Excess Molar volumes and Densities of the binary mixtures of Acetone with Chloroalkanes at temperatures between (288.15 and 318.15) K

1. NIRMAL KUMAR, National Degree College, Purnea
2. RAMAN GUNJAN, National Degree College, Purnea

Abstract

The experimental densities of binary mixture of Acetone with 1,1,2,2- tetrachloroethane, 1,1,1-trichloroethane, trichloromethane, 1.2- dichloroethane,1,3-dichloropropane, 1.4-dichlorobutane and 1-chlorobutane have been measured at T=(288.15, 298.15, 308.15 and 318.15) K and atmospheric pressure over the wghole composition range. Frome these results, excess molor volumes, V^E , have been calculated and fitted redlich—Kister polynomial equation. The excess molor volumes are negative for the Acetone +1,1,2,2-tetrachloroethane, 1,1,1- trichloroethane, trichloromethane, and 1-chlorobutane systems and positive for the other three systems, over the whole composition range and at all investigated temperatures. The variation of these properties with rhe composition of the binary mixtures is discussed ion the terms of molecular interactions between components and structural effects.

Introduction

The physicochemical properties of liquid mixtures have attracted much attention from the point of view of both theoretical and engineering applications. Many engineering applications require quantitative data on the density of liquid mixtures. They also provide information about the nature and molecular interactions between liquid mixture components.

Acetone is a versatile solvent, having a globular molecule and being used in the synthesis of pharmaceuticals, is agricultural chemistry and as a solvent for polymers. Mono- and polychloroalkanes represent a class of technically important compounds, used in industry as intermediates or as final products. Both acetone and chloroalkanes are polar and practically unassociated liquids. These compounds are also interesting from a theoretical aspect because of the inter- and intramolecular effects. A fundamental understanding of the mixture behavior of Acetone with chloroalkanes is therefore important from the technical and engineering standpoint. The present work us a continuation of the studies devoted to the physicochemical properties of various nonelectrolyte systems. [1-3] Concerning the volumetric behavior of ketones with chloroalkanes mixtures, so far we have studies systems of linear ketones(propan-2-one, eentan-3-one) with several chloroalkanes, [1-3] and here we report density date for mixtures of a cyclic ketone with mone-, di-, and tetrachloroalkanes at temperatures between (288.15 and 318.15) K and atmospheric pressure. The values of the excess molor volumes of the studied systems and reported with the aim to discuss the results in terms of structural effects and molecular interactions between components.

A survey of the literature indicates that volumetric properties of binary mixtures of Aceton + 1,1,1-trichloroethane, trechloromethane and dechloroethane have been studied by other authors [4-10]at (298.15, 303.15 and 308.15) K for the other four systems presented here, the density data are not available in literature.

Experimental Section

Materials. All the substances used were commercial products from Aldrich of the first grade purity. The purity of substances, checked by gas chromatograpy was not less than 99.8% in mole fraction. The liquids were dries and stored over 4A molecular sieves and were used without further purification. Experimental densities of the pure components are in agreement with the literature values, as can be seen in Table-1.

Table 1.

Comparison of Measured Densities with Literature Values for Pure Components at *T*) (298.15 and 308.15) K

10^{-3} F/kg · m^{-3}

T **) 298.15 K**			***T*** **) 308.15 K**	
Component	exptl	lit.	exptl	lit.
cyclohexanone	0.94276	0.94251[8] 0.9424[11] 0.94207[12]	0.93380	0.9424[11]
1,1,2,2-tetrachloroethane	1.58918	1.58655[12] 1.588539[13] 1.5876[14]	1.57357	1.572901[13]
1,1,1-trichloroethane	1.32827	1.32929[8] 1.3314[15] 1.32955[16] 1.3287[17]	1.31145	
trichloromethane	1.47316	1.47988[12] 1.472435[13] 1.4717[18] 1.47156[19]	1.45407	1.460025[20]
1,2-dichloroethane	1.24548	1.24561[3] 1.2458[12] 1.245290[13] 1.2455[21]	1.23083	1.230566[13] 1.2309[21]
1,3-dichloropropane	1.17958	1.1818[15] 1.17922[22] 1.17908[23]	1.16716	
1,4-dichlorobutane	1.13257	1.13402[3] 1.1353[15] 1.1337[21] 1.1328[24]	1.12161	1.1224[21]
1-chlorobutane	0.88105	0.8809[12,24] 0.8810[18] 0.88079[25]	0.86986	0.86962[25]

Apparatus and Procedure. The binary mixtures were prepared by mixing rhe appropriate volumes of liquids in airtight glass bottle and weighted using a HR-120 (A&D Japan) electronic balance with a precision of 0.1 · 10^{-6} kg. The experimental uncertainty in mole fractions was estimated to be less than ± 0.0002. The density measurement of the pure solvements and of the mixtures were performed by means of an Anton Paar DMA 4500 densimeter with a precision of ± 0.05 kg.m^{-3}, between (288.15 and 318.15) K. The DMA cell was calibrated with dry air and ultra pure water at atmospheric pressure. The sample thermostat ting was controlled to ± 0.01 K. The uncertainty in the density determination is ± 0.05 kg·m^{-3} and for the V^E calculation is less than ± 10^{-8} m^3·mol^{-1}.

Results and Discussion.

The measured densities, p, for the binary mixtures of Acetone with chloroalkanes at T= (288.15, 298.15, 308.15 and 318.15) K over the whole composition range are listed in Table 2.

The experimental excess molor volumes, V^E, for these binary mixtures were obtained from the following relation:

$$V^E = x_1 M_1 \left(\frac{1}{p} - \frac{1}{p1}\right) + x_2 M_2 \left(\frac{1}{p} - \frac{1}{p2}\right) \quad (1)$$

Where x_1 and x_2 are the mnole fractions, M_1 and M_2 are molar masses and p_1 and p_2 are the densities of the pure liquid components 1 and 2 respectively. The determined V^E values are indicated also in Table 2.

Table 2. Experimental Densities, G, and Molar Excess Volumes, V^E, for Binary Mixtures of Chloroalkanes with Acetone at Temperatures of (288.15, 298.15, 308.15, and 318.15) K

$X1$	T = 288.15 K		T = 298.15 K		T = 308.15 K		T = 318.15 K	
	10^{-3} F	$10^6 V^E$	10^{-3} F	$10^6 V^E$	10^{-3} F	$10^6 V^E$	10^{-3} F	$10^6 V^E$
	kg · m^{-3}	m^3 ·mol^{-1}	kg · m^{-3}	m^3 ·mol^{-1}	kg · m^{-3}	m^3 ·mol^{-1}	kg · m^{-3}	m^3 ·mol^{-1}
1,1,2,2-Tetrachloroethane +Acetone								
0.0000	0.95169	0.000	0.94276	0.000	0.9338	0.000	0.92482	0.000
0.1147	1.02934	-0.181	1.01979	-0.198	1.0102	-0.214	1.00058	-0.230
0.2121	1.09487	-0.295	1.08477	-0.322	1.07462	-0.348	1.06444	-0.374
0.3045	1.15678	-0.383	1.14613	-0.416	1.13543	-0.448	1.1247	-0.481
0.4052	1.2238	-0.447	1.21252	-0.482	1.2012	-0.519	1.18984	-0.555
0.4996	1.28607	-0.469	1.27418	-0.505	1.26226	-0.543	1.2503	-0.581
0.5909	1.3458	-0.463	1.33331	-0.499	1.32077	-0.534	1.3082	-0.570
0.6868	1.40773	-0.410	1.39458	-0.442	1.38138	-0.474	1.36814	-0.505
0.7820	1.4685	-0.323	1.45464	-0.347	1.44076	-0.373	1.42683	-0.398
0.8798	1.53011	-0.197	1.51552	-0.213	1.50089	-0.229	1.48623	-0.245
1.0000	1.60475	0.000	1.58918	0.000	1.57357	0.000	1.55794	0.000
1,1,1-Trichloroethane + Acetone								
0.0000	0.95169	0.000	0.94276	0.000	0.9338	0.000	0.92482	0.000
0.1151	0.99674	-0.137	0.98713	-0.146	0.97749	-0.157	0.96781	-0.168
0.2288	1.04175	-0.271	1.03143	-0.289	1.02106	-0.308	1.01065	-0.329
0.3155	1.07619	-0.352	1.06528	-0.374	1.05433	-0.398	1.04333	-0.425
0.4163	1.1163	-0.419	1.10468	-0.445	1.09301	-0.474	1.08128	-0.505
0.5167	1.15617	-0.447	1.14381	-0.475	1.13139	-0.507	1.1189	-0.542
0.6059	1.19152	-0.442	1.17845	-0.470	1.16533	-0.502	1.15212	-0.537
0.7081	1.23185	-0.398	1.21794	-0.424	1.20395	-0.453	1.18986	-0.485
0.8062	1.2703	-0.314	1.25552	-0.334	1.24064	-0.357	1.22564	-0.382
0.8979	1.30581	-0.186	1.29016	-0.198	1.27441	-0.214	1.25851	-0.229
1.0000	1.34495	0.000	1.32827	0.000	1.31145	0.000	1.29447	0.000
Trichloromethane + Acetone								
0.0000	0.95169	0.000	0.94276	0.000	0.9338	0.000	0.92482	0.000
0.1198	1.00415	-0.086	0.99458	-0.103	0.98497	-0.122	0.97532	-0.141
0.2362	1.05819	-0.182	1.04793	-0.213	1.03761	-0.249	1.02725	-0.287
0.3050	1.09164	-0.241	1.08094	-0.281	1.07016	-0.325	1.05932	-0.372
0.4235	1.15188	-0.331	1.14029	-0.379	1.12862	-0.434	1.11688	-0.493
0.5103	1.19822	-0.384	1.18589	-0.435	1.17348	-0.495	1.16097	-0.559
0.6047	1.25045	-0.399	1.23716	-0.446	1.22378	-0.503	1.21028	-0.564
0.6953	1.30306	-0.412	1.28880	-0.457	1.27442	-0.513	1.2599	-0.573
0.8109	1.3721	-0.312	1.35630	-0.341	1.34036	-0.381	1.32423	-0.423
0.9089	1.43335	-0.188	1.41612	-0.204	1.39868	-0.227	1.38101	-0.252
1.0000	1.49186	0.000	1.47316	0.000	1.45407	0.000	1.43472	0.000
1,2-Dichloroethane +Acetone								
0.0000	0.95169	0.000	0.94276	0.000	0.9338	0.000	0.92482	0.000
0.1142	0.97881	0.046	0.96950	0.039	0.96016	0.032	0.95078	0.026
0.2318	1.00861	0.067	0.99888	0.054	0.9891	0.040	0.97928	0.027
0.3197	1.0321	0.078	1.02200	0.063	1.01186	0.046	1.00167	0.029
0.4227	1.06102	0.091	1.05047	0.072	1.03986	0.053	1.02919	0.032
0.5190	1.0895	0.105	1.07846	0.085	1.06736	0.065	1.05619	0.043
0.6155	1.1197	0.107	1.10812	0.089	1.09648	0.067	1.08475	0.046
0.7061	1.14967	0.103	1.13752	0.086	1.1253	0.067	1.11298	0.048
0.8134	1.18743	0.084	1.17453	0.071	1.16153	0.056	1.14842	0.042
0.9145	1.2255	0.052	1.21176	0.046	1.19792	0.039	1.18396	0.030
1.0000	1.26001	0.000	1.24548	0.000	1.23083	0.000	1.21604	0.000
1-Chlorobutane+ Acetone								
0.0000	0.95169	0.000	0.94276	0.000	0.93380	0.000	0.92482	0.000
0.1152	0.94558	-0.086	0.93647	-0.098	0.92734	-0.112	0.91817	-0.127
0.2084	0.94043	-0.134	0.93118	-0.154	0.92188	-0.176	0.91254	-0.200
0.3068	0.93495	-0.179	0.92551	-0.203	0.91603	-0.232	0.90650	-0.264
0.4067	0.92927	-0.212	0.91965	-0.241	0.90997	-0.275	0.90022	-0.311
0.5041	0.92360	-0.229	0.91378	-0.260	0.90389	-0.295	0.89392	-0.333
0.5841	0.91886	-0.233	0.90886	-0.263	0.89878	-0.297	0.88863	-0.336
0.6920	0.91228	-0.216	0.90202	-0.242	0.89168	-0.273	0.88125	-0.308
0.7881	0.90618	-0.173	0.89571	-0.196	0.88512	-0.221	0.87442	-0.249
0.8820	0.90011	-0.117	0.88937	-0.129	0.87854	-0.147	0.86757	-0.166
1.0000	0.89210	0.000	0.88105	0.000	0.86986	0.000	0.85852	0.000

The experimental value of V^E were fitted to the Redlich –Kister type polynomials:

$$V^E = x_1 x_2 + \sum_{k=0}^{p} A_k (x_1 x_2)^k \quad (2)$$

Where p = 2 is the degree of polynomial expansion. The adjustable parameters A_k obtained by fitting the equations to the experimental values with a least squ-squares type algorithm are given in Table 3, along with the standard deviation, σ, defined as follows:

$$\sigma) \left[\sum_{i=1}^{n} (V_{Exp,i} - V_{Ealc,i})^2/(n-m)\right]^{0.5} \quad (3)$$

Table-3

Coefficients A_k of the fitting Equation (2) and standard Deviations σ

T	$10^6 A_o$	$10^6 A_1$	$10^6 A_2$	$10^6 A\sigma$
K	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$
	1,1,2,2-Tetrachloroethane + Acetone			
288.15	-18821	0.1058	0.1272	0.003
298.15	-2.0279	0.1058	0.1100	0.003
308.15	-2.1773	0.0898	0.0965	0.003
318.15	-2.3270	0.0832	0.0895	0.003
	1,1,1-Trichloroethane + Acetone			
288.15	-17860	0.4085	0.1322	0.003
298.15	-18963	0.4343	0.1208	0.003
308.15	-2.0216	0.4683	0.1084	0.003
318.15	-2.1588	-0.5062	0.1069	0.003
	Trichloromethane + Acetone			
288.15	-15070	0.9382	0.0013	0.007
298.15	-17090	0.9587	0.0521	0.008
308.15	-19436	-10225	0.0673	0.009
318.15	-2.1957	-10893	0.0907	0.010
	1,2-Dichloroethane + Acetone			
288.15	0.4005	0.1469	0.2041	0.003
298.15	0.3229	0.1333	0.2063	0.003
308.15	0.2388	0.1165	0.2086	0.003
318.15	0.1518	0.0973	0.2142	0.003
	1-Chlorobutane + Acetone			
288.15	-0.9137	0.2019	0.0849	0.002
298.15	-1037	0.2123	0.0819	0.002
308.15	-11753	0.2263	0.0994	0.002
318.15	-13308	0.2478	-0.1082	0.002

Where n is the number of experimental data and m = 3 is the number of parameters.

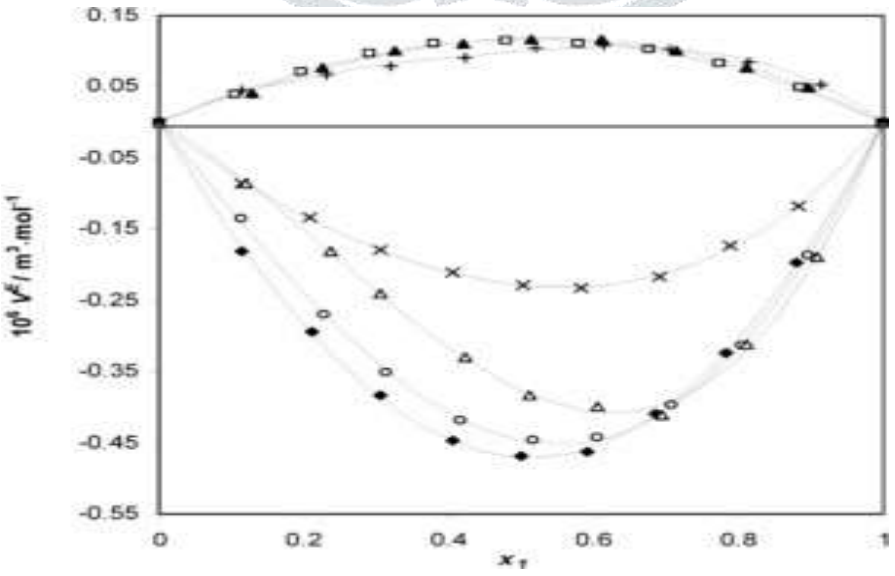

Figure 1. Excess molar volumes, V^E, for the chloroalkanes (1) + acetone (2) mixtures at 288.15 K: ♦, 1,1,2,2-tetrachloroethane; O, 1,1,1-trichloroethane; +, 1,2-dichloroethane; ▲, 1-chlorobutane; ▲, trichloromethane; solid line, Redlich-Kister correlation.

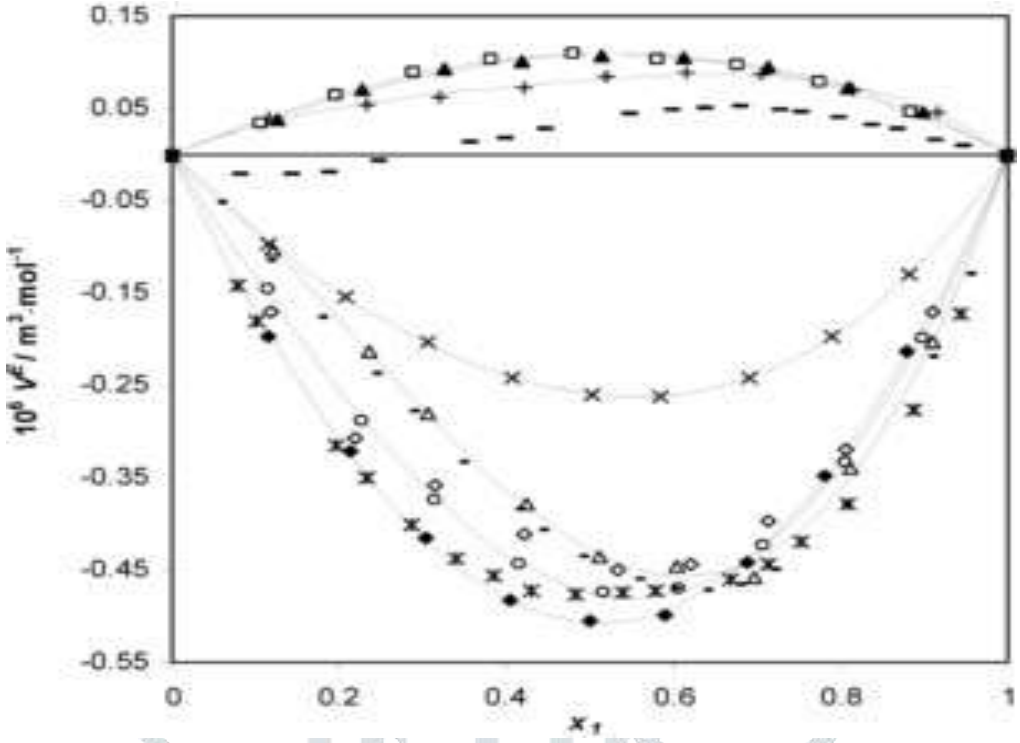

Figure 2. Excess molar volumes, V^E, for the chloroalkanes (1) + Acetone (2) mixtures at 298.15 K: ♦, 1,1,2,2-tetrachloroethane; O, 1,1,1-trichloroethane; +, 1,2-dichloroethane;; ×, 1-chlorobutane; ▲, trichloromethane; solid line, Redlich-Kister correlation; *, 1,1,1-trichloroethane (ref 6); short dashed line, trichloromethane (ref 6); long dashed line, 1,2-dichloroethane (ref 6); ◊, 1,1,1-trichloroethane (ref 8).

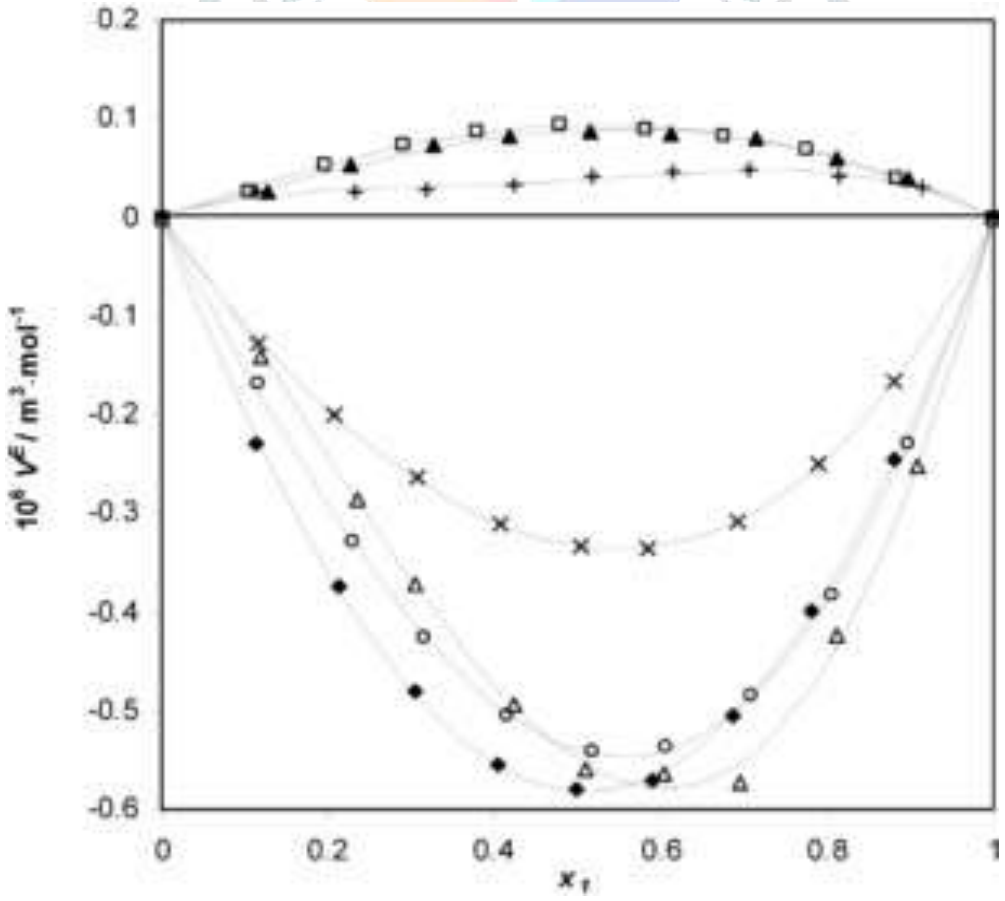

Figure 3. Excess molar volumes, V^E, for the chloroalkanes (1) Acetone (2) mixtures at 318.15 K: ♦, 1,1,2,2-tetrachloroethane; O, 1,1,1-trichloroethane; ▲, 1,2-dichloroethane; ×, 1-chlorobutane; ▲, trichloromethane; solid line, Redlich-Kister correlation

It can be observed from the experimental results in Table 2 and Figures l,2 and 3 that the excess molar volume values are negative for the acetone +1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, and 1-chlorobutane systems and positive for the Acetone + 1,2-dichloroethane system, the excess volume curves for the other six systems are slightly asymmetric about x = 0.5.

It seems that intermolecular interactions are the predominant factors in deciding the sign of V^E for the mixtures of Acetone with the studied tetra- and trichloroalkanes. The most negative values of V^E for Acetone + 1,1,2,2-tetrachloroethane +1,1,1-trichlorethane, or + trichloromethane systems show that strong intermolecular complexes are formed between components, probably favored by an increased number of chlorine atoms to one carbon atom in these chloroalkanes. The Acetone + 1-chlorobutane system presents less negative values for V^E, comparative with the above-mentioned systems.

Surprisingly, the values of V^E for the systems of Acetone with 1,2-dichloreethane. and 1A are small, positive and nearly identical. For such systems of acetone with a,ω −dichloroalkanes, the positive values of suggest the presence of weak interaction between the component molecules and the unfavorable packing of unlike molecules into each other's structure because of almost equal molar volumes: Acetone ($10.4\cdot10^{-5}$m^3·mol^{-1}), 1,2-dichloroethane ($7.9\cdot10^{-5}$ m^3·mol^{-1}), ($9.5\cdot10^{-5}$m^3·mol^{-1}), and ($11.2\cdot10^{-5}$m^3·mol^{-1}), at 298.15K. Besides, a possible explanation of the positive values of V^E could be the breaking of dipole−depoleinteractions between the with a,ω −dichloroalkanes molecules from the pure state.

The excess molar volumes of the studied binary mixtures of Acetone with chloroalkanes follow the general order: 1,2-dichloroethane >1-chlorobutane > trichloromethane > 1,1,1-trichloroethane > 1,1,2,2-tetrachloroethane, with both positive and negative observed values.

For a better illustration of the system's nonideality and a better evaluation of the uncertainty in the data at high and low mole fraction, [26] we also plot the quantity

$V^E = x_1(1 - x_1)$ versus x_1 at, for example, 298.15 K in figure 5. In addition, this plot furnishes an approximation of the partial molar excess quantities at infinite dilution when no measurement has been made in the dilute regions. Crude extrapolations yield different values of $V^E = x_1(1 - x_1)$ for acetone at infinite dilution, indicating that the behavior of the Acetone in the solvent bulk is influenced by the shape and nature of the chlorocompound, being less significant in the series of with a,ω −dichloroalkanes.

From the Figure 2 and 5 it is obvious that our V^E data compare well with literature data[8] for the 1,1,1-trichlorethane system, when the same experimental method is used. Also, the comparison with other sources[5,6] indicate satisfactory results at (298.15 and 308.15) K (Figure 2 and 3) for the trichloromethane and 1,1,1-trichloroethane systems , when the dilatometric method is involved. The differences between our and literature data[5,6] for the 1,2-dichloroethane system could be due to the very small V^E values. Other literature data[27] for the trichloromethane system at 308.15 K do not compare well with neither our nor above mentioned data,[5] They are more negative with a deviation of about $0.13\cdot10^{-6}$m^3·mol^{-1} around equimolar composition.

The V^E values become more negative for all of the studied systems as the temperature of the systems increase from (288.15 to 318.15) K. Such behavior could be explained by the packing effect which became more dominant and increases with temperature, as it was observed for other systems in literature. [28]

Conclusion

The densities of the binary Acetone with 1,1,2,2- tetrachloroethane, 1,1,1- trichloroethane, trichloromethane, 1.2- dichloroethane and 1-chlorobutane systems have been measured as a function of composition at temperatures between (288.15 to 318.15) K and atmospheric pressure. The excess molar volumes obtained from densities are negative for the Acetone +1,1,2,2- tetrachloroethane, 1,1,1-trichloroethane, trichloromethane and 1-chlorobutane systems and positive for the acetone + 1.2-dichloroethane systems and become more negative as the temperature increases from from (288.15 to 318.15) K.

The interactional factor seems to be predominant for the systems with negative excess molar volumes, while for the systems small positive V^E values the structural effects prevail.

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