The heat capacity data for molten $NaNO_2$ show a slight negative temperature dependence over the temperature range investigated (570-670 K). Attempts to extend the measurements to higher temperatures were unsuccessful, due to the onset of higher noise-to-signal levels, and due to sample-pan seal ruptures. For a discussion of the possible factors contributing to these difficulties, see ref *5*.

Inspection of the heat capacity data reported for $NaNO_2$ by Voskresenskaya et al. (*7*) shows that for the solid state the agreement is good with the presently reported values; however, for the liquid state there is marked disagreement. Thus, from 570 to 630 K, Voskresenskaya et al. (*7*) reported that the C_p values decrease from 42.1 to 39.2 cal mol^{-1} deg^{-1}; the results from the present measurements are, in comparison, as follows: 570 K, 28.6 cal mol^{-1} deg^{-1}; 630 K, 28.2 cal mol^{-1} deg^{-1}, respectively. During the preparation of our present communication, density and heat capacity data for the molten $NaNO_2$–KNO_3 system were reported by Iwadate et al. (*9*); as part of their investigation, measurements for molten $NaNO_2$ were also undertaken. For $NaNO_2$, C_p was found to be 27.89 cal mol^{-1} deg^{-1} and to be constant at this value ($\sim \pm 1\%$) over the temperature range 571-630 K. The accuracy of our method is estimated to be $\sim \pm 2.0\%$ in heat capacity measurements; i.e., the results are in accord with ref *9* within the limits of accuracy of the measurement technique.

Acknowledgment

We acknowledge with pleasure the continued interest and helpful comments of Dr. Derek J. Rogers throughout the course of this work.

Registry No. KNO_3, 7757-79-1; $NaNO_2$, 7632-00-0; $NaNO_3$, 7631-99-4.

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Received for review September 23, 1982. Accepted December 27, 1982. The DSC facility in this laboratory was made possible in large part through support received from the U.S. Department of Energy, Division of Materials Research.

Excess Enthalpies of Cycloheptane + *n*-Alkane and Cyclooctane + *n*-Alkane

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Molar excess enthalpies H^E have been measured as a function of composition at 298.15 K and atmospheric pressure for each of the binary liquid mixtures cycloheptane ($c\text{-}C_7H_{14}$) + *n*-heptane, + *n*-nonane, + *n*-tetradecane, and cyclooctane ($c\text{-}C_8H_{16}$) + *n*-heptane, + *n*-nonane, and + *n*-tetradecane with a flow calorimeter of the Picker design, equipped with separators. In both series H^E increases with increasing chain length *n* of the *n*-alkane, with the increments per CH_2 group being smaller for the cyclooctane series than for the cycloheptane series. At equimolar composition, $H^E(x = 0.5)/(J\ mol^{-1})$ of $c\text{-}C_7H_{14}$ + $n\text{-}C_nH_{2n+2}$ is 234.2 for $n = 7$, 267.0 for $n = 9$, and 357.6 for $n = 14$, respectively, and that of $c\text{-}C_8H_{16}$ + $n\text{-}C_nH_{2n+2}$ is 226.6 for $n = 7$, 249.3 for $n = 9$, and 322.8 for $n = 14$.

Introduction

In a series of articles (*1-6*), we recently reported molar excess enthalpies H^E of binary liquid mixtures composed of either a five- or a six-membered cyclic ether and various second components, ranging from *n*-alkanes to *n*-alkanoic acids.

In addition, molar excess volumes were determined, as a function of temperature, for several mixtures of cyclic ether + *n*-alkane (*7*). In order to obtain more information as to the influence of (a) ring size and (b) chain length of the *n*-alkane, we measured calorimetrically H^E for the six binary mixtures cycloheptane ($c\text{-}C_7H_{14}$) + *n*-heptane, + *n*-nonane, + *n*-tetradecane, and cyclooctane ($c\text{-}C_8H_{16}$) + *n*-heptane, + *n*-nonane, and + *n*-tetradecane at 298.15 K and atmospheric pressure, thus complementing literature data on cyclopentane + *n*-alkane (*8*) and cyclohexane + *n*-alkane (*9*). These measurements will be used later for a comprehensive discussion, in terms of group-contribution theory (*10*), of the thermodynamic behavior of mixtures containing cyclic ethers.

Table I. Experimental Densities ρ of Pure Liquids at 298.15 K and Comparison with Selected Literature Data

	$\rho/(kg\ m^{-3})$	
compd	exptl	lit.
cycloheptane	806.9	806.56 (*13*)
cyclooctane	832.1	832.02 (*13*)
n-heptane	679.3	679.51 (*14*)
n-nonane	713.9	713.81 (*14*)
n-tetradecane	759.3	759.3 (*14*)

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Table II. Molar Excess Enthalpy H^E of Cycloalkane + *n*-Alkane at 298.15 K[a]

x	H^E/(J mol^{-1})	x	H^E/(J mol^{-1})
	x c-C_7H_{14} + $(1-x)$ *n*-C_7H_{16}		
0.0502	34.0	0.5606	240.2
0.0953	62.7	0.6425	239.7
0.1577	101.8	0.7282	222.3
0.1930	123.0	0.8107	187.0
0.2909	171.8	0.8579	158.5
0.3829	207.0	0.9359	88.0
0.4742	229.7		
	x c-C_7H_{14} + $(1-x)$ *n*-C_9H_{20}		
0.0605	44.8	0.6085	274.6
0.1857	134.0	0.6865	266.9
0.3333	216.7	0.7655	242.4
0.4305	252.3	0.8392	200.4
0.5235	270.5	0.9467	91.8
	x c-C_7H_{14} + $(1-x)$ *n*-$C_{14}H_{30}$		
0.0857	79.2	0.6933	354.8
0.2491	239.3	0.7610	334.6
0.4210	336.3	0.8260	294.0
0.5237	361.7	0.8836	235.6
0.6151	365.8	0.9628	103.6
	x c-C_8H_{16} + $(1-x)$ *n*-C_7H_{16}		
0.0455	31.0	0.5351	230.3
0.0868	57.7	0.6185	232.4
0.1445	93.1	0.7074	218.2
0.1775	113.6	0.7944	187.6
0.2702	159.8	0.8449	161.7
0.3589	195.3	0.9294	94.3
0.4486	218.5		
	x c-C_8H_{16} + $(1-x)$ *n*-C_9H_{20}		
0.0549	40.0	0.5838	254.1
0.1707	120.4	0.6639	249.1
0.3109	197.1	0.7465	228.7
0.4055	231.1	0.8248	191.8
0.4978	249.2	0.9413	90.4
	x c-C_8H_{16} + $(1-x)$ *n*-$C_{14}H_{30}$		
0.0779	77.1	0.6710	321.9
0.2304	212.4	0.7418	305.0
0.3961	300.1	0.8107	272.8
0.4980	324.3	0.8726	225.6
0.5904	329.5	0.9589	107.5

[a] Mole fraction of cycloalkane is x.

Experimental Section

Materials. Cycloheptane (puriss. quality) was from Fluka and cyclooctane (gold label quality) was from Aldrich, both with purity $\geq$ 99 mol %; the *n*-alkanes were from Fluka (puriss. quality) with stated purities of $\geq$99.5 and >99 mol %, respectively. They were used without further purification. Prior to 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 (*11*, *12*) and are summarized in Table I. Agreement with reliable literature values is satisfactory for all substances.

Calorimetry. Molar excess enthalpies were determined as described previously (*6*) with a flow microcalorimeter of the Picker design, equipped with separators and operated in the discontinuous mode. The liquids were partially degassed before being transferred to the separators.

Results and Discussion

Results of our measurements of H^E at 298.15 K are given in Table II. For each binary mixture, the excess enthalpies were fitted with a Redlich-Kister-type smoothing function

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

by the method of (unweighted) least squares, where x denotes the mole fraction of cycloalkane. Values of the coefficients A_i and standard deviations $\sigma(H^E)$ are summarized in Table III. No literature data could be found for comparison.

Table III. Coefficients A_i and Standard Deviations $\sigma(H^E)$ for Representation of Molar Excess Enthalpies H^E of Cycloalkane + *n*-Alkane at 298.15 K by Eq 1[a]

	A_0	A_1	A_2	A_3	$\sigma(H^E)$/ (J mol^{-1})
x c-C_7H_{14}					
+ $(1-x)$ *n*-C_7H_{16}	936.8	292.1	181.3	167.3	0.9
+ $(1-x)$ *n*-C_9H_{20}	1067.8	318.4	249.1	310.3	1.3
+ $(1-x)$ *n*-$C_{14}H_{30}$	1430.3	328.2	446.9	799.8	2.4
x c-C_8H_{16}					
+ $(1-x)$ *n*-C_7H_{16}	906.5	243.5	197.5	209.8	1.4
+ $(1-x)$ *n*-C_9H_{20}	997.2	243.4	234.9	302.0	1.1
+ $(1-x)$ *n*-$C_{14}H_{30}$	1291.4	218.0	514.6	731.4	4.6

[a] Mole fraction of cycloalkane is x.

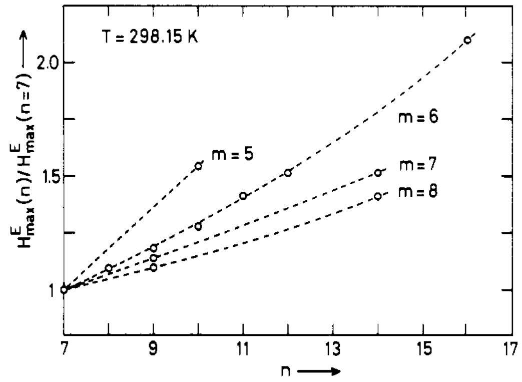

Figure 1. Plot of $H^E_{max}(n)/H^E_{max}(n = 7)$ against chain length n of the n-alkane for the series cycloalkane (c-C_mH_{2m}) + n-alkane (n-C_nH_{2n+2}). The circles represent interpolated experimental results at 298.15 K.

For the investigated range of *n*-alkanes, we observe in all series an almost linear increase of H^E with increasing n (see also ref *1* and *15*–*18*). The average increment per CH_2 group at 298.15 K, evaluated at $x = 0.5$, is about 17.7 J mol^{-1} for the cycloheptane series and about 13.9 J mol^{-1} for the cyclooctane series. The relative variation of H^E with chain length n of the *n*-alkane n-C_nH_{2n+2} is shown for each series in Figure 1, where we plotted the ratio $H^E_{max}(n)/H^E_{max}(n = 7)$ against n with the ring size m of c-C_mH_{2m} as parameter; H^E_{max} denotes the maximum value of the molar excess enthalpy with respect to mole fraction. For the sake of comparison we also included results from the literature on the series with c-C_5H_{10} (*8*) and c-C_6H_{12} (*9*).

Registry No. Cycloheptane, 291-64-5; cyclooctane, 292-64-8; *n*-heptane, 142-82-5; *n*-nonane, 111-84-2; *n*-tetradecane, 629-59-4.

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Received for review October 27, 1982. Accepted November 18, 1982. Financial support within the frame of the Austrian-French treaty for scientific and technical cooperation is gratefully acknowledged by E.W.

Osmotic and Activity Coefficients of Lithium and Tetramethylguanidinium Sulfamates at 298.15 K

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Osmotic and activity coefficient data are reported for the lithium and tetramethylguanidinium salts of sulfamic acid. These coefficients are compared with those of the previously reported sodium and potassium salts and with the corresponding salts of methanesulfonic acid.

Osmotic and activity coefficient data have been previously reported (*1*) for sulfamic acid and for its sodium and potassium salts. At that time, the coefficients of the two salts were compared with the coefficients of the corresponding salts of methanesulfonic acid. Since the coefficients of the sulfamate salts were appreciably smaller, it was suggested that there might be linear association of the sulfamate anion, especially if resonance structures of the type $H_2N^+{=}SO_3^{2-}$ are at all important. Coefficients for the two salts being presently reported were measured to obtain further information to enable a better understanding of the sulfamate system.

Method

The sulfamic acid was purchased as the "certified" grade with lot analysis from Fisher Scientific Co. Solutions of this acid were carefully neutralized with solutions of C.P. grade lithium carbonate or the free base tetramethylguanidine and evaporated to dryness over H_2SO_4 in vacuum desiccators. The salts were recrystallized several times from alcohol-water mixtures, again dried over H_2SO_4, and stored under vacuum over P_4O_{10}. The molecular weights of the salts were measured by exchange of known weights of the salts on a sulfonate strong-acid ion-exchange resin and titration of the released hydrogen ion. The salts were not hydrates and the molecular weights agreed with the calculated formula weights within the reproducibility of the titration (about 0.1%).

The isopiestic equilibration of these solutions was performed in the usual manner (*2*). It was established that equilibrium was reached when the concentrations of identical samples were within 0.1% agreement with one sample losing solvent and the other gaining solvent to attain equilibrium.

Results and Discussion

The primary isopiestic equilibration data are presented in Table I. These data have an accuracy of approximately 0.1%. The osmotic and activity coefficients at rounded concentrations are reported in Table II. Osmotic coefficients were calculated from the equation (*3*)

$$\phi = R\phi_{\text{ref}}$$

and activity coefficients from the relationship

$$\ln \gamma = \ln \gamma_{\text{ref}} + \ln R + 2\int_0^{m_{\text{ref}}} (R - 1)\, d\ln (m\gamma)_{\text{ref}}^{1/2}$$

where $R = m_{\text{ref}}/m$.

Table I. Molalities of Isopiestic Solutions

	sulfamate			sulfamate	
NaCl	Li	Me$_4$Gu[a]	NaCl	Li	Me$_4$Gu[a]
0.1963	0.1928	0.1968	2.923	2.881	2.946
0.3925	0.3825	0.3946	3.393	3.376	3.441
0.5872	0.5113	0.5901	3.896	3.907	3.987
0.8875	0.8616	0.8910	4.586	4.651	4.728
1.206	1.170	1.211	5.304	5.455	5.582
1.600	1.550	1.605	5.897	6.147	6.271
1.959	1.907	1.963	5.953	6.228	6.363
2.450	2.293	2.459			

[a] Me$_4$Gu = tetramethylguanidinium.

Table II. Osmotic and Activity Coefficients of Sulfamate Salts at 298.15 K

	Li		Me$_4$Gu[a]	
m	ϕ	γ	ϕ	γ
0.1	0.944	0.796	0.930	0.775
0.2	0.943	0.764	0.922	0.730
0.3	0.943	0.747	0.918	0.703
0.4	0.944	0.736	0.915	0.685
0.5	0.946	0.729	0.916	0.674
0.6	0.949	0.725	0.918	0.664
0.7	0.953	0.722	0.921	0.658
0.8	0.957	0.720	0.924	0.653
0.9	0.961	0.720	0.928	0.650
1.0	0.966	0.720	0.932	0.648
1.2	0.975	0.723	0.939	0.645
1.4	0.985	0.728	0.947	0.644
1.6	0.994	0.734	0.958	0.647
1.8	1.003	0.741	0.970	0.653
2.0	1.012	0.749	0.981	0.658
2.5	1.035	0.771	1.009	0.677
3.0	1.060	0.788	1.035	0.697
3.5	1.085	0.825	1.061	0.721
4.0	1.112	0.858	1.085	0.745
4.5	1.139	0.895	1.109	0.772
5.0	1.162	0.930	1.132	0.800
5.5	1.185	0.967	1.152	0.827
6.0	1.203	1.003	1.163	0.855

[a] Me$_4$Gu = tetramethylguanidinium.

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