$$V^E/[x(1-x)] = \sum A_i(2x-1)^i \qquad (1)$$

where x is the mole fraction of *o*-xylene for all of the systems. The solid lines of Figure 1 are those calculated from the smoothing equation. The coefficients of eq 1, their respective standard deviations, and the standard deviations for the excess volumes are given in Table II.

The results for these systems can be compared with those obtained for benzene + *n*-alkanes (*5*) and *p*-xylene + *n*-alkanes (*4*). Both *o*-xylene and *p*-xylene + *n*-alkanes systems show a very similar behavior. Excess volumes are slightly smaller for those systems were *p*-xylene is one of the compounds. The most remarkable difference is that the excess volume for *o*-xylene + *n*-octane changes sign (from positive to negative) as the mole fraction of *o*-xylene increases, while *p*-xylene + *n*-octane always shows a positive excess volume.

The excess volumes for benzene + *n*-alkanes are always positive and are larger than those found for xylene + *n*-alkanes. These systems show a more ideal behavior which is probably due to the methyl groups in the aromatic ring.

Literature Cited

(1) Timmermans, J. "Physico-Chemical Constants of Binary Systems"; Interscience: New York, 1959; Vol. 1.
(2) Battino R. *Chem. Rev.* **1971**, *71*, 5.
(3) Handa, Y. P.; Benson G. C. *Fluid Phase Equilib.* **1979**, *3*, 185.
(4) Cáceres Alonso, M.; Nuñez Delgado, J. *J. Chem. Thermodyn.* **1981**, *13*, 1133.
(5) Diaz Peña, M.; Nuñez Delgado, J. *An. Quim.* **1974**, *70*, 678.
(6) Diaz Peña, M.; Nuñez Delgado, J. *An. Quim.* **1977**, *73*, 24.
(7) Diaz Peña, M.; Nuñez Delgado, J. *J. Chem. Thermodyn.* **1975**, *7*, 201.
(8) Dreisbach, R. R. "Advances in Chemistry Series"; American Chemical Society: Washington, DC, 1955; No. 15, p 14.

Received for review October 26, 1981. Accepted March 29, 1982.

Excess Enthalpies of Binary Systems of Cyclic Ether + Cyclohexene

Jean-Pierre E. Grolier,[*†] **Americo Inglese,**[‡] **and Emmerich Wilhelm**[*§]

Centre de Thermodynamique et de Microcalorimétrie du C.N.R.S., F-13003 Marseille, France

The molar excess enthalpy H^E has been measured as a function of mole fraction x at atmospheric pressure and 298.15 K for the binary liquid systems cyclohexene (c-C_6H_{10}) + oxolane (tetrahydrofuran, C_4H_8O), + oxane (tetrahydropyran, $C_5H_{10}O$), + 1,3-dioxolane (1,3-$C_3H_6O_2$), + 1,4-dioxane (1,4-$C_4H_8O_2$), and + cyclohexane (c-C_6H_{12}), by using a flow calorimeter of the Picker design. The mixtures with cyclic diethers exhibit relatively large positive excess enthalpies: for 1,3-$C_3H_6O_2$ + c-C_6H_{10}, $H^E(x = 0.5) = 1155.5$ J mol^{-1}; and for 1,4-$C_4H_8O_2$ + c-C_6H_{10}, $H^E(x = 0.5) = 909.7$ J mol^{-1}. The excess enthalpy for C_4H_8O + c-C_6H_{10} is considerably smaller, i.e., $H^E(x = 0.5) = 285.5$ J mol^{-1}, and $C_5H_{10}O$ + c-C_6H_{10} shows S-shaped dependence of H^E on x, with the very small negative section being located at small mole fractions of the cyclic ether ($x < 0.0899$). For c-C_6H_{12} + c-C_6H_{10} the excess enthalpy is rather symmetric, with $H^E(x = 0.5) = 97.3$ J mol^{-1}.

Introduction

Excess enthalpies of binary liquid mixtures composed of either five- or six-membered cyclic ethers and various second components (ranging from *n*-alkanes to alkanoic acids) were reported in ref *1–5*. As a sequel, we present here measurements of the molar excess enthalpy H^E at 298.15 K of the binary systems cyclohexene (c-C_6H_{10}) + oxolane (tetrahydrofuran, C_4H_8O), + oxane (tetrahydropyran, $C_5H_{10}O$), + 1,3-dioxolane (1,3-$C_3H_6O_2$), + 1,4-dioxane (1,4-$C_4H_8O_2$), and + cyclohexane (c-C_6H_{12}). These measurements will be used later to assess, in terms of group-contribution theory (*6*), the influence of various structural parameters (ring size, proximity of oxygen in diethers, n–π interaction, etc.) on the thermodynamic behavior of such mixtures.

Table I. Densities (ρ) of Pure Component Liquids at 298.15 K

	ρ/(kg m^{-3})	
compd	exptl	lit.
cyclohexene	806.0	806.09 (*9*), 806.3,[a] 805.66 (*11*), 805.9 (*12*), 805.70 (*13*)
cyclohexane	773.9	773.89 (*14*)
oxane	879.1	879.22[b]
oxolane	881.9	881.97 (*16*)
1,4-dioxane	1028.2	1028.21 (*17*), 1027.97 (*18*)
1,3-dioxolane	1059.1	1053.8[c]

[a] Interpolated value from ref *10*. [b] Interpolated value from ref *15*. [c] Extrapolated value from ref *19*.

Table II. Comparison of Experimental Molar Excess Enthalpies H^E at 298.15 K of the Test System Benzene (x) + Cyclohexane ($1-x$) with the Results of Marsh (*20*)

	H^E/(J mol^{-1})		
x	exptl	Marsh (*20*)	δ[a]
0.2118	519.3	523.8	−0.9
0.3064	667.2	669.7	−0.4
0.4015	756.2	761.8	−0.7
0.4920	793.7	798.5	−0.6
0.5768	779.9	787.2	−0.9
0.6581	729.3	733.8	−0.6
0.7400	638.3	636.2	+0.3
0.9334	214.6	214.7	0.0

[a] Percentage deviation $\delta = 100(H^E_{\text{exptl}} - H^E_{\text{Marsh}})/H^E_{\text{Marsh}}$.

Experimental Section

Materials. Source and treatment of the cycloethers have been given previously (*1*). Cyclohexene (from Fluka, puriss.,

---

[†] Present address: Laboratoire de Thermodynamique et Cinétique Chimique, Université de Clermont II, F-63170 Aubière, France.

[‡] Present address: Istituto di Chimica Fisica, Università di Bari, Bari, Italy.

[§] On leave from Institut für Physikalische Chemie, Universität Wien, Währingerstrasse 42, A-1090 Wien, Austria.

0021-9568/82/1727-0333$01.25/0

Table III. Molar Excess Enthalpy H^E for Cyclic Ether + Cyclohexene and for Cyclohexane + Cyclohexene at 298.15 K[a]

x	H^E/(J mol^{-1})	x	H^E/(J mol^{-1})
	x c-C_6H_{12} + $(1-x)$ c-C_6H_{10}		
0.0451	14.4	0.5431	97.3
0.1442	45.0	0.6297	91.7
0.1883	58.0	0.7265	80.0
0.2738	75.9	0.8238	60.0
0.3604	88.7	0.9178	31.5
0.4512	95.2		
	x $C_5H_{10}O$ + $(1-x)$ c-C_6H_{10}		
0.0495	−11.5	0.5825	148.1
0.0794	−1.5	0.6697	136.6
0.2270	69.8	0.7540	114.3
0.3195	109.4	0.8704	66.9
0.4965	148.5	0.9597	18.4
	x C_4H_8O + $(1-x)$ c-C_6H_{10}		
0.0591	14.6	0.6126	279.2
0.1831	132.5	0.6935	251.2
0.2358	181.4	0.7794	207.0
0.3341	242.2	0.8615	144.6
0.4285	276.8	0.9369	69.4
0.5224	286.0		
	x 1,4-$C_4H_8O_2$ + $(1-x)$ c-C_6H_{10}		
0.0899	362.7	0.6151	850.7
0.2518	755.1	0.6990	762.7
0.3498	860.4	0.7784	629.8
0.5304	900.3	0.8850	368.0
	x 1,3-$C_3H_6O_2$ + $(1-x)$ c-C_6H_{10}		
0.1080	520.4	0.7400	898.3
0.2920	1008.3	0.8115	726.3
0.3973	1133.9	0.9042	414.3
0.5806	1112.7	0.9709	133.7
0.6620	1028.4		

[a] Mole fraction of cyclic ether or cyclohexane is x.

purity > 99.5 mol %) was shaken with mercury and distilled in its presence (*7*). Cyclohexane was from Fluka (puriss.), with stated purity > 99.5 mol%. It was used without further purification. Before actual measurement, all liquids were dried with molecular sieve (Union Carbide Type 4A, beads, from Fluka). Densities of the pure liquids were determined with a vibrating-tube densimeter (*8*) and are compared with reliable literature values (*9–19*) in Table I.

Calorimetry**.** Molar excess enthalpies were determined as previously (*1–5*) with a flow calorimeter of the Picker design equipped with separators and operated in the discontinuous mode. The liquids were partially degassed before being transferred to the separators. The performance of the calorimeter was checked by measuring H^E of some well-investigated test mixtures, such as tetrachloromethane + benzene, and benzene + cyclohexane. Agreement with literature data (*20*) was generally within 1%, as evidenced by representative results obtained for the latter system (Table II).

Results and Discussion

Results of our measurements of H^E for the five binary systems at 298.15 K are listed in Table III and are graphically presented in Figure 1. These results were fitted by unweighted least-squares polynomial regression according to

$$H^E/(\mathrm{J\ mol^{-1}}) = x(1-x)\sum_{i=0}^{n-1} A_i(2x-1)^i \qquad (1)$$

where x denotes the mole fraction of either cyclic ether or cyclohexane. Values of the coefficients A_i and standard deviations $\sigma(H^E)$ are summarized in Table IV. With the exception of the system oxane + cyclohexene, $|\sigma(H^E)/H^E_{extr}| < 0.01$, where H^E_{extr} is the extreme value of the molar excess enthalpy with respect to mole fraction. The curves in Figure 1 were calculated from eq 1 with these coefficients.

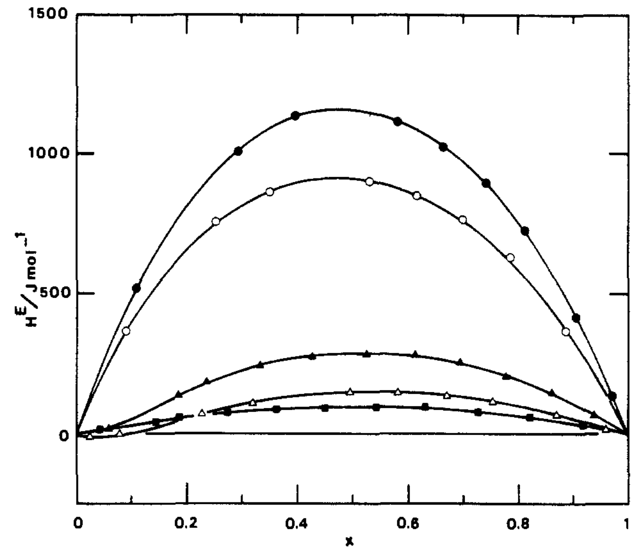

Figure 1. Molar excess enthalpies H^E of binary mixtures of cyclic ether + cyclohexene, and cyclohexane + cyclohexene, at 298.15 K, plotted against mole fraction x of cyclic ether or cyclohexane. Points denote experimental results: (■) cyclohexane + cyclohexene; (△) oxane + cyclohexene; (▲) oxolane + cyclohexane; (○) 1,4-dioxane + cyclohexene; (●) 1,3-dioxolane + cyclohexene. Curves are least-squares representations of results by eq 1 with parameters from Table IV.

Literature data for comparison could only be found for cyclohexane + cyclohexene (*12*, *21*, *22*). The results of Günzel and Bittrich (*21*), i.e., $H^E(x = 0.5) = 54.5$ J mol^{-1}, are much lower than ours, whereas the excess enthalpies presented by Letcher and Sack (*22*) have to be regarded as being too high: at $x = 0.5$ their value for H^E deviates by 18 J mol^{-1} from our $H^E = 97.3$ J mol^{-1}. Though we are unable to explain these differences, we note that densities reported earlier by Letcher and Marsicano (*23*) are in variance with literature data (*9–13*) and with the density determined by us: at 298.15 K these authors give $\rho = 815.5$ kg m^{-3}, which is larger by about 9 kg m^{-3} than any value given in Table I. On the other hand, the measurements of Wóycicki (*12*) are in reasonable accord with ours, though slightly smaller: at 298.15 K he reports H^E/(J mol^{-1}) = $x(1-x)[368.0 - 4.9(2x - 1) + 5.1(2x - 1)^2]$.

The series of systems formed by mixing oxane, oxolane, 1,4-dioxane, and 1,3-dioxolane with cyclohexene exhibits values of H^E which become progressively more positive (oxane + cyclohexene shows S-shaped dependence on x, with the very small negative section located at $x < 0.0899$). This behavior

Table IV. Coefficients A_i and Standard Deviations $\sigma(H^E)$ for Representation of Excess Enthalpies H^E at 298.15 K by Eq 1

	A_0	A_1	A_2	A_3	A_4	$\sigma(H^E)$/(J mol^{-1})
$(1-x)$ c-C_6H_{10}						
$+x$ c-C_6H_{12}	389.3	15.1	5.7	35.7		0.7
$+x$ $C_5H_{10}O$	592.3	106.6	−149.0	341.9	−476.8	1.8
$+x$ C_4H_8O	1142.0	54.4	77.8	539.8	−788.0	2.7
$+x$ 1,4-$C_4H_8O_2$	3638.9	−284.6	650.7	−312.3		5.2
$+x$ 1,3-$C_3H_6O_2$	4622.0	−334.3	781.9			6.0

parallels the increase of the relative oxygen content of the ether molecules. We note that, in general, the excess enthalpy of cyclic ether + cyclohexene is distinctly smaller than that of the corresponding system cyclic ether + cyclohexane (*2*, *24*, *25*): at $x = 0.5$, these increments vary between ca. −400 and −700 J mol^{-1}.

Literature Cited

(1) Inglese, A.; Wilhelm, E.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.* **1980**, *12*, 217.
(2) Inglese, A.; Wilhelm, E.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.* **1980**, *12*, 1047.
(3) Inglese, A.; Wilhelm, E.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.* **1981**, *13*, 229.
(4) Wilhelm, E.; Inglese, A.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.* **1982**, *14*, 33.
(5) Wilhelm, E.; Inglese, A.; Grolier, J.-P. E.; Kehiaian, H. V. *J. Chem. Thermodyn.*, in press.
(6) Kehiaian, H. V.; Grolier, J.-P. E.; Benson, G. C. *J. Chim. Phys. Phys.-Chim. Biol.* **1978**, *75*, 1031.
(7) Andrews, A.; Morcom, K. W.; Duncan, W. A.; Swinton, F. L.; Pollock, J. M. *J. Chem. Thermodyn.* **1970**, *2*, 95.
(8) Wilhelm, E.; Grolier, J.-P. E.; Karbalai Ghassemi, M. H. *Monatsh. Chem.* **1978**, *109*, 369.
(9) Forziati, A. F.; Camin, D. I.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* (*U.S.*) **1950**, *45*, 406.
(10) Timmermans, J. "Physico-Chemical Constants of Pure Organic Compounds"; Elsevier: New York, 1950; Vol. 1.
(11) Harris, K. R.; Dunlop, P. J. *J. Chem. Thermodyn.* **1970**, *2*, 813.
(12) Wőycicky, W. *J. Chem. Thermodyn.* **1980**, *12*, 165.
(13) Letcher, T. M. *J. Chem. Thermodyn.* **1977**, *9*, 661.
(14) Riddick, J. A.; Bunger, W. B. "Techniques of Chemistry", 3rd ed.; Weissberger, A., Ed.; Wiley-Interscience: New York, 1970; Vol. 2.
(15) Landolt-Börnstein, Zahlenwerte und Funktionen, 2 Band, 1 Teil, 6 Auflage; Springer: West Berlin, 1971.
(16) Kiyohara, O.; D'Arcy, P. J.; Benson, G. C. *Can. J. Chem.* **1979**, *57*, 1006.
(17) Anand, S. C.; Grolier, J.-P. E.; Kiyohara, O.; Benson, G. C. *Can. J. Chem.* **1973**, *51*, 4140.
(18) Hammond, B. R.; Stokes, R. H. *Trans. Faraday Soc.* **1955**, *51*, 1641.
(19) Beilstein, "Handbuch der Organischen Chemie", 19 Band, 1 Ergänzungswerk, 4 Auflage; Springer: Berlin, 1934, p 609.
(20) Stokes, R. H.; Marsh, K. N.; Tomlins, R. P. *J. Chem. Thermodyn.* **1969**, *1*, 211. Marsh, K. N. *Int. Data Ser., Sel. Data Mixtures, Ser. A* **1973**, 2, 3.
(21) Günzel, K.; Bittrich, H. J. *Z. Phys. Chem.* (*Leipzig*) **1977**, *258*, 1073.
(22) Letcher, T. M.; Sack, J. *J. S. Afr. Chem. Inst.* **1975**, *28*, 316.
(23) Letcher, T. M.; Marsicano, F. *J. Chem. Thermodyn.* **1974**, *6*, 509.
(24) Andrews, A. W.; Morcom, K. W. *J. Chem. Thermodyn.* **1971**, *3*, 519.
(25) Cabani, S.; Ceccanti, N. *J. Chem. Thermodyn.* **1973**, *5*, 9.

Received for review November 3, 1981. Accepted April 13, 1982. Financial support within the frame of the Austrian–French treaty for scientific and technical cooperation is gratefully acknowledged by E.W.

Heat Capacities of Aqueous Solutions of $NiCl_2$ and $NiCl_2 \cdot 2NaCl$ from 0.12 to 3.0 mol kg^{-1} and 321 to 572 K at a Pressure of 17.7 MPa

David Smith-Magowan,† Robert H. Wood,* and David M. Tillett

Department of Chemistry, University of Delaware, Newark, Delaware 19711

The heat capacity of aqueous $NiCl_2$ and aqueous $NiCl_2 \cdot 2NaCl$ has been measured at temperatures from 321 to 572 K at a pressure of 17.7 MPa by using a new flow calorimeter. The results for $NiCl_2$ do not show the large negative apparent molar heat capacities characteristic of strong electrolytes at high temperatures and low molalities. This indicates that $NiCl_2$ at 572 K is mainly un-ionized. The apparent molar heat capacity of $NiCl_2 \cdot 2NaCl$ could be predicted with reasonable accuracy, by using Young's rule and the apparent molar heat capacities of pure $NiCl_2$ and NaCl. This success indicates that Young's rule can be used to calculate the heat capacity of $NiCl_2$ in any mixture with NaCl. Equations are derived which allow the present results together with room-temperature data to be used to calculate enthalpies and free energies of aqueous $NiCl_2$ at high temperatures. The integrals of the apparent molar and partial molar heat capacities needed in these equations are tabulated.

Introduction

This investigation of the heat capacities of $NiCl_2$ solutions at high temperatures, complementing our previous study of NaCl heat capacities (*1*), was undertaken for two reasons. First, we wanted to contrast the relatively simple behavior of NaCl solutions at high temperatures with a system more likely to exhibit complex thermodynamic behavior. Ludeman and Franck (*2*), in their spectroscopic investigation of aqueous $NiCl_2$ solutions, for example, found dramatic changes in the absorption spectrum near 200 °C. Second, we wanted to demonstrate that our calorimeter could be used to investigate industrial problems associated with high-temperature aqueous systems. Extensive use of nickel-containing alloys in nuclear power plants has resulted in several corrosion problems, yet very little is known about aqueous nickel species at high temperatures. These problems include stress-corrosion cracking which may result from $NiCl_2$ concentrations in crevices and sludge piles (*3*). Postlewait's investigation implicates chloride in the corrosion of nickel at temperatures up to 274 °C (*4*). Migration of radioactivity throughout steam-generating circuits is a serious problem which is dependent on nickel speciation at high temperatures (*5–7*).

Table I. Densities of the Solutions at 1 atm and 25 °C[a]

m/(mol kg^{-1})	d/(g cm^{-3})		m/(mol kg^{-1})	d/(g cm^{-3})	
	$NiCl_2$	$NiCl_2 \cdot$ 2NaCl		$NiCl_2$	$NiCl_2 \cdot$ 2NaCl
0.1202	0.985 45	0.976 11	0.9940	0.885 42	0.899 32
0.5286	0.937 78	0.949 44	2.995	0.681 25	0.821 32

[a] The density of water used was 0.997 04 g cm^{-3}.

The measurements reported here allow the calculation of the apparent molar and partial molar heat capacities, the change in the enthalpy and the partial molar enthalpy, and the change in the chemical potential as functions of molality and temperature for aqueous $NiCl_2$ and $NiCl_2 \cdot 2NaCl$. The results allow the calculation of equilibria involving aqueous $NiCl_2$ alone or in the presence of NaCl at molalities from 0.12 to 3.0 mol kg^{-1} and temperatures from 298 to 575 K.

Experimental Section

Solutions. A stock solution of approximately 3.0 mol kg^{-1} $NiCl_2$ was prepared from Fisher certified $NiCl_2 \cdot 2H_2O$, the actual

---

† Current address: Westinghouse Research and Development Center, Pittsburgh, PA 15235.

0021-9568/82/1727-0335$01.25/0