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Thermophysical properties of dimethyl sulfoxide + cyclic and linear ethers at 308.15 K
Application of an extended cell model

Romolo Francesconi [a], Fabio Comelli [b,∗], Adriana Bigi [a], Katia Rubini [a]

[a] *Dipartimento di Chimica "G. Ciamician", Università degli Studi, via Selmi 2, I-40126 Bologna, Italy*
[b] *I.S.O.F.-C.N.R., c/o Dipartimento di Chimica "G. Ciamician", via Selmi 2, I-40126 Bologna, Italy*

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Abstract

Excess molar enthalpies and heat capacities of dimethyl sulfoxide + 1,4-dioxane, dimethyl sulfoxide + 1,3-dioxolane, dimethyl sulfoxide + tetrahydropyran, dimethyl sulfoxide + tetrahydrofuran, dimethyl sulfoxide + 1,2-dimethoxyethane, and dimethyl sulfoxide + 1,2-diethoxyethane have been measured at 308.15 K and at atmospheric pressure using an LKB micro-calorimeter and a Perkin-Elmer differential scanning calorimeter. Heat capacities of pure components were determined in the range ($293.15 < T/K < 423.15$). The results of excess molar enthalpies were fitted to the Redlich–Kister polynomial equation to derive the adjustable parameters and standard deviations, and were used to study the nature of the molecular interactions in the mixtures. Results of excess molar enthalpy were interpreted by an extended modified cell model.

Keywords: Excess molar enthalpy; Heat capacity; Liquid mixtures; Cell model

1. Introduction

The use of dimethyl sulfoxide (DMSO) has stimulated great interest in recent years because of its wide range of applicability as a solvent in chemical and biological processes, in pharmaceutical applications, in veterinary medicine and microbiology [1–3]. The importance of DMSO in medicine is various: in fact DMSO stabilizes membranes and cuts pain by blocking peripheral c fibres [4], it reduces inflammation by several mechanisms, it is an antioxidant, a scavenger of the free radical that gather at the site of injury [5]. DMSO was also successfully utilized in the treatment of several pathologies, including scleroderma [6], and arthritis [7]. Moreover, several properties of this substance have gained attention in relation to cancer [8].

As a part of our research of investigating the physical properties of binary liquid mixtures containing DMSO [9–11], in this paper we present experimental data of excess molar enthalpies, H_m^E, and molar heat capacities, C_p, of DMSO + cyclic and linear ethers, namely 1,4-dioxane, 1,3-dioxolane, oxane, oxolane, 1,2-dimethoxyethane, and 1,2-diethoxyethane, respectively. The aim of this work is to provide information about the molecular interactions in the liquid state with a special attention focussed on the differences of the excess properties of cyclic and linear species.

DMSO is a highly polar aprotic solvent because of its S=O group and has a large dipole moment and relative permittivity ($\mu = 4.06$ D and $\varepsilon = 46.45$ at 298.15 K [12]). Cyclic and linear ethers, on the other hand, have relatively low values of relative permittivity and dipole moment. The thermodynamic properties of DMSO + cyclic and linear ethers should be related to the interactions between the S=O group provided by DMSO and the OR group of the cyclic and linear ethers. However, just a few papers at 298.15 K are available in the literature [13–15], reporting thermo-chemical data.

2. Experimental

DMSO (analytical grade >99.5 mol%), 1,4-dioxane and 1,2-diethoxyethane (analytical grade 99.8 mol% for both products)

∗ Corresponding author. Tel.: +39 051 2094326; fax: +39 051 2094325.
E-mail address: comelli@isof.cnr.it (F. Comelli).

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were obtained from Fluka, while 1,3-dioxolane, tetrahydropyran (THP), and tetrahydrofuran (THF) ((analytical grade (99.8, 99, and 99.9) mol%, respectively)) were from Aldrich.

All liquids were used without further purification.

Before use, the components were degassed ultrasonically (ultrasonic bath, Hellma, type 460, Milan, Italy) and dried over molecular sieves (Aldrich, type 3A) to remove any traces of moisture. Purities of all products were checked using a Hewlett-Packard G.CX. Model 5890 supplied by an HP (cross-linked 5% ME siloxane) capillary column and the obtained values complied with purchaser specifications.

In order to have a better comparison with the data of literature, measurements of refractive indices, n_D (sodium D-line), of pure components were obtained using a thermo-stated Abbe refractometer (Carl Zeiss, model G, Jena, Switzerland) with accuracy less than ± 0.0001 units.

Experimental values of densities, ρ, refractive indices, n_D, and heat capacities, C_p, of the pure components were compared with literature data [12,16–26], as shown in Table 1.

A flow micro-calorimeter (LKB, model 2107, Producer AB, Bromma, Sweden), thermo-stated at (308.15 ± 0.01) K, was used to measure the excess molar enthalpies, H_m^E. The apparatus consists of a flow-mixing cell, a reference cell, a thermostatic water bath, a data acquisition unit, and two automatic burets (ABU, Radiometer, Copenhagen, Denmark) necessary to pump the pure liquids into the mixing cell of the calorimeter. The temperature of the bath was controlled within ± 0.01 K. Details of its experimental setup and operational procedure were described previously [27,28]. The performance and reliability of the micro-calorimeter were checked by the test mixtures hexane + cyclohexane, benzene + cyclohexane, and methanol + water. The experimental values of H_m^E agreed with literature data [29] within 1%. Miscibility of the components was tested prior to measurements and components were found to be completely miscible over the whole concentration range. Mole fractions of mixtures were computed from densities. Density measurements of pure components, necessary to calculate flow rates of mixtures have been determined using a digital density meter (Anton Paar, model DMA 60, Graz, Austria) equipped with a measuring cell (Anton Paar, type 602) described elsewhere [30].

All measurements have been determined at a constant temperature using an external ultra-thermostat bath circulator (Heto, type 01 DTB 623, Birkeròd, Denmark), precision ±0.005 K, and temperatures have been detected by a digital thermometer (Anton Paar, type CTK 100). Before each series of measurements, the apparatus was calibrated at atmospheric pressure using double-distilled water and dry air, whose densities were taken from literature [31,32]. The uncertainty in density was $\pm 1.5 \times 10^{-5}$ g cm^{-3} at 308.15 K. Volumetric flow rates of components, selected to cover the entire mass fraction range, were stated by the automatic burettes. The total flow rates were usually kept at about 0.4 cm^3 min^{-1}, but in the dilute region the total flow rates may increase up to 0.8 cm^3 min^{-1}. The experimental uncertainties in H_m^E were estimated to be less than 0.5% over the most of the composition range.

The H_m^E values were computed from the following relationship:

$$H_m^E = \frac{I^2 R(E/E_c)}{f} \quad (1)$$

where I and R are the electrical current and resistance in the electrical calibration experiments, E and E_c are the voltage readings for measurements and electrical calibration, respectively, and f is the molar flow rate of the mixture.

The molar flow rate f_i of the i-th component flowing into the mixing cell is obtained from the formula

$$f_i = \frac{\rho_i V_i}{M_i} \quad (2)$$

where ρ_i and M_i are the density and molar mass, respectively, and V_i is the volumetric flow rate of component i. Experimental data of excess molar enthalpies, H_m^E, are reported in Table 2 and represented in Figs. 1 and 2.

Table 1
Densities, ρ, refractive indices, n_D, and heat capacities, C_p, of pure components, and comparison with literature data

Compound	T (K)	ρ (g cm^{-3}) Exp.	Lit.	n_D Exp.	Lit.	C_p (J mol^{-1} K) Exp.	Lit.
DMSO	298.15	1.09558	1.09569 [16]	1.4775	1.47754 [12]	152.4	153.18 [12]
	308.15	1.08550	1.08548 [17]	1.4729	1.4729 [18]	154.6	
1,4-Dioxane	298.15	1.02796	1.02797 [12]	1.4202	1.42025 [12]	151.0	150.65 [12]
	308.15	1.01699	1.017 [19]	1.4154		153.7	
1,3-Dioxolane	298.15	1.05879	1.05865 [20]	1.3983		121.7	121.56 [21]
	308.15	1.04640		1.3934		124.4	
Oxane	298.15	0.87931	0.8791 [20]	1.4188	1.41862 [12]	147.9	149.2 [21]
	308.15	0.86885	0.8688 [22]	1.4142		151.7	
Oxolane	298.15	0.88190	0.88193 [23]	1.4048	1.40496 [12]	123.8	123.9 [12]
	308.15	0.87099		1.4002		131.4	
1,2-Dimethoxyethane	298.15	0.86190	0.8620 [24]	1.3781	1.37811 [12]	191.1	191.22 [25]
	308.15	0.85128	0.85082 [26]	1.3726		193.4	
1,2-diethoxyethane	298.15	0.83511	0.83510 [12]	1.3897	1.3898 [12]	257.5	259.4 [12]
	308.15	0.826026		1.3853		258.7	

Table 2
Excess molar enthalpies, H_m^E, for binary mixtures containing DMSO + cyclic and linear ethers at 308.15 K

x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})	x_1	H_m^E (J mol^{-1})
DMSO (1) + 1.4-dioxane (2)					
0.0478	133	0.3757	409	0.8280	272
0.0911	222	0.4451	417	0.8784	207
0.1308	281	0.5462	404	0.9059	167
0.1671	320	0.6437	383	0.9353	116
0.2313	365	0.7066	356	0.9665	66
0.2863	386	0.7831	310		
DMSO (1) + 1,3-dioxolane (2)					
0.0394	61	0.3297	250	0.7973	217
0.0757	107	0.3959	263	0.8551	179
0.1095	140	0.4959	271	0.8872	148
0.1408	171	0.5961	264	0.9219	112
0.1974	200	0.6630	255	0.9594	65
0.2469	226	0.7469	235		
DMSO (1) + oxane (2)					
0.0543	376	0.4079	1144	0.8464	685
0.1148	670	0.4786	1165	0.8921	508
0.1469	781	0.5708	1128	0.9168	412
0.1867	896	0.6739	1035	0.9429	295
0.2562	1016	0.7337	946	0.9706	157
0.3146	1091	0.8051	796		
DMSO (1) + oxolane (2)					
0.0457	213	0.3651	853	0.8215	588
0.0875	372	0.4339	870	0.8735	474
0.1257	490	0.5349	874	0.902	400
0.1608	579	0.6332	839	0.9325	291
0.2233	699	0.6970	773	0.965	163
0.2771	765	0.7753	682		
DMSO (1) + 1,2-dimethoxyethane (2)					
0.0577	77	0.4238	361	0.8547	230
0.1092	142	0.4950	366	0.8982	182
0.1553	193	0.5953	364	0.9217	142
0.1969	231	0.6882	338	0.9464	105
0.2689	285	0.7463	316	0.9725	57
0.3290	326	0.8153	265		
DMSO (1) + 1,2-diethoxyethane (2)					
0.0765	342	0.4985	893	0.8883	397
0.1421	532	0.5698	883	0.9227	293
0.1990	648	0.6653	835	0.9408	245
0.2488	720	0.7489	726	0.9598	160
0.3320	803	0.7990	638	0.9795	83
0.3986	843	0.8564	502		

The heat capacity measurements, C_p, were performed using a Perkin-Elmer DSC-7 differential scanning calorimeter, equipped with a model PII intercooler.

The instrument was calibrated with high-purity standards (indium and cyclohexane) at 5 K min^{-1}.

The temperature was known to within ±0.1 K. The samples, approximately 10 mg, determined to ± 0.01mg, were encapsulated in hermetic pans. The weight of the closed pans did not change before and after measurements. The heat capacity of the samples was obtained by means of three consecutive DSC runs at scanning rate of 5 K min^{-1}: the sample run, the blank run and the standard sample (sapphire) run [33]. Care was taken to ensure that for all three scans, sample, blank, and standard, similar initial and final isotherm levels were reached. The heat capacity data were obtained by means of the commercial software supplied by Perkin-Elmer.

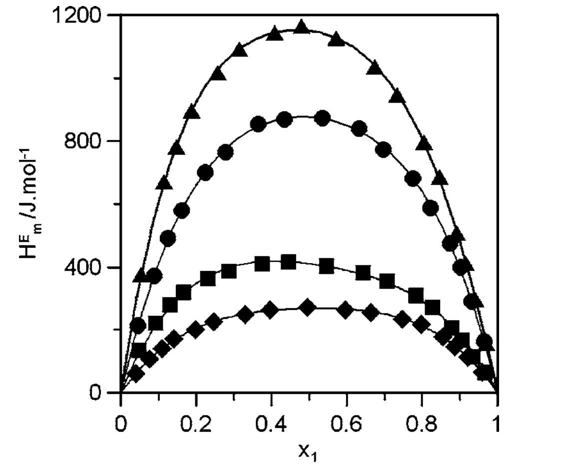

Fig. 1. Excess molar enthalpies, H_m^E, for binary mixtures of DMSO (1) + cyclic ethers (2) at 308.15 K). ■, ♦, ▲, ● refer to mixtures containing 1,4-dioxane, 1,3-dioxolane, oxane, and oxolane, respectively. Full line, Eq. (4).

The experimental and calculated heat capacities, C_p, of pure liquids (from 293.15 to 423.15) K at atmospheric pressure are listed in Table 3 and represented in Fig. 3. The expression used to fit the heat capacities C_p is

$$\frac{C_p}{J} \times \mathrm{mol}^{-1} \times K^{-1} = c_0 + c_1\left(\frac{T}{K}\right) + c_2\left(\frac{T}{K}\right)^2 \quad (3)$$

Values of the parameters c_k are listed in Table 4 together with the standard deviations σ (C_p). Values of molar heat capacities are reported in Table 5 and graphically represented in Figs. 4 and 5.

The precision of the heat capacity measurements is better than ±0.1%, as stated by the instructions of Perkin-Elmer DSC and checked by experimental data of this paper.

Experimental enthalpies, H_m^E were fitted by the method of least squares, with all points weighted equally, to the smoothing

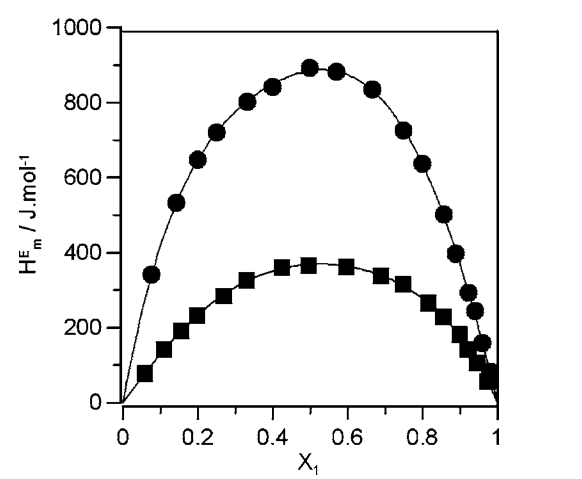

Fig. 2. Excess molar enthalpies, H_m^E, for binary mixtures of DMSO (1) + linear ethers (2) at 308.15 K). ■, ● refer to mixtures containing 1,2-dimethoxyethane, and 1,2-diethoxyethane, respectively. Full line, Eq. (4).

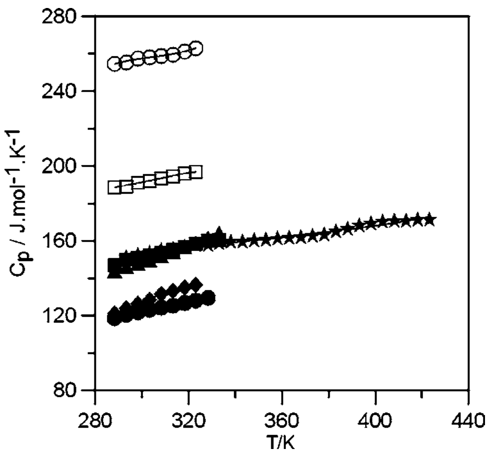

Fig. 3. Liquid heat capacities, C_p, of pure components at 308.15 K. DMSO. *, ♦, ■, ▲, ●, □, ○ refer to DMSO, 1,4-dioxane, 1,3-dioxolane, oxane, oxolane, 1,2-dimethoxyethane, and 1,2-diethoxyethane, respectively. Full line, Eq. (3).

Redlich–Kister polynomial

$$H_m^E = x_1 x_2 \sum_{k \geq 0} a_k (x_1 - x_2)^k \quad (4)$$

The adjustable parameters, a_k, were determined by a least-squares method, fitting the experimental values to Eq. (4) and the results are given in Table 6. The standard deviations, σ (H_m^E), reported in Table 6 were defined as:

$$\sigma(H_m^E) = \left| \frac{\phi_{min}}{(N-n)} \right|^{0.5} \quad (5)$$

with N and n the number of experimental points and parameters, respectively, whereas ϕ_{min} is the minimum value of the objective function ϕ defined as:

$$\phi = \sum_{k=1}^{N} \eta k^2 \quad (6)$$

where $\eta_k = H_{m,calcd}^E - H_m^E$. H_m^E is the experimental value and $H_{m,calcd}^E$ is evaluated through Eq. (4).

Table 4
Adjustable parameters of Eq. (3) and standard deviation, σ (C_p)

Component	c_0	c_1	c_2	σ (C_p) (J mol^{-1} K^{-1})
DMSO	129.4653	0.0268	0.0001	0.9
1,4-Dioxane	−58.0289	1.0707	−0.0012	0.6
1,3-Dioxolane	−1.4222	0.5548	−0.0005	0.2
Oxane	230.5906	−0.9462	0.0022	0.2
Oxolane	−349.9378	2.6910	−0.0037	0.2
1,2-Dimethoxyethane	106.5516	0.3183	−0.0001	0.3
1,2-Diethoxyethane	284.7413	−0.3994	0.0010	0.5

Table 3
Experimental liquid heat capacities, C_p, of DMSO, 1,4-dioxane, 1,3-dioxolane, oxane, oxolane, 1,2-dimethoxyethane, and 1,2-diethoxyethane at atmospheric pressure

T (K)	DMSO	1,4-Dioxane	1,3-Dioxolane	Oxane	Oxolane	1,2-Dimethoxy-ethane	1,2-Diethoxy-ethane
	C_p (J mol^{-1} K^{-1})						
288.15		146.7	118.8	143.9	121.1	188.7	254.5
293.15	151.2	150.0	120.3	146.3	123.8	189.0	255.3
298.15	152.4	151.0	121.7	147.9	126.4	191.0	257.5
303.15	153.4	152.1	123.3	149.7	128.5	192.2	257,9
308.15	154.8	153.7	124.4	151.7	131.4	193.4	258.7
313.15	155.4	155.3	125.3	154.3	133.2	194.5	259.5
318.15	156.6	156.5	126.8	156.5	135.2	195.8	261.2
323.15	157.7	158.4	128.1	159.1	136.6	196.9	262.9
328.15	157.8	160.2	129.5	161.6			
333.15	158.5	160.4		164.2			
338.15	159.3						
343.15	159.5						
348.15	160.2						
353.15	160.3						
358.15	161.3						
363.15	161.5						
368.15	161.7						
373.15	162.6						
378.15	163.3						
383.15	164.8						
388.15	166.3						
393.15	168.3						
398.15	169.1						
403.15	170.3						
408.15	170.4						
413.15	170.6						
418.15	171.1						
423.15	171.2						

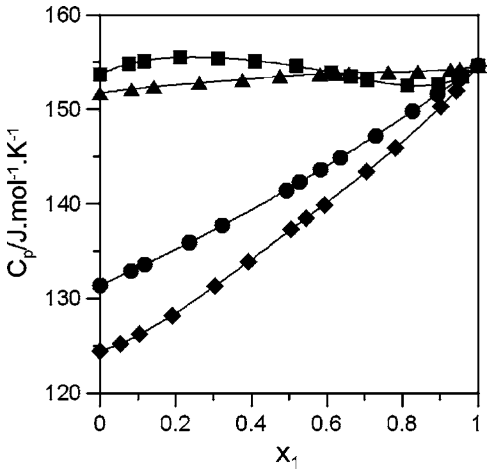

Fig. 4. Heat capacities, C_p, for binary mixtures containing DMSO (1) + cyclic ethers (2) at 308.15 K. ■, ♦, ▲, ● refer to mixtures containing 1,4-dioxane, 1,3-dioxolane, oxane, and oxolane, respectively. Full line, Eq. (3).

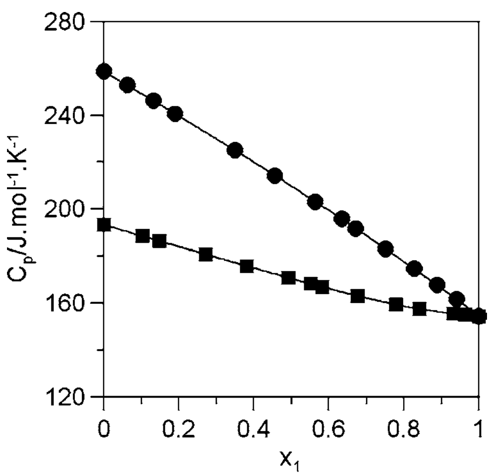

Fig. 5. Heat capacities, C_p, for binary mixtures containing DMSO (1) + linear ethers (2) at 308.15 K. ■, ● refer to mixtures containing 1,2-dimethoxyethane, and 1,2-diethoxyethane, respectively. Full line, Eq. (3).

3. The cell model

An attempt to describe the systems studied in this paper by means of the cell model, elaborated by Prigogine and co-workers [34–36], Salsburg and Kirkwood [37] and Rowlinson [38,39] was carried out, starting from the theoretical expression for H_m^E

$$H_m^E = x_1 x_2 E_{11} z \left[-1.44\theta + 10.76 \left(\frac{RT}{zE_{11}} \right)^2 \times (-2\theta - \delta^2 + 4\delta\theta x_2 + 4x_1 x_2 \theta^2) \right] \quad (7)$$

where

$$\delta = \frac{(E_{22} - E_{11})}{E_{11}} \quad (8)$$

$$\theta = \left(E_{12} - \frac{(E_{11} + E_{22})/2}{E_{11}} \right) \quad (9)$$

Table 5
Experimental heat capacities, C_p, Eq. (3), for binary mixtures containing DMSO + cyclic and linear ethers at 308.15 K

x_1	C_p (J mol^{-1} K^{-1})	x_1	C_p (J mol^{-1} K^{-1})
DMSO (1) + 1,4-dioxane (2)			
0.0749	154.8	0.6108	153.9
0.1148	155.1	0.6637	153.5
0.2112	155.5	0.7064	153.2
0.3130	155.4	0.8128	152.5
0.4096	155.1	0.8952	152.7
0.5185	154.6	0.9586	153.5
DMSO (1) + 1,3-dioxolane (2)			
0.0532	125.2	0.5455	138.5
0.1036	126.2	0.5936	139.9
0.1897	128.2	0.7053	143.4
0.3044	131.3	0.7810	145.9
0.3922	133.9	0.9015	150.3
0.5058	137.3	0.9431	152.0
DMSO (1) + oxane (2)			
0.0834	152.1	0.6249	153.8
0.1416	152.4	0.6590	153.8
0.2619	152.8	0.7619	153.9
0.3760	153.1	0.8405	154.0
0.4572	153.5	0.9268	154.2
0.5817	153.7	0.9520	154.3
DMSO (1) + oxolane (2)			
0.0807	132.9	0.5833	143.6
0.1171	133.6	0.6359	144.9
0.2353	135.9	0.7298	147.2
0.3233	137.7	0.8269	149.8
0.4932	141.4	0.8930	151.6
0.5284	142.3	0.9507	153.2
DMSO (1) + 1,2-dimethoxyethane (2)			
0.1017	188.6	0.5831	166.9
0.1471	186.5	0.6770	163.1
0.2718	180.8	0.7788	159.4
0.3811	175.8	0.8414	157.6
0.4923	170.8	0.9315	155.5
0.5507	168.3	0.9626	155.0
DMSO (1) + 1,2-diethoxyethane (2)			
0.0627	252.8	0.6350	195.8
0.1317	246.0	0.6718	191.9
0.1895	240.7	0.7514	183.1
0.3500	225.0	0.8274	174.7
0.4563	214.4	0.8881	167.7
0.5642	203.2	0.9410	161.6

where z is the number of nearest neighbours in the quasi-lattice model, E_{ij} the interaction energy between molecules i and j, δ and θ the normalized parameters.

The results do not show any appreciable variation in the range of z values from 8 to 12.

Values of δ have been calculated from Eq. (8) with E_{11} and E_{22} evaluated as the heats of vaporization reported in the literature [12]. Fig. 6, refers to DMSO + 1,2-diethoxyethane mixture, is an example of the result of the above cited theory.

Table 7 shows the interaction energy values, E_{ij}, between the molecules for the mixtures studied in this paper with the dipole moments, μ/D, and relative permittivities, ε of pure components.

Table 6
Adjustable parameters, a_k, Eq. (4), and standard deviations σ (H_m^E), Eq. (5), of DMSO + linear and cyclic ethers at 308.15 K

Function	a_0	a_1	a_2	a_3	σ (H_m^E)
DMSO (1) + 1,4-dioxane (2)					
H_m^E (J mol^{-1})	1639.9	−106.5	1009.7	−473.9	3.3
DMSO (1) + 1,3-dioxolane (2)					
H_m^E (J mol^{-1})	1071.3	37.5	656.9		2.3
DMSO (1) + oxane (2)					
H_m^E (J mol^{-1})	4605.5	−285.0	2236.7	−901.7	6.0
DMSO (1) + oxolane (2)					
H_m^E (J mol^{-1})	3505.2	−108.5	1542.1		5.7
DMSO (1) + 1,2-dimethoxyethane (2)					
H_m^E (J mol^{-1})	1474.7	110.5	355.1	323.8	2.3
DMSO (1) + 1,2-diethoxyethane (2)					
H_m^E (J mol^{-1})	3540.1	289.9	1311.7	−986.1	5.9

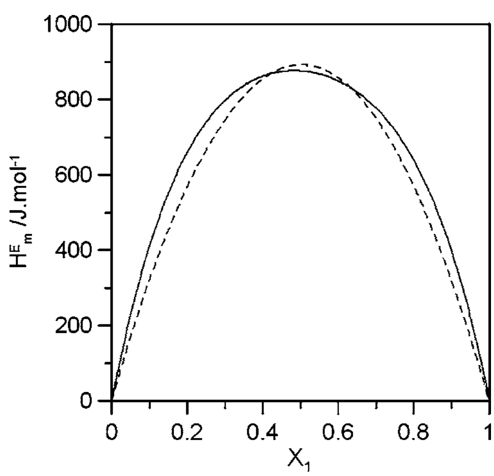

Fig. 6. Example of comparison between the Redlich–Kister fit, Eq. (4) (full line) and the cell model theory, Eq. (7) (dashed line) of DMSO (1) + 1,2-diethoxyethane (2) at 308.15 K.

4. Results and conclusions

Figs. 1 and 2 show the H_m^E data for cyclic ethers and linear ethers, respectively. Linear diethers, 1,2-dimethoxyethane and 1,2-diethoxyethane make possible a comparison with the cyclic diether dioxolane, since the three molecules have two O groups separated by a CH_2–CH_2 chain.

A second useful comparison may be between cyclic mono ethers and cyclic diethers and, finally, also a comparison between 6-atom ring and 5-atom ring cyclic ethers, with the same number of ethereal atoms, may be of interest.

In any case, a qualitative explanation can be achieved by considering the approximate expression $H_m^E \propto E_{11} + E_{22} - 2E_{12}$, where E_{ij} are the interaction energies between molecules i and j, and Table 7, reporting the E_{ij}s evaluated from experimental data by means of the cell model, Eq. (7). These energies E_{ij} imply interactions between S=O and ethereal groups of DMSO and ethers, respectively, as well as dipole–dipole and dipole–quadrupole interactions. Table 7 reports values of dipole moments, μ, among which the large value of μ for DMSO id evident.

As can be seen from Figs. 1 and 2, the H_m^Es for the mixtures of dioxane and 1,2-dimethoxyethane with DMSO are very close (maximum values about 400 J mol^{-1}), thus indicating that opening the ring of dioxane does not influence the interactions between ethereal atoms and DMSO. Instead the mixture 1,2-diethoxyethane + DMSO has values of H_m^E greatly larger (maximum value about 900 J mol^{-1}).

Table 7 shows a decrease of both E_{22} and E_{12} in passing from 1,4-dioxane to 1,2 dimethoxyethane, due to the less availability of ethereal atoms when the ring is open. Thus, H_m^E is quite the same. Instead, in the 1,2-diethoxyethane molecule, the C_2H_5 group induce a negative charge on oxygen atoms larger than the one induced by the CH_3 group and indeed, we observe very strong values of interaction energies E_{22} and E_{12}, the former quite twice the E_{22}s for 1,2-dimethoxyethane.

When we compare cyclic monoethers and cyclic diethers, the larger values of E_{22} and E_{12} for the latter compounds is clearly a consequence of doubling the number of oxygen atoms, but the DMSO molecule, with a very active S=O group, will stress the increase of E_{12} for the cyclic diethers, which show H_m^E very smaller than the corresponding values for cyclic monoethers.

As to the effect of the increase of the ring atoms, with the same number of ethereal atoms, we remark that 1,4-dioxane and 1,3-dioxolane show the same values of E_{22} (obtained from the experimental H_v [12]) and of E_{12} (see Table 7) which is close to the arithmetic mean $(E_{11} + E_{22})/2$. In this case, the less number of CH_2 in the 5-atom ring is balanced by the stronger positive charge induced to CH_2 group having the two O atoms adjacent to it.

In the second case, oxolane and oxane, the oxygen atom in the 5-atom ring of oxane has a smaller negative charge and, thus, smaller values of both E_{22} and E_{12} are observed, see Table 7. The term E_{22}–$2E_{12}$ is larger for oxolane. The correlation between

Table 7
Values of interaction energies, E_{ij} (kJ mol^{-1}), Eq. (7), dipole moments, μ, and permittivities, ε, for DMSO + cyclic and linear ethers

	E_{11}	E_{22}	E_{12}	$E_{11} + E_{22} - 2E_{12}$	μ/D	ε
1,4-Dioxane	52.9	35.6	44.1	0.3	0.45 [12]	2.209 [12]
1,3-Dioxolane	52.9	35.6	44.1	0.3	1.47 [12]	7.13 [37]
Oxane	52.9	34.9	43.5	0.8	1.63 [12]	5.61 [12]
Oxolane	52.9	32.0	42.1	0.7	1.75 [12]	7.58 [12]
1,2-Dimethoxyethane	52.9	28.9	40.7	0.4	1.71 [12]	7.20 [12]
1,2-Diethoxyethane	52.9	43.2	47.7	0.7	0.7 [12]	5.10 [12]
DMSO	52.9				4.06 [12]	46.45 [12]

dipole moments, μ, and values of H_m^E is not straightforward. For example, the larger value of μ for 1,2-dimethoxyethane, when compared with that of 1,2-diethoxyethane, is consistent with larger value of E_{12} and then lower values of H_m^E. However, in the case of cyclic ethers, ring opening, doubling of oxygen atoms and steric effects cannot be simply connected with dipole moments: for example in 1,4-dioxane molecule, the two oxygen atoms in a symmetric structure lead to a low value of μ. From Table 5, we deduce that the C_ps data, as a function of DMSO molar fraction, display the same trend given by H_m^E values, that is an increase of C_p in the order 1,3-dioxolane, 1,4-dioxane, oxane, oxolane. Also the linear ethers show the same trend in C_p and H_m^E. However, values of C_p for the latter ethers are greatly larger than the ones for the series of cyclic ethers.

We may conclude that interactions energies E_{ij} are able to ensure an at least approximated interpretation of the H_m^E data, whereas dipole moments, surely entering in the overall value of $E_{ij,}$ have not a simple correlation with E_{ij}. Finally, though resulting C_ps match with H_m^Es, their interpretation in term of molecular interaction was impossible.

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