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DIMETHYL CARBONATE WITH ETHERS:THERMOPHYSICAL STUDY

Abstract

Viscosities, densities of liquid-liquid combinations of dimethyl carbonate with (Butyloxy) ethylene, 2-isopropoxypropane, methyl phenyl ether, and 1-Butoxybutane have been calculated through the entire compositions radius at temperatures (303.15, 308.15 and 313.15)K. The empirical values have been employed to measure the deflection in viscosity $\Delta\theta$, excess Gibb's free energy. The excess property has estimated and adapted to the Redlich-Kister polynomials. Their outputs are explained in terms of molecular interactions present in mixtures.

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

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I. INTRODUCTION

To the better perceiving of the intermolecular and intramolecular interactions present between the different species in a solution, the studies on thermodynamic properties of binary liquid-liquid combinations are important.The study provides detailed knowledge regarding changes with reference to structure and in packing efficiencies that occurred in solution while blending process[1].Such research work has been carried out on this properties of non- electrolyte solutions. Thrilling evolutions in this field of non-electrolyte solution has shown great efforts by Patterson-Delmas[2-5], concerning how impact of molecular size affect the thermodynamic properties of binary liquid-liquid combinations. In chemical, pharmaceutical and engineering disciplines[6], investigational computations of viscosities, densities and free energy of activations information play very vital role in these industries. So study of these properties from practical and theoretical point of view is crucial for binary liquid-liquid combinations. In expanding separation techniques like HPLC, capillary electrophoresis[7], and designing of processes including separation of chemical substances, fluid flow, mass and heat transport processes, viscosities and densities data are required.

Carbonic ester of dimethyl is an eco friendly solvent. It is employed to prepare platings, stickings, and rinsing negotiators. It is employed as a starting compound for many biotic manufacturing. It is a green reagent because of its nontoxicity and its biodegradability in nature. Dimethyl sulphate, carbonyl chloride, iodomethane, are very toxic but dimethyl carbonate can be plyed instead of them in methylation and carbonylation synthesis. Dimethyl carbonate easily catch the fire because of its low turning point (290.15 K).So there is restrictions for using in indoor applications. But DMC is safer than other organic solvents like, propanone, methyl ethanoate, 3-pentanone concerning catching fire perspective. Dimethyl carbonate (DMC), has higher activity, less persistence[8], good natured solvent qualities so it is employed in many industries. Dimethyl carbonates have revealed to

be most beneficial in the recharging battery technique of lithium. It is also used in gasoline industry.

Ethers are tremendously used as trading solvents and moving agent for Greece oil, pastes, compound containing carbon and hydrogen, organic base compound containing Nitrogen, lubricants, wax, colouring agent, plastics, covering, and tints. They are employed as to remove wax. n-Butoxy ethylene is generally employed as active diluting agent, in the radiation restoring of cross-breed plastic coatings for colours, pigments, adherents, etc, Diisopropyl ether have wide variety of applications. It is mostly used as a solvent as derived from oil solutions easily liquefy in this. This create it is authentic base for various stains, waxes, colours and fixatives. It is commonly utilized as a solvent in colour slimmers and spot erasers. In the constructing of manufactured colors and polymers diethyl ether is employed as a solvent it was introduced as sedative agent in many countries but now it was replaced. Methoxy benzene is a pale yellow colored to faded solvent with a little tangy smell. It is employed in scents, as a added flavor in nourishments, and in the preparation of different chemical agents.

Density, vicinity and free enthalpy of the mixtures containing dimethyl carbonate give information about how to develop the injection system and inspect the flowing liquid, it assist in good understanding the molecular interactions of the mixture.

There are many works are obtainable in letters on thermodynamic and thermophysical characteristics of dual liquid-liquid combinations containing dimethyl carbonate in association of different organic liquids. M.V.Rathnam et al[9] have studied densities, viscosities and index of refraction of binary liquid-liquid combinations of dimethyl carbonate with with acetyl benzene, ketocyclopentane, cyclohexyl ketone, and diethyl ketone along the complete range of configuration at the temperatures 303.15, 308.15 and 313.15 K and at barometric pressure. The index of refraction information have been corresponded by utilizing Lorentz–Lorentz,

Weiner, Newton, Gladstone–Dale, Eykman, and Eyring–John relations.

Jaime Wisniaka et al[10] have studied densities of the dual systems of dimethyl carbonate with butyl-2-methylpropenoate, cis-cyclooctane-1,2-diol, vinyl benzene, and acetic acid vinyl ester over the entire range of the concentrations at (293.15, 303.15, and 313.15) K at barometric pressure, employing an Anton Paar DMA 5000 oscillating U-tube densitometer. They correlated the intentional excess molar volumes with the Redlich–Kister equation and with a series of Legendre polynomials. A clarification of the outputs is provided depending on the FT-IR (ATR) spectra of several combinations of the various systems. Michael A. Pacheco and Christopher L. Marshall[11] have reported, the propellant properties and studied chemical blending plans for DMC are assessed. E. R. Lopez et al[12] have measured densities γ and excess molar volumes of (dimethyl carbonate + methyl benzene) at the temperatures (278.15, 288.15, 298.15, 308.15, 318.15, and 323.15) K and using an Anton-Paar DMA602HP densitometer. The observed data were employed for the computation by analytical differentiation of the backing 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 binate combinations of dimethyl carbonate + (Butyloxy)ethylene, 2-isopropoxypropane, methyl phenyl ether, and 1-Butoxybutane at temperature (303.15,308.15 and 313.15) K with respect to mole fractions are measured.

II. PRACTICAL

1. Chemicals

Dimethyl carbonate, (Butyloxy)ethylene, 2-isopropoxypropane, methyl phenyl ether, and 1-Butoxybutane (mass little bit purity >99.10%) every one of the obtained from Sigma-Aldrich. The clarity of every one of the these compounds were estimated by vapor phase chromatography (VPC-8610,) and the investigation clarity were

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discovered to be > 99.6%.These compounds were collected over 0.4 nm molecular sieves to minimize aqua content and refined fair prior to work.

2. Methods

The dual liquid-liquid combinations were developed by blending fixed amount of unadulterated liquids in closed ground stoppered glass so as to decrease dispersal deprivations. The mass estimations were correct to ± 0.01 mg were done on a well programmed electronic balance (Mettler AE 240, Switzerland).Unreliability of observed molar proportion were determined which is lower than $\pm$ 0.0001.

First densitometer (DDM -2910, Rudolph Research Analytical) was set by utilizing distilled water. The temperature of densitometer is fixed at required value. Internal thermostat had good precision $\pm$ 0.1. There is inbuilt air pressure in densitometer that help in drying the estimating cell after washing it. There should not be air bubbles in estimating cell while taking the readings. First clean the estimation cell with sample to expel the impurities if, present. Then final sample of mixture is introduced into estimation cell by using syringe.In this way densities of sterling chemicals and their dual combinations were taken.The density measurements were accurate to $\pm$ 0.00005 $g.cm^{-3}$.

Ubbelohde viscometer is thoroughly washed and completely dried it. First, flow time of water was calculated at desired temperatures. Well programmed stopwatch was used having unreliability of ± 0.04s.The sterling liquid compounds and their combinations viscidity were evaluated at the barometric pressure and the required temperature. Its arms were sealed by inert lids for stopping of vanishing solvents. The viscometer was put in water bath having thermic steadiness of $\pm$ 0.02 K.It was placed for 25 min. Minimum three readings were taken. The viscosity (θ) was estimated from outflow pattern ‘m’ by considering the equation.

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$$\Theta = \gamma(Xm\text{-}Y/m) \quad (1)$$

where, γ is the density and X and Y are the characteristic constants of the viscometer.X and Y are fixed by using water as setting solvents. The unreliability in the viscosity was got to be ± 0.005 m.Pas.

III. OUTCOMES

Gibb's free energy, density γ, viscosity θ, of the binary mixtures are measured against the mole fragments x_1 of dimethyl carbonate for the calculated dual combinations at (303.15, 308.15 and 313.15)K.

The deviations in viscosity Δθ were measured by following relation.

$$\Delta\theta = \theta_{12} - (x_1\,\theta_1 + x_2\theta_2) \quad (2)$$

where x_1, θ_1, θ_2 and θ_{12} are proportionately the mole fragment, viscosity of pure compounds and their combinations.

The viscosities (θ), deviations in viscosities ($\Delta\theta$) for the dual liquid-liquid combinations of dimethyl carbonate are calculated at T = (303.15, 308.15 and 313.15) K. The deviation in viscosities ($\Delta\theta$) obtained by using the equation (2) have been graphically represented in Figures 1. From the graphs it was found that for the combinations of dimethyl carbonate + (Butyloxy)ethylene, 2-isopropoxypropane, and 1-Butoxybutane, the $\Delta\theta$ values are found to be negative while, for dimethyl carbonate + anisole $\Delta\theta$ values are got positive across the entire concentrations and at the studied temperatures. Observed negative Δθ values indicates dispersion or weak dipole-dipole interactions among the molecules in the mixtures.[13-14] The negative curves for Δθ indicate there are different molecular size of molecules in components of the mixture.[15-16] From these tables it is observed that for dimethyl carbonate + butyl vinyl ether,+ dibutyl ether the values of viscosity decreases with rising of temperature, for dimethyl carbonate + diisopropyl ether , + anisole the values of viscosity rises with growing of temperature.

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The negative Δθ values for (Butyloxy)ethylene, 2-isopropoxypropane, methyl phenyl ether, and 1-Butoxybutane follows the order 1-Butoxybutane < 2-isopropoxypropane < (Butyloxy) ethylene < methyl phenyl ether.

The Gibb's free energy was obtained by following equation

$$\Delta G^{*E}=RT[\ln\theta_{12}\nu_{12}-(x_1\ln\theta_1\nu_1+x_2\ln\theta_2\nu_2) \quad (3)$$

where R is the universal gas constant , T is absolute temperature, $\theta_{12,}\nu_{12}$ are viscosity and molar volume of the combinations respectively, $\theta_{1,}\nu_{1,}$ $\theta_{2,}$ and ν_2 are the viscosity and molar volumes and of pure compounds 1 and 2 respectively. The molar volume of dual liquid-liquid combinations (ν_{12}) is obtained from the density of the combination using the equation.

$$N_{12=}(x_1m_1+x_2m_{2)}/\ \gamma_{12} \quad (4)$$

The excess Gibb's free energy of activation of viscous flow ΔG was obtained by utilizing the equation (3) and these values are graphically shown in Figures 2. It was found that for dimethyl carbonate + (Butyloxy) ethylene, 2-isopropoxypropane, 1-Butoxybutane the curves for ΔG are negative and for anisole the ΔG value is positive along the whole concentration at every one of the observed temperatures. The ΔG values for dimethyl carbonate + (Butyloxy) ethylene, + 2-isopropoxypropane, + 1-Butoxybutane decreases with increasing temperature. While for dimethyl carbonate + anisole curves values increases in rising 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 study of excess Gibb's free energy, viscosity deviations are important for determining the molecular interactions between components in combinations.The studied positive ΔG value may be due to the flow of system is hard as compared to flow of pure components[17]. Also the positive values of it indicate there are powerful specific interactions between unlike molecules. The negative ΔG value may be due to easier flow of binary system[18].

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The outcomes of Δθ and ΔG for dual liquid-liquid combinations at (303.15, 308.15 and 313.15) K are diagrammatically shown in figures 1-2. Then outcomes were fitted to the Redlich-Kister [5] polynomial relation by the procedure of least squares to get the dual solution coefficients B0, B1, and B2.

$$\Delta Y = x_1 x_2 [B0 + B1(x_1 - x_2) + B2(x_1 - x_2)^2] \quad (5)$$

where ΔY indicate the discussed characteristics. The standard deviations for Δθ and ΔG were measured by following relation.

$$\Sigma(Y) = [\sum (Yexpt - Ycal)^2/(P - p)]^{1/2} \quad (6)$$

where 'P' is the number of data points and p is the number of coefficients. The measured values of the polynomial coefficients B0, B1, and B2 along with their standard deviations σ are given in Table 1.

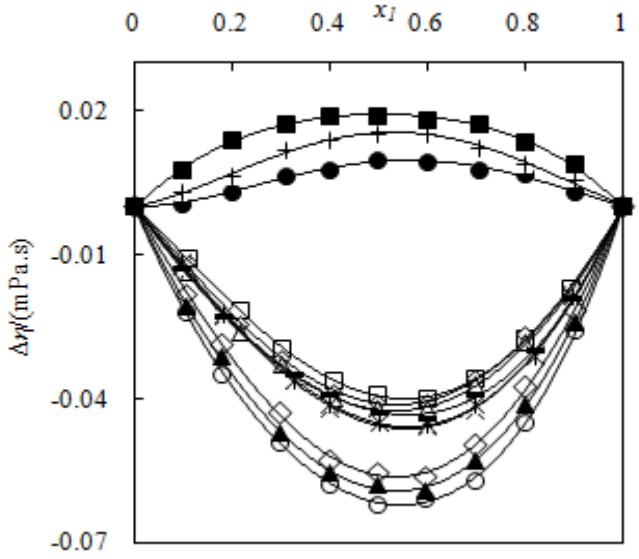

Figure.1: Deviation in viscosity ($\Delta\theta$) Vs mole fraction (x_1) for the binary combinations of
Dimethyl carbonate + (Butyloxy)ethylene at (□, 303.15 ; ◊,308.15 ; Δ,313.15) K,

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Dimethyl carbonate + 2-isopropoxypropane at (×, 303.15; ж, 308.15 ; ▬,313.15) K,
Dimethyl carbonate + Methoxy benzene at (●,303.15; +, 308.15 ;■, 313.15) K,
Dimethyl carbonate + 1-Butoxybutane at (◊,303.15; ▲,308.15 ; O, 313.15) K.

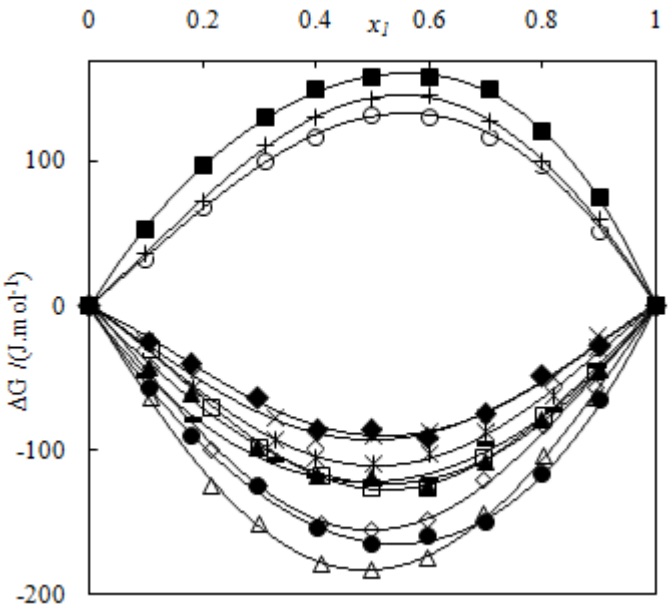

Figure 2: Excess free energy of activation (ΔG)Vs mole fraction for the binarymixture of ,

Dimethyl carbonate + (Butyloxy)ethylene at (□, 303.15 ;◊,308.15 ; Δ, 313.15) K,
Dimethyl carbonate + 2-isopropoxypropane at (×,303.15 ; ж,308.15 ; ▬,313.15)K
Dimethyl carbonate + Methoxy benzene at (O, 303.15; +, 308.15 ; ■, 313.15)K
Dimethyl carbonate + 1-Butoxybutane at (■,303.15;▲, 308.15 ;●,313.15) K

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Table 1: Derived parameters by Redlich-Kister relation for excess properties for different functions and Standard deviation (σ) for the dual system

Function	***T*/K**	***B0***	***B1***	***B2***	**σ**	***B0***	***B1***	***B2***	**Σ**
Dimethyl carbonate (1) + Butyl vinyl ether (2)						**Dimethyl carbonate(1)+ Diisopropyl ether(2)**			
Δ*G*	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)**			
Δ*G*	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

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VII. CONCLUSION

Density, viscosity, Gibb's free energy of activation for dual liquid-liquid combinations of Dimethyl carbonate + (Butyloxy) ethylene, + 2-isopropoxypropane , + Methoxy benzene, + 1-Butoxy -butane are calculated along the whole concentration at (303.15, 308.15 and 313.15) K. Utilizing observed data excess Gibb's free energy of activation of viscous flow ΔG, deviation in viscosity $\Delta\theta$, were measured. These excess or deviation properties were fitted to Redlich-Kister polynomial equation. From these excess or deviation properties it is concluded that there will be weak interactions means less dispersion forces between Dimethyl carbonate and + (Butyloxy) ethylene,2-isopropoxypropane,and 1-Butoxybutane whereas for (Dimethyl carbonate + methoxy benzene) combinations,there is perticular interactions for example charge transfer complex are demanded.

The present article gives extensive collection data of physico-chemical characteristics of the dual combinations 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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