

Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Dimethyl Carbonate with Methanol, Chloroform, Carbon Tetrachloride, Cyclohexane, and Dichloromethane in the Temperature Interval (298.15–308.15) K

Tejraj M. Aminabhavi* and Kamalika Banerjee

Department of Chemistry, Karnatak University, Dharwad-580 003, India

Experimental values of density, viscosity, and refractive index at (298.15, 303.15, and 308.15) K and the speed of sound data at 298.15 K for the binary mixtures of dimethyl carbonate with methanol, chloroform, carbon tetrachloride, cyclohexane, and dichloromethane are presented over the whole range of mixture composition. From these data, excess molar volume, deviations in viscosity, speed of sound, isentropic compressibility, and Lorenz–Lorentz molar refractivity have been calculated. These results are fit to the Redlich–Kister type polynomial equation of the third degree to derive the binary coefficients. The standard error values are estimated between the calculated and experimental data points.

Introduction

Dimethyl carbonate (DMC) is a versatile solvent used in the synthesis of pharmaceuticals (Martindale, 1989) and agrochemicals and as a solvent for many synthetic and natural resins as well as polymers (The Merck Index, 1989). A fundamental understanding of the mixing behavior of DMC with common solvents such as methanol, chloroform, carbon tetrachloride, cyclohexane, or dichloromethane is therefore important from a technical and engineering viewpoint. A survey of the literature showed that several papers have been published on the binary mixtures of DMC (Comelli et al., 1996; Comelli and Francesconi, 1994a,b; Francesconi and Comelli, 1994, 1995a,b, 1996). However, none of these papers are concerned with the mixtures studied in this paper. Herein, we report the results of density, ρ , viscosity, η , and refractive index, n_D , with the sodium D-line at 298.15, 303.15, and 308.15 K for the binary mixtures of DMC with methanol, chloroform, carbon tetrachloride, cyclohexane, and dichloromethane over the entire range of mixture composition. The values of speed of sound, u , are measured only at 298.15 K. Using the density, viscosity, and speed of sound data, excess molar volumes, V^E , deviations in viscosity, $\Delta\eta$, and deviations in speed of sound data, Δu , have been, respectively, calculated on the basis of the mole fraction, x_1 , of DMC. Also, from the speed of sound and refractive index data, deviations in isentropic compressibility, Δk_S , and Lorenz–Lorentz molar refractivity, ΔR , have been computed using volume fraction, ϕ_1 , of DMC. These results are graphically presented and compared with the values calculated from the Redlich–Kister type polynomial equation (Redlich and Kister, 1948). The standard deviations for the least-squares fits are also presented for all the binary mixtures and at all the temperatures.

Experimental Section

Materials. High-purity spectroscopic and analytical grade samples of dimethyl carbonate, methanol, chloro-

form, carbon tetrachloride, and cyclohexane were procured from s.d Fine Chemicals Ltd., Mumbai, India. Dichloromethane of HPLC grade was purchased from Qualigens, Mumbai. All the samples were used without further purification because their purities (except dimethyl carbonate) exceeded 99% as tested by gas chromatography (HP 6890 series) using a flame ionization detector with a packed column (see Table 1). Experimental values of ρ and n_D of the pure liquids are compared in Table 1 at 298.15 K, and these values agree well with the published results. Mixtures were prepared by mass in specially designed glass-stoppered bottles, and the properties were measured on the same day. An electronic Mettler balance, model AE 240 (Switzerland), with a precision of ± 0.01 mg was used for mass measurements. The error in mole fraction is around ± 0.0002 .

Measurements. Densities of single liquids and their mixtures were measured using a pycnometer having a bulb volume of 15 cm³ and a capillary bore with an internal diameter of 1 mm. Density values are accurate to ± 0.0002 g·cm⁻³.

Refractive indices for the sodium D-line were measured using a thermostatically controlled Abbe refractometer (Atago 3T, made in Japan). A minimum of three independent readings were taken for each composition. The refractive index values are accurate to ± 0.0001 units. Calibration procedures of the pycnometer and refractometer are the same as given earlier (Aminabhavi et al., 1993; Aminabhavi and Bindu, 1994; Aralaguppi et al., 1991).

Viscosities were measured using a Schott-Gerate viscometer, model AVS 350. The unit performs automated measurements of the flow-through times in capillary viscometers. Efflux times were determined on a digital display at an accuracy of ± 0.01 s. An AVS/S measuring stand was used for optoelectronic sensing of the meniscus. The LED in the upper part of the measuring stand generates light in the near-infrared range, which is transmitted through a glass fiber cable to the measuring levels. The light beam passes through viscometer and reaches the input end of another light guide cable on the other side,

* Author for correspondence: Fax, 91-836-747884; E-mail, rrist@bgl.vsnl.net.in.

Table 1. Comparison of Experimental Densities (ρ) and Refractive Indices (n_D) of Pure Liquids with the Literature Values at 298.15 K

liquid (mol % purity)	molar volume/ (cm ³ /mol)	ρ (g·cm ⁻³)		n_D	
		exptl	lit.	exptl	lit.
dimethyl carbonate (98.0)	84.8	1.0622	1.0633 ^a	1.3684	1.3671 ^a
methanol (99.2)	40.8	0.7860	0.7868 ^b	1.3282	1.3265 ^b
chloroform (99.0)	80.9	1.4758	1.4760 ^c	1.4434	1.4432 ^d
carbon tetrachloride (99.7)	97.1	1.5840	1.5844 ^e	1.4579	1.4574 ^e
cyclohexane (99.7)	109.0	0.7724	0.7739 ^f	1.4249	1.4235 ^f
dichloromethane (99.8)	64.5	1.3163	1.3161 ^g	1.4228	1.4212 ^h

^a Comelli and Francesconi (1994b). ^b Nikam et al. (1995). ^c Asfour and Dullien (1981). ^d Aminabhavi and Patil (1998). ^e Riddick et al. (1986). ^f Fuente et al. (1995). ^g Comelli and Francesconi (1995). ^h Zurita et al. (1986).

which conducts light to a receiver in the upper part of the measuring stand. When liquid meniscus passes through the measuring level, the light beam is darkened briefly by the optical lens effect of the meniscus and thereafter intensified for a brief period. This fluctuation of light beam produces a measuring signal that can be evaluated precisely.

The temperature of the bath (Schott Geräte, model CT 050/2) was maintained constant within ± 0.01 K. The estimated error in viscosity measurement was ± 0.001 mPa·s. Approximately 5 cm³ volume of the liquid was taken in the viscometer. The liquid was allowed to equilibrate to the desired bath temperature ranging from 7 to 10 min depending upon the viscosity of the liquid. The viscosity of the liquid/mixture was calculated using

$$\eta = t \cdot k \cdot \rho \quad (1)$$

where k is viscometer constant (0.010 35 mm²/s²), ρ is density of the liquid, and t is the efflux time in seconds. The viscometer constant k was determined by using comparative measurements with the reference viscometers, of which the constants were determined from the Physikalisch-Technischen Bundesanstalt, D-38116 Braunschweig. The instrument constant is valid for liquids with a surface tension of 20 to 30 mN/m and an acceleration of the fall of 9.8125 m/s². For temperatures up to 373.15 K, it is not necessary to pay attention to the heat expansion of the viscometer.

The speed of sound values were measured using a variable path single-crystal interferometer (Mittal Enterprises, model M-84, New Delhi) as described earlier by Aralaguppi et al. (1991). The interferometer was used at a frequency of 4 kHz and was calibrated using water and benzene. The speed of sound values are accurate to ± 2 m·s⁻¹. From the speed of sound data, the values of isotropic compressibilities, k_S , have been calculated as $k_S = 1/u^2 \rho$. This relation has been used earlier by a large number of investigators (Aralaguppi et al., 1991; Afanasyev and Zyatkova, 1996).

In all the property measurements except viscosity, an INSREF model 016 AP thermostat was used and the desired temperature in this thermostat was controlled to ± 0.01 K. The results of ρ , η , n_D , and u compiled in Table 2 represent the averages of three independent measurements for each composition of the mixture.

The Julabo immersion cooler (FT 200), Julabo Labortechnik GmbH, Germany, was employed to cool the water bath. This unit was installed at the intake of a heating circulator to draw the heat away from the circulating bath liquid. The immersion probe was connected to the instrument with a flexible and insulated tube. To prevent the immersion probe from icing, it was completely immersed into the bath liquid.

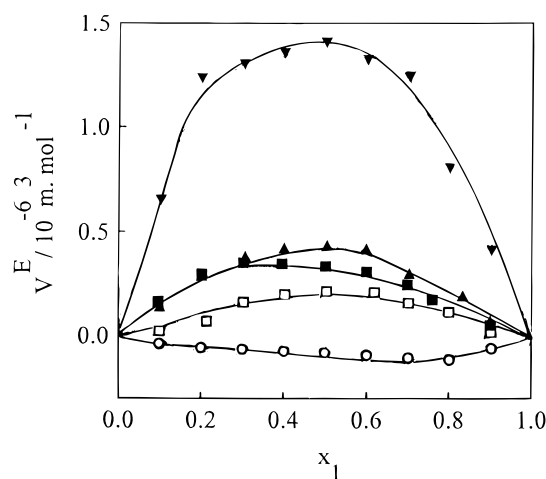


Figure 1. Plots of excess molar volume vs mole fraction of dimethyl carbonate (1) at 298.15 K for the mixtures of dimethyl carbonate with (○) methanol, (□) chloroform, (▲) carbon tetrachloride, (▼) cyclohexane, and (■) dichloromethane.

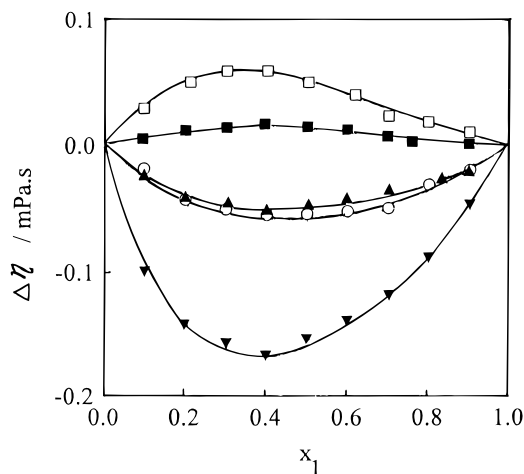


Figure 2. Plots of deviation in viscosity vs mole fraction of dimethyl carbonate (1) at 298.15 K for the same mixtures given in Figure 1.

Results and Discussion

From the results of densities given in Table 2, excess molar volumes have been calculated as

$$V^E = V_m - V_1 x_1 - V_2 x_2 \quad (2)$$

where V_m is the mixture molar volume, V_1 and V_2 are the molar volumes of components 1 and 2 of the mixture, and x_i represents the mole fraction of the i th component in the mixture. From the values of η , n_D , u , and k_S of the

Table 2. Experimental Values of Density (ρ), Refractive Index (n_D), Viscosity (η), and Speed of Sound (u) of the Binary Mixtures at Different Temperatures

x_1	$\rho/(\text{g}\cdot\text{cm}^{-3})$	n_D	$\eta/(\text{mPa}\cdot\text{s})$	$u/(\text{m}\cdot\text{s}^{-1})$	x_1	$\rho/(\text{g}\cdot\text{cm}^{-3})$	n_D	$\eta/(\text{mPa}\cdot\text{s})$	$u/(\text{m}\cdot\text{s}^{-1})$
Dimethyl Carbonate (1) + Methanol (2)									
298.15 K									
0.0000	0.7860	1.3282	0.497	1080	0.6002	0.9966	1.3584	0.468	1176
0.0989	0.8381	1.3353	0.482	1110	0.7016	1.0168	1.3613	0.474	1177
0.2009	0.8819	1.3416	0.462	1130	0.8015	1.0344	1.3636	0.496	1177
0.3008	0.9176	1.3471	0.458	1156	0.9028	1.0494	1.3654	0.511	1177
0.4008	0.9479	1.3514	0.457	1166	1.0000	1.0622	1.3684	0.534	1178
0.5000	0.9738	1.3554	0.462	1175					
303.15 K									
0.0000	0.7814	1.3272	0.463		0.6002	0.9909	1.3563	0.439	
0.0989	0.8331	1.3332	0.443		0.7016	1.0105	1.3587	0.447	
0.2009	0.8765	1.3386	0.432		0.8015	1.0287	1.3614	0.459	
0.3008	0.9102	1.3499	0.427		0.9028	1.0428	1.3630	0.480	
0.4008	0.9422	1.3493	0.429		1.0000	1.0566	1.3648	0.503	
0.5000	0.9676	1.3532	0.459						
308.15 K									
0.0000	0.7755	1.3234	0.432		0.6002	0.9846	1.3534	0.421	
0.0989	0.8251	1.3309	0.415		0.7016	1.0024	1.3562	0.419	
0.2009	0.8681	1.3370	0.406		0.8015	1.0219	1.3588	0.433	
0.3008	0.9040	1.3426	0.404		0.9028	1.0363	1.3608	0.456	
0.4008	0.9362	1.3469	0.403		1.0000	1.0500	1.3628	0.474	
0.5000	0.9603	1.3514	0.406						
Dimethyl Carbonate (1) + Chloroform (2)									
298.15 K									
0.0000	1.4758	1.4434	0.495	985	0.6187	1.2122	1.3880	0.559	1128
0.0987	1.4328	1.4289	0.528	990	0.7021	1.1791	1.3824	0.546	1147
0.2134	1.3831	1.4192	0.553	999	0.7996	1.1404	1.3762	0.545	1152
0.3031	1.3436	1.4125	0.566	1000	0.9013	1.1011	1.3686	0.541	1162
0.4027	1.3014	1.4042	0.570	1028	1.0000	1.0622	1.3684	0.534	1178
0.5031	1.2596	1.3968	0.565	1052					
303.15 K									
0.0000	1.4664	1.4402	0.471		0.6187	1.2049	1.3909	0.523	
0.0987	1.4240	1.4316	0.501		0.7021	1.1721	1.3847	0.514	
0.2134	1.3747	1.4226	0.525		0.7996	1.1333	1.3784	0.513	
0.3031	1.3360	1.4150	0.530		0.9013	1.0944	1.3709	0.509	
0.4027	1.2941	1.4071	0.536		1.0000	1.0566	1.3648	0.503	
0.5031	1.2524	1.3998	0.531						
308.15 K									
0.0000	1.4570	1.4368	0.452		0.6187	1.1964	1.3880	0.493	
0.0987	1.4149	1.4289	0.475		0.7021	1.1633	1.3824	0.484	
0.2134	1.3660	1.4192	0.494		0.7996	1.1249	1.3762	0.480	
0.3031	1.3278	1.4125	0.504		0.9013	1.0876	1.3686	0.480	
0.4027	1.2860	1.4042	0.507		1.0000	1.0500	1.3628	0.474	
0.5031	1.2432	1.3968	0.502						
Dimethyl Carbonate (1) + Carbon Tetrachloride (2)									
298.15 K									
0.0000	1.5840	1.4579	0.821	918	0.5982	1.2830	1.4036	0.608	1035
0.0994	1.5359	1.4492	0.770	932	0.7031	1.2287	1.3945	0.585	1069
0.2010	1.4855	1.4398	0.724	947	0.8330	1.1571	1.3824	0.557	1110
0.3063	1.4329	1.4306	0.689	965	0.8997	1.1203	1.3763	0.543	1144
0.4005	1.3854	1.4218	0.656	986	1.0000	1.0622	1.3684	0.534	1178
0.5036	1.3325	1.4126	0.631	1010					
303.15 K									
0.0000	1.5748	1.4552	0.768		0.5982	1.2754	1.4008	0.572	
0.0994	1.5268	1.4462	0.719		0.7031	1.2207	1.3918	0.548	
0.2010	1.4768	1.4366	0.680		0.8330	1.1506	1.3801	0.520	
0.3063	1.4246	1.4276	0.646		0.8997	1.1134	1.3741	0.511	
0.4005	1.3776	1.4192	0.614		1.0000	1.0566	1.3648	0.503	
0.5036	1.3248	1.4100	0.588						
308.15 K									
0.0000	1.5650	1.4512	0.717		0.5982	1.2674	1.3982	0.536	
0.0994	1.5160	1.4432	0.676		0.7031	1.2120	1.3892	0.516	
0.2010	1.4671	1.4335	0.633		0.8330	1.1430	1.3778	0.493	
0.3063	1.4151	1.4245	0.604		0.8997	1.1064	1.3716	0.481	
0.4005	1.3685	1.4160	0.575		1.0000	1.0500	1.3628	0.474	
0.5036	1.3160	1.4066	0.551						

Table 2. Continued

Dimethyl Carbonate (1) + Cyclohexane (2)									
298.15 K									
0.0000	0.7724	1.4249	0.814	1249	0.5996	0.9157	1.3873	0.507	1170
0.1010	0.7908	1.4186	0.686	1220	0.7039	0.9469	1.3822	0.499	1168
0.1993	0.8096	1.4115	0.616	1208	0.8005	0.9831	1.3771	0.502	1171
0.3026	0.8349	1.4048	0.572	1186	0.9028	1.0221	1.3726	0.515	1175
0.3999	0.8596	1.3988	0.535	1178	1.0000	1.0622	1.3684	0.534	1178
0.5000	0.8864	1.3927	0.520	1174					
303.15 K									
0.0000	0.7685	1.4216	0.749		0.5996	0.9097	1.3855	0.475	
0.1010	0.7861	1.4147	0.636		0.7039	0.9438	1.3794	0.470	
0.1993	0.8062	1.4079	0.573		0.8005	0.9772	1.3745	0.472	
0.3026	0.8298	1.4018	0.533		0.9028	1.0158	1.3697	0.491	
0.3999	0.8541	1.3961	0.500		1.0000	1.0566	1.3648	0.503	
0.5000	0.8807	1.3901	0.485						
308.15 K									
0.0000	0.7640	1.4201	0.692		0.5996	0.9032	1.3823	0.445	
0.1010	0.7801	1.4125	0.590		0.7039	0.9377	1.3764	0.442	
0.1993	0.8010	1.4063	0.535		0.8005	0.9695	1.3723	0.444	
0.3026	0.8245	1.3999	0.498		0.9031	1.0093	1.3672	0.457	
0.3999	0.8474	1.3946	0.463		1.0000	1.0500	1.3628	0.474	
0.5000	0.8754	1.3874	0.455						
Dimethyl Carbonate (1) + Dichloromethane (2)									
298.15 K									
0.0000	1.3163	1.4228	0.380	1035	0.5996	1.1432	1.3829	0.485	1105
0.0957	1.2821	1.4141	0.400	1050	0.6992	1.1214	1.3788	0.495	1110
0.2018	1.2475	1.4049	0.423	1072	0.7599	1.1090	1.3760	0.500	1125
0.3029	1.2179	1.3980	0.441	1080	0.9005	1.0812	1.3713	0.520	1145
0.3958	1.1930	1.3930	0.458	1085	1.0000	1.0622	1.3684	0.534	1178
0.5009	1.1665	1.3873	0.472	1096					
303.15 K									
0.0000	1.3064	1.4198	0.369		0.5996	1.1363	1.3813	0.461	
0.0957	1.2736	1.4111	0.384		0.6992	1.1145	1.3771	0.470	
0.2018	1.2402	1.4036	0.400		0.7599	1.1020	1.3740	0.478	
0.3029	1.2109	1.3967	0.419		0.9005	1.0747	1.3691	0.490	
0.3958	1.1859	1.3914	0.431		1.0000	1.0566	1.3648	0.503	
0.5009	1.1592	1.3860	0.447						
308.15 K									
0.0000	1.2972	1.4171	0.362		0.5996	1.1291	1.3781	0.430	
0.0957	1.2649	1.4082	0.374		0.6992	1.1077	1.3740	0.440	
0.2018	1.2317	1.3999	0.385		0.7599	1.0950	1.3706	0.448	
0.3029	1.2028	1.3940	0.399		0.9005	1.0676	1.3667	0.461	
0.3958	1.1780	1.3887	0.409		1.0000	1.0500	1.3628	0.474	
0.5009	1.1513	1.3830	0.420						

individual components as well as of the binary mixtures, $\Delta\eta$, ΔR , Δu , and Δk_S have been calculated from

$$\Delta Y = Y_m - Y_1 C_1 - Y_2 C_2 \quad (3)$$

For calculating $\Delta\eta$ and Δu , we have used mole fraction, x_i , for C_i . Similarly, following the conventional practice in the literature (Aralaguppi et al., 1991), to compute ΔR and Δk_S , the volume fraction, $\phi_i [(x_i V_i)/(\sum x_i V_i)]$, was used.

Each set of functions computed from eqs 2 and 3 has been fit to the Redlich and Kister (1948) type polynomial equation

$$V^E \text{ (or } \Delta Y) = C_1 C_2 \sum_{j=1}^{k=3} A_{j-1} (C_2 - C_1)^{j-1} \quad (4)$$

to estimate the parameter values A_0 , A_1 , and A_2 by the method of least squares using the Marquardt algorithm (1963). It was found that the best fits were obtained for the solution of eq 4 with only three adjustable parameters for all the functions.

The standard deviations, σ , between the fitted quantities (eq 4) and the computed quantities (eqs 2 and 3) have been

calculated using

$$\sigma = \left(\frac{\sum (V_{\text{cal}}^E \text{ (or } \Delta Y_{\text{cal}}) - V_{\text{obs}}^E \text{ (or } \Delta Y_{\text{obs}}))^2}{(n - m)} \right)^{1/2} \quad (5)$$

where n represents the number of data points and m the number of coefficients. The fitted parameter values along with the standard deviations are presented in Table 3. Smoothed curves of the various quantities, viz., V^E , $\Delta\eta$, ΔR , Δu , and Δk_S vs mixture compositions as presented respectively in Figures 1 to 5, have been calculated from eq 4, while the points represent those calculated from eqs 2 and 3.

Excess molar volumes of the binary mixtures displayed in Figure 1 at 298.15 K are positive for all the mixtures except DMC + methanol. The positive V^E values follow the sequence cyclohexane > carbon tetrachloride > dichloromethane > chloroform. This trend is not consistent with the molar volumes of the second components of the mixture. An extremely large value of V^E observed for DMC + cyclohexane may be attributed to the weak dispersion type interactions when compared to other mixtures. On the other hand, the negative V^E values exhibited by the DMC + methanol mixture is attributed to specific interactions of the H-bond type. For the remaining mixtures, the

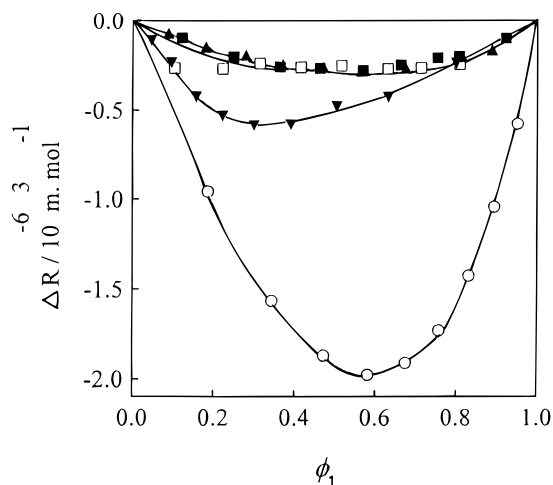


Figure 3. Plots of deviation in Lorenz-Lorentz molar refractivity vs volume fraction of dimethyl carbonate (1) at 298.15 K for the same mixtures given in Figure 1.

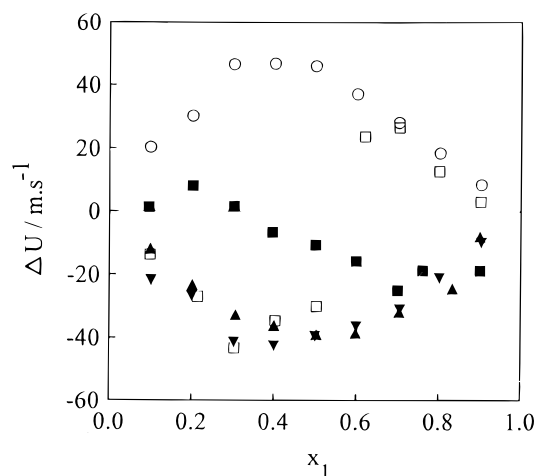


Figure 4. Deviation in speed of sound vs mole fraction of dimethyl carbonate (1) at 298.15 K for the same mixtures given in Figure 1. The solid curves are not drawn to avoid intermixing.

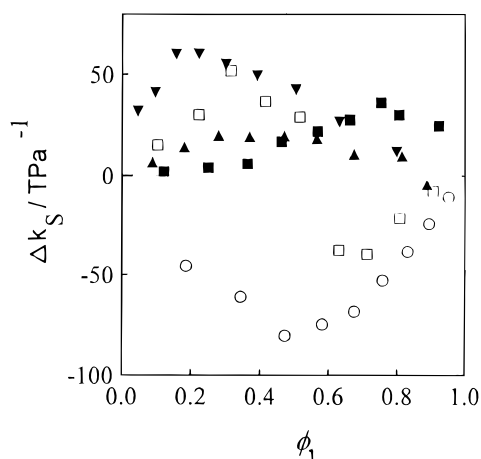


Figure 5. Deviation in isentropic compressibility vs volume fraction of dimethyl carbonate (1) at 298.15 K for the same mixtures as given in Figure 1. The solid curves are not drawn to avoid intermixing.

values are slightly positive over the entire scale of composition.

The plots of $\Delta\eta$ vs x_1 at 298.15 K are displayed in Figure 2. For DMC + chloroform, or + dichloromethane, the $\Delta\eta$

Table 3. Derived Parameters of Excess Functions for Mixtures

function	temp/K	A_0	A_1	A_2	σ
Dimethyl Carbonate (1) + Methanol (2)					
$V^E/10^{-6}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	298.15	-0.329	0.236	-0.492	0.007
	303.15	-0.145	0.320	-0.137	0.050
	308.15	-0.115	0.459	0.791	0.068
$\Delta\eta/(\text{mPa}\cdot\text{s})$	298.15	-0.222	-0.025	-0.012	0.003
	303.15	-0.169	-0.024	-0.181	0.009
	308.15	-0.181	-0.020	-0.063	0.004
$\Delta R/10^{-6}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	298.15	-7.61	-2.84	-1.58	0.023
	303.15	-7.30	-2.54	-1.91	0.058
	308.15	-7.41	-2.78	-1.15	0.023
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	298.15	180.2	82.7	-47.3	2.34
$\Delta k_s/(\text{TPa}^{-1})$	298.15	-310.2	-4.6	79.9	3.62
Dimethyl Carbonate (1) + Chloroform (2)					
$V^E/10^{-6}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	298.15	0.893	-0.135	-0.994	0.014
	303.15	0.857	-0.543	-0.465	0.014
	308.15	1.075	-1.028	-0.569	0.037
$\Delta\eta/(\text{mPa}\cdot\text{s})$	298.15	0.203	0.169	0.017	0.003
	308.15	0.174	0.154	0.043	0.003
	308.15	0.154	0.137	-0.013	0.003
$\Delta R/10^{-6}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	298.15	-0.915	-0.036	-2.637	0.044
	303.15	0.085	0.057	-0.188	0.014
	308.15	0.094	0.119	-0.014	0.022
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	298.15	-60.9	-287.6	55.5	15.4
$\Delta k_s/(\text{TPa}^{-1})$	298.15	58.8	-372.5	-108.8	19.1
Dimethyl Carbonate (1) + Carbon Tetrachloride (2)					
$V^E/10^{-6}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	298.15	1.74	0.434	-0.688	0.027
	303.15	1.85	0.138	-0.327	0.015
	308.15	1.98	0.254	0.156	0.027
$\Delta\eta/(\text{mPa}\cdot\text{s})$	298.15	-0.182	-0.053	-0.079	0.002
	303.15	-0.175	-0.038	-0.069	0.003
	308.15	-0.166	-0.043	-0.041	0.003
$\Delta R/10^{-6}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	298.15	-1.090	-0.341	-0.316	0.010
	303.15	-1.001	0.040	-0.088	0.011
	308.15	-0.983	-0.118	0.318	0.018
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	298.15	-157.7	5.5	32.9	2.68
$\Delta k_s/(\text{TPa}^{-1})$	298.15	79.0	-52.2	-47.1	3.37
Dimethyl Carbonate (1) + Cyclohexane (2)					
$V^E/10^{-6}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	298.15	5.67	1.25	1.59	0.117
	303.15	6.04	1.47	1.22	0.038
	308.15	6.35	1.62	2.23	0.097
$\Delta\eta/(\text{mPa}\cdot\text{s})$	298.15	-0.620	-0.282	-0.289	0.004
	303.15	-0.564	-0.259	-0.217	0.005
	308.15	-0.517	-0.220	-0.197	0.004
$\Delta R/10^{-6}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	298.15	-2.34	-0.072	0.658	0.037
	303.15	-2.04	0.072	0.277	0.021
	308.15	-2.17	-0.096	0.594	0.038
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	298.15	-163.8	-52.9	-1.50	2.60
$\Delta k_s/(\text{TPa}^{-1})$	298.15	213.2	-152.5	47.7	3.44
Dimethyl Carbonate (1) + Dichloromethane (2)					
$V^E/10^{-6}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	298.15	1.374	0.712	-0.081	0.015
	303.15	1.312	0.128	-0.096	0.005
	308.15	1.325	0.157	-0.067	0.017
$\Delta\eta/(\text{mPa}\cdot\text{s})$	298.15	0.061	0.046	-0.045	0.001
	303.15	0.046	-0.001	-0.038	0.001
	308.15	0.009	0.013	-0.011	0.001
$\Delta R/10^{-6}$ ($\text{m}^3\cdot\text{mol}^{-1}$)	298.15	-1.103	-0.138	-0.119	0.012
	303.15	-0.811	0.160	0.061	0.012
	308.15	-0.894	0.040	-0.278	0.021
$\Delta u/(\text{m}\cdot\text{s}^{-1})$	298.15	-42.7	140.4	-36.9	3.34
$\Delta k_s/(\text{TPa}^{-1})$	298.15	65.5	177.4	104.0	4.26

values are positive over the entire composition of the mixture. In case of DMC + methanol, or + carbon tetrachloride mixtures, the $\Delta\eta$ values are negative but show almost similar trends. On the other hand, the $\Delta\eta$ values for mixtures of DMC + cyclohexane are more negative than those for other mixtures, a quite opposite trend to those of V^E curves discussed before. This further supports the presence of weaker interactions.

The results of ΔR vs ϕ_1 at 298.15 K presented in Figure 3 are negative for all the mixtures. It may be noted that the deviation in molar refractivity represents the electronic perturbation induced owing to mixing of the two components in a binary mixture. Therefore, the nature of the

ΔR vs ϕ_1 curves depends on the electronic structure of the mixing components. This is clearly indicated in the case of mixtures of DMC + chloroform, + carbon tetrachloride, or + dichloromethane (all of which contain chlorine atoms) for which the ΔR vs ϕ_1 curves are quite identical. Hence, a single curve is drawn to show their dependencies. On the other hand, the ΔR for DMC + methanol shows the highest negative deviation when compared to all the other mixtures.

The plots of Δu vs x_1 at 298.15 K are displayed in Figure 4. The Δu values are positive for DMC + methanol, but for mixtures of DMC + chloroform, or + dichloromethane, the sigmoidal trends are observed. The negative values of Δu for the binary mixtures of DMC + carbon tetrachloride, or + cyclohexane, vary almost identically. The plots of Δk_S vs volume fraction, ϕ_1 , of DMC with all the liquids, i.e., methanol, chloroform, carbon tetrachloride, cyclohexane, and dichloromethane, are presented at 298.15 K in Figure 5. A large negative Δk_S is observed for DMC + methanol mixture, while for the remaining mixtures, the dependency is not very systematic as displayed. This is also suggestive of the specific interactions arising due to H-bond forces between DMC and alkanols.

Acknowledgment

The authors are grateful to Prof. V. G. Pangarkar (UDCT, Bombay) for supplying dimethyl carbonate used in this study.

Literature Cited

- Afanasyev, V.; Zyatkov, L. Speed of Sound, Densities, and Viscosities for Solutions of Lithium Hexafluoroarsenate in Tetrahydrofuran at 283.15, 298.15, and 313.15 K. *J. Chem. Eng. Data* **1996**, *41*, 1315–1318.
- Aminabhavi, T. M.; Phayde, H. T. S.; Khinnavar, R. S.; Bindu, G. Densities, Refractive Indices, Speeds of Sound, and Viscosities of Diethylene Glycol Dimethyl Ether + Butyl Acetate at 298.15, 303.15, 308.15, 313.15, and 318.15 K. *J. Chem. Eng. Data* **1993**, *38*, 542–545.
- Aminabhavi, T. M.; Bindu, G. Densities, Shear Viscosities, Refractive Indices, and Speeds of Sound of Bis(2-methoxyethyl) Ether with Nonane, Decane, Dodecane, Tetradecane, and Hexadecane at 298.15, 308.15, and 318.15 K. *J. Chem. Eng. Data* **1994**, *39*, 529–534.
- Aminabhavi, T. M.; Patil, V. B. Density, Viscosity, Refractive Index, and Speed of Sound in Binary Mixtures of Ethenylbenzene with *N,N*-Dimethylacetamide, Tetrahydrofuran, *N,N*-Dimethylformamide, 1,4-Dioxane, Dimethyl Sulfoxide, Chloroform, Bromoform, and 1-Chloronaphthalene. *J. Chem. Eng. Data* **1998**, *43*, 497–503.
- Aralaguppi, M. I.; Aminabhavi, T. M.; Balundgi, R. H.; Joshi, S. S. Thermodynamic Interactions in Mixtures of Bromoform with Hydrocarbons. *J. Phys. Chem.* **1991**, *95*, 5299–5308.
- Asfour, A. F. A.; Dullien, F. A. L. Viscosities and Densities of Four Binary Liquid Systems at 25.00 °C. *J. Chem. Eng. Data* **1981**, *26*, 312–316.
- Comelli, F.; Francesconi, R. Densities and Excess Molar Volumes of Dimethyl Carbonate + Six Methyl *n*-Alkyl Ketones at 298.15 K and Atmospheric Pressure. *J. Chem. Eng. Data* **1994a**, *39*, 108–110.
- Comelli, F.; Francesconi, R. Isothermal Vapor–Liquid Equilibria, Densities, Refractive Indices, Excess Molar Volumes, and Excess Molar Enthalpies of Dimethyl Carbonate + 1,2-Dichloromethane and 1,1,1-Trichloroethane. *J. Chem. Eng. Data* **1994b**, *39*, 560–564.
- Comelli, F.; Francesconi, R. Excess Molar Enthalpy of Binary Mixtures of Diethyl Carbonate + Nine Chloroalkanes at 298.15 K and Atmospheric Pressure. *J. Chem. Eng. Data* **1995**, *40*, 509–511.
- Comelli, F.; Francesconi, R.; Ottan, S. Isothermal Vapor–Liquid Equilibria of Dimethyl Carbonate + Diethyl Carbonate in the Range (313.15 to 353.15) K. *J. Chem. Eng. Data* **1996**, *41*, 534–536.
- Francesconi, R.; Comelli, F. Excess Molar Volumes of Binary Mixtures Containing Dimethyl Carbonate + Linear and Cyclic Ethers. *J. Chem. Eng. Data* **1994**, *39*, 106–107.
- Francesconi, R.; Comelli, F. Excess Molar Enthalpies, Densities, and Excess Molar Volumes of Binary Mixtures Containing Esters of Carbonic Acid at 298.15 and 313.15 K. *J. Chem. Eng. Data* **1995a**, *40*, 811–814.
- Francesconi, R.; Comelli, F. Excess Molar Enthalpies of Binary Mixture Containing Dialkylcarbonates + Cyclic Ketones at 298.15 K or 313.15 K. *Thermochim. Acta* **1995b**, *258*, 49–57.
- Francesconi, R.; Comelli, F. Vapor–Liquid Equilibria, Excess Molar Enthalpies, and Excess Molar Volumes of Dimethyl Carbonate + 1,2-Epoxybutane at 298.15 or 313.15 K. *J. Chem. Eng. Data* **1996**, *41*, 736–740.
- Fuente, I. G.; Gonzalez, J. A.; Cobos, J. C.; Casanova, C. Excess Molar Volumes of Diethyl Carbonate with Hydrocarbons or Tetrachloromethane at 25 °C. *J. Solution Chem.* **1995**, *24*, 827–835.
- Martindale, W. *The Extra Pharmacopoeia*; Pharmaceutical Press: London, 1989.
- Marquardt, D. W. An Algorithm for Least-squares Estimation of Nonlinear Parameters. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431–441. *The Merck Index*; Merck Co. Inc.: Rahway, NJ, 1989.
- Nikam, P. S.; Jadhav, M. C.; Hasan, M. Density and Viscosity of Mixtures of Nitrobenzene with Methanol, Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, 2-Methylpropan-1-ol, and 2-Methylpropan-2-ol at 298.15 and 303.15 K. *J. Chem. Eng. Data* **1995**, *40*, 931–934.
- Redlich, O.; Kister, A. T. Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ind. Eng. Chem.* **1948**, *40*, 345–348.
- Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Techniques of Chemistry, Organic Solvents, Physical Properties and Methods of Purification*; John Wiley & Sons: New York, 1986; Vol. II.
- Zurita, J. L.; Soria, M. L. G.; Postigo, M. A.; Katz, M. Vapor–Liquid Equilibrium for the *n*-Pentane–Dichloromethane System at 298.15 K. *J. Chem. Eng. Data* **1986**, *31*, 389–390.

Received for review June 26, 1998. Accepted September 9, 1998. The authors thank the Department of Science and Technology, New Delhi, Grant No. SP/S1/H-26/96(PRU), for a major funding.

JE980145+