J. Chem. Eng. Data **1993**, *38*, 221–223

Excess Molar Enthalpies for the Binary Systems 1-Methylnaphthalene + Linear and Cyclic Ethers

Romolo Francesconi*

Dipartimento di Chimica "G. Ciamician", Universitá degli Studi, via Selmi 2, I-40126 Bologna, Italy

Fabio Comelli

Centro di Studio per la Fisica delle Macromolecole del CNR, via Selmi 2, I-40126 Bologna, Italy

---

The excess molar enthalpies H^E for the binary liquid mixtures of 1-methylnaphthalene + six ethers (oxolane, oxane, 1,3-dioxolane, 1,4-dioxane, dimethoxymethane, and 1,2-dimethoxyethane) were determined at atmospheric pressure and at 298.15 K. The experimental data have been correlated by means of the Redlich–Kister equation, and results are interpreted in terms of molecular interactions. The influence of the structural parameters on H^E has been assessed.

Introduction

As a large part of continuing studies of excess molar enthalpies for the binary systems containing cyclic ethers, excess enthalpies of mixtures formed by cyclic ethers with halothane and 1-chloronaphthalene have been previously reported (*1*, *2*). In this paper, excess molar enthalpies at 298.15 K for the binary systems 1-methylnaphthalene + oxolane, oxane, 1,3-dioxolane, 1,4-dioxane, and two linear ethers, namely, dimethoxymethane and 1,2-dimethoxyethane, are presented with the aim of correlating the experimental data by the Redlich–Kister equation and studying the influence of the aromatic and linear structure on the calorimetric behavior. A comparison with the H^E's of the 1-chloronaphthalene + cyclic ethers (*2*) will be made in the Discussion of the Results and Conclusions of this paper.

Experimental Section

Purity of Components. Cyclic ethers considered in this paper are the same as those used in refs 1 and 2, and their purifications are there described. 1-Methylnaphthalene and dimethoxymethane, two Aldrich products, analytical grade 98% and 99%, respectively, have been purified by two fractional distillations through a 120 theoretical plate column. 1,2-Dimethoxyethane, an Aldrich product, analytical grade 99.9%, was used without further purification. All products were dried by using Union Carbide Type 4A molecular sieves by Fluka and kept in dark bottles after this treatment. 1-Methylnaphthalene is component 1.

Density Measurements of Pure Components. Density values of pure components, necessary to evaluate flow rates and hence mole fractions in the calorimetric measurements, have been measured at different temperatures by means of a two-capillary glass pycnometer (volume 31.41 mL at 297.45 K) calibrated with distilled mercury and thermostated in a water bath at 298.15 ± 0.02 K, as described in ref 3.

The experimental data of densities ρ_i of pure components, determined at atmospheric pressure, are fitted as a function of temperature T, by means of the following equation:

$$\rho_i = A + B(T/\mathrm{K} - 273.15) \qquad (1)$$

Coefficients A and B were obtained by the least-squares method.

Table I collects the experimental density data with their coefficients A and B, correlation coefficients $|R|$, and standard deviation $\sigma(\rho)$. Literature values are also reported in this table, in parentheses, and are in good agreement, with those of this paper. In this table, only density values of 1-methylnaphthalene, dimethoxymethane, and 1,2-dimethoxyethane are reported; those of cyclic ethers have been obtained in previous papers (*2–4*).

Table I. Densities of 1-Methylnaphthalene, Dimethoxymethane, or 1,2-Dimethoxyethane as a Function of Temperature *T*, Coefficients *A* and *B*, Equation 1, Standard Deviation $\sigma(\rho)$, and Correlation Coefficient $|R|$[a]

	1-methylnaphthalene		dimethoxymethane		1,2-dimethoxyethane	
	T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})	T/K	ρ/(kg m^{-3})
	291.70	1021.3	288.15	866.4 (866.5)	291.15	871.1
	293.15	1020.2 (1020.3)	289.8	864.3	293.15	868.9 (869.1)
	294.60	1019.2	290.85	862.9	295.00	866.7
	295.95	1018.3	292.55	860.8	296.65	865.1
	297.40	1017.2	294.05	858.9	298.15	863.6 (863.7)
	298.15	1016.7 (1016.8)	296.45	855.8	299.70	861.8
	299.50	1015.7	298.15	853.8	301.05	860.3
	300.85	1014.7	300.25	851.0	302.65	858.6
	302.20	1013.8	302.45	848.4	303.15	858.0
	303.55	1012.9	303.15	847.4 (847.5)	304.15	857.0
A	1034.4		885.3		890.6	
B	−0.7104		−1.2629		−1.0847	
$\sigma(\rho)$	0.04		0.07		0.05	
$\|R\|$	0.999 91					

[a] Literature values in parentheses (*8*).

0021-9568/93/1738-0221$04.00/0

Table II. Excess Molar Enthalpies H^E of 1-Methylnaphthalene + Linear and Cyclic Ethers at 298.15 K as a Function of the Mole Fraction x_1 of 1-Methylnaphthalene

x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})	x_1	H^E/(J mol^{-1})
	1-Methylnaphthalene + Dimethoxymethane						1-Methylnaphthalene + Oxane				
0.0504	32.5	0.2982	106.0	0.7927	68.7	0.0553	−82.4	0.3188	−347.0	0.8082	−239.2
0.0738	45.7	0.3892	115.2	0.8360	55.2	0.0807	−117.8	0.4125	−387.8	0.8489	−196.6
0.0960	55.2	0.4887	115.2	0.8843	39.4	0.1047	−149.4	0.5130	−395.8	0.8939	−144.5
0.1374	70.4	0.5604	112.2	0.9386	20.5	0.1493	−204.3	0.5841	−382.5	0.9440	−80.0
0.1752	83.4	0.6566	99.7			0.1896	−247.0	0.6781	−341.1		
0.2416	99.7	0.7182	87.6			0.2598	−306.9	0.7374	−298.0		
	1-Methylnaphthalene + 1,2-Dimethoxyethane						1-Methylnaphthalene + 1,3-Dioxolane				
0.0301	−52.7	0.3322	−421.1	0.8174	−299.6	0.0400	14.1	0.2501	9.7	0.7501	−101.8
0.0585	−98.0	0.4273	−475.8	0.8565	−248.3	0.0588	18.6	0.3334	−14.3	0.8001	−92.6
0.1106	−179.1	0.5282	−492.5	0.8995	−183.5	0.0769	20.7	0.4228	−43.5	0.8572	−80.5
0.1572	−250.8	0.5988	−479.4	0.9471	−109.7	0.1111	24.7	0.5001	−66.7	0.9231	−52.0
0.1992	−296.0	0.6912	−430.4			0.1429	25.0	0.6001	−89.7		
0.2717	−373.4	0.7490	−378.0			0.2001	19.3	0.6668	−99.1		
	1-Methylnaphthalene + Oxolane						1-Methylnaphthalene + 1,4-Dioxane				
0.0464	−130.1	0.2800	−576.6	0.7778	−417.5	0.0249	7.8	0.2347	18.5	0.7104	−71.9
0.0680	−189.7	0.3685	−657.0	0.8236	−331.1	0.0486	15.4	0.2902	8.2	0.7863	−71.7
0.0886	−231.9	0.4667	−689.0	0.8751	−235.8	0.0712	20.1	0.3801	−16.1	0.8307	−68.2
0.1273	−316.3	0.5385	−675.2	0.9331	−129.9	0.0927	23.8	0.4926	−44.6	0.8804	−59.5
0.1628	−391.7	0.6364	−610.1			0.1321	26.2	0.5508	−55.7	0.9364	−40.2
0.2258	−507.5	0.7000	−536.9			0.1697	25.7	0.6479	−69.5	0.9515	−34.4

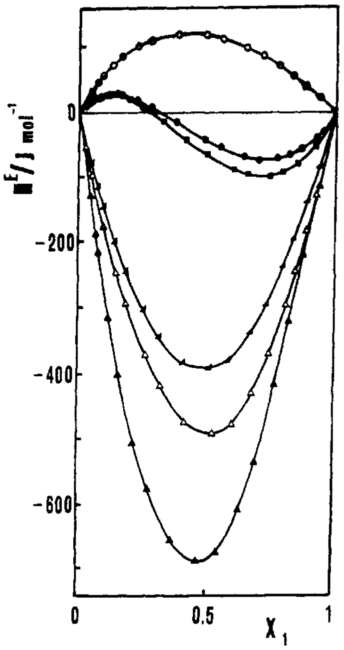

Figure 1. Excess molar enthalpies H^E for the 1-methylnaphthalene + oxolane (▲), + oxane ( ), + 1,3-dioxolane (■), + 1,4-dioxane (●), + dimethoxymethane (○) or + 1,2-dimethoxyethane (△) systems at 298.15 K. Curves calculated from eq 2 with coefficients from Table III.

Calorimetric Measurements. Molar excess enthalpies H^E were determined at 298.15 ± 0.005 K with a flow microcalorimeter, model 2107, LKB Produkter AB (Bromma, Sweden), as described in ref 5 while details of electrical calibration and analytical measurements are given in ref 3. The performance of the calorimeter was checked by measuring H^E of the well-investigated test mixture cyclohexane–hexane (*6*) over the whole composition range (about 0.5% is the agreement with the literature in the central range of composition).

The experimental molar excess enthalpies H^E of the six mixtures are listed in Table II and graphically represented in Figure 1. The dependence of H^E on composition may be expressed by the Redlich–Kister equation of the form

Table III. Coefficients a_k and Standard Deviations $\sigma(H^E)$ for 1-Methylnaphthalene (1) + Linear or Cyclic Ethers (2)

component 2	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)$
dimethoxy-methane	462.1	−70.6	68.9	−141.3		0.70
1,2-dimethoxy-ethane	−1954.6	−159.7				2.54
oxolane	−2754.3	356.9	368.6	191.5		3.90
oxane	−1586.1	50.0	44.3			1.08
1,3-dioxolane	−267.9	−566.9	124.1	−64.9	−73.9	0.81
1,4-dioxane	−184.2	−432.4	203.6	−177.2	−280.0	0.65

$$H^E/(\text{J mol}^{-1}) = x_1x_2\sum_{k=0}^{n}a_k(x_1-x_2)^k \qquad (2)$$

where a_k are the adjustable parameters and x_1 and x_2 the mole fractions of components 1 and 2, respectively. The values of the parameters obtained by the least-squares method are collected in Table III along with the standard deviation $\sigma(H^E)$, defined as described in ref 7.

Discussion of the Results and Conclusions

Figure 1 shows the curves H^E vs x_1 for the six systems of this paper. The mixtures of 1-methylnaphthalene with oxane, oxolane, and dimethoxymethane give negative H^E, and the one with 1,2-dimethoxyethane gives positive H^E whereas 1,4-dioxane and 1,3-dioxolane show an inversion of sign for H^E. The curves indicate for the monoethers more negative H^E than for the diethers. Furthermore, an increasing ring size leads to a marked difference in H^E for monoethers and to nearly the same H^E for diethers. These results may be compared with those of 1-chloronaphthalene + cyclic ethers (*2*) and attest the complexity of molecular interactions and steric effects occurring in these systems.

Glossary

a_k	parameters in eq 2
A,B	parameters in eq 1
H^E	excess molar enthalpy, J mol^{-1}
R	correlation coefficient, Table I
T	absolute temperature, K
x_i	mole fraction of component i (i = 1, 1-methylnaphthalene; i = 2, ethers)

Greek Letters

ρ_i	density of component *i*, kg m^{-3}
$\sigma(\rho)$, $\sigma(H^E)$	standard deviations, Tables I and III, respectively

Literature Cited

(1) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1990**, *36*, 288.
(2) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1991**, *36*, 382.
(3) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1986**, *31*, 250.
(4) Francesconi, R.; Comelli, F. *J. Chem. Eng. Data* **1988**, *33*, 80.
(5) Monk, P.; Wadsö, I. *Acta Chem. Scand.* **1968**, *22*, 1842.
(6) Benson, G. C. *Int. DATA Ser., Sel. Data Mixtures, Ser. A.* **1974**, 19.
(7) Comelli, F.; Francesconi, R. *J. Chem. Eng. Data* **1991**, *36*, 32.
(8) Riddik, A.; Bunger, W. B.; Sakano, T. K. *Organic Solvent*, 4th ed.; Wiley-Interscience: New York, 1986; Vol. II.

Received for review May 8, 1992. Revised October 6, 1992. Accepted November 5, 1992.