

Thermodynamics of Binary Mixtures Containing Organic Carbonates.

4. Liquid-Liquid Equilibria of Dimethyl Carbonate + Selected *n*-Alkanes[†]

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Liquid-liquid equilibrium (LLE) data are reported for dimethyl carbonate + *n*-decane, + *n*-dodecane, + *n*-tetradecane, or + *n*-hexadecane at atmospheric pressure, between 277 K and the upper critical temperatures. The solubility curve of pure solid *n*-hexadecane in liquid dimethyl carbonate is also presented. The coexistence curves are very asymmetrical with respect to mole fraction, the asymmetry increasing with the size of the *n*-alkane. The critical solution points vary almost linearly with the number of carbon atoms of the *n*-alkane. The data are used in the framework of regular solution theory to obtain the solubility parameter of dimethyl carbonate.

Introduction

In part 1 of this series (2), we reported excess molar enthalpies H^E for dimethyl carbonate + selected *n*-alkanes, + cyclohexane, + benzene, + toluene, or + tetrachloromethane. H^E for diethyl carbonate with the same solvents have been published previously (3). In parts 2 and 3, the isothermal vapor-liquid equilibria (VLE) for both carbonates with cyclohexane, benzene, or tetrachloromethane were reported (4, 5). In continuation of this systematic study on the thermodynamic properties of binary mixtures containing organic carbonates, we present the liquid-liquid equilibrium (LLE) diagrams of dimethyl carbonate + *n*-decane, + *n*-dodecane, + *n*-tetradecane, or + *n*-hexadecane. We have also measured the solubility curve of solid *n*-hexadecane in dimethyl carbonate.

Experimental Section

Materials. Dimethyl carbonate (purum, >99 mol %), *n*-decane (purum, >99 mol %), and *n*-tetradecane (puriss, >99 mol %), from Fluka, were stored over molecular sieves (Union Carbide Type 4A from Fluka). *n*-Dodecane and *n*-hexadecane (both >99 mol %) were obtained from Aldrich (packaged under nitrogen in Sure/Seal bottles). All these chemicals were used without further purification. The densities ρ and refractive indexes n_D (Table I) were in good agreement with published values (6-8). Water contents, determined by the Karl-Fisher method, are 0.33, 0.15, 0.02, 0.19, and 0.25 mol % or 0.092, 0.027, 0.003, 0.025, and 0.029 vol % for dimethyl carbonate, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane, respectively. Conversion to molar quantities is based on the relative atomic mass table of 1975, issued by IUPAC.

Apparatus and Procedure. The coexistence curves of the binary mixtures were determined visually (9-12), with 0.9-cm-i.d. and about 4-cm-length Pyrex tubes. Mixtures were prepared by weight, with weighings accurate to 0.0001 g.

The samples were placed in a thermostated bath a few hundredths of degree above the expected temperature, and the appearance of a second phase upon cooling was noted. The separation temperatures were reproducible to ± 0.03 K.

Table I. Refractive Index n_D and Density of Pure Compounds

compound	$n_D(298.15 \text{ K})$		$\rho(298.15 \text{ K})/(\text{kg m}^{-3})$	
	this study	lit.	this study	lit.
dimethyl carbonate	1.3665	1.3687 ^a	1063.4	1069.4 ^a
<i>n</i> -decane	1.4097	1.40967 ^b	726.47	726.35 ^b
<i>n</i> -dodecane	1.4196	1.41952 ^b	745.27	745.18 ^b
<i>n</i> -tetradecane	1.4270	1.42685 ^c	759.22	759.17 ^c
<i>n</i> -hexadecane	1.4326	1.43250 ^c	770.07	769.96 ^c

^a Reference 6 (293.15 K). ^b Reference 7. ^c Reference 8.

Table II. Coexistence Temperatures T for Dimethyl Carbonate (1) + *n*-Alkanes (2) at Atmospheric Pressure as a Function of Mole Fraction x_1

x_1	T/K	x_1	T/K	x_1	T/K
<i>n</i> -Decane					
0.4100	281.16	0.5955	286.35	0.7879	285.91
0.4683	283.57	0.6288	286.48	0.8180	284.97
0.4853	284.16	0.6719	286.60	0.8383	284.13
0.5126	284.88	0.6919	286.55	0.8505	283.23
0.5452	285.70	0.7026	286.60	0.8716	281.27
0.5641	285.94	0.7547	286.41		
0.5777	286.08	0.7841	285.92		
<i>n</i> -Dodecane					
0.3225	280.09	0.5652	295.94	0.7811	297.57
0.3681	284.54	0.6084	296.93	0.8001	297.41
0.4092	287.87	0.6294	297.15	0.8299	296.95
0.4434	290.16	0.6744	297.56	0.8395	296.69
0.4659	291.23	0.6858	297.70	0.8460	296.43
0.4931	292.77	0.7055	297.84	0.8870	293.56
0.5213	294.37	0.7211	297.84	0.8966	291.96
0.5503	295.45	0.7387	297.85	0.9284	285.48
<i>n</i> -Tetradecane					
0.2910	279.85	0.5882	304.87	0.8576	306.84
0.3163	283.09	0.6081	305.57	0.8882	305.05
0.3438	286.87	0.6622	306.72	0.9047	303.16
0.3670	288.88	0.6900	307.11	0.9191	301.41
0.4108	292.82	0.7141	307.41	0.9296	299.26
0.4773	298.52	0.7665	307.73	0.9339	298.25
0.5008	300.18	0.8044	307.65	0.9558	290.00
0.5615	303.47	0.8220	307.50	0.9743	277.13
<i>n</i> -Hexadecane					
0.0000	291.15 ^a	0.4748	303.28	0.8105	316.21
0.0908	289.92 ^a	0.4906	304.67	0.8338	316.13
0.1491	289.00 ^a	0.4944	304.94	0.8579	315.96
0.1666	288.74 ^a	0.5218	306.98	0.8737	315.61
0.1801	288.59 ^a	0.5546	309.52	0.8994	314.37
0.1973	288.21 ^a	0.6184	312.72	0.9066	313.46
0.2361	287.74 ^a	0.6352	313.49	0.9116	313.16
0.2753	286.92 ^a	0.6597	314.41	0.9157	312.67
0.2930	286.50 ^a	0.6707	314.59	0.9288	310.90
0.3209	286.12	0.6991	315.40	0.9513	304.36
0.3597	291.22	0.7274	315.92	0.9714	292.72
0.3944	295.56	0.7660	316.16		
0.4150	297.87	0.7902	316.24		

^a Solid-liquid equilibria.

The temperature was measured with an accuracy of ± 0.05 K, by using a digital thermometer tested against a calibrated Hewlett-Packard Model 2804A quartz thermometer.

[†] This paper is a contribution to the Tom Project (1).

Table III. Number of Direct Experimental Values, N , Coefficients, a_i , in Equation 1 and Standard Deviations $\sigma(T)$, Equation 2, for Dimethyl Carbonate (1) + n -Alkane (2)

n -alkane	N	a_0	a_1	a_2	a_3	a_4	a_5	$\sigma(T)/K$
n -decane	19	286.62	-7.771	-47.695	0.6864			0.06
n -dodecane	24	297.82	-7.776	-53.801	0.7379			0.13
n -tetradecane	24	307.61	-6.225	-57.252	0.7825			0.42
n -hexadecane	29	316.21	-4.951	-78.662	101.217	-119.696	0.8137	0.43

Table IV. Upper Critical Solution Temperature T^c and Composition x_1^c for Dimethyl Carbonate (1) + n -Alkane (2) Systems

n -alkane	T^c/K	x_1^c	n -alkane	T^c/K	x_1^c
n -decane	286.62	0.6864	n -tetradecane	307.61	0.7825
n -dodecane	297.82	0.7379	n -hexadecane	316.21	0.8137

Results and Discussion

The transition temperatures are plotted in Figure 1 versus x_1 , the mole fraction, and in Figure 2 versus Φ_1 , the volume fraction, of dimethyl carbonate. Table II gives the numerical results.

Experimental data were fitted by a least-squares method, all the points equally weighted, to the equation

$$T_{\text{calc}} = \sum_{i=0}^{n-2} a_i \left[\frac{x_1/x_1^c - x_2/x_2^c}{x_1/x_1^c + x_2/x_2^c} \right]^{2i}; \quad a_0 = T^c, \quad a_n = x_1^c \quad (1)$$

where n is the number of adjustable coefficients, a_i , N is the number of direct experimental values, and $\sigma(T)$ is the standard deviation (Table III)

$$\sigma(T) = [\sum (T_{\text{calc}} - T)^2 / (N - n)]^{1/2} \quad (2)$$

The critical temperatures and compositions, listed in Table IV, vary almost linearly with the number of carbon atoms of the n -alkanes.

We examined experimentally the influence of adding small amounts of water, the main impurity in our systems, on T^c . As expected, water being more soluble in one of the mixture components (dimethyl carbonate) than in the other (alkane), T^c increases with the volume of water added (12-15). This increase is almost linear. So, a 0.1 vol % amount of water, the maximum amount present in the investigated mixtures, increases T^c about 1.95 K in the dimethyl carbonate (1) + n -decane (2) system and 1.85, 1.75, and 1.65 K in the dimethyl carbonate (1) + n -dodecane (2), dimethyl carbonate (1) + n -tetradecane (2), and dimethyl carbonate (1) + n -hexadecane (2) mixtures, respectively.

The solubility of solid n -hexadecane in liquid dimethyl carbonate is well represented by the ideal solubility equation

$$\ln x_2 = -\frac{\Delta H_f}{R} [1/T - 1/T_f] \quad (3)$$

where $T_f = 291.15$ K and $\Delta H_f = 53.371$ kJ mol⁻¹ are the experimental temperature and the molar enthalpy of fusion (β) of n -hexadecane. The good agreement between experimental and calculated values indicates (Figure 1) that the activity coefficient of n -hexadecane is close to 1 at $x_1 < 0.4$ as the result of intermolecular enthalpy-combinatorial entropy compensation.

We have used the experimental T^c data to obtain the solubility parameter of dimethyl carbonate, δ_1 , using Hildebrand's formula (16)

$$RT^c = \frac{2x_1^c x_2^c V_1^2 V_2^2 (\delta_1 - \delta_2)^2}{(x_1^c V_1 - x_2^c V_2)^3} \quad (4)$$

where δ_2 is the solubility parameter of the n -alkane. The latter has been evaluated from

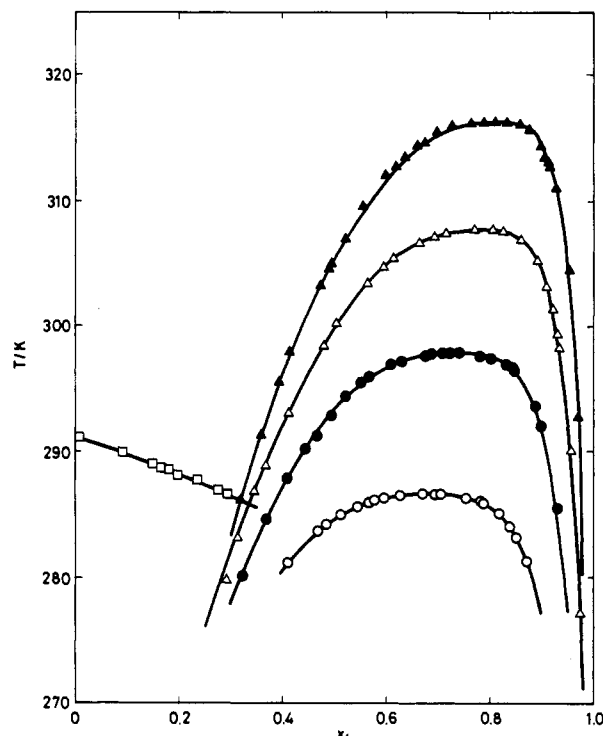


Figure 1. Coexistence curves (temperature T versus x_1 , the mole fraction of dimethyl carbonate) of dimethyl carbonate (1) + n -alkanes (2): O, n -decane; ●, n -dodecane; Δ, n -tetradecane; ▲, n -hexadecane. Full lines: calculated from eq 1. The solubility of n -hexadecane is represented by □, with full lines calculated from eq 3.

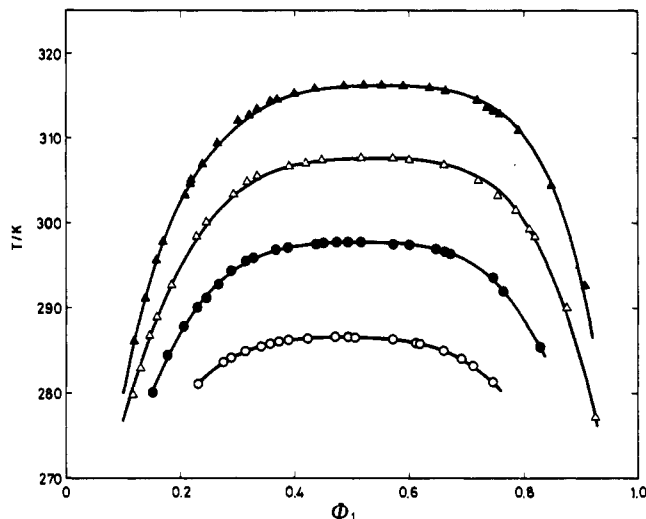


Figure 2. Coexistence curves (temperature T versus Φ_1 , the volume fraction of dimethyl carbonate) of dimethyl carbonate (1) + n -alkanes (2): O, n -decane; ●, n -dodecane; Δ, n -tetradecane; ▲, n -hexadecane. Full lines: calculated from eq 1.

$$\delta_2 = \left(\frac{\Delta H_v - RT}{V} \right)^{1/2} \quad (5)$$

where ΔH_v is the molar enthalpy of vaporization at 298.15 K (17) and V the molar volume. The values for δ_1 (J^{1/2} cm^{-3/2}) obtained are 21.65, 21.62, 21.56, and 21.50 for dimethyl car-

bonate + *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane, respectively. The value found in the literature is $\delta_1 = 20 \text{ J}^{1/2} \text{ cm}^{-3/2}$ (6).

Glossary

<i>a</i>	coefficients in eq 1
<i>x</i>	mole fraction
<i>H</i>	molar enthalpy, J mol^{-1}
<i>T</i>	temperature, K
<i>R</i>	molar gas constant, $\text{J K}^{-1} \text{ mol}^{-1}$
<i>V</i>	molar volume, $\text{m}^3 \text{ mol}^{-1}$

Greek Letters

δ	solubility parameter, $\text{J}^{1/2} \text{ cm}^{-3/2}$
Φ	volume fraction, $\Phi_i = x_i V_i / (x_1 V_1 + x_2 V_2)$ (<i>i</i> = 1, 2)
σ	standard deviation, eq 2

Subscripts

<i>i</i>	property of component <i>i</i> (<i>i</i> = 1, 2)
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Superscripts

<i>E</i>	excess property
<i>c</i>	critical point property

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Received for review March 29, 1990. Revised August 24, 1990. Accepted November 25, 1990.

Transport Properties in the Molten Binary System $\text{CH}_3\text{NH}_3\text{Cl}-\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$

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As the simplest case in a series of molten binary systems containing alkylammonium chlorides, the system $\text{CH}_3\text{NH}_3\text{Cl}-\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$ [(MA)Cl-(EA)Cl] was investigated. The liquidus curve is of the simple eutectic type, with $T_e = 347 \pm 3 \text{ K}$ and eutectic composition of 0.710 in ethylammonium chloride. Densities, conductivities, and viscosities of molten mixtures were measured in the whole composition range, for $0 < x_2 < 1$. From the results obtained, one can conclude that the behavior of the system is not ideal. Owing to its interesting transport properties, the eutectic mixture can be proposed as a convenient molten electrolyte above 353 K.

Introduction

In a series of previous papers, the transport properties of binary molten mixtures formed with alkylammonium halides (1, 2) and sodium and potassium acetates (3) were investigated.

The interest of these works lays in the fact that salts formed with organic ions, alkylammonium in particular, can find wide application in electrochemistry, not only as supporting electrolytes in nonaqueous solvent systems but also in several electrochemical methods of analytical and industrial importance.

However, with physicochemical information about this class of molten systems being still fragmentary [see, e.g., a recent review (4)], it seemed worthy to extend the investigation to

further systems containing alkylammonium chlorides. It is well-known that the formation of a binary mixture of salts with organic ions usually involves changes in molar volumes, conductivities, and viscosities. The determination of these properties could allow one to evaluate the influence of ion size, acid-base characteristics, and intermolecular interactions on the structure of the melts in the mixture.

In this paper, the molar volumes, conductivities, and viscosities of nine mixtures in one of the simplest systems of this type, viz., the binary formed with $\text{CH}_3\text{NH}_3\text{Cl}$ [(MA)Cl] and $\text{C}_2\text{H}_5\text{NH}_3\text{Cl}$ [(EA)Cl], are reported and discussed in connection with the phase diagram of the system.

Experimental Section

Materials. The salts were obtained by neutralization of the amines (both Fluka, purum) with HCl (Polskie Odczynniki Chemiczne (P.O.Ch.), Gliwice, Poland; czysty). After evaporation of the aqueous solutions, the salts were recrystallized at least twice from ethanol (P.O.Ch.; absolutny); their melting point was checked by microscopic observation with a Boettius type apparatus. The pure salts, as well as the binary mixtures, prepared by melting the preweighed components under nitrogen, were stored under vacuum before measurements.

The salts employed for determining the phase diagram were reagent grade chemicals supplied by Aldrich. They were kept in a vacuum oven for 48 h at $\sim 80 \text{ }^\circ\text{C}$ before use.