refraction (R/R_{H_2O}) as a function of solution concentration is shown in Figure 3. Obviously, with an increase in solution concentration both R and R/R_{H_2O} decrease. One also notes from Tables XIV and XV that with an increase in temperature the values of A_2, A_4, B_2, and B_4 decrease while those of A_3 and B_3 increase. One also finds that at a constant temperature t, $A_2 = R_{H_2O}$, $B_2 = A_2/R_{H_2O}$, $B_3 = A_3/R_{H_2O}$, and $B_4 = A_4/R_{H_2O}$ because the molar refraction of solid $LiIO_3$ is practically constant in the investigated range of temperature.

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Glossary

A_0, A_1–A_4	constants in eq 13 and 14
a_0, a_1–a_4	constants in eq 1 and 3
B_0, B_1–B_4	constants in eq 15 and 16
b_0, b_1–b_4	constants in eq 2 and 4
c	solution concentration, M
d	corrected density of solution, g/cm^3
d_m	measured density of solution, g/cm^3
$d_0(c)$, d_0'	concentration-dependent constants in eq 3 and 5, g/cm^3
$d_0(t)$	temperature-dependent constants in eq 1, g/cm^3
d_{H_2O}	density of water, g/cm^3
n	refractive index of solution
$n_0(c)$, n_0'	concentration-dependent constants in eq 4 and 6
$n_0(t)$	temperature-dependent constant in eq 2
n_{H_2O}	refractive index of water
R	specific refraction of solution, cm^3/g
R_{H_2O}	specific refraction of water, cm^3/g
T	temperature, K
T_0', T_0''	constants in eq 5 and 6, K
t	temperature, °C
α_0, α_1–α_5	constants in eq 7 and 9
β_0, β_1–β_5	constants in eq 8 and 10
β', β''	concentration-dependent constants in eq 5 and 6, K^{-2}

Registry No. $LiIO_3$, 13765-03-2.

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Thermodynamics of Binary Mixtures Containing Organic Carbonates. 1. Excess Enthalpies of Dimethyl Carbonate + Hydrocarbons or + Tetrachloromethane[†]

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Molar excess enthalpy H^E data at 298.15 K are reported for the binary liquid systems dimethyl carbonate + hexane, + heptane, + octane, + decane, + cyclohexane, + methylcyclohexane, + benzene, + toluene, or + tetrachloromethane.

Introduction

Esters of carbonic acid, dialkyl carbonates $CH_3(CH_2)_{n-1}O$-CO-$O(CH_2)_{m-1}CH_3$ and polymethylene carbonates O-CO-O-$(CH_2)_n$, are used in the syntesis of pharmaceuticals, agricultural chemicals, and dyestuffs. They are also used as solvents for many synthetic and natural resins and polymers, and some of them are used in photoengraving as assist agents for silicon circuitry.

In spite of the potential applications of carbonic acid esters there are only a few experimental thermodynamics studies on this class of substances, mainly on cyclic derivatives (*3–5*). In particular, to our knowledge, no data exist on the properties of binary mixtures of dialkyl carbonates $(CH_3(CH_2)_{n-1}O)_2CO$ with normal alkanes. Accordingly, no interaction parameters are yet

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[†] This paper is a contribution to the TOM Project (*1*,*2*).

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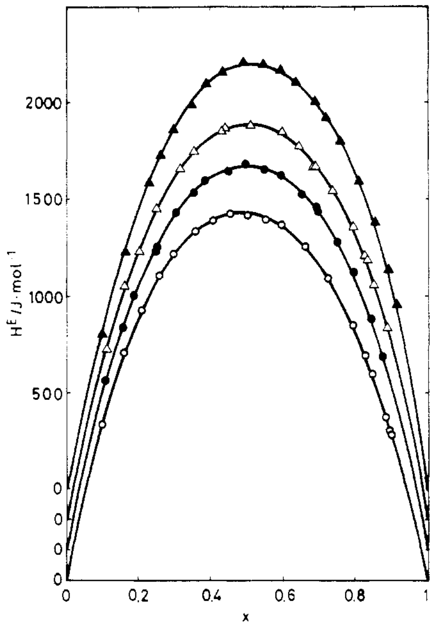

Figure 1. Excess molar enthalpy H^E for dimethyl carbonate (1) + n-alkane (2) mixtures versus x_1, the mole fraction of component 1: (○) hexane; (●) heptane; (△) octane; (▲) decane. Full curves represent the smoothing eq 1 with the coefficients of Table III.

available for the carbonate group, -O-CO-O- in the frame of predictive group-contribution methods, such as UNIFAC (*6*). For these reasons we have initiated a systematic study of the thermodynamic properties of mixtures containing dialkyl or polymethylene carbonates.

In this paper we report excess molar enthalpies H^E for dimethyl carbonate (1) + hexane (2), + heptane (2), + octane (2), + decane (2), + cyclohexane (2), + methylcyclohexane (2), + benzene (2), + toluene (2), or + tetrachloromethane (2) at 298.15 K and atmospheric pressure. Vapor-liquid equilibrium data have been reported in the literature (*7*) for dilute solutions ($x_1 < 0.15$) of dimethyl carbonate (1) in methylcyclohexane (2) or toluene (2).

Experimental Section

A standard Calvet type microcalorimeter, equipped with a batch mixing cell with small (<2%) vapor phase, and the experimental technique of Paz Andrade et al. (*8*) were used to determine the excess enthalpies over the entire mole fraction, x_1, range. The microcalorimeter was calibrated electrically and the calibration was checked by determining the molar excess enthalpy of hexane + cyclohexane, benzene + cyclohexane, and tetrachloromethane + benzene at 298.15 K over the whole mole fraction range. Our results differ by less than 1% from those of the literature near $x_1 = 0.5$ (*9-11*). It was found that the corrections in H^E and x_1 due to the vapor phase are smaller than 0.1 J mol^{-1} and 0.0002, respectively. The calorimeter was thermostated at 298.15 ± 0.005 K; the accuracy of H^E is better than 2% over the central range of concentration.

All the chemicals used were from Fluka. Dimethyl carbonate (purum, >99 mol %), hexane (puriss p.a., >99.5 mol %), heptane (puriss p.a., >99.5 mol %), octane (purum, >99 mol %), decane (purum, >99 mol %), cyclohexane (puriss p.a., >99.5 mol %), methylcyclohexane (purum, >98 mol %), benzene (puriss p.a., >99.5 mol %), toluene (puriss p.a., >99.5 mol %), and tetrachloromethane (puriss p.a., >99.5 mol %) were used without further purification. Prior to the actual measurements, all liquids were dried over molecular sieves (Union Carbide Type 4A from Fluka). The results of the measurements of their densities and refractive indexes are in Table I and were in good agreement with published values (*12*,*13*).

Table I. Physical Properties of Pure Compounds

compound	refractive index $\eta(\mathrm{D}_2, 298.15\ \mathrm{K})$ this study	lit.	density $\rho(298.15\ \mathrm{K})/\mathrm{kg\ m}^{-3}$ this study	lit.
dimethyl carbonate	1.3667	1.3687[a]	1063.6	1069.4[a]
hexane	1.3723	1.37226	654.7	654.84
heptane	1.3851	1.38511	679.5	679.46
octane	1.3951	1.39505	698.5	698.62
decane	1.4097	1.40967	726.3	726.35
cyclohexane	1.4235	1.42354	773.9	773.89
methylcyclohexane	1.4206	1.42058	765.1	765.06
benzene	1.4979	1.49792	873.7	873.6
toluene	1.4941	1.49396	862.4	862.2
tetrachloromethane	1.4574	1.4570	1584.4	1584.3

[a] Reference *13* (293.15 K).

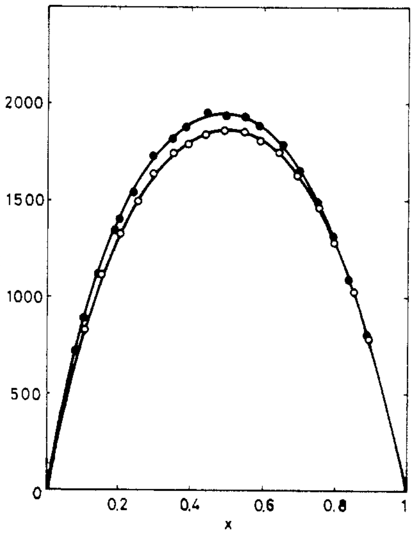

Figure 2. Excess molar enthalpy H^E for dimethyl carbonate (1) + cyclic alkanes (2) mixtures versus x_1, the mole fraction of component 1: (●) cyclohexane; (○) methylcyclohexane. Full curves represent the smoothing eq 1 with the coefficients of Table III.

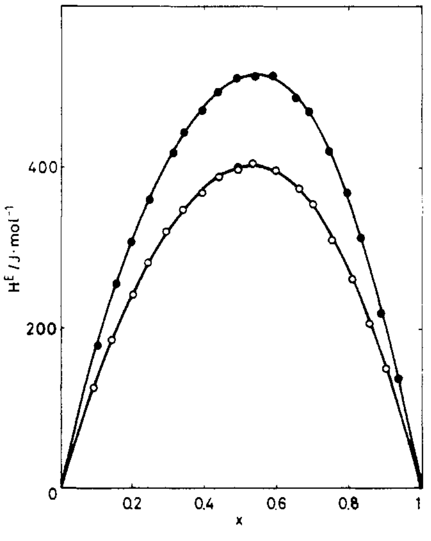

Figure 3. Excess molar enthalpy H^E for dimethyl carbonate (1) + aromatic hydrocarbons (2) mixtures versus x_1, the mole fraction of component 1: (○) benzene; (●) toluene. Full curves represent the smoothing eq 1 with the coefficients of Table III.

Conversion to molar quantities is based on the relative atomic mass table of 1975, issued by IUPAC.

Results and Discussion

Table II gives experimental results of H^E as a function of the mole fraction x_1 of dimethyl carbonate. These data were fitted

Table II. Molar Excess Enthalpy H^E for Dimethyl Carbonate (1) + Solvents (2) at 298.15 K

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}
Hexane							
0.0984	803	0.3528	1804	0.5913	1835	0.8464	1073
0.1583	1175	0.4006	1862	0.6593	1731	0.8856	846
0.2059	1395	0.4507	1896	0.7244	1568	0.8961	775
0.2563	1579	0.4998	1893	0.7916	1323	0.8992	754
0.2941	1688	0.5491	1870	0.8272	1162		
Heptane							
0.1078	871	0.3004	1748	0.5453	1971	0.7480	1595
0.1548	1148	0.3470	1850	0.5912	1938	0.7922	1439
0.1860	1314	0.3822	1914	0.6486	1839	0.8421	1197
0.2458	1547	0.4450	1959	0.6882	1774	0.8741	1000
0.2484	1565	0.4939	1997	0.6938	1749		
Octane							
0.1092	884	0.3478	1905	0.6374	1935	0.8205	1368
0.1600	1207	0.4271	2016	0.6830	1830	0.8260	1348
0.1989	1389	0.4328	2031	0.6857	1840	0.8484	1221
0.2467	1602	0.5073	2047	0.7335	1705	0.8827	994
0.3095	1818	0.5928	2005	0.7898	1520		
Decane							
0.0956	800	0.3418	1997	0.5880	2171	0.8080	1584
0.1584	1220	0.3825	2100	0.6296	2102	0.8484	1374
0.2273	1585	0.4266	2163	0.6861	2006	0.8861	1140
0.2545	1725	0.4833	2213	0.7131	1929	0.9106	956
0.2942	1863	0.5391	2205	0.7529	1795		
Cyclohexane							
0.0788	719	0.2394	1540	0.4964	1938	0.7489	1495
0.1024	890	0.2942	1726	0.5459	1930	0.7929	1312
0.1401	1115	0.3474	1814	0.5877	1885	0.8366	1090
0.1875	1337	0.3853	1877	0.6529	1783	0.8880	804
0.1991	1403	0.4432	1948	0.6994	1653		
Methylcyclohexane							
0.1040	823	0.3466	1740	0.5445	1850	0.7522	1462
0.1529	1110	0.3898	1789	0.5894	1807	0.7957	1282
0.2013	1321	0.4396	1836	0.6413	1749	0.8493	1026
0.2503	1495	0.4874	1860	0.6941	1626	0.8927	780
0.2953	1631						
Benzene							
0.0917	125	0.3387	347	0.5322	404	0.7527	310
0.1425	185	0.3910	369	0.5972	396	0.8093	260
0.1986	241	0.4395	387	0.6628	373	0.8561	206
0.2417	281	0.4904	397	0.7003	354	0.9014	149
0.2916	320	0.4923	397				
Toluene							
0.1018	178	0.3414	444	0.5869	513	0.7949	368
0.1519	255	0.3911	470	0.6517	487	0.8325	312
0.1949	307	0.4367	493	0.6872	469	0.8912	218
0.2438	359	0.4857	510	0.7441	421	0.9380	137
0.3124	418	0.5376	514				
Tetrachloromethane							
0.0940	239	0.3102	496	0.5608	514	0.7508	374
0.1129	275	0.3556	516	0.6053	492	0.7983	325
0.1538	343	0.4030	533	0.6574	453	0.8518	252
0.2041	408	0.4515	535	0.7034	418	0.9073	169
0.2598	458	0.5161	520				

by unweighted least-squares polynomial regression to the equation

$$H^E/\mathrm{J\ mol^{-1}} = x_1(1 - x_1)\sum_{i=0}^{k} A_i(2x_1 - 1)^i \qquad (1)$$

The coefficients A_i and the standard deviations $\sigma(H^E)$

$$\sigma(H^E) = |\sum(H^E_{\mathrm{calcd}} - H^E_{\mathrm{exptl}})^2/(N - n)|^{1/2} \qquad (2)$$

where N is the number of direct experimental values and n the number of coefficients of the polynomial, are summarized in Table III. For all the mixtures $\sigma(H^E)/H^E(\mathrm{max}) < 0.01$, where $H^E(\mathrm{max})$ denotes the maximum value of the H^E with respect to x_1. The direct experimental results and the curves calculated from eq 1 are represented graphically in Figures 1–4. No literature data exist for comparison.

For all the systems studied H^E is positive over the whole concentration range. Comparing H^E of dimethyl carbonate, CH_3-O-CO-O-CH_3, with H^E of other structurally related molecules, viz., methyl acetate, CH_3-O-CO-CH_3, and acetone, CH_3-CO-CH_3, with the same solvents, normal alkanes, cyclohexane, benzene, and CCl_4, we note the typical behavior of polar + nonpolar or polar + polarizable solvent mixtures. With saturated alkanes H^E is large, ca. 1900 J mol^{-1} at $x_1 = 0.5$ for dimethyl carbonate + hexane, whereas H^E of acetone or methyl acetate + hexane is only ca. 1600 J mol^{-1}. The difference would be even more important if we compare dimethyl carbonate with homomorphic molecules, diethyl ketone, CH_3–

Table III. Coefficients A_i in Eq 1 and Standard Deviations $\sigma(H^E)$, Eq 2, at 298.15 K for Dimethyl Carbonate (1) + Solvents (2)

solvent	A_0	A_1	A_2	A_3	$\sigma(H^E)$/ J mol^{-1}
hexane	7608.9	-375.4	1887.8	-166.7	8
heptane	7953.5	-54.7	1959.1	426.8	9
octane	8210.7	-24.5	2070.2	852.3	10
decane	8818.9	151.4	2269.1	2001.8	10
cyclohexane	7786.9	-203.4	1640.7	-1243.2	9
methylcyclohexane	7449.6	-21.0	1740.5	-698.4	7
benzene	1602.4	200.7	-3.2	-171.5	2
toluene	2046.7	327.4	135.4	-224.5	3
tetrachloromethane	2109.6	-373.4	424.5	-172.2	3

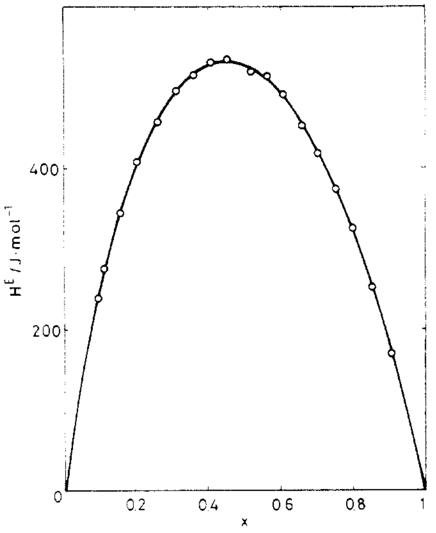

Figure 4. Excess molar enthalpy H^E for dimethyl carbonate (1) + tetrachloromethane (2) mixture versus x_1, the mole fraction of component 1. Full curve represents the smoothing eq 1 with coefficients of Table III.

CH_2-CO-CH_2-CH_3, ca. 1000 J mol^{-1}, and methyl propionate, CH_3-CH_2-CO-O-CH_3, ca. 1200 J mol^{-1} (*14*-*16*). There is no direct correlation between H^E and the molecular dipole moment: 2.88 D (acetone), 1.72 D (methyl acetate), and 0.90 D (dimethyl carbonate), all the dipole moments for the gas phase (*17*). Obviously each O atom attached to CO, while decreasing the overall electric dipole moment, increases the dissimilarity between the force fields of the polar compounds and the alkane, and hence also H^E.

With nonpolar but strongly polarizable solvents such as benzene and CCl_4 the H^E ($x_1 = 0.5$) values of dimethyl carbonate, methyl acetate, and acetone are ca. 1400–1500 J mol^{-1} smaller, due to the exothermic dipole-induced dipole interaction. For the series with the normal alkane H^E increases as the chain length of the alkane.

A quantitative treatment in terms of DISQUAC, an extended quasi-chemical group contribution method (*2*), of these results and of additional H^E measurements on diethyl carbonate (*18*), will be presented in a forthcoming paper.

Registry No. CH_3-O-CO-O-CH_3, 616-38-6; hexane, 110-54-3; heptane, 142-82-5; octane, 111-65-9; decane, 124-18-5; cyclohexane, 110-82-7; methylcyclohexane, 108-87-2; benzene, 71-43-2; toluene, 108-88-3; tetrachloromethane, 56-23-5.

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Thermodynamic Properties of Methanol from 288 to 503 K and at 8.3 MPa

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Specific heats of methanol have been measured from 393 to 503 K and at 8.3 MPa, using a high-temperature and high-pressure flow heat capacity calorimeter. These data have been supplemented with specific heats at lower temperatures, taken from the literature and corrected to 8.3 MPa, to obtain a consistent set of molar heat capacities from 288 to 503 K. The heat capacities have been fitted to a four-parameter equation and the equation has been employed to evaluate $H_T - H_{298}$ and $S_T - S_{298}$ for methanol from 298 to 503 K at 8.3 MPa.

Introduction

Methanol is a major solvent in the chemical industry, and energy crises of the past several years have increased its importance as a fuel additive and as a potential solvent in absorption type refrigerators and air conditioners. Notwithstanding this increased interest, the thermodynamic properties of methanol, especially at elevated temperatures and pressures, are sparse. Precise heat capacities of the saturated liquid have been measured from low temperatures to 325 K by Carlson (*1*), from 323 to 353 K by Hough, Mason, and Sage (*2*), and at 298

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