Hindawi International Journal of Chemical Engineering Volume 2018, Article ID 8689534, 10 pages https://doi.org/10.1155/2018/8689534



Research Article

Densities, Apparent Molar Volume, Expansivities, Hepler's Constant, and Isobaric Thermal Expansion Coefficients of the Binary Mixtures of Piperazine with Water, Methanol, and Acetone at T = 293.15 to 328.15 K

Qazi Mohammed Omar [0], 1 Jean-Noël Jaubert [0], 2 and Javeed A. Awan [0]

 $Correspondence\ should\ be\ addressed\ to\ Jean-No\"{e}l\ Jaubert;\ jean-noel.\ jaubert@univ-lorraine.fr\ and\ Javeed\ A.\ Awan;\ javeedawan@yahoo.com$

Received 11 May 2018; Revised 26 July 2018; Accepted 2 September 2018; Published 14 November 2018

Academic Editor: Gianluca Di Profio

Copyright © 2018 Qazi Mohammed Omar et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The properties of 3 binary mixtures containing piperazine were investigated in this work. In a first step, the densities for the two binary mixtures (piperazine + methanol) and (piperazine + acetone) were measured in the temperature range of 293.15 to 328.15 K and 293.15 to 323.15 K, respectively, at atmospheric pressure by using a Rudolph research analytical density meter (DDM 2911). The concentration of piperazine in the (piperazine + methanol) mixture was varied from 0.6978 to 14.007 mol/kg, and the concentration of piperazine in the (piperazine + acetone) mixture was varied from 0.3478 to 1.8834 mol/kg. On the other hand, the density data for the (piperazine + water) mixture were taken from the literature in the temperature range of 298.15 to 328.15 K. In a second step, for the 3 investigated systems, the apparent molar volume (V_{ϕ}) and the limiting apparent molar volume (V_{ϕ}^{0}) at infinite dilution were calculated using the Redlich–Mayer equation. The limiting apparent molar volumes (V_{ϕ}^{0}) were used to study the influence of the solute-solvent and solute-solute interactions. The temperature dependency of the apparent molar volumes was used to estimate the apparent molar expansibility, Hepler's constant $(\partial^{2}V_{\phi}^{0}/\partial T^{2})_{\rm p}$, and isobaric thermal expansion coefficients $\alpha_{\rm p}$.

1. Introduction

Information about the physical properties of solutions in the vast range of solute concentrations at different temperatures is greatly important for physicochemical processes (separation process, crystallization, vaporization, desalination, waste aqua treatment, environment protection, oil retrieval, etc.) and the natural environment [1, 2].

The apparent molar volumes are particularly relevant to determine the molecular interactions (solute to solute, solute to solvent, and solvent to solvent) happening in solutions [3]. Also, the apparent molar volumes of solutions at infinite dilution are useful to obtain information regarding solute to solvent and solvent to solvent interactions. However, the apparent molal volumes depend on strength of solution that

can be used for the determination of solute to solute interactions [4–6].

The thermophysical properties of piperazine + water is important for the design of gas processing technology [7] like in the treatment of natural gas having significant amount of $\rm H_2S$ and in processing of refinery waste gases as well as synthesis gas for manufacturing of NH₃, where solution of piperazine + water is used as a solvent for the removal of acidic gases (carbon dioxide and hydrogen sulfide). The highly effective removal of $\rm CO_2$ from industrial gases can also be performed by mixing piperazine with an alcohol such as the 2-amino-2-methyl-1-propanol [7, 8], which suggests that the alcoholic solutions of piperazine are also important in many separation processes. As another example, the separation of o- and p-chlorobenzoic acids from

¹Institute of Chemical Engineering and Technology, Faculty of Engineering and Technology, University of the Punjab, Lahore, Pakistan

²Université de Lorraine, Ecole Nationale Supérieure des Industries Chimiques, Laboratoire Réactions et Génie des Procédés (UMR CNRS 7274), 1 rue Grandville, 54000 Nancy, France

their eutectic blend usually uses a mixture of (piperazine + methanol) [9] as the solvent. In chemical processes, piperazine is present with crude products and has to be separated. In such a case, acetone is classically used due to its stronger molecular interaction with piperazine as compared to the higher molecular weight ketone [10].

In conclusion, the thermophysical properties of the 3 binary systems (piperazine + water), (piperazine + acetone), and (piperazine + methanol) are involved in many separation processes and thus need to be known. Consequently, it was decided to measure the densities of the (piperazine + acetone) and (piperazine + methanol) systems in the temperature range of 293.15 to 328.1 K and 293.15 to 323.15 K, respectively, since they are not available in the open literature. The concentration of piperazine was varied from 0.6978 to 14.007 mol/kg and from 0.3478 to 1.8834 mol/kg for methanol and acetone, respectively. The density data for (piperazine + water) were taken from literature in the temperature range of 298.15 to 328.15 K. [11]. For the 3 investigated binary systems, the density data were used for the calculation of the apparent molar volume, limiting apparent molar volume, apparent molar expansivities, Hepler's constant, and isobaric thermal expansion coefficient.

2. Experimental Work

2.1. Materials. The chemicals used in this work are piperazine (purity \geq 99%), methanol (\geq 99.4%), and acetone (\geq 99.8%). They were provided by Sigma-Aldrich (Germany) and were used without any further purification or treatment. The purity of these chemicals used along with their source and CAS number are tabulated in Table 1. The deionized water has been prepared in lab through alfa-pore machine (WAP-4).

2.2. Measurement of the Density. An analytical digital vibrating glass U-tube densitometer (DDM-2911, Rudolph) with an accuracy of 0.05 kg/m³ was used to measure the density of the 2 mixtures: piperazine + methanol and piperazine + acetone. A schematic diagram of the used densitometer is illustrated in Figure 1. The binary mixtures were prepared by weight using a Sartorius analytical weight balance with an uncertainty of ±0.00029 g (the corresponding uncertainty in molality was ±0.0004 mol/kg). The densities of the pure solvents and their blends with piperazine were measured in a temperature range varying from 298.15 to 333.15 K. The calibration of the apparatus was conducted by comparing the density of air and water at 293.15 K and the barometric pressure. Air was provided through a suction tube filled with silica balls to ensure a provision of dry air, and double-distilled water was injected through a syringe into the density meter. Silica balls were regularly heated to remove the moisture content absorbed from the atmospheric air. Once calibrated, the U-tube densitometer was washed with distilled water and dried with acetone and air. The density data reported in this study are an average of at least three runs. To remove the air bubbles from the samples, all the solutions were sonicated by using a universal ultrasonic cleaner for 30 min. Later, the samples were stored in vials and placed into a desiccator for 10 minutes for proper mixing and settling. For each

TABLE 1: List of chemicals used in this work.

Chemicals	Purity	Source	CAS number
Piperazine	≥99%	Merck	110-85-0
Methanol	≥99.4%	Merck	67-56-1
Acetone	≥99.8%	Merck	67-64-1

measurement, the tube was washed with water and dried with acetone. During the measurements, the air pump was always turned off to avoid irregularities due to vibrations.

Table 2 shows the densities of the pure solvents (methanol and acetone) measured in this study in the temperature range of 293.1–328.15 K along with values reported in the literature. An average deviation of approximately 0.03% is observed between both sets of data, which suggests that our data are consistent with previously measured densities and that our equipment is reliable.

3. Results and Discussion

The densities of all three binary mixtures (piperazine + water), (piperazine + methanol), and (piperazine + acetone) a function of the molality of piperazine and temperature are presented in Table 3 and plotted in Figures 2-4. The experiments cover the commercially significant concentration range of piperazine with water, methanol, and acetone, that is, concentrations that are important for industrial applications like the design of gas processing technology, liquid-liquid extraction, and leaching. More specifically, the mixtures of piperazine + methanol were prepared in a concentration range of 2.187 wt.% to 30.978 wt.% (0.6978 mol/kg to 14.007 mol/kg). Similarly, mixtures of piperazine + acetone were prepared in concentration range from 1.98 wt.% to 9.86 wt.% (0.3478 mol/kg to 1.8834 mol/kg). It is observed that the density of the mixture increases with an increase in the concentration of piperazine. However, the density decreases with an increase in the temperature.

The apparent molar volumes [26] (V_{ϕ}) (in m³/mol) of piperazine were calculated from the densities of the solutions by using the equation given below:

$$V_{\phi} = \frac{M}{\rho} + \frac{\rho_0 - \rho}{m \cdot \rho \cdot \rho_0},\tag{1}$$

where m is the molality of piperazine (mol/kg), ρ and ρ_0 are densities (in kg/m³) of the solution and pure solvent, respectively, and M is the molar mass of piperazine (in kg/mol). The apparent molar volume (V_{ϕ}) of all three binary mixtures (piperazine + water), (piperazine + methanol), and (piperazine + acetone) calculated from Equation (1) as a function of molality of piperazine and temperature is tabulated in Table 4 and plotted in Figures 5–7 (denoted by markers). Figures 5–7 show that V_{ϕ} values rise with rise in temperature for each binary mixture, highlighting that the overall order of the structure is improved or increased in solution with rising temperature [27]. The influence of the molality depends on the studied system, that is, the apparent molar volumes may rise, decrease, or progress through a maximum. Our data were correlated with the Redlich–Mayer equation [28]:

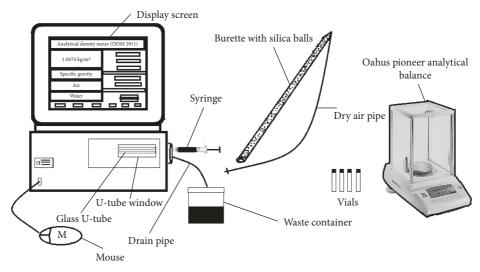


FIGURE 1: Schematic diagram of the experimental setup (analytical density meter (DDM 2911)).

Table 2: Comparison of the densities of the pure solvents measured in this study with those reported previously at various temperatures and at atmospheric pressure with standard uncertainties: $u(T) = \pm 0.01 \text{ K } u(\rho) = \pm 0.1 \text{ kg/m}^3$, $u(m) = \pm 0.004 \text{ mol/kg}$, and $u(P) = \pm 0.002 \text{ atm}$.

	Density (ρ_0) kg/m ³										
		Meth		Acetone							
T/K	This work	Lit. value	(Reference)	T/K	This work	Lit. value	(Reference)				
293.15	791.6	791.9	(Papanastasiou and Ziogas [12])	293.15	789.9	790.02	(Kinart et al. [13])				
		791.65	(Gonfa et al. [14])			790.355	(Janz and Tomkins [15])				
298.15	786.9	786.884	(Anwar and Yasmeen [16])	298.15	784.2	784.45	(Kinart et al. [13])				
		786.68	(Tu et al. [17])			784.638	(Janz and Tomkins [15])				
303.15	782.2	782.158	(Anwar and Yasmeen [16])	303.15	778.5	778.7	(Fan et al. [18])				
		781.9	(Tu et al. [19])			778.57	(Enders et al. [20])				
308.15	777.2	777.2	(Tu et al. [17])	308.15	773.0	773.0	(Hafez and Hartland [21])				
		777.414	(Anwar and Yasmeen [16])			773.065	(Janz and Tomkins [15])				
313.15	772.4	772.3	(Tu et al. [19])	313.15	767.3	767.03	(Fan et al. [18])				
		772.64	(Anwar and Yasmeen [16])			767.21	(Estrada-Baltazar et al [22])				
318.15	767.5	767.6	(Tu et al. [17])	318.15	761.6	761.288	(Janz and Tomkins [15])				
		767.844	(Anwar and Yasmeen [16])			761.3	(Hafez and Hartland [21])				
323.15	762.7	762.7	(Bhuiyan and Uddin [23])	323.15	755.7	755.14	(Fan et al. [18])				
		763.028	(Anwar and Yasmeen [16])			755.31	(Estrada-Baltazar et al [22])				
328.15	757.7	759.2	(Cai et al. [24])			755.54	(Wu et al. [25])				

$$V_{\phi} = V_{\phi}^{0} + S_{\mathbf{v}}\sqrt{m} + B_{\mathbf{v}} \cdot m, \tag{2}$$

where V_{ϕ}^0 is the limiting apparent molar volume of the piperazine mixtures and $S_{\rm v}$ and $B_{\rm v}$ are two regression parameters. Figures 6 and 7 highlight that our data are accurately correlated with such a simple model. The corresponding values of V_{ϕ}^0 , $S_{\rm v}$, and $B_{\rm v}$ are tabulated in Table 5. From this table, notably, the V_{ϕ}^0 values rise with rise in temperature for each binary mixture. As highlighted by [29], this behavior characterizes the presence of strong solute to solvent interactions that are strengthened with the rise in temperature. It is worth noting that this behavior was also observed for many systems. We can cite the (methanol + methyl acetate) system reviewed by [30], the (methanol + ethyl acetate), the (ethanol + methyl acetate) and (ethanol + ethyl acetate) systems studied by [29], the (methanol + isopropyl alcohol), the (methyl salicylate + DMSO) and (hydroxamic acid + DMSO) examined by [31]. The V_{ϕ}^0 values of the mixtures rise in the

following order: (piperazine + methanol) < (piperazine + water) < (piperazine + acetone), which could be due—as explained by [29]—to an enhancement in the strengths of the solute to solvent interactions. This enhancement results in an increase of contraction in the volume.

The values of $S_{\rm V}$ and $B_{\rm V}$ are also tabulated in Table 5. The $S_{\rm V}$ values are negative for (piperazine + acetone) and positive for the (piperazine + water) and (piperazine + methanol) systems at each temperature. The $S_{\rm V}$ value decreases with rise in temperature for each binary system. The strength of the solute to solute interactions of each system increases in the following order: (piperazine + methanol) > (piperazine + water) > (piperazine + acetone). The solute to solute interaction decreases with an increase in temperature for each binary system. The $B_{\rm V}$ values are negative for the (piperazine + acetone) mixture at each temperature. The $B_{\rm V}$ values rise with rise in temperature for each binary system. The negative $B_{\rm V}$ values show rise in solute to solute interactions for

Table 3: Densities (kg/m³) of the binary mixtures (piperazine + water), (piperazine + methanol), and (piperazine + acetone) as a function of the molality and temperature at atmospheric pressure. A global uncertainty calculation was performed on each point and the corresponding values are given in parentheses.

Temperature (K)	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15			
Molality (mol/kg) of piperazine		Binary sys	stem densities	(kg/m ³) with g	lobal uncertain	ty (kg/m³) in p	parentheses				
		Systen	ı (piperazine +	water) (Muhar	nmad et al. [11	.])					
0.9838	_	998.3	996.9	995.2	993.4	991.4	989.2	986.8			
3.0226	_	999.4	997.9	996.3	994.4	992.4	990.1	987.8			
6.4138	_	1001.3	999.8	998.0	996.1	994.0	991.7	989.3			
System (piperazine + methanol) (this work)											
0.6978	805.8 (0.02)	801.2 (0.01)	796.4 (0.02)	791.3 (0.007)	786.5 (0.02)	781.7 (0.01)	776.6 (0.01)	771.3 (0.01)			
1.4000	817.4 (0.04)	812.9 (0.02)	808.2 (0.03)	803.5 (0.01)	798.6 (0.02)	793.6 (0.01)	788.4 (0.02)	783.2 (0.01)			
2.2148	829.6 (0.03)	825.2 (0.02)	820.5 (0.03)	815.7 (0.02)	810.9 (0.02)	805.9 (0.02)	800.8 (0.02)	795.6 (0.02)			
3.0544	840.7 (0.04)	836.3 (0.02)	831.7 (0.04)	827.0 (0.04)	822.1 (0.03)	817.2 (0.03)	812.1 (0.03)	806.9 (0.02)			
3.7151	849.0 (0.04)	844.6 (0.02)	840.0 (0.04)	835.3 (0.04)	830.5 (0.04)	825.6 (0.03)	820.5 (0.04)	815.4 (0.02)			
5.1007	862.6 (0.05)	858.2 (0.03)	853.7 (0.04)	849.0 (0.05)	844.5 (0.04)	839.6 (0.04)	834.6 (0.04)	829.5 (0.03)			
5.9003	870.3 (0.05)	866.0 (0.03)	861.5 (0.05)	856.9 (0.05)	852.1 (0.05)	847.2 (0.04)	842.2 (0.05)	837.1 (0.04)			
7.4725	881.4 (0.06)	877.1 (0.03)	872.6 (0.05)	868.0 (0.06)	863.2 (0.06)	858.4 (0.05)	853.4 (0.06)	848.3 (0.04)			
9.2198	893.9 (0.06)	889.6 (0.04)	885.2 (0.05)	880.6 (0.06)	875.8 (0.06)	871.0 (0.05)	866.1 (0.07)	861.1 (0.05)			
14.007	912.6 (0.06)	908.4 (0.05)	903.9 (0.06)	899.3 (0.06)	894.6 (0.07)	889.6 (0.05)	884.2 (0.07)	879.3 (0.06)			
			System (pipera	zine + acetone)	(this work)						
0.3478	792.4 (0.01)	786.5 (0.005)	780.8 (0.01)	774.9 (0.006)	768.8 (0.002)	762.7 (0.002)	756.3 (0.002)	_			
0.8416	796.7 (0.02)	791.0 (0.02)	785.2 (0.02)	779.3 (0.02)	773.3 (0.008)	767.2 (0.01)	760.9 (0.01)	_			
1.0951	799.3 (0.03)	793.5 (0.02)	787.7 (0.03)	781.6 (0.02)	775.5 (0.01)	769.1 (0.02)	762.7 (0.02)	_			
1.3359	802.3 (0.03)	797.0 (0.03)	790.7 (0.03)	784.6 (0.03)	778.4 (0.02)	772.1 (0.02)	765.6 (0.02)	_			
1.8834	807.5 (0.03)	802.0 (0.04)	795.9 (0.03)	789.9 (0.03)	784.1 (0.02)	778.2 (0.03)	772.1 (0.03)	_			

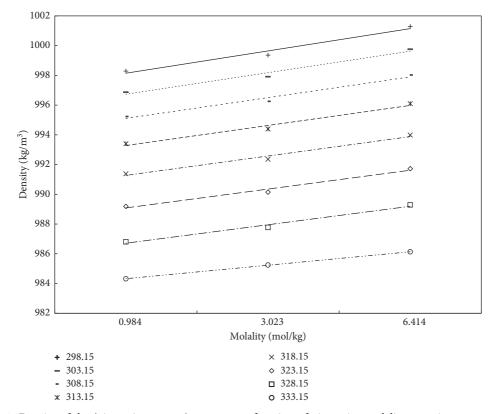


FIGURE 2: Density of the (piperazine + water) system as a function of piperazine molality at various temperatures.

mixtures that is, (piperazine + water) and (piperazine + methanol). The positive $B_{\rm V}$ values indicate strong solute to solute interactions for the (piperazine + acetone) system.

The temperature dependence of the limiting apparent molar volume (V_ϕ^0) can be expressed in terms of the following equation [26]:

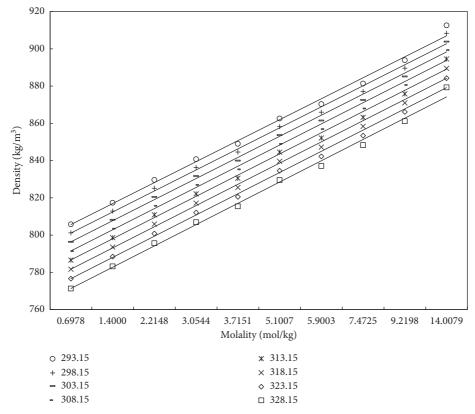


FIGURE 3: Density of the (piperazine+methanol) system as a function of piperazine molality at various temperatures.

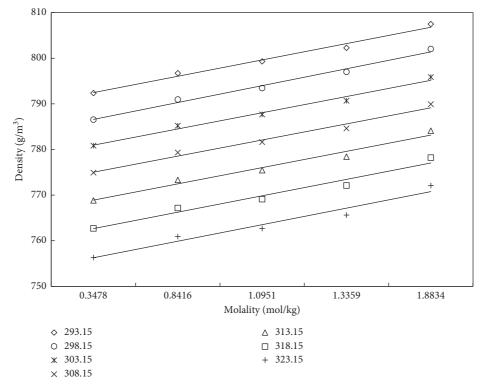


FIGURE 4: Density of the (piperazine + acetone) system as a function of piperazine molality at various temperatures.

Table 4: Apparent molar volume (m³/mol) of the binary mixtures (piperazine + water), (piperazine + methanol), and (piperazine + acetone) as a function of the molality and temperature at atmospheric pressure with the standard uncertainty: $u(V_{\phi}) = \pm 0.35 \times 10^{-6} \text{ m}^3/\text{mol}$.

Temperature (K)	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15
Molality (mol/kg) of piperazine		Bir	nary system a	pparent mol	ar volumes 10	$0^6 \times V_\phi \text{ (m}^3/\text{n}$	nol)	
		System	(piperazine	+ water)				
0.9838		85.02	85.16	85.32	85.49	85.67	85.88	86.13
3.0226	_	85.43	85.57	85.72	85.89	86.08	86.28	86.50
6.4138		85.37	85.52	85.68	85.87	86.06	86.27	86.50
		System (piperazine +	methanol)				
0.6978	75.02	75.24	75.50	75.84	76.07	76.38	77.32	78.39
1.4000	76.96	77.05	77.18	77.15	77.48	77.97	78.69	79.32
2.2148	77.69	77.84	78.02	78.13	78.44	78.83	79.39	79.88
3.0544	78.29	78.46	78.65	78.78	79.11	79.48	79.98	80.41
3.7151	78.48	78.66	78.86	79.03	79.31	79.67	80.11	80.49
5.1007	79.49	79.70	79.93	80.13	80.30	80.66	81.07	81.45
5.9003	79.61	79.82	80.04	80.24	80.54	80.90	81.29	81.68
7.4725	80.52	80.75	81.00	81.23	81.55	81.89	82.29	82.68
9.2198	80.69	80.92	81.18	81.43	81.77	82.11	82.47	82.84
14.007	82.43	82.71	83.01	83.31	83.66	84.07	84.55	84.93
		System	(piperazine +	acetone)				
0.3478	97.37	98.38	99.39	102.11	104.76	107.33	110.96	_
0.8416	95.20	95.88	96.72	98.09	99.43	100.86	102.50	_
1.0951	94.14	94.91	95.75	97.22	98.65	100.24	101.94	_
1.3359	92.75	92.69	94.15	95.49	96.78	98.16	99.71	_
1.8834	92.02	92.32	93.37	94.36	95.06	95.77	96.69	_

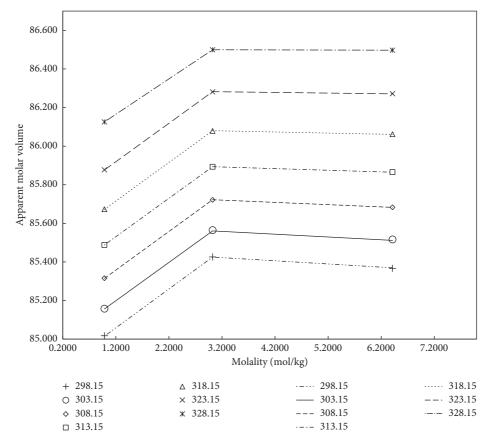


FIGURE 5: Apparent molar volume (V_{ϕ}) of the binary mixture (piperazine+water) as a function of piperazine molality at different temperatures.

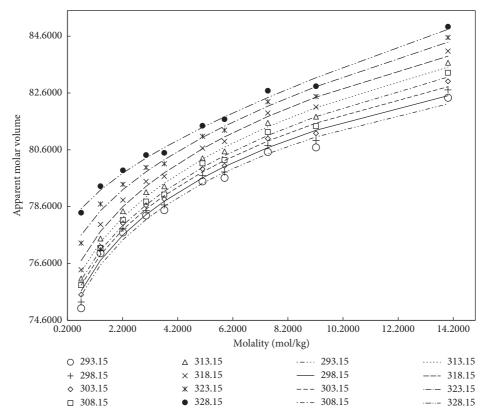


FIGURE 6: Apparent molar volume (V_{ϕ}) of the binary mixture (piperazine + methanol) as a function of piperazine molality at different temperatures. The correlations performed with the Redlich–Mayer equation are plotted as solid/dashed lines.

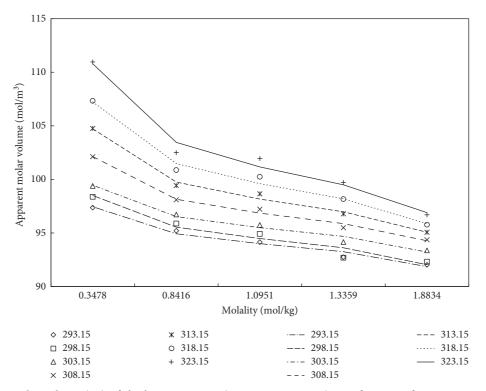


Figure 7: Apparent molar volume (V_{ϕ}) of the binary mixture (piperazine + acetone) as a function of piperazine molality at different temperatures. The correlations performed with the Redlich–Mayer equation are plotted as solid/dashed lines.

• •		-						
Temperature (K)	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15
		Sy.	stem (piperazi	ne + water)				
$10^6 \times V_{\phi}^0 \text{ (m}^3 \cdot \text{mol}^{-1}\text{)}$		83.78	83.94	84.11	84.30	84.49	84.71	85.07
$10^6 \times S_v (m^3 \cdot kg^{1/2} \cdot mol^{-3/2})$	_	1.65	1.61	1.60	1.57	1.56	1.53	1.39
$10^6 \times B_{\rm v} \ ({\rm m}^3 \cdot {\rm kg} \cdot {\rm mol}^{-2})$	_	-0.40	-0.39	-0.39	-0.38	-0.37	-0.36	-0.33
		Syste	em (piperazin	e + methanol)				
$10^6 \times V_{\phi}^0 \text{ (m}^3 \cdot \text{mol}^{-1}\text{)}$	72.57	72.75	72.99	73.27	73.57	74.01	75.48	77.05
$10^6 \times S_v (m^3 \cdot kg^{1/2} \cdot mol^{-3/2})$	3.72	3.69	3.63	3.47	3.45	3.38	2.58	1.67
$10^6 \times B_{\rm v} \ ({\rm m}^3 \cdot {\rm kg} \cdot {\rm mol}^{-2})$	-0.31	-0.29	-0.27	-0.22	-0.21	-0.20	-0.05	0.11
		Sys	tem (piperazir	ie + acetone)				
$10^6 \times V_{\phi}^0 \text{ (m}^3 \cdot \text{mol}^{-1}\text{)}$	102.68	104.72	105.89	111.82	117.01	121.20	129.50	_
$10^{6} \times V_{\phi}^{0} \text{ (m}^{3} \cdot \text{mol}^{-1})$ $10^{6} \times S_{v} \text{ (m}^{3} \cdot \text{kg}^{1/2} \cdot \text{mol}^{-3/2})$	-9.60	-11.54	-12.17	-19.19	-24.51	-27.62	-37.74	_
$10^6 \times B_v \text{ (m}^3 \cdot \text{kg} \cdot \text{mol}^{-2}\text{)}$	1.26	1.68	2.14	4.66	6.21	6.67	10.19	_

Table 5: Values of the limiting apparent molar volume (V_{ϕ}^{0}) along with the S_{v} and B_{v} parameters to be used in the Redlich–Mayer equation for each of the 3 binary systems as a function of temperature.

Table 6: The limiting apparent molar expansibility (E_{ϕ}^{0}) and isobaric thermal expansion coefficient $\alpha_{\rm p}$.

				,				
Temperature (K)	293.15	298.15	303.15	308.15	313.15	318.15	323.15	328.15
Binary mixtures								
			$10^6 \times E_{\phi}^0 \text{ (m}^3$	\cdot mol ⁻¹ ·K ⁻¹)				
Piperazine + water	_	2.64	3.24	3.84	4.44	5.04	5.64	6.24
Piperazine + methanol	-0.04	0.03	0.10	0.16	0.23	0.29	0.35	0.41
Piperazine + acetone	25.38	46.78	68.18	89.58	110.98	132.38	153.78	_
			$10^3 \times \alpha_{\rm I}$	(K ⁻¹)				
Piperazine + water	_	0.31	0.39	0.46	0.53	0.60	0.67	0.73
Piperazine + methanol	-0.39	0.28	0.95	1.62	2.28	2.93	3.52	4.08
Piperazine + acetone	2.47	4.47	6.44	8.01	9.48	10.92	11.88	_

$$V_{\phi}^{0} = A + BT + CT^{2},\tag{3}$$

where A, B, and C are empirical parameters and T is the temperature. The limiting apparent molar expansibility (E_ϕ^0) can be obtained by differentiating Eq. (3) with respect to the temperature:

$$E_{\phi}^{0} = \left(\frac{\partial V_{\phi}^{0}}{\partial T}\right) = B + 2CT,\tag{4}$$

The (E_{ϕ}^{0}) values for each binary system are tabulated in Table 6 which gives important information related to the solute to solvent interactions [32]. Table 6 depicts that, at each temperature, the (E_{ϕ}^{0}) values are positive for all three binary systems and decrease with rise in temperature.

According to Hepler's theory [33] the so-called Hepler's constant, $(\partial^2 V_\phi^0/\partial T^2)$, can be used to classify a solute into two categories, whether solute can act as a builder of structure or as a breaker of structure. If the $(\partial^2 V_\phi^0/\partial T^2)$ value is positive, then the solute is favorable in development or making of structure. Conversely, if the $(\partial^2 V_\phi^0/\partial T^2)$ value is negative, then the solute will act as a structure breaker. The values of $(\partial^2 V_\phi^0/\partial T^2)$ are -0.33, -2.89, and -12.25 for the binary mixtures, that is, (piperazine + water), (piperazine + methanol), and (piperazine + acetone), respectively. Thus, piperazine acts as a structure breaker in solution. The proof for the effect of Hepler's constant on microscopic structure is discussed in the literature [34].

The isobaric thermal expansion coefficient, α_p , of the solute was calculated using the apparent molar volume and apparent molar expansibility at infinite dilution data:

$$\alpha_{\rm p} = \frac{1}{V_{\phi}^0} \left(\frac{\partial V_{\phi}^0}{\partial T} \right) = \frac{E_{\phi}^0}{V_{\phi}^0}.$$
 (5)

The isobaric thermal expansion coefficient, α_p , is also tabulated in Table 6. A higher value of α_p was obtained for acetone, and lower value of α_p was obtained for water.

4. Conclusion

In this work, new density data for 2 binary mixtures (piperazine+methanol) and (piperazine+acetone) were measured from 293.15 K to 328.15 K. It was found that the density of both the mixtures increases with increase in temperature but decreases with increase in concentration. Similarly, V_{ϕ} values rise with increase in concentration of piperazine in methanol but decreases in case of acetone. Also, the apparent molar volume (V_{ϕ}^0) , limiting apparent molar volume (V_{ϕ}^0) , apparent molar expansibility (E_{ϕ}^0) , Hepler's constant, and isobaric thermal expansion coefficient $(\alpha_{\rm P})$ were calculated and reported in this work. The limiting apparent molar volume V_{ϕ}^0 increases with temperature, which highlights the strong interactions of the solute with the solvent. The positive apparent molar expansibility (E_{ϕ}^0) decreases with temperature, which indicates

that the interactions increase with a rise in the temperature of the solution. The negative values of the Helper's constant suggest that piperazine acts as a structure breaker in the solvent. The Redlich–Mayer equation was used to correlate the apparent molar volume with the standard deviation, $\mathbf{u}(V_{\phi}) = \pm 0.35 \times 10^{-6} \, \mathrm{mol/m^3}$.

Nomenclature

- V_{ϕ} : Apparent molar volume
- V_{ϕ}^{0} : Apparent molar volume at infinite dilution
- ρ : Density of the solution
- ρ_0 : Density of the pure solvent
- S_V: Empirical parameter of the apparent molar volume
- $B_{\rm V}$: Empirical parameter of the apparent molar volume
- $\alpha_{\rm p}$: Isobaric thermal expansion coefficient
- E_{ϕ}^{0} : Limiting apparent molar volume expansibility
- \dot{M} : Molar mass of the solute
- *m*: Molality of the solute.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

This research was performed as part of the employment of the authors. Consequently, University of the Punjab and University of Lorraine are warmly thanked. The work described in this paper has been presented at the Chisa 2018 International Conference that took place in Prague (Czech Republic) in August 2018.

References

- [1] S. Gupta and J. D. Olson, "Industrial needs in physical properties," *Industrial & Engineering Chemistry Research*, vol. 42, no. 25, pp. 6359–6374, 2003.
- [2] K. S. Pitzer, "Thermodynamics of natural and industrial waters," *Journal of Chemical Thermodynamics*, vol. 25, no. 1, pp. 7–26, 1993.
- [3] F. J. Millero, "Molal volumes of electrolytes," *Chemical Reviews*, vol. 71, no. 2, pp. 147–176, 1971.
- [4] Y. Marcus, Ion Solvation, Wiley, New York, NY, USA, 1985.
- [5] F. J. Millero, Water and Aqueous Solutions, Structure, Thermodynamics, and Transport Properties, Chapter 13, R. A. Horne, Ed., Wiley Interscience, New York, NY, USA, 1972..
- [6] R. Perkins, T. Andersen, J. O. M. Bockris, and B. E. Conway, Modern Aspects of Electrochemistry, Kluwer Academic Publishers, Norwell, MA, USA, 1969.
- [7] A. Samanta and S. S. Bandyopadhyay, "Density and viscosity of aqueous solutions of piperazine and (2-amino-2-methyl-1-propanol + piperazine) from 298 to 333 K," *Journal of Chemical & Engineering Data*, vol. 51, no. 2, pp. 467–470, 2006.

- [8] A. L. Kohl and R. Nielsen, *Gas Purif*, Gulf Professional Publishing, Houston, TX, USA, 1997.
- [9] A. Lashanizadegan, N. S. Tavare, M. Manteghian, and D. M. Newsham, "Ternary phase equilibrium diagrams for o-and p-chlorobenzoic acids and their complex with piperazine in methanol," *Journal of Chemical & Engineering Data*, vol. 45, no. 6, pp. 1189–1194, 2000.
- [10] G. R. Bond, "Determination of piperazine as piperazine diacetate," *Analytical Chemistry*, vol. 32, no. 10, pp. 1332– 1334, 1960.
- [11] A. Muhammad, M. I. A. Mutalib, T. Murugesan, and A. Shafeeq, "Thermophysical properties of aqueous piperazine and aqueous (N-methyldiethanolamine + piperazine) solutions at temperatures (298.15 to 338.15) K," *Journal of Chemical & Engineering Data*, vol. 54, no. 8, pp. 2317–2321, 2009.
- [12] G. E. Papanastasiou and I. I. Ziogas, "Physical behavior of some reaction media. 3. Density, viscosity, dielectric constant, and refractive index changes of methanol + dioxane mixtures at several temperatures," *Journal of Chemical & Engineering Data*, vol. 37, no. 2, pp. 167–172, 1992.
- [13] C. M. Kinart, W. J. Kinart, and A. Ć. wiklińska, "Density and viscosity at various temperatures for 2-methoxyethanol+acetone mixtures," *Journal of Chemical & Engineering Data*, vol. 47, no. 1, pp. 76–78, 2002.
- [14] G. Gonfa, M. A. Bustam, N. Muhammad, and S. Ullah, "Density and excess molar volume of binary mixture of thiocyanate-based ionic liquids and methanol at temperatures 293.15–323.15 K," *Journal of Molecular Liquids*, vol. 211, pp. 734–741, 2015.
- [15] G. J. Janz and R. P. T. Tomkins, Nonaqueous Electrolytes Handbook, Vol. 1, Academic Press, New York, NY, USA, 1972.
- [16] N. Anwar and S. Yasmeen, "Volumetric, compressibility and viscosity studies of binary mixtures of [EMIM][NTf2] with ethylacetate/methanol at (298.15–323.15) K," *Journal of Molecular Liquids*, vol. 224, pp. 189–200, 2016.
- [17] C. H. Tu, H. C. Ku, W. F. Wang, and Y. T. Chou, "Volumetric and viscometric properties of methanol, ethanol, propan-2-ol, and 2-methylpropan-2-ol with a synthetic C₆₊ mixture from 298.15 K to 318.15 K," *Journal of Chemical & Engineering Data*, vol. 46, no. 2, pp. 317–321, 2001.
- [18] X. H. Fan, Y. P. Chen, and C. S. Su, "Densities and viscosities of binary liquid mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate with acetone, methyl ethyl ketone, and N-methyl-2-pyrrolidone," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 61, pp. 117–123, 2016.
- [19] C. H. Tu, S. L. Lee, and I. H. Peng, "Excess volumes and viscosities of binary mixtures of aliphatic alcohols (C1–C4) with nitromethane," *Journal of Chemical & Engineering Data*, vol. 46, no. 1, pp. 151–155, 2001.
- [20] S. Enders, H. Kahl, and J. Winkelmann, "Surface tension of the ternary system water + acetone + toluene," *Journal of Chemical & Engineering Data*, vol. 52, no. 3, pp. 1072–1079, 2007.
- [21] M. Hafez and S. Hartland, "Densities and viscosities of binary systems toluene-acetone and 4-methyl-2-pentanone-acetic acid at 20, 25, 35, and 45. degree. C," *Journal of Chemical & Engineering Data*, vol. 21, no. 2, pp. 179–182, 1976.
- [22] A. Estrada-Baltazar, A. De León-Rodríguez, K. R. Hall, M. Ramos-Estrada, and G. A. Iglesias-Silva, "Experimental densities and excess volumes for binary mixtures containing propionic acid, acetone, and water from 283.15 K to 323.15 K at atmospheric pressure," *Journal of Chemical & Engineering Data*, vol. 48, no. 6, pp. 1425–1431, 2003.

- [23] M. M. H. Bhuiyan and M. H. Uddin, "Excess molar volumes and excess viscosities for mixtures of N, N-dimethylformamide with methanol, ethanol and 2-propanol at different temperatures," *Journal of Molecular Liquids*, vol. 138, no. 1–3, pp. 139–146, 2008.
- [24] D. Cai, J. Yang, H. Da, L. Li, H. Wang, and T. Qiu, "Densities and viscosities of binary mixtures N, N-dimethyl-N-(3-sulfopropyl) cyclohexylammonium tosylate with water and methanol at T = (303.15 to 328.15) K," *Journal of Molecular Liquids*, vol. 229, pp. 389–395, 2017.
- [25] J. Y. Wu, Y. P. Chen, and C. S. Su, "The densities and viscosities of a binary liquid mixture of 1-n-butyl-3-methylimidazolium tetrafluoroborate, ([Bmim][BF4]) with acetone, methyl ethyl ketone and N, N-dimethylformamide, at 303.15 to 333.15 K," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 45, no. 5, pp. 2205–2211, 2014.
- [26] M. T. Zafarani-Moattar and H. Shekaari, "Apparent molar volume and isentropic compressibility of ionic liquid 1-butyl-3-methylimidazolium bromide in water, methanol, and ethanol at T = (298.15 to 318.15) K," *Journal of Chemical Thermodynamics*, vol. 37, no. 10, pp. 1029–1035, 2005.
- [27] P. Khanuja, V. R. Chourey, and A. A. Ansari, "Apparent molar volume and viscometric study of glucose in aqueous solution," *Journal of Chemical and Pharmaceutical Research*, vol. 4, pp. 3047–3050, 2012.
- [28] O. Redlich and D. M. Meyer, "The molal volumes of electrolytes," *Chemical Reviews*, vol. 64, no. 3, pp. 221–227, 1964.
- [29] I. Bahadur, N. Deenadayalu, and D. Ramjugernath, "Effects of temperature and concentration on interactions in methanol+ ethyl acetate and ethanol+ methyl acetate or ethyl acetate systems: Insights from apparent molar volume and apparent molar isentropic compressibility study," *Thermochimica Acta*, vol. 577, pp. 87–94, 2014.
- [30] I. Bahadur and N. Deenadayalu, "Apparent molar volume and isentropic compressibility for the binary systems {methyltrioctylammoniumbis(trifluoromethylsulfonyl)imide + methyl acetate or methanol} and (methanol + methyl acetate) at T = 298.15, 303.15, 308.15 and 313.15 K and atmospheric pressure," *Journal of Solution Chemistry*, vol. 40, pp. 1528–1543, 2011.
- [31] R. S. Sah, P. Pradhan, and M. N. Roy, "Solute–solvent and solvent–solvent interactions of menthol in isopropyl alcohol and its binary mixtures with methyl salicylate by volumetric, viscometric, interferometric and refractive index techniques," *Thermochimica Acta*, vol. 499, pp. 149–154, 2010.
- [32] H. Shekaari, S. S. Mousavi, and Y. Mansoori, "Thermophysical properties of ionic liquid, 1-pentyl-3-methylimidazolium chloride in water at different temperatures," *International Journal of Thermophysics*, vol. 30, no. 2, pp. 499–514, 2009.
- [33] L. G. Hepler, "Thermal expansion and structure in water and aqueous solutions," *Canadian Journal of Chemistry*, vol. 47, no. 24, pp. 4613–4617, 1969.
- [34] P. K. Thakur, S. Patre, and R. Pande, "Thermophysical and excess properties of hydroxamic acids in DMSO," *Journal of Chemical Thermodynamics*, vol. 58, pp. 226–236, 2013.



















Submit your manuscripts at www.hindawi.com











International Journal of Antennas and

Propagation











