibutyl ether	5913	49.2	74.73	74.76
tetraethylene glycol dimethyl ether	6151	51.2	76.16	77.35
hexadecane	6652	55.3	81.40	82.79
octadecane	7458	62.0	91.40	91.54
18-crown-6	7001	58.2	–	86.58
eicosane	8286	68.9	101.80	100.5

[a] Correlation between ($\Delta_s^v H_m$) and ($\Delta_{vap}H$(298.15)). Correlation equation: $\Delta_{vap}H_m$ (298,15) $= 1.306\Delta_s^v H_m + 10.57$; Correlation coefficient: 0.991.

Table 3
Summary of all correlations between $\Delta_s^v H_m$ and $\Delta_{vap}H_m$ (298.15 K); kJ mol^{-1}

Compoud	Run CE1	Run CE2	Run CE3	Run CE4	Run CE5	Run CE6	Run CE7	Run CE8	Run CE9	Run CE10	Run CE11	Run CE12	Run CE13	Run CE14	Run CE15	Run CE16	Run CE17	$\Delta_{vap}H$ (298 K) gc-corr[a]	$\Delta_{vap}H$ (298 K) lit
$C_6H_{10}O_3$ cis/trans 2,5 dimethoxy-2,5-dihydrofuran																44.3	44	44.2±0.3	
$C_6H_{14}O_3$ bis(2-methoxyethyl) ether												47.5	48			48.1	48.2	48.0±0.6	47.7[b]
$C_8H_{16}O_4$ 12-crown-4		67.1	64.1	63.8	68.4		65.9				64.6							65.7±3.7	65.7[c]
$C_8H_{18}O_4$ 1,2 bis(2-methoxyethoxy) ethane			65.1	65.1		65.4						61.8		62.0		63.0		63.7±3.3	
$C_8H_{18}O_3$ bis(2-ethoxyethyl) ether												54.0	53.9			55.1	55.2	54.6±1.4	53.1[d,j]
$C_9H_{12}O_3$ 1,3,5-trimethoxybenzene														67.6	68.9			68.2±2.0	
$C_{10}H_{22}O_5$ tetraethylene glycol dimethyl ether			77.4	77	73.5	77.2		78.7	77.9		77.4	76.7	77.5	76.7	76.8			76.9±2.6	76.2[e,j]
$C_{10}H_{22}$ decane														52.8	51.8	49.9	49.9	51.1±3.9	51.4[f]
$C_{10}H_{20}O_5$ 15-crown-5	75.1			75.6		75.7		76.7		74.1			75.6					75.7±1.7	79.6[c]
$C_{12}H_{16}O_6$ benzo-12-crown-4	81.6									82.5	83.9							82.7±2.3	
$C_{12}H_{24}O_6$ 18-crown-6	87.6	77.7	86.6	86.4	84.9			87.3	88.4	88.0	88.2							86.1±6.7	
$C_{12}H_{26}O$ dihexyl ether								63.5						63.1	64		63.8	63.6±0.8	63.5[g,j]
$C_{12}H_{26}O_3$ diethylene glycol dibutyl ether			74.8	74.5		73.8		73.1	74.0		74.6	73.4	72.3					73.8±1.7	74.7[h,j]
$C_{12}H_{26}$ dodecane													60.8	59.9	60.4	60.6	60	60.3±0.8	61.5[f]
$C_{14}H_{20}O_5$ benzo-15-crown-5	98.5									99.4								98.9±1.3	
$C_{14}H_{30}$ tetradecane				73.6	72.1	71.8						70.7						72±2.4	71.7[f]
$C_{16}H_{34}$ hexadecane			82.8					81.6	81.3	80.9	81.9	82.4	82.1	81.5	81			81.8±1.3	81.4[f]
$C_{18}H_{38}$ octadecane	90.9		91.5	91.7		91.2		91.4	89.8		91.6							91.4±1.3	91.4[f]
$C_{20}H_{24}O_6$ dibenzo-18-crown-6	141.0	136.4					133.6											137±7.4	
$C_{20}H_{36}O_6$ dicyclohexano-18-crown-6 (syn-cis/anti-cis)		125.8			125.4		121.4											124.2±4.0	
$C_{20}H_{42}$ eicosane			100.5	100.9	100.3			101.1		102.9	100.9							101.1±2.0	101.8[i]

Table 3 (*Continued*)

Compoud	Run CE1	Run CE2	Run CE3	Run CE4	Run CE5	Run CE6	Run CE7	Run CE8	Run CE9	Run CE10	Run CE11	Run CE12	Run CE13	Run CE14	Run CE15	Run CE16	Run CE17	$\Delta_{vap}H$ (298 K) gc-corr[a]	$\Delta_{vap}H$ (298 K) lit
$C_{23}H_{48}$ tricosane	120.7	118					120.1			119.9								119.7±2.3	120.5[i]
$C_{24}H_{50}$ tetracosane	126.5	125								125.5								125.7±1.6	125.6[i]
$C_{25}H_{52}$ pentacosane					127.9		127.4											127.6±0.8	126.9[i]
$C_{28}H_{58}$ octacosane	150.7	151.4					149.6											150.7±1.7	151.4[i]
$C_{30}H_{62}$ triacontane		164.6					164.4											164.5±0.4	162.9[i]

[a] The uncertainties represent two standard deviations.

[b] Calculated from the Antoine constants from [27] (vaporization enthalpies were calculated from the Antoine constants and adjusted to 298 K using the relationship: $\Delta_{vap}H_m(298.15\ K)=\Delta_{vap}H_m(T_m)+(10.58+0.26\ Cp_l)(T_m-298.15)$; where T_m is the mean temperature of the measurements) over the temperature range 286–316 K.

[c] From [16].

[d] From [27], (330–360) K.

[e] From [27], (419–449) K.

[f] From [28].

[g] From [27], (372–402) K.

[h] From [27], (463–493) K.

[i] From [12].

[j] Adjusted to 298.15 K using the relationship given in footnote b.

Table 4
Correlation between $\Delta_s^v H_m$ and $\Delta_{vap}H$ (298.15 by c-gc) of the crown ethers in kJ mol^{-1a}

Compound	$\Delta_s^v H_m$	$\Delta_{vap}H_m$(c-gc)^b (298.15 K)	$\Delta_{vap}H_m$(calc)^c (298.15 K)	$\Delta_{vap}H_m$(lit)^d (298.15 K)
$C_8H_{16}O_4$ 12-crown-4	37.1	65.7	64.6	65.7
$C_{10}H_{20}O_5$ 15-crown-5	44.6	75.7	76.5	79.6
$C_{12}H_{16}O_4$ benzo[12-crown-4]	48.9	82.7	83.4	
$C_{12}H_{24}O_6$ 18-crown-6	52.0	87.3	88.3	
$C_{14}H_{20}O_5$ benzo[15-crown-5]	57.8	98.9	97.5	

[a] Correlation equation: $\Delta_{vap}H_m = (1.588\pm0.086)\Delta_s^v H_m + (5.74\pm1.34)$; Correlation coefficient (r^2): 0.9913.

[b] This work.

[c] From [25].

[d] From [16].

A vaporization enthalpy of 79.57 kJ mol^{-1} has been reported for 15-crown-5 by Byström and Månsson [16]. The values derived from the correlation equations consistently deviated from the literature value by approximately 4 kJ/mol as shown for $C_{10}H_{20}O_5$ in Table 3. The vaporization enthalpy of 15-crown-5 was therefore treated as an unknown in all these mixtures. As can be seen from Table 3, the calculated vaporization enthalpy of 15-crown-5, derived from a variety of different standards (75.7±1.7) kJ mol^{-1}, is consistently lower than the literature value[2]. With a similar compound, 12-crown-4, the value we obtain, (65.7±3.7) kJ mol^{-1}, compares very favorably to the vaporization enthalpy reported by Byström and Månsson [16] in the same study, 65.7 kJ mol^{-1}. Although the Byström and Månsson value lies outside of the uncertainty generated by the statistics cited in Table 3, we note here that this value falls just within two standard deviations when the standard error is calculated from the uncertainty in slope associated with each correlation equation.

The commercial sample of dicyclohexano-18-crown-6 in runs CE2, CE5 and CE7 was measured as a *syn-cis*/*anti-cis* mixture. Similarly, 2,5-dimethoxy-2,5-dihydrofuran also commercially available, was measured as a *cis-trans* mixture. Under the conditions of the chromatographic measurements, the two isomers of both substances were not resolved but eluted as a single peak. The property measured for these two compounds is not a true vaporization enthalpy but rather some composite of the vaporization and mixing enthalpies. At lower temperatures the column was able to separate the two isomers of dicyclohexano-18-crown-6.

The vaporization enthalpy of 18-crown-6 was evaluated in nine different mixtures. The uncertainty of one of the results, that for CE2, deviated by more than three standard deviations of from the remaining eight values and was not used in computing the mean.

As a test to evaluate the internal consistency of the vaporization enthalpies measured for the crown ethers, a mixture of all them was analyzed. The experimental data are presented in run CE18 and the results are summarized in Table 4. Column 2 in this table records the enthalpy of transfer from solution to the vapor while column 3 lists the vaporization enthalpies measured in this study. The correlation between $\Delta_s^v H_m$ and $\Delta_{vap}H_m$ (298.15 K) is illustrated in Fig. 4. The solid line represents the results of the linear regression analysis. The parameters associated with this correlation are described at the bottom of Table 4 and were used to calculate the entries reported in the fourth column of the Table. The solid square in Fig. 4 represents the vaporization enthalpy of 15-crown-5 which was not used in the analysis as discussed earlier. The correlation obtained suggests that the vaporization enthalpies of all the crown ethers are internally consistent and in good agreement with the values cited in Table 3.

Several of the crown ethers in this study are solids at room temperature. Consequently, the sublimation

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[2] We have measured the vaporization enthalpy of this material using a technique we refer to as transpiration gas chromatography. A vaporization enthalpy of 75.5 ± 4.8 kJ mol^{-1} was measured by this technique (unpublished results from [17]).

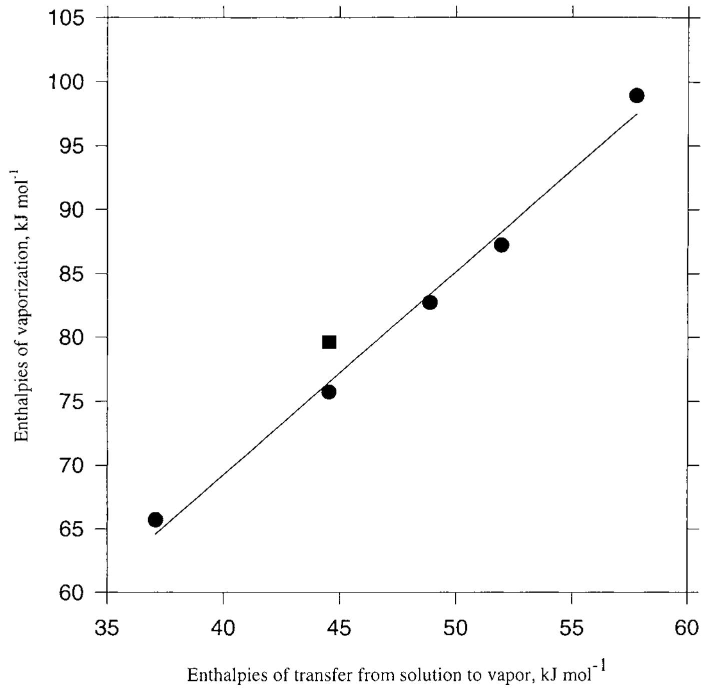

Fig. 4. Correlation of vaporization enthalpies at 298.15 K vs enthalpies of transfer for the crown ethers.

enthalpies of these materials at 298.15 K are of thermochemical interest. Sublimation enthalpies have been calculated by combining fusion and vaporization enthalpies. Fusion enthalpies for several of these materials have been measured in this work and others are available from the literature. Fusion enthalpies were adjusted to 298.15 using the following equation [18]:

$$\Delta_{\text{fus}}H_{\text{m}}\,(298.15\,\text{K}) = \Delta_{\text{fus}}H_{\text{m}}(T_{\text{fus}}) + (0.75 + 0.15\,\text{Cp}_{\text{c}}) \times (T_{\text{fus}} - 298.15) + (10.58 + 0.26\,\text{Cp}_{\text{l}}) \times (298.15 - T_{\text{fus}})\,\text{J}\,\text{mol}^{-1}.$$

This equation has been used successfully in adjusting fusion enthalpies of a variety of different materials

Table 5
Experimental fusion, vaporization and sublimation enthalpies of some solid crown ethers

	T_{fus}/K	$\Delta_{\text{fus}}H_{\text{m}}(T_{\text{fus}})$ (kJ mol^{-1})	$\Delta_{\text{vap}}H_{\text{m}}$ (298.15 K) (kJ mol^{-1})	Cp_{l} (J mol^{-1} K^{-1})	Cp_{c} (J mol^{-1} K^{-1})	$\Delta_{\text{sub}}H_{\text{m}}$ (298.15 K) (kJ mol^{-1})
$C_8H_{16}O_4$ 12-crown-4	290.7	22.5^{a}	65.7±3.7	306	236	88.5±3.7
$C_{12}H_{16}O_4$ benzo[12-crown-4]	321.2	23.1±1.2^{b}	82.7±2.3	372	273	104.3± 2.6
$C_{12}H_{24}O_6$ 18-crown-6	312.2	40.9±1.9^{b}	87.3±2.3^{c}	458	353	128.1±2.3^{c}
		37.1^{a}				124.3
$C_{14}H_{20}O_5$ benzo[15-crown-5]	351.2	28.3±1.5^{b}	98.9±1.3	448	332	123.2±2.0
$C_{20}H_{24}O_6$ dibenzo[18-crown-6]	440.0	55.4±3.2^{b}	137.0±7.4	590	429	178.4±6.9
		57.5^{a}				180.2

[a] From [22].
[b] This work.
[c] Average of runs in Table 3 and including mix CE18.

Table 6
Estimated fusion, vaporization and sublimation enthalpies of some solid crown ethers[a]

	$\Delta_{tpce}S$ (J mol^{-1} K^{-1})	$\Delta_{fus}H_m(T_{fus})$ (kJ mol^{-1})	$\Delta_{vap}H_m$ (298.15 K) (kJ mol^{-1})	$\Delta_{sub}H_m$ (298.15 K) (kJ mol^{-1})	$\Delta_{sub}H_m$ (298.15 K) (kJ mol^{-1}) (from Table 5)
$C_8H_{16}O_4$ 12-crown-4	71.5 [33.4+9×3.7+4×1.2]	20.8	65.0 [8×4.69+3.0+2.9+4×5×1.08]	86.3	88.6
$C_{12}H_{16}O_4$ benzo-12-crown-4	76.5 [33.4+9×3.7+4×1.2+4×7.4–2×12.3]	24.6	82.6 [12×4.69+3.0+2×5×(1.08+0.85)/2+2×5×1.08+2.9]	105.7	104.3
$C_{12}H_{24}O_6$ 18-crown-6	96.1 [33.4+15×3.7+6×1.2]	30.0	94.6 [12×4.69+3.0+2.9+6×5×1.08]	123.5	128.1
$C_{14}H_{20}O_5$ benzo-15-crown-5	88.8 [33.4+12×3.7+5×1.2+4×7.4–2×12.3]	31.2	97.4 [14×4.69+3.0+2×5×(1.08+0.85)/2+3×5×1.08+2.9]	124.5	123.1
$C_{20}H_{24}O_6$ dibenzo-18-crown-6	106.1 [33.4+15×3.7+6×1.2+8×7.4–4×12.3]	46.2	13.0 [20×4.69+3.0+4×5×(1.08+0.85)/2+2×5×1.08+2.9]	162.4	179.8

[a] The terms in brackets in this table are a device to illustrate the calculation; for a description of the protocol see [25].

[19]. The terms Cp_l and Cp_c refer to the heat capacity of the liquid and solid respectively. Heat capacity values were estimated for both phases [20]. They are listed in columns 5 and 6 of Table 5.

Sublimation enthalpies for the compounds in Table 5 have not been measured directly except for 18-crown-6. A value of 133.2 kJ mol^{-1} has been reported by Briggner and Wadso [21]. No uncertainty is associated with their measurement. This value is slightly larger than the value of 128.2±3.0 kJ mol^{-1} listed in Table 5 that we obtain from the sum of the vaporization and fusion enthalpies. The fusion enthalpy of 18-crown-6 is the average of three DSC measurements performed in our laboratory. Our value is slightly larger than the value cited by Domanska [23,24][3]. No uncertainty is cited in this work but both values are in reasonable agreement. Efforts to measure the sublimation enthalpy of 18-crown-6 by head space analysis were not successful. The volatility of the solid proved to be too low for our apparatus.

As noted above, with the exception of 18-crown-6, sublimation enthalpies for the crown ethers listed in Table 5 have not been reported previously. For purposes of comparison, estimated fusion, vaporization and sublimation properties for all the solid crown ethers investigated in this study are summarized in Table 6. These estimations were obtained using a protocol previously reported [25]. Column 2 of this table reports an estimate of the total phase change entropy (the phase change entropy change associated in going from the solid at 0 K to the liquid at the melting point) was calculated for each compound. Multiplication of this column by the experimental melting point results in an estimate of the fusion enthalpy listed in the third column. Adjusting this value to 298.15 K and adding the vaporization enthalpy results in an estimate of the sublimation that is in reasonably good agreement with the experimental results obtained in this study. Only the value for dibenzo-18-crown-6 has a substantial absolute error. We have previously observed that the protocol used to estimate vaporization enthalpies shows a tendency to underestimate the vaporization enthalpy of molecules approaching the size of dibenzo-18-crown-6 [25,26].

A comparison of experimental and estimated vaporization enthalpies of the remaining liquid ethers of Table 3 is provided in Table 7. In this case also the estimated values are in good agreement with the experimental results. The terms in brackets illustrate the estimation.

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[3] A fusion enthalpy of 35.7 and a phase transition of 1.4 kJ mol^{-1}, are reported. The temperature for the phase transition was not reported (private communication by J.-P.E. Grolier, cited in [24]).

Table 7
A Comparison of Estimated and Experimental Vaporization Enthalpies (kJ mol^{-1})

Compounds	$\Delta_{vap}H_m$(298.15 K)[a] [estimated]	$\Delta_{vap}H_m$(298 K) (this work)	$\Delta_{vap}H_m$ (298 K) (lit)
$C_6H_{14}O_3$ bis(2-methoxyethyl) ether	50.0 [6×(4.69)+3+5×1.082×5×(1.62+1.08)/2]	48.0	47.4
$C_8H_{18}O_4$ 1,2-bis(2-methoxyethoxy) ethane	64.8 [8×(4.69)+3+2×5×1.082×5×(1.62+1.08)/2]	63.7	
$C_8H_{18}O_4$ bis(2-ethoxyethyl) ether	56.7 [8×4.69+3+3×5×1.08]	54.6	53.1
$C_9H_{12}O_3$ 1,3,5-trimethoxybenzene	63.7 [9×(4.69)+3+3×5×(1.62+0.85)/2]	68.2	
$C_{10}H_{22}O_5$ tetraethylene glycol dimethyl ether	79.6 [10×(4.69)+3+3×5×1.08+2×5×(1.08+1.62)/2]	76.9	76.2
$C_{10}H_{20}O_5$ 15-crown-5	79.8 [10×(4.69)+3+5×5×1.08+2.9]	75.7	79.6
$C_{12}H_{26}O$ hexyl ether	64.7 [12×4.69+3+5×1.08]	63.6	63.5
$C_{12}H_{26}O_3$ diethylene glycol dibutyl ether	75.5 [12×4.69+3+3×5×1.08]	73.8	74.7

[a] The terms in brackets are a device to illustrate the estimation; see [25] for a description of the protocol used in the estimation.

4. Conclusions

The results of this study indicate that despite the fact that crown ethers are excellent complexing agents that strongly interact with metal ions often with high selectivity, they are quite similar to their acyclic counterparts and analogous hydrocarbons as far as the thermodynamics of their phase changes are concerned. Their properties seem to be modeled quite well by methods designed for general use. Similar conclusions have been reached by others examining other thermodynamic properties of crown ethers in solution [21].

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