Dimethyl carbonate with ethers:Thermophysical study

Ajit N. Bhumkar
Department of Chemistry
VPM's B.N. Bandodkar College of Science(Autonomous),Thane
Thane,Maharashtra-India
ajitnanabhumkar@gmail.com

ABSTRACT

Viscosities, and densities of binary liquid mixtures of dimethyl carbonate with butyl vinyl ether, diisopropyl ether, anisole, and dibutyl ether have been calculated over the entire concentration range at temperatures (303.15, 308.15 and 313.15)K. The experimental data have been used to measure the deviation in viscosity *Δη,* excess Gibb's free energy. The excess property has been evaluated and fitted to the Redlich-Kister polynomials and the results are interpreted in terms of molecular interactions present in mixtures.

Keywords- Density; Viscosity; dimethyl carbonate, Gibbs free energy, Redlich-Kister equation.

1. INTRODUCTION

The studies on thermodynamic properties of binary liquid-liquid mixtures contribute to the understanding of the intermolecular interactions existing between the various species in a solution. The study provides information about changes with respect to composition and in packing efficiencies that take place in solution during mixing process[1]. Such research work has been carried out on this properties of non- electrolyte solutions. One of the most exciting developments in the whole field of non-electrolyte solutions has been work of Patterson-Delmas[2-5], concerning the effect of molecular shape on the thermodynamic properties of binary mixtures. Viscosity and density data for binary liquids are important from practical and theoretical point of view. Experimental measurements of these properties of binary mixtures have gained much importance in many chemical industries and engineering disciplines[6]. Knowledge of the viscosity is very important in many chemical applications, such as mass and heat transfer operations, fluid flow, molecular structure and design involving chemical separations, developing separation methods like HPLC and capillary electrophoresis[7].

Dimethyl carbonate is an eco friendly solvent used to prepare coatings, adhesives, and cleaning agents. DMC is also used as a raw material for many organic synthesis. Dimethyl carbonate (DMC) is considered to be a green solvent. It is a nontoxic substance and is used as a replacement for dimethyl sulphate, methyl halide, and phosgene in methylation and carbonylation reactions. Dimethyl carbonate is a flammable liquid with a flash point of 17 °C (63 °F).so there is restrictions for using in indoor applications. But DMC is safer than other organic solvents like, propanone, methyl acetate and methyl ethyl ketone from a flammability point of view. Dimethyl carbonate (DMC), one of the carbonic acid esters, has been used as an environmentally benign solvent because of its higher activity, and lower persistence[8]. Dimethyl carbonates have shown to be most beneficial in the lithium battery technology. It is also used in gasoline industry.

Ethers are tremendously used as commercial solvents and extractants for esters, gums, hydrocarbons, alkaloids, oils, resins, dyes, plastics, lacquers, and paints. They are used as dewaxing. Butyl Vinyl Ether is generally used as reactive diluent, for example in the radiation curing of hybrid polymer coatings for paints, inks, adhesives, etc., Diisopropyl ether have wide variety of applications. It is mostly used as a solvent as oil-based solutions dissolve in it. This create it the authentic base for many paints, waxes, dyes and resins. It is commonly utilised as a solvent in paint thinners and stain removers. Diethyl ether is a component of starting fluids and is used as a solvent in the manufacture of synthetic dyes and plastics. It was used as anesthetic agent in many countries but now it was replaced. Methoxy benzene is a straw-colored to colorless liquid with a little spicy-sweet odor. It is used in perfumes, as a flavoring in food, and in the manufacture of other chemicals.

Density, viscosity and gibb's free energy of the mixtures containing dimethyl carbonate give information about how to design the injection system and analyse the fluid flow, but also can help better understanding the molecular interactions of the solutions.

There have been many studies available in literature on thermodynamic and thermophysical properties of binary mixtures containing dimethyl carbonate with different organic liquids. M.V.Rathnam et al[9] have studied densities, viscosities and refractive indices of binary mixtures of dimethyl carbonate with with acetophenone, cyclopentanone, cyclohexanone, and 3-pentanone over the entire range of composition at the temperatures 303.15, 308.15 and 313.15 K and at atmospheric pressure. The refractive indices data have been correlated using Lorentz–Lorentz, Weiner, Newton, Gladstone–Dale, Eykman, and Eyring–John equations .

Jaime Wisniaka et al[10] have studied densities of the binary systems of dimethyl carbonate with butyl methacrylate, allyl methacrylate, styrene, and vinyl acetate over the entire range of the composition at (293.15, 303.15, and 313.15) K at atmospheric pressure, using an Anton Paar DMA 5000 oscillating U-tube densimeter. They correlated the calculated excess molar volumes with the Redlich–Kister equation and with a series of Legendre polynomials. An explanation of the results is offered based on the FT-IR (ATR) spectra of several mixtures of the different systems. Michael A. Pacheco and Christopher L. Marshall[11] have reported, the fuel characteristics and known chemical synthesis schemes for DMC are reviewed.E. R. Lopez et al[12] have measured densities ρ and excess molar volumes of (dimethyl carbonate + toluene) at the temperatures (278.15, 288.15, 298.15, 308.15, 318.15, and 323.15) K and of (dimethyl carbonate + toluene) at the temperatures (288.15, 298.15, 308.15, 318.15, and 323.15) K using an Anton-Paar DMA602HP densimeter. The experimental data were used for the calculation by analytical differentiation of the following quantities: the cubic expansion coefficient, the excess cubic expansion of coefficient, (∂VE m/∂T)p and (∂HE m/∂p)T . Gibb's free energy for the binary mixtures of dimethyl carbonate +butyl vinyl ether, diisopropyl ether, anisole, dibutyl ether at temperature (303.15,308.15 and 313.15) K with respect to mole fractions are measured.

2. Experimental

2.1 Materials

Dimethyl carbonate, butyl vinyl ether, diisopropyl ether, anisole, and dibutyl ether (mass fraction purity >99.0%) all are obtained from Sigma-Aldrich. The purity of all these chemicals was checked by Gas chromatography (GC-8610,) and the analysis of the purity was found to be > 99.4%.These chemicals were stored over 0.4 nm molecular sieves to reduce water content and distilled just before use.

2.2 Methods

The binary liquid mixtures were prepared by mixing known masses of pure liquids in airtight stoppered bottles in order to minimise evaporation losses. All mass measurements were made using a Mettler one-pan balance (AE, 240, Switzerland). The resulting mole fraction uncertainty was estimated to be less than ± 0.0001.

Densities of pure and their binary mixtures were determined using a density meter (DDM -2910, Rudolph Research Analytical). The instrument has high precision platinum thermometer in the density sensor for the accurate measuring temperature. The instrument was calibrated frequently before the start of the actual experiments, using doubly distilled water and dry air. The density measurements were accurate to ± 0.00005 $g.cm^{-3}$.

Viscosities of the pure liquids and their mixtures were determined at the atmospheric pressure and the required temperature by using Ubbelohde viscometer. The viscometer bulb has a capacity of about 15 ml and the capillary tube with a length of about 90 mm and 0.5 mm internal diameter. The viscometer thoroughly cleaned and perfectly dried is filled with the sample liquid and its limbs were closed with teflon caps to avoid evaporation. The viscometer is kept in a transparent walled water bath with a thermal stability of ± 0.01K for about 20 min to obtain thermal equilibrium. An electronic digital stopwatch with an uncertainty of ± 0.01s was used for flow time measurements. At least 3-4 repetitions of each mixture reproducible to ± 0.05s were obtained and the results were averaged. The viscosity was calculated from efflux time't' using the following relation

$$\eta=\rho\,(At-B/t) \tag{1}$$

Where, ρ is the density and A and B are the characteristic constants of the viscometer, which are determined by taking water and benzene as the calibrating liquids. The uncertainty in the viscosity thus estimated was found to be ± 0.005 m.Pas.

3. Results and Discussion

Densities ρ, viscosities η, and gibb's free energy of the binary mixtures are measured against the mole fractions x_1 of dimethyl carbonate for the studied binary mixtures at (303.15, 308.15 and 313.15)K.

The deviations in viscosity Δη were calculated using equation.

$$\Delta\eta = \eta_{12} - (x_1\,\eta_1 + x_2\eta_2) \tag{2}$$

Where x_1, η_1, η_2 and η_{12} are respectively the mole fraction, viscosity of pure components and mixture.

The viscosities (η), deviations in viscosities ($\Delta\eta$) for the binary mixtures of dimethyl carbonate are calculated at T = (303.15, 308.15 and 313.15) K. The deviation in viscosities ($\Delta\eta$) obtained by using the equation (2) have

been graphically represented in Figures 1. From the graphs it is observed that for the systems of dimethyl carbonate + butyl vinyl ether, + diisopropyl ether,+ dibutyl ether the $\Delta\eta$ values are found to be negative while, for dimethyl carbonate + anisole $\Delta\eta$ values are found to be positive across the entire whole composition and at the studied temperatures. The negative Δη values indicates dispersion or weak dipole-dipole interactions between the component molecules.[13-14] Also negative Δη values may be due to the different molecular size of components in mixture.[15-16] From these tables it is observed that for dimethyl carbonate + butyl vinyl ether,+ dibutyl ether the values of viscosity decreases with increase in temperature, for dimethyl carbonate + diisopropyl ether , + anisole the values of viscosity increases with increase in temperature.
The negative Δη values for butyl vinyl ether, diisopropyl ether, anisole, dibutyl ether follows the order
Dibutyl ether < Diisopropyl ether < Butyl vinyl ether < Anisole.

The Gibb's free energy was obtained by following equation

$$\Delta G^{*E} = RT[\ln\eta_{12}v_{12}-(x_1 \ln\eta_1 v_1+ x_2\ln\eta_2 v_2) \quad (3)$$

where R is the gas constant , T is absolute temperature, η_{12}, v_{12} are viscosity and molar volume of the mixture respectively, $\eta_1, v_1,$ $\eta_2,$ and v_2 are the viscosity and molar volumes and of pure components 1 and 2 respectively. The molar volume of binary mixture (v_{12}) is obtained from the density of the mixture using the equation.

$$N_{12} = (x_1 m_1 + x_2 m_2) /\rho_{12} \quad (4)$$

The excess Gibb's free energy of activation of viscous flow ΔG^{*E} was calculated by using the equation (3) and these values are graphically represented in Figures 2. It is observed that for dimethyl carbonate + butyl vinyl ether, diisopropyl ether, dibutyl ether the ΔG^{*E} values are negative and for anisole the ΔG^{*E} value is positive across the composition range at all the studied temperatures. The ΔG^{*E} values for dimethyl carbonate + butyl vinyl ether,+ diisopropyl ether,+ dibutyl ether decreases with increase of temperature. While for dimethyl carbonate + anisole these values increases with increase of temperature across the composition of ester at all the studied temperature. The minima for dimethyl carbonate + butyl vinyl ether is at $x_1 = 0.4995$. The excess Gibbs free energy of activation of viscous flow, like viscosity deviation, can be used to detect molecular interactions. The observed positive ΔG^{*E} value may be due to the flow of system is hard as compared to flow of pure components[17]. On the other hand, positive values of it suggest strong specific interactions (like hydrogen bonding and dipole-dipole interactions) between unlike molecules.The negative ΔG^{*E} value may be due to easier flow of binary system[18].
The results of Δη and ΔG^{*E} for the binary mixtures at (303.15, 308.15 and 313.15) K are graphically represented in figs 1-2. Further these results were fitted to the Redlich-Kister [5] polynomial equation by the method of least squares to derive the binary solution coefficients A_0, A_1, and A_2.

$$\Delta Y=x_1x_2[A_0+A_1(x_1-x_2)+A_2(x_1-x_2)^2] \quad (5)$$

Where ΔY represents the concerned property. The standard deviations for Δη and ΔG^{*E} were calculated using the relation.

$$\Sigma(Y) = [\sum(Yexpt – Ycal)^2/(N – n)]^{1/2} \quad (6)$$

Where 'N' is the number of data points and n is the number of coefficients. The calculated values of the polynomial coefficients A_0, A_1, and A_2 along with their standard deviations σ are given in Table 1.

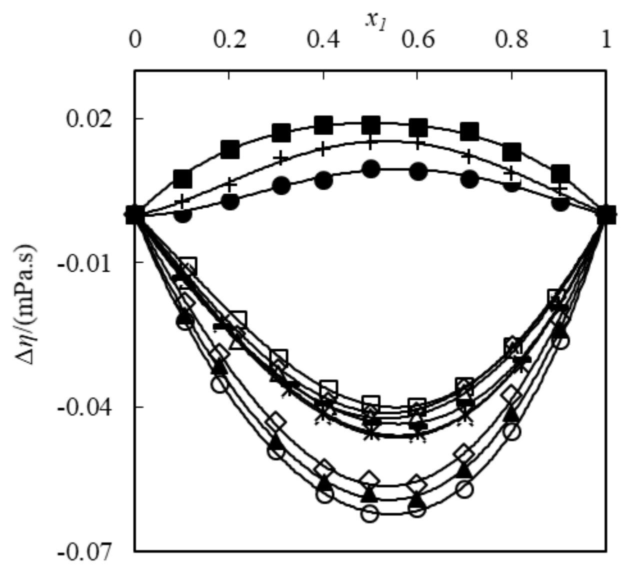

Figure.1: Curves of deviation in viscosity ($\Delta\eta$) Vs mole fraction (x_1) for the binary mixtures of Dimethyl carbonate + Butyl vinyl ether at (□, 303.15 ; ◊,308.15 ; Δ,313.15) K ,Dimethyl carbonate + Diisopropyl ether at (×, 303.15;ж, 308.15 ; ▬,313.15) K, Dimethyl carbonate + Anisole at (●,303.15; +, 308.15 ;■, 313.15) K, Dimethyl carbonate + Dibutyl ether at (◊,303.15; ▲,308.15 ; O, 313.15) K.

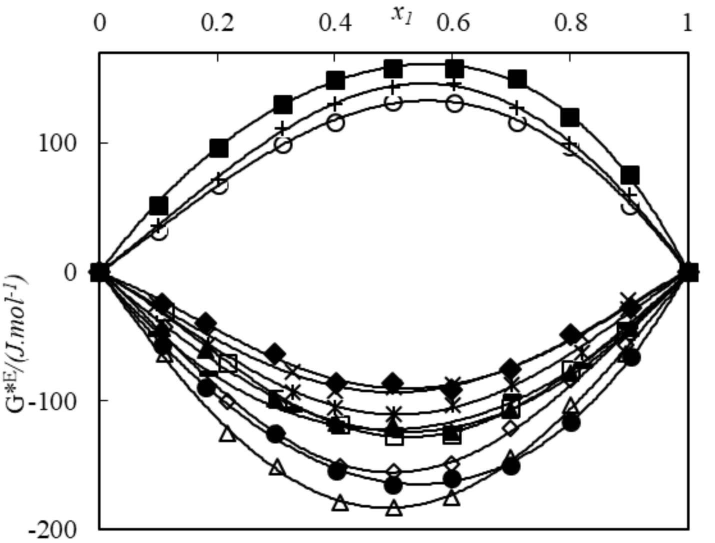

Figure 2: Curves of excess free energy of activation(ΔG^{*E})Vs mole fraction for the binary mixture of ,
Dimethyl carbonate + Butyl vinyl ether at (□, 303.15 ;◊,308.15 ; Δ,313.15) K,
Dimethyl carbonate + Diisopropyl ether at (×,303.15 ; ж,308.15 ; ▬,313.15)K
Dimethyl carbonate + Anisole at (O, 303.15; +, 308.15 ; ■, 313.15)K
Dimethyl carbonate + Dibutyl ether at (■,303.15;▲,308.15 ;●,313.15) K

Table 1: Derived parameters by Redlich-Kister equation for excess properties for various functions and Standard deviation (σ) for the binary system

Function	*T*/K	A_0	A_1	A_2	σ	A_0	A_1	A_2	Σ
Dimethyl carbonate (1) + Butyl vinyl ether (2)						**Dimethyl carbonate(1)+ Diisopropyl ether(2)**			
ΔG^{*E}	303.15	-732.4	36.084	124.7	3.413	-374.05	3.1266	129.57	3.510
	308.15	-622.63	2.758	189.4	5.822	-443.00	-17.840	160.735	3.516
	313.15	-511.4	-71.80	190.4	2.600	-489.14	26.15	-15.2955	3.583
Dimethyl carbonate (1) + Anisole (2)						**Dimethyl carbonate (1) + Dibutyl ether (2)**			
ΔG^{*E}	303.15	523.64	142.88	-60.384	1.802	-361.11	-41.480	151.43	3.420
	308.15	577.58	143.87	-88.624	2.335	-495.24	-52.512	56.446	3.612
	313.15	638.05	132.88	120.73	2.322	-654.90	-107.14	-29.67	2.588

4.Conclusion

Density, viscosity and Gibb's free energy of activation for binary systems of Dimethyl carbonate + butyl vinyl ether, +diisopropyl ether, + anisole, + dibutyl ether have been determined over the entire range of composition at (303.15, 308.15 and 313.15) K. Using these experimental data excess Gibb's free energy of activation of viscous flow ΔG^{*E} , deviation in viscosity $\Delta\eta$, were calculated. These excess or deviation properties were fitted to Redlich-Kister polynomial equation. From these excess or deviation properties it is concluded that the presence of weak interactions (dispersion forces) between Dimethyl carbonate and butyl vinyl ether, diisopropyl ether,and dibutyl ether, whereas for (Dimethyl carbonate + anisole) mixtures the presence of specific interactions such as charge transfer complex are involved.

The present article gives extensive collection data of physico-chemical properties of the binary mixtures which are used in chemical and other related industries. The results by using this data can be used in the field of solution chemistry. The experimental mixing property data presented here are entirely new and will add a new wealth of information to the existing database.

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