

studies (15, 17) that were based on use of high-purity NiCl_2 .

Acknowledgment

We thank John G. Albright for the loan of his pycnometers, Sue Frumentini for typing the manuscript, and John G. Albright and Donald G. Miller for assistance with calculations.

Glossary

d	density of solution, g cm^{-3}
d^0	density of pure water, g cm^{-3}
m	molal concentration of solute, $\text{mol (kg of H}_2\text{O)}^{-1}$
c	molar concentration of solute, mol dm^{-3}
ϕ_v	apparent molal volume of solute, $\text{cm}^3 \text{ mol}^{-1}$
M_2	molecular weight of solute, g mol^{-1}
B_j	least-squares coefficients for eq 2
X	denotes m or c in eq 2
σ	standard deviation of eq 2

Registry No. NiCl_2 , 7718-54-9.

Literature Cited

- (1) Millero, F. J. In "Activity Coefficients in Electrolyte Solutions"; Pytkowicz, R. M., Ed.; CRC Press: Boca Raton, FL, 1979; Vol. II, Chapter 2.
- (2) Rard, J. A.; Miller, D. G. *J. Chem. Eng. Data* **1980**, *25*, 211-215; **1981**, *26*, 38-43; **1982**, *27*, 169-173.

- (3) Rard, J. A.; Miller, D. G. *J. Solution Chem.* **1979**, *8*, 701-716, 755-766; **1983**, *12*, 413-425.
- (4) Rard, J. A.; Miller, D. G. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 887-896.
- (5) Miller, D. G.; Rard, J. A.; Eppstein, L. B.; Albright, J. G. *J. Phys. Chem.* **1984**, *88*, 5739-5748.
- (6) Rard, J. A. *J. Chem. Eng. Data* **1984**, *29*, 443-450.
- (7) Rard, J. A.; Miller, D. G. *J. Chem. Eng. Data* **1984**, *29*, 151-156.
- (8) Rard, J. A.; Miller, D. G. *J. Solution Chem.* **1985**, *14*, 271-299.
- (9) Rard, J. A.; Miller, D. G. *Z. Phys. Chem. N. F.* **1984**, *142*, 141-155.
- (10) Hunt, J. P.; Friedman, H. L. In "Progress in Inorganic Chemistry"; Lip-pard, S. J., Ed.; Wiley Interscience: New York, 1983; Vol. 30.
- (11) Weingartner, H.; Müller, C.; Hertz, H. G. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 2712-2734.
- (12) Karapet'yants, M. Kh.; Vasil'ev, V. A.; Sanaev, E. S. *Russ. J. Phys. Chem. (Engl. Transl.)* **1977**, *51*, 1281-1283.
- (13) Pearce, J. N.; Eckstrom, H. C. *J. Phys. Chem.* **1937**, *41*, 563-565.
- (14) Spitzer, J. J.; Singh, P. P.; McCurdy, K. G.; Hepler, L. G. *J. Solution Chem.* **1978**, *7*, 81-86.
- (15) Stokes, R. H.; Phang, S.; Mills, R. *J. Solution Chem.* **1979**, *8*, 489-500.
- (16) Lo Surdo, A.; Millero, F. J. *J. Phys. Chem.* **1980**, *84*, 710-715.
- (17) Perron, G.; Roux, A.; Desnoyers, J. E. *Can. J. Chem.* **1981**, *59*, 3049-3054.
- (18) Rard, J. A., unpublished data.
- (19) Rard, J. A.; Miller, D. G., unpublished data.
- (20) Kell, G. S. *J. Chem. Eng. Data* **1975**, *20*, 97-105.
- (21) Richardson, J. T. *J. Phys. Chem.* **1963**, *67*, 1377-1378.

Received for review July 15, 1985. Accepted October 14, 1985. This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

Thermodynamics of Binary Mixtures Containing Cyclic Alkanones.

1. Excess Enthalpies of Cyclopentanone and Cyclohexanone + n -Alkanes, + Cyclohexane, + Benzene, and + Tetrachloromethane

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A Tian-Calvet type calorimeter has been used to determine molar excess enthalpies, H^E , as a function of concentration at atmospheric pressure and 298.15 K for some binary liquid mixtures containing cycloalkanones (cyclopentanone and cyclohexanone) with n -alkanes, $\text{CH}_3-(\text{CH}_2)_{m-2}-\text{CH}_3$ ($m = 6, 7, 12, 16$), cyclohexane, C_6H_{12} , benzene, C_6H_6 , and tetrachloromethane, CCl_4 . The experimental H^E results are interpreted in terms of molecular interactions and the Patterson effect.

Introduction

This work is part of a systematic study of the thermodynamic properties of organic mixtures, T.O.M. Project (1-8), with the purpose of characterizing the type and magnitude of molecular interaction in the binary liquid mixtures and to improve the group contribution models currently used to predict thermodynamic properties (1, 8).

Moreover, the study of mixtures containing cycloalkanones offers an opportunity to test the applicability of the energy interchange parameters determined from mixtures of n -alkanes (9-11).

Furthermore, there are many intriguing problems related to binary liquid mixtures containing n -alkanes (12-15). For example, mixtures of n -alkanes with spherical nonpolar molecules, such as cyclohexane (16), have been discussed by Patterson (12) in terms of destruction of partial order assumed to exist in pure liquid n -alkanes of sufficient chain length. Such an effect will manifest itself by a positive contribution to the excess enthalpy, H^E . In view of this, cycloalkanones + n -alkane mixtures were regarded as interesting in that by formally replacing $-\text{CH}_2-$ groups of cycloalkanes by the $-\text{CO}-$ group, the influence exerted by group dipole moments and shape upon the thermodynamic excess functions can be further investigated.

No experimental excess Gibbs free energy or excess enthalpy data could be found in the literature for these mixtures. In order to characterize the behavior of the "cycloalkanone" group with respect to the main functional groups of organic chemistry, it was decided to measure excess enthalpies in a systematic way for mixtures of cyclopentanone and cyclohexanone with n -alkanes of general formula



and with cyclohexane, benzene, and tetrachloromethane.

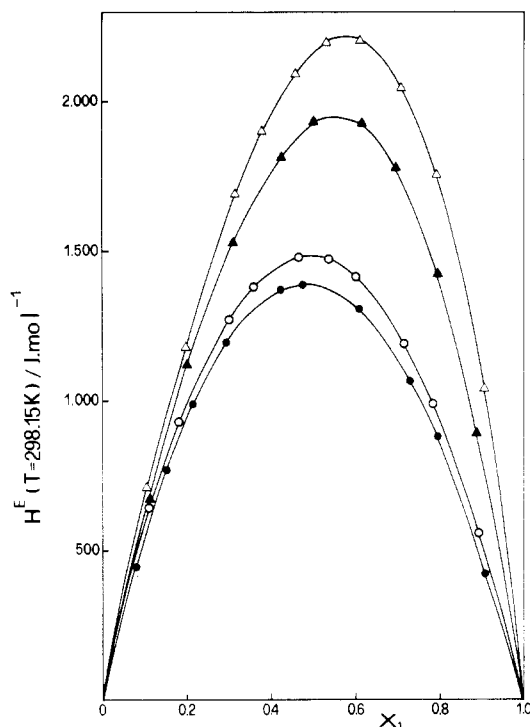


Figure 1. Experimental excess enthalpies H^E of cyclopentanone (1) + n -alkanes (2) mixtures at 298.15 K vs. x_1 , the mole fraction of cyclopentanone: ●, + n -hexane; ○, + n -heptane; ▲, + n -dodecane; Δ, + n -hexadecane.

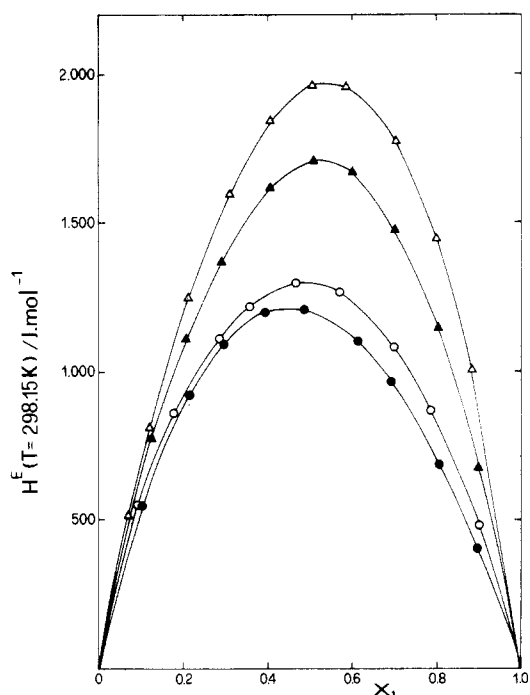


Figure 2. Experimental excess enthalpies H^E of cyclohexanone (1) + n -alkanes (2) mixtures at 298.15 K vs. x_1 , the mole fraction of cyclohexanone: ●, + n -hexane; ○, + n -heptane; ▲, + n -dodecane; Δ, + n -hexadecane.

These systems were chosen for possible comparison with n -alkanones in terms of molecular surface interaction (10), and also to compare the electron-donor ability of these carbonyl compounds with benzene and tetrachloromethane.

Experimental Section

The excess enthalpies, H^E , were measured with a Tian-Calvet ("CRMT") type calorimeter which was manually titrated.

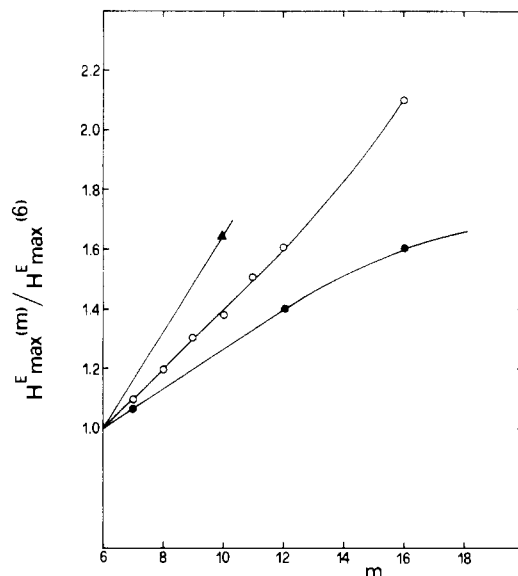


Figure 3. Plot of $H^E_{\max}(m)/H^E_{\max}(6)$ against chain length m of the n -alkane at 298.15 K for the cyclopentane + n -alkane mixtures (○), for the cyclohexene + n -alkane mixtures (Δ), and for the cycloalkanones + n -alkanes mixtures (●). The results for the two cycloalkanones series are not distinguishable on the scale of graph.

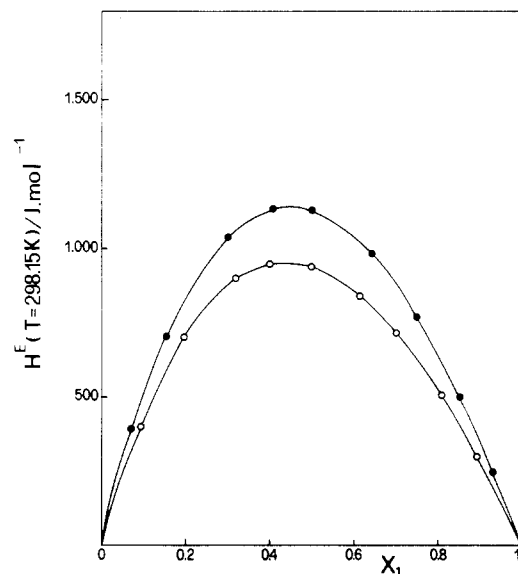


Figure 4. Experimental excess enthalpies H^E of cycloalkanones (1) + cyclohexane (2) mixtures at 298.15 K vs. x_1 , the mole fraction of cycloalkane: ●, cyclopentanone; ○, cyclohexanone.

The batch mixing cell and the experimental procedure are reported in the literature (17). The calorimeter was calibrated by the Joule effect and the calibration was repeated after each experiment. Comparison of measurements for the benzene + cyclohexane system with literature data (18) indicated that the precision of our results is 2%. All measurements were made at an average temperature of 298.15 ± 0.10 K.

The experimental values, H^E_{exptl} , reported in Tables I and II, were fitted to the smoothing equation

$$H^E_{\text{sm}} = x_1 x_2 \sum_{j=0}^{N-1} a_j (x_1 - x_2)^j \quad (1)$$

where x_1 is the mole fraction of cycloalkane and x_2 that of n -alkane (or cyclohexane, benzene, tetrachloromethane). Values for the standard deviations $\sigma(H^E)$ are given by

$$\sigma(H^E) = [\sum (H^E_{\text{sm}} - H^E_{\text{exptl}})^2 / (N - n)]^{1/2} \quad (2)$$

where N is the number of experimental points and n is the

Table I. Experimental Values of the Excess Enthalpies H^E for Binary Mixtures of Cycloalkanones (1) with n -Alkanes (2) at 298.15 K

x_1	$H^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H^E/\text{J}\cdot\text{mol}^{-1}$
Cyclopentanone + C_6H_{14}		Cyclohexanone + C_6H_{14}	
0.0788	445	0.1032	550
0.1511	772	0.2113	925
0.2126	991	0.2929	1096
0.2904	1193	0.3935	1198
0.4224	1370	0.4859	1210
0.4751	1389	0.6192	1100
0.6076	1306	0.6964	967
0.7285	1066	0.8068	689
0.7912	878	0.8910	409
0.9087	419		
Cyclopentanone + C_7H_{16}		Cyclohexanone + C_7H_{16}	
0.1100	644	0.0951	553
0.1811	930	0.1786	862
0.3013	1268	0.2844	1110
0.3597	1377	0.3569	1220
0.4649	1480	0.4667	1295
0.5322	1475	0.5715	1270
0.6015	1414	0.7031	1083
0.7158	1193	0.7878	869
0.7856	987	0.8971	480
0.8949	560		
Cyclopentanone + $\text{C}_{12}\text{H}_{26}$		Cyclohexanone + $\text{C}_{12}\text{H}_{26}$	
0.1117	673	0.1212	780
0.2025	1123	0.2072	1111
0.3083	1527	0.2925	1371
0.4233	1818	0.4081	1618
0.5000	1924	0.5065	1710
0.6138	1923	0.6013	1671
0.6959	1782	0.7024	1479
0.7927	1430	0.8016	1148
0.8850	896	0.9001	675
Cyclopentanone + $\text{C}_{16}\text{H}_{34}$		Cyclohexanone + $\text{C}_{16}\text{H}_{34}$	
0.1087	708	0.0702	521
0.1975	1179	0.1213	813
0.3154	1695	0.2146	1250
0.3768	1903	0.3105	1597
0.4556	2102	0.4090	1845
0.5294	2201	0.5033	1964
0.6049	2208	0.5841	1960
0.7083	2047	0.6990	1779
0.7918	1757	0.7984	1445
0.9052	1044	0.8821	1010

number of coefficients a_i . The values for the coefficients a_i [eq 1] and the standard deviations $\sigma(H^E)$ [eq 2] determined by least-squares analysis, are reported in Tables III and IV.

Discussion

(a) Mixtures with n -Alkanes and with Cyclohexane. As shown in Figures 1–4, the values of H^E are large and positive, this behavior is mainly due to the breaking of dipole–dipole interactions between the cycloalkanones molecules. Since the dipole moments for the two cycloalkanones are similar, it is the dispersive interactions between the unlike molecules which determine the decrement of H^E with increasing number of $-\text{CH}_2-$ groups in the cycloalkanone.

The most striking feature of the reported data is the dependence of the excess enthalpy values upon the chain length m of the n -alkane. This behavior is shown in Figure 3, where the quantity $H^E_{\text{max}}(m)/H_{\text{max}}(6)$ is plotted against m . For sake of comparison the results for cycloalkane + n -alkane (16, 19) are also included.

Within the range $6 \leq m \leq 14$, the cycloalkane series shows a substantial increase of H^E_{max} with increasing m . Analysis of

Table II. Experimental Values of the Excess Enthalpy H^E for Binary Mixtures of Cycloalkanones (1) with Cyclohexane (C_6H_{12}), Benzene (C_6H_6), and Tetrachloromethane (CCl_4) at 298.15 K

x_1	$H^E/\text{J}\cdot\text{mol}^{-1}$	x_1	$H^E/\text{J}\cdot\text{mol}^{-1}$
Cyclopentanone (1) + C_6H_{12} (2)		Cyclohexanone (1) + C_6H_{12} (2)	
0.0715	390	0.0922	400
0.1536	705	0.1975	702
0.3000	1034	0.3211	899
0.4071	1136	0.4007	948
0.4997	1129	0.5000	939
0.6424	984	0.6124	843
0.7489	770	0.6983	718
0.8500	500	0.8056	507
0.9286	251	0.8910	302
Cyclopentanone (1) + C_6H_6 (2)		Cyclohexanone (1) + C_6H_6 (2)	
0.0871	-92	0.1145	-102
0.1924	-187	0.1873	-150
0.3012	-264	0.3212	-221
0.4636	-320	0.3866	-245
0.5517	-320	0.4606	-268
0.6983	-276	0.5320	-274
0.8340	-185	0.6117	-270
0.9128	-108	0.6951	-241
Cyclopentanone (1) + CCl_4 (2)		Cyclohexanone (1) + CCl_4 (2)	
0.1020	-142	0.0911	-109
0.2176	-265	0.2100	-221
0.2895	-324	0.3055	-290
0.4232	-393	0.4876	-361
0.4918	-412	0.6014	-348
0.6040	-400	0.6748	-316
0.6997	-356	0.8040	-226
0.8133	-270	0.8805	-150
0.9200	-142		

the data (16, 20, 21) indicates behavior in accordance with the Patterson effect.

For linear alkanones + n -alkane mixtures the excess enthalpy values increase with the value of m , as expected from group contribution theory (10).

The behavior of cycloalkanones + n -alkane is quite similar as evidenced by the dependence of H^E_{max} upon m . However, there appears to be a rather smooth transition from cycloalkane series to the cyclic alkanones series.

Preliminary calculations by the DISQUAC model, using the interchange energy coefficients previously determined from mixtures of n -alkanones + n -alkanes (9, 10) and from mixtures of n -alkanones + cyclohexane (11), have shown that, for increasing values of m , the experimental data are systematically higher than the calculated values.

This extra-endothermic contribution referred to as Patterson effect is attributed to the destruction of orientational order in n -alkanes during the process of mixing with branched or cyclic molecules.

The excess enthalpy with cyclohexane is larger and positive as with n -alkanes which is due to the rather unspecific interaction between the cycloalkanone and cyclohexane.

However, the excess enthalpy of cycloalkanones + cyclohexane is less positive ($\Delta H^E \approx 250 \text{ J}\cdot\text{mol}^{-1}$) than those of n -alkane mixtures of comparable size, and this suggests the existence of particular structural factors in liquid cyclohexane.

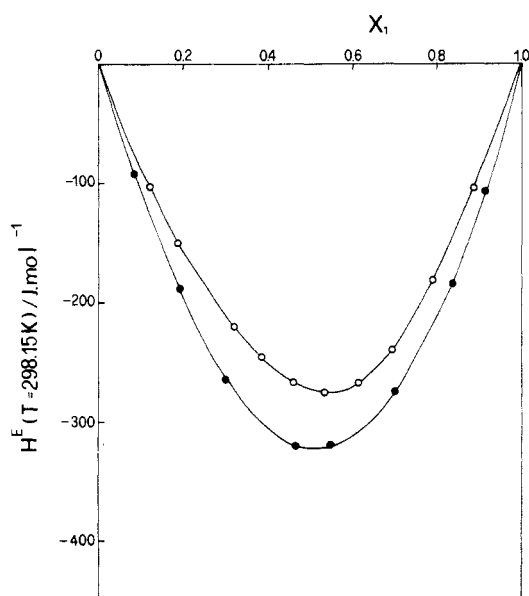
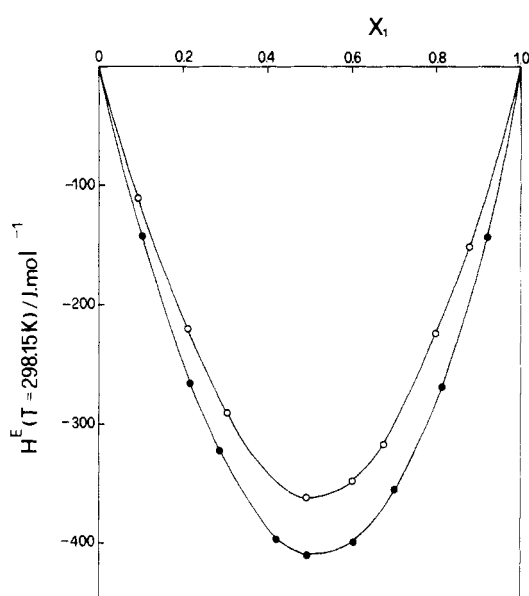
(b) Mixtures with Benzene and Tetrachloromethane. In these solvents (see Figures 5 and 6) a marked decrease in H^E occurs. Such behavior of excess properties can be explained as a consequence of two competing effects in these mixtures. The breaking of the cycloalkanone structure by dilution with benzene or tetrachloromethane leads to an endothermic effect, and on the other hand specific interactions between unlike

Table III. Values for the Coefficients a_i , Eq 1, and the Standard Deviations, $\sigma(H^E)$, Eq 2. Binary Systems: Cycloalkanones (1) with n -Alkanes (2) at 298.15 K

cycloalkanone	m	T/K	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)/J\cdot mol^{-1}$
cyclopentanone	6	298.15	5546	-384	384	-406	-517	0.9
	7	298.15	5933	-126	-73	-461	1013	1.0
	12	298.15	7692	1732	767	-725	-1001	0.8
	16	298.15	8696	2453	543	828	1696	1.1
cyclohexanone	6	298.15	4817	-795	761	-468	-575	1.4
	7	298.15	5194	-136	616	-944	504	1.2
	12	298.15	6837	782	-293	-1226	2125	1.9
	16	298.15	7850	1242	292	145	1940	1.8

Table IV. Values for the Coefficients a_i , Eq 1, and the Standard Deviations, $\sigma(H^E)$, Eq 2. Binary Systems: Cycloalkanones (1) with Cyclohexane (C_6H_{12}), Benzene (C_6H_6), and Tetrachloromethane (CCl_4), at 298.15 K

cycloalkanone (1)	solvent (2)	T/K	a_0	a_1	a_2	a_3	a_4	$\sigma(H^E)/J\cdot mol^{-1}$
cyclopentanone	C_6H_{12}	298.15	4527	-851	127	-457	392	2.7
	C_6H_6	298.15	-1290	-57	54	-103		0.7
	CCl_4	298.15	-1640	-119	72	-170	-341	2.3
cyclohexanone	C_6H_{12}	298.15	3756	-932	200	-145	82	1.0
	C_6H_6	298.15	-1092	-217	145	345		1.4
	CCl_4	298.15	-1447	-89	353	-7	-411	1.9

**Figure 5.** Experimental excess enthalpies H^E of cycloalkanones (1) + benzene (2) mixtures at 298.15 K vs. x_1 , the mole fraction of cycloalkanone: ●, cyclopentanone; ○, cyclohexanone.**Figure 6.** Experimental excess enthalpies H^E of cycloalkanones (1) + tetrachloromethane (2) mixtures at 298.15 K vs. x_1 , the mole fraction of cycloalkanone: ●, cyclopentanone; ○, cyclohexanone.

molecules leads to an exothermic effect. The balance between the two contributions is a function of inductive and steric effects. Thermodynamic excess properties of n -alkanes + benzene have been qualitatively discussed in terms of specific n - π interactions (22), and observed differences between mixtures containing a cyclic alkanone and mixtures with a corresponding n -alkane are plausibly attributed to a larger exposed surface of the $-CO-$ group in cyclic alkanones relative to the n -alkanes.

Specific interactions of the n - σ type have been postulated for alkanones + CCl_4 .

A detailed interpretation of these results in terms of the DISQUAC model (β) of molecular surface interaction will be presented separately.

Glossary

a_i	coefficients of eq 1
G	molar Gibbs energy, $J\cdot mol^{-1}$
H	molar enthalpy, $J\cdot mol^{-1}$
m	number of C atoms in the n -alkane
n	number of coefficients a_i of eq 1
N	number of experimental points
T	temperature

$\sigma(H^E)$ standard deviations, eq 2

Superscript

E excess properties

Subscripts

i type of molecule (component)

exptl experimental

sm smoothing

Registry No. CCl_4 , 56-23-5; C_6H_6 , 71-43-2; C_6H_{12} , 110-82-7; C_6H_{14} , 110-54-3; C_7H_{16} , 142-82-5; $C_{12}H_{26}$, 112-40-3; $C_{16}H_{34}$, 544-76-3; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1.

Literature Cited

- (1) Kehiaian, H. V. *Ber. Bunsenges. Phys. Chem.* **1977**, *81*, 908-921.
- (2) Ferino, I.; Maronglu, B.; Solinas, V.; Torrazza, S.; Kehiaian, H. V. *Fluid Phase Equilib.* **1982**, *9*, 49-65.
- (3) Ferino, I.; Maronglu, B.; Solinas, V.; Torrazza, S.; Kehiaian, H. V. *Fluid Phase Equilib.* **1982**, *9*, 213-233.
- (4) Ferino, I.; Maronglu, B.; Solinas, V.; Torrazza, S. *Gazz. Chim. Ital.* **1983**, *113*, 413-418.
- (5) Ferino, I.; Maronglu, B.; Solinas, V.; Torrazza, S.; Kehiaian, H. V. *Fluid Phase Equilib.* **1983**, *11*, 1-12.
- (6) Ferino, I.; Maronglu, B.; Solinas, V.; Torrazza, S.; Kehiaian, H. V. *Fluid Phase Equilib.* **1983**, *12*, 125-142.

- (7) Maronglu, B.; Ferino, I.; Sollnas, V.; Torrazza, S.; Kehalain, H. V. *J. Therm. Anal.* **1984**, *29*, 711-717.
- (8) Kehalain, H. V.; Maronglu, B. *Fluid Phase Equilib.* **1985**, *21*, 197-209.
- (9) Kehalain, H. V.; Grollier, J.-P. E.; Kechavarz, M.-R.; Benson, G. C.; Kiyohara, O.; Handa, Y. P. *Fluid Phase Equilib.* **1981**, *5*, 159-189.
- (10) Kehalain, H. V.; Grollier, J.-P. E.; Kechavarz, M.-R.; Benson, G. C.; Kiyohara, O.; Handa, Y. P. *Fluid Phase Equilib.* **1981**, *7*, 95-120.
- (11) Kehalain, H. V.; Maronglu, B. *Fluid Phase Equilib.* submitted for publication.
- (12) Patterson, D. *Pure Appl. Chem.* **1978**, *47*, 305-314.
- (13) Tancrede, P.; Bothorel, P.; St. Romain, P.; Patterson, D. *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 15-28.
- (14) Tancrede, P.; Patterson, D.; Bothorel, P.; *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 29-39.
- (15) Barbe, M.; Patterson, D. *J. Phys. Chem.* **1978**, *82*, 40-46.
- (16) Heintz, A.; Lichtenthaler, R. N. *Ber. Bunsenges. Phys. Chem.* **1977**, *81*, 921-925.
- (17) Bares, D.; Soulle, M.; Metzger, J. *J. Chim. Phys.* **1973**, *70*, 1531-1539.
- (18) Marsh, K. N. *Int. DATA Ser., Sel. Data Mixtures, Ser. A* **1973**, *1*, 2.
- (19) Inglese, A.; Grollier, J.-P.E. *Int. DATA Ser. Sel. Data Mixtures, Ser. A*, **1975**, *1*, 98-109.
- (20) Kehalain, H. V.; Grollier, J.-P.E.; Benson, G. C. *J. Chim. Phys.* **1978**, *75*, 1031-1048.
- (21) Lane, V. T.; Picker, P.; Patterson, D.; Tancrede, P. *J. Chem. Soc., Faraday Trans. 2* **1974**, *70*, 1465-1478.
- (22) Kehalain, H. V. In "MTP International Review of Science. Thermochemistry and Thermodynamics"; Butterworth: London, 1972; Vol. X, Chapter 5.

Received for review July 1, 1985. Accepted November 6, 1985. We gratefully acknowledge the support of the Ministero Pubblica Istruzione of Italy.

An Empirical Equation of State for Pure Water in the Oceanographic Region of Temperature and Pressure Determined from Direct Measurements[†]

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Polynomial regression fits to the results of measurements on distilled water of the thermal expansion at a number of pressures and of the compression at a single temperature are combined to form an empirical equation of state which is valid in the ranges $T \leq 0-30^\circ\text{C}$ and atmospheric pressure to 1000 bars. The specific volume from the equation has a standard error of $3 \times 10^{-6} \text{ cm}^3/\text{g}$ or better over the entire region and its inaccuracy is estimated to be not worse than $25 \times 10^{-6} \text{ cm}^3/\text{g}$ at 1000 bars. The measurements are direct volumetric ones which are based on calibrations using mercury $P-V-T$ data. The equation of state for water presented agrees within $20 \times 10^{-6} \text{ cm}^3/\text{g}$ with two recent equations derived from sound speed measurements. Some properties derived from the equation are compared with those found by others.

The results of direct measurements of the volume properties of pure water in the oceanographic region of temperature and pressure are presented here. They are summarized as an empirical equation of state using polynomial least-squares fits. The data on which they are based was part of our contribution to the data set used in the formulation of an empirical equation of state for seawater (1) which has been endorsed by the UNESCO Joint Panel on Oceanographic Tables and Standards. The remaining pure water data used in that data set was that from Chen, Fine, and Millero's (2) equation of state for water, determined from Wilson's (3) sound speed data, for the 0-100 °C, atmospheric pressure to 1000 bar region. Our pure water data consist of compressions to 1000 bars at 10 °C IPTS-48 and isopiestic thermal expansions in the temperature range $T \leq 0-30^\circ\text{C}$ at pressures up to ~1000 bars. The compression data was published earlier (4), but the thermal expansion data has not been published before. The water data is important not only as a necessary component in the formulation of a seawater equation which goes to zero salt concentration but also by itself, because an accurate water equation can be used in calibrations of instruments for future measurements of the

$P-V-T$ relations in seawater and other aqueous solutions. Our measurements, in particular, have value because they provide, within the experimental differences between the two, a confirmation of the sound speed based results by a direct volumetric method and because they yield specific volumes below 0 °C, where the temperatures of maximum density lie at higher pressures.

Kell and Whalley (5) also determined precisely the $P-V-T$ properties of water by direct volumetric measurement to 1000 bars over a much larger temperature range, 0-150 °C. There are differences, however, of over 100 ppm of the specific volume at 1000 bars between their values and those determined from Wilson's (3) sound speeds; this was pointed out by Fine and Millero (6) from results of their determination of compressions from sound speeds. Later, more accurate determinations of compressions from sound speeds by Kell and Whalley (7) and by Chen, Fine, and Millero confirmed this, as do our own results from direct measurements.

Experimental Section

Apparatus and Procedures. The apparatus and the experimental and data workup procedures used for our measurements on water were described in detail earlier (4, 8, 9). The change in sample volume with temperature or with pressure was measured in a dilatometer, by which means the change can be measured to a high resolution from the change in length in a small-diameter, precision-bore tubing whose volume is continuous with that of the main sample volume. Two different fused-quartz dilatometers were used, one for the thermal expansion and one for the compression measurements. In the thermal expansion and compression determinations a 1 ppm change in the sample volume ($\sim 45 \text{ cm}^3$) corresponded to ~ 14 and $\sim 2 \mu\text{m}$, respectively, change in length along the dilatometer capillary. The sample was separated from the pressure transmitting fluid (distilled water) in the pressure vessel which enclosed the dilatometer by mercury, which extended from the bottom of the main volume of the dilatometer up into the measuring section of the precision-bore capillary. The height of the mercury in the measuring section was followed by measuring the position of a small, magnetic-steel cylinder

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