Iranian Journal of Organic Chemistry Vol. 12, No. 4 (2020) 2961-2969

Thermodynamic Properties of pure and mixtures isopropyl alcohol with water and CO_2 by Molecular dynamics simulation

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Received: August 2020; Revised: September 2020; Accepted: September 2020

Abstract: In this study the changes in the values of thermodynamic quantities like enthalpies (ΔH), entropies (ΔS), heat capacities (ΔCp), and changes in the Gibbs free energies (ΔG) of pure water, isopropyl alcohol, carbon dioxide, and their mixtures in temperature range T = 293.15- 320.15 K at atmospheric pressure were calculated using MD simulation. The obtained values of enthalpy change for the mixture is higher than their pure components.

We have observed that the maximum values of ΔCp in all cases belong to the mixtures. It is obvious that the values of ΔS for the mixture, pure water, carbon dioxide, and isopropyl alcohol increase by temperature increasing. For the mixing processes in this study, the values of ΔG are negative at 303.15 K, 308.15 K, 313.15 K, and 320.15 K temperatures. Increasing temperature, the first peak heights of the radial distributions functions lower, local structure order lower, coordination numbers lower then mutual diffusion coefficient and self- diffusion coefficients increases. Also, the results show, the mutual- diffusion coefficients are inversely proportional to the coordination numbers.

Keywords: Enthalpy, Diffusion Coefficients, Thermodynamic, Molecular dynamics.

Introduction

The carbon dioxide and water systems are highly important in investigations into the natural environment and industrial applications [1,2]. The solubility of carbon dioxide in water is an order of magnitude larger than that of many other simple gases. As a consequence, dissolved carbon dioxide is an important component and chemical participant in geological hydrothermal systems [3,4]. Carbon dioxide has become an important substance in chemical technology, particularly in its use as a supercritical solvent and reaction medium [5]. Isopropyl is used as a cosolvent and in manufacturing other chemicals and pharmaceutical and cosmetic formulations [6].

Most drugs are polar compounds, and given that carbon dioxide is not soluble due to its non- polar structure, it has limitation while exposed to drugs, in order to improve the solubility of carbon dioxide, supercritical is used with other solvents, which is called “Cosolvent” The role of cosolvents is the change in the polarity of the solvent [7]. Increasing the amount of cosolvent increases the ability of supercritical carbon dioxide solubility in polar compounds, drugs, lipids, and dyes. Alcohol, for example, and other compounds [8-11] are used as a cosolvent for the extraction of drugs. Jun-su Jin et al., studied the solubility of benzene sulfonamide in a carbon dioxide solvent, along with ethanol, ethylene glycol and ethyl acetate cosolvents [12]. Ran Ran Zhou et al., have used methanol, ethanol and acetone as cosolvents for the extraction of steroidal drugs [10]. Bozorgmehr also reported study of the effects of methanol, ethanol and propanol alcohols as

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Co- solvents on the interaction of methimazole, propranolol and phenazopyridine with carbon dioxide in supercritical conditions by molecular dynamics [13]. Development of thermodynamic models to predict solubility of gases in pure solvents as well as solvent mixtures is still a demanding task in fluid phase equilibrium thermodynamics. In several recent papers, it has been demonstrated that good to excellent predictions of the thermodynamic data of pure fluids and mixtures in the whole fluid region could be obtained by molecular simulations [14,15]. The ternary mixtures carbon dioxide –water- alcohol is extremely important in the natural environment and industrial applications [15]. Heat capacity is a basic thermodynamic property, which could be used to characterize a liquid. It is directly linked to temperature derivatives of other basic thermodynamic functions and is therefore indispensable for calculation of differences in these functions between different temperatures. This invaluable information is widely used in physics and chemistry for establishing energy balances in thermodynamics to obtain entropy and enthalpy values, and to calculate changes in interaction enthalpies with temperature. Since the knowledge of heat capacities is also required to evaluate the effect of temperature on phase and interaction equilibria, variations in heat capacities serve as a sensitive indicator of phase transitions and are an important tool to understand changes in the structure of liquid solutions [16]. Properties measurement of the mixtures is extremely expensive, and finding a way to predict these properties would be very beneficial and cost-effective [17]. In this work, the thermodynamic properties of carbon dioxide, isopropanol, water, their mixtures and their interaction were calculated in the thermal equilibrium state, and the temperature dependence of these properties was studied. Furthermore, we will present the details of the simulations. The obtained results and their meaning are discussed in subsequent sections.

Result and Discussion

In this study the changes in the values of thermodynamic quantities for pure compound and mixture composed of under thermal equilibrium condition at temperature range of T = 293.15 K to T= 320.15 K and at atmospheric pressure were calculated using MD simulation.

At constant pressure, change of enthalpy (ΔH) can be obtained from the following equation:

$$\Delta H = \Delta U + P\Delta V \qquad (3)$$

In this theoretical study, all studied systems are closed. Usually the values of ΔH increase with temperature growth. It is well known that in closed systems, ΔV and ΔU and hence ΔH have positive values. For our studied systems, the obtained values of ΔH (at various temperatures) have been plotted in Fig. 1. The figure shows the ΔH’s for the pure isopropyl, and mixture will be increased with temperature and this effect has also been observed earlier [38, 44]. As Fig. 1 shows, for the mixture is higher than their pure components. The result of the pure water and carbon dioxide were taken from [38, 44].

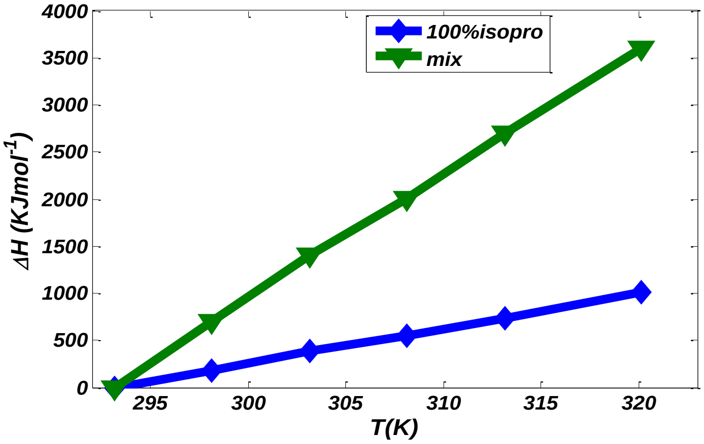

Figure 1: enthalpy change of the mixture, pure isopropyl alcohol as a function of temperature in pressure 1 bar

The values of ΔH for systems of this study can be fitted by the following equation:

$$\Delta H = a_0 + a_1 T + a_2 T^2 \qquad (4)$$

The purpose of this work, the values of the mixture and the pure isopropyl are obtained and reported in Table **1**[38, 44].

Table 1: The values of a_0, a_1, a_2 (according to equation 4) for mixture, pure isopropyl alcohol, in pressure 1 bar

	a_0	a_1	a_2
mix	-5.702×10^4	251	-0.1926
Pure isopropanol	-8308	20.15	0.02796

The change of specific heat capacity or specific heat (ΔC_p) is obtained by the following equation:

$$\Delta C_P = \left(\frac{d\Delta H}{dT}\right)_P \quad (5)$$

We can obtain equation 6 by considering equations 5 and 4:

$$\Delta C_P = a_1 + 2a_2 T \quad (6)$$

Equation **6** can be used to calculate the variations of the specific heats for the studied systems. Obtained data are listed in Table **2** and also plotted in Figure **2** for more clearance. We can see that the maximum values of ΔC_p in all cases belong to the mixtures. Entropy change can be calculated by:

$$\Delta S = \int_{273.15}^{320.15} nC_P \frac{dT}{T} \quad (7)$$

For the systems of this work, the obtained values of ΔS have been plotted in Figure **3** at different temperatures. In this figure it is obvious that the values of ΔS for the mixture and isopropanol increase by temperature increasing. As can be seen in Fig. 3, the lowest entropy changes are for pure water and carbon dioxide and the maximum value is for their mixtures. Obtained data of the pure water and carbon dioxide has been reported from ref. [38, 44].

The change of Gibbs free energy (ΔG) can be calculated by the following equation:

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

Using Equation 8, the values of ΔG were calculated and listed in Table **2**.

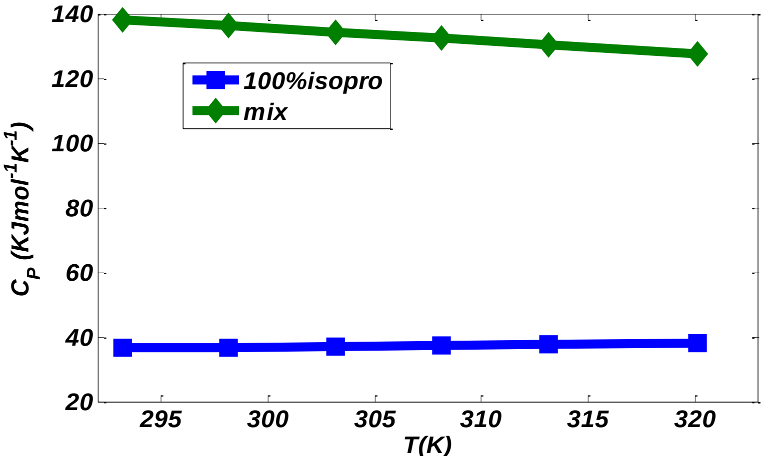

Figure 2: specific heat change of the mixture, pure isopropyl alcohol as a function of temperature.

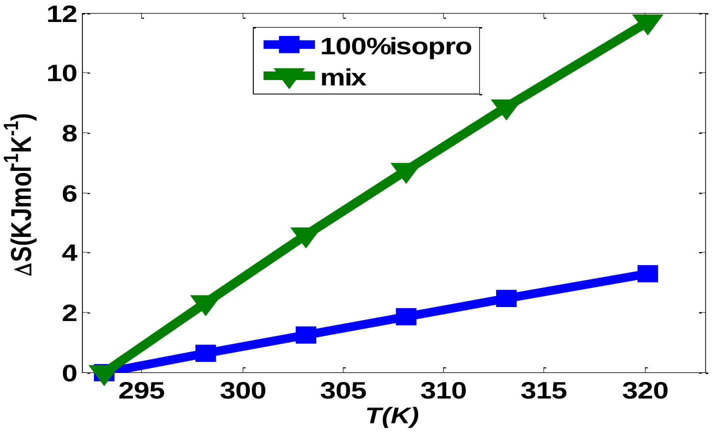

Figure 3: entropy change of mixture, pure isopropyl alcohol as a function of temperature

Table 2: The values of Gibbs free energy change ($KJ.mol^{-}.K^{-1}$) at different temperature for mixture, mixing processes, pure isopropyl alcohol

T(K)	293.15	298.15	303.15	308.15	313.15	320.15
ΔG_{iso}	0	-6.1723	9.9794	-21.3700	-28.1851	-41.2568
ΔG_{mix}	0	8.599	15.4018	-79.2174	-75.0062	-148.649
$\Delta G_{mixing\ process}$	0	8.2985	-4.4758	-38.3886	-55.2814	-99.3306

As it can be seen in Table 2, for the mixing processes in this study, the values of ΔG are negative at all temperatures except at 298 K. Therefore, the mixing processes will be possible only at 303.15 K, 308.15 K, 313.15 K, and 320.15 K. Fig. 4,5 show the self-diffusion coefficients (Ds) and mutual diffusion coefficients (Dm) for isopropyl alcohol and mixture at various temperatures. The values show the self-diffusion coefficients for water, and the mutual diffusion coefficients for CO2 are maximum. The result of the pure water and carbon dioxide were taken from ref. [38,44]. Figs show that by increasing temperature, the Ds and Dm increase. Radial distribution function (RDF) is one of the important tools to characterize the local structure of dense fluids, reflecting the effective pair wise interaction, i.e., the potential of mean force between the two species. In Figure **6-9** the RDFs between various atoms in carbon dioxide/ isopropyl /water mixture and pure isopropyl at T = (293.15 and 320.15) K are obtained to study the local structure. Fig.s 6,7 indicate that the oxygen of water (Ow) have a maximum interaction with water oxygen (Ow) and oxygen of isopropyl alcohol (Oi). It shows the most interaction among atoms of water and isopropyl alcohol and also water molecules are in mixture. Figure **8** and **9** and The results of the pure water and carbon dioxide [38, 44] show the correlation between pure water atoms is lower than isopropyl alcohol and carbon dioxide atoms, then bond between atoms in pure water is weaker than isopropyl alcohol and carbon dioxide. The first peak heights between various atoms in pure isopropyl alcohol, carbon dioxide and water and their mixture are obtained [38, 44] and shown at temperature range of T = 293.15 K to T= 320.15 K in Table 3. We observe that the first peak heights of the radial distributions functions become higher when temperature are decreasing, Table **3**. The higher the first peak heights, the stronger are the interactions atoms. Hence, for higher first peaks the self-diffusion coefficients will decrease. The corresponding coordination numbers (Nc(r)) i.e., the number of molecules contained in the first shell around a central molecule, determined by integration of the pair radial distribution functions.

$$N_C(r) = 4\pi\rho\int_{r_0}^{R_{\min}} RDF(r)r^2 d(r) \qquad (9)$$

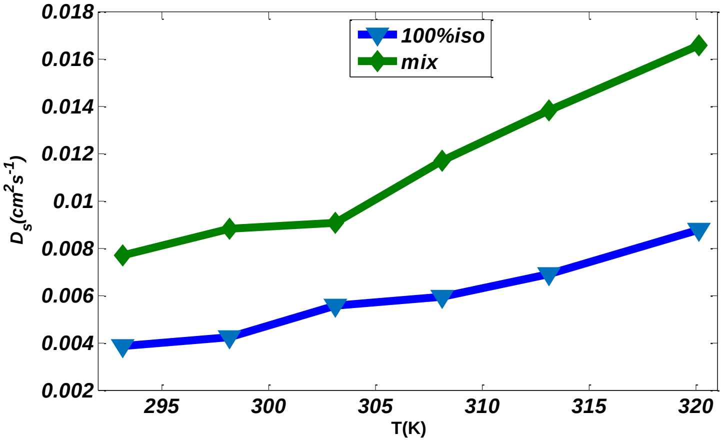

Figure 4: Self- diffusion coefficients (D_s) for pure isopropyl alcohol and mixture

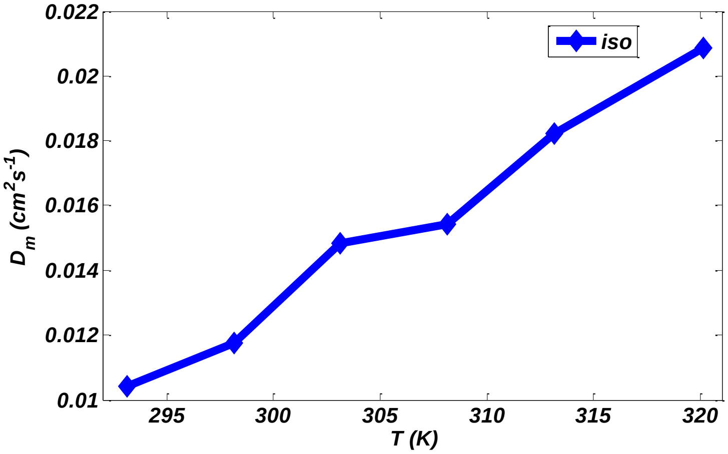

Figure 5: mutual- diffusion coefficients (D_m) for pure isopropyl alcohol

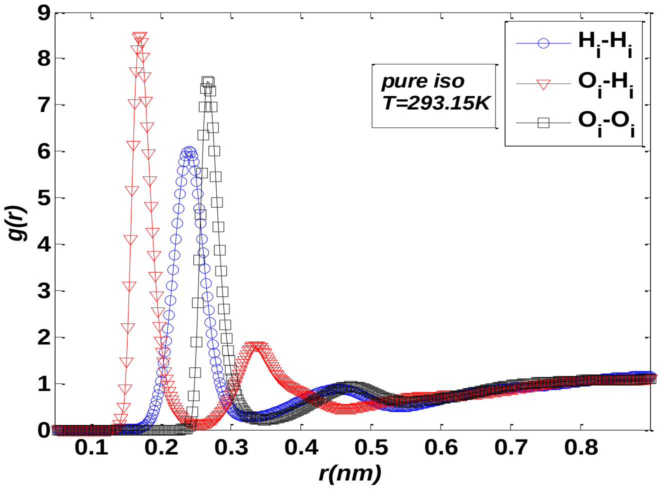

Figure 6: The partial radial distribution functions between various atoms in pure isopropyl at 293.15K

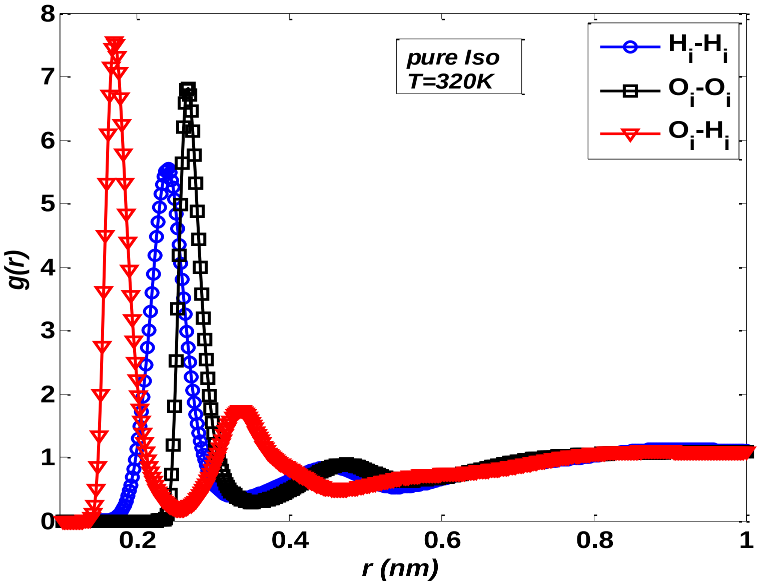

Figure 7: The partial radial distribution functions between various atoms in pure isopropyl at 320.15K

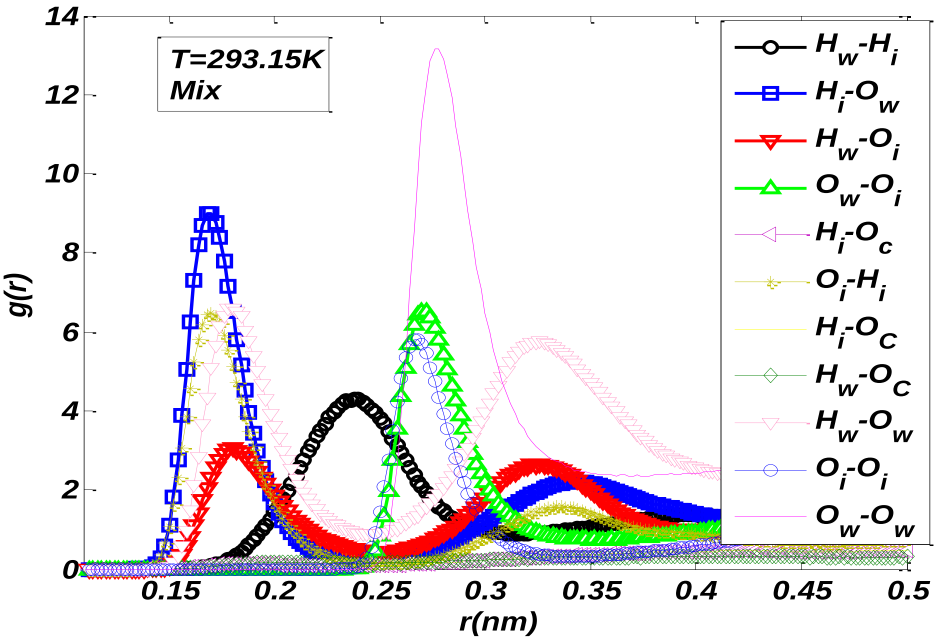

Figure 8: The partial radial distribution functions between various atoms in CO2/ isopropyl /water mixture at 293.15K

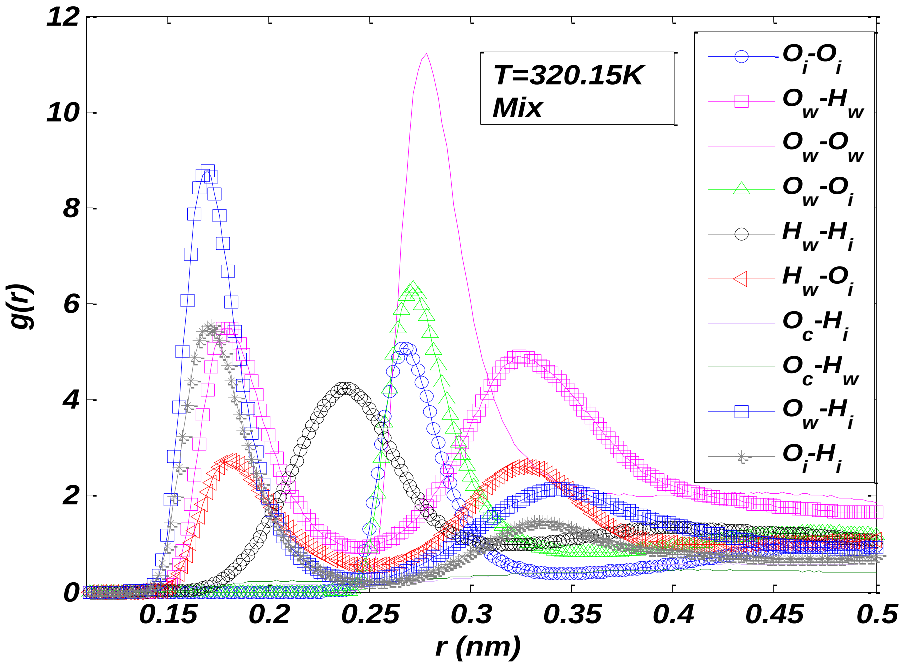

Figure 9: The partial radial distribution functions between various atoms in CO2/ isopropyl /water mixture at 320.15K

Table 3: The coordination numbers ($N_c(r)$) and the first peak heights of the radial distributions functions for mixture, pure isopropyl alcohol

Interaction	Molecule	N_C	first peak heights in RDF (nm)	Temperature(K)
O_W-O_W	mixture	7.29	13.16	293.15
H_I-O_W	mixture	1.40	9	293.15
O_I-H_I	mixture	1.12	6.48	293.15
O_W-H_W	mixture	1.53	6.6	293.15
O_W-O_I	mixture	3.24	6.51	293.15
O_W-O_W	mixture	6.71	11.21	320.15
H_I-O_W	mixture	1.44	8.75	320.15
O_I-H_I	mixture	1.06	5.52	320.15
O_W-H_W	mixture	1.36	5.49	320.15
O_W-O_I	mixture	3.26	6.32	320.15
H_I-H_I	Pure Isopropanol	1.97	6.01	293.15
O_I-O_I	Pure Isopropanol	1.91	7.51	293.15
O_I-H_I	Pure Isopropanol	0.96	8.48	293.15
H_I-H_I	Pure Isopropanol	1.97	5.54	320.15
O_I-O_I	Pure Isopropanol	1.88	6.80	320.15
O_I-H_I	Pure Isopropanol	0.93	7.55	320.15

Where $N_c(r)$ is the corresponding coordination numbers and R_{min} is the distance between the first zero value after RDF peak. The coordination numbers ($N_c(r)$) is obtained from Equation (9) is presented in Table 3. With enhancement of coordination numbers, more molecules participate in the reaction. Increasing temperature, the first peak heights of the radial distributions functions lower, local structure order lower, coordination numbers lower then mutual diffusion coefficient and self- diffusion coefficients increases. Fig. 4 and table 3 show the self-diffusion coefficients for water is more than carbon dioxide, isopropyl alcohol and their mixture [38, 44] . With enhancement of coordination numbers, more molecules participate in the reaction, hence stronger bounds are formed between molecules. The result of the pure water and carbon dioxide were taken from ref. [38, 44] and Table 3 show maximum coordination numbers among particle pure for water and minimum it for carbon dioxide. As Fig. 5 and table 3 and the result were taken from ref. [38, 44] show, the mutual- diffusion coefficients are inversely proportional to the coordination numbers.

Conclusion

In this study the changes in the values of thermodynamic quantities like enthalpies (ΔH), entropies (ΔS), heat capacities (ΔC_p), and change of Gibbs free energies (ΔG) for pure water, isopropyl, carbon dioxide, their mixture under thermal equilibrium condition at different temperature and atmospheric pressure were calculated using MD simulation. Results show that the ΔH's for the pure isopropyl, CO_2, water, and their mixture will be increased with temperature. The obtained values ΔH for the mixture is higher than their pure components. We have observed that the maximum values of ΔC_p in all cases belong to the mixtures. It is obvious that the values of ΔS for the mixture, pure water, carbon dioxide, and isopropyl alcohol increase by temperature increasing. For the mixing processes in this study, the values of ΔG are negative at 303.15 K, 308.15 K, 313.15 K, and 320.15 K temperatures. Also, it showed that the self-diffusion coefficient and the mutual diffusion coefficients increase by increasing temperature. The results show in mixture is the most interaction among atoms of water and isopropyl alcohol.

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