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Thermodynamic properties of binary mixtures of water with alkanols

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Abstract
Excess molar volumes, V^E and speeds of sound, u data of water (1) + propane 1,2 diol or propane 1,3 diol (2) binary mixtures have been measured over entire mole fraction range at 298.15 and 308.15K. Speeds of sound have been utilized to predict isentropic compressibilities changes of mixing κ_S^E. The observed V^E and κ_S^E data have been analyzed in term of Graph theory. Analysis of V^E data of (1+2) mixtures in terms of Graph theory suggest that water (1) + propane 1, 2 diol or propane 1,3 diol (2) exist as an associated molecular entities. It has been observed that V^E and κ_S^E predicted by Graph theory compare well with their corresponding experimental values.

Keywords: Excess molar volumes, V^E; isentropic compressibilities changes of mixing, κ_S^E; interaction energy parameter, χ

Introduction
There has been an increasing interest in the study of molecular interactions existing in mixtures and a number of experimental techniques have been used to extract information about the interactions operating among the components of binary and ternary liquid mixtures. Thermodynamic properties like excess molar volumes, V^E and isentropic compressibilities changes of mixing, κ_S^E have extensive applications in chemical engineering, design calculations for heat transfer, mass transfer and fluid flow [1]; process simulation, solution theory and molecular dynamics . These thermodynamic properties provide a base for the selection of physico-chemical methods of analysis in the field of petrochemicals and chemical industry. These properties are important from practical and theoretical point of view to understand the molecular interactions in multicomponent liquid mixtures. In recent studies, [2-6] topology of the constituents of binary or ternary mixtures has been employed to predict excess molar volumes, excess molar enthalpies and isentropic compressibility changes of mixing of binary or ternary liquids mixtures. In continuation of our studies [7-9] on thermodynamic properties of binary or ternary mixtures containing water as one of the component, we report here excess molar volumes and speeds of sound of water + propane 1,2 diol or propane 1,3 diol binary mixtures.

Experimental Section
Water, propane 1, 2 diol (A) (Fulka, 99 mol %), propane 1,3 diol (Fluka, 98 mol %), were purified by standard methods [10]. The purities of the purified liquids were checked by measuring their densities [recorded in Table 1] using bicappillary pycnometer at 298.15±0.01K and these agreed to within ±0.05 kg.m^{-3} with their literature values [11, 12]. Excess molar volumes, V^E were determined in a V-shaped dilatometer in the manner as described elsewhere [13]. The change in liquid level of dilatometer capillary was measured with a cathetometer that could read to ± 0.001 cm. The uncertainties in the measured V^E values are 0.5%. Speeds of sound, u (at frequency 2 MHz) in binary mixtures were measured using a variable path interferometer (Model M84, Mittal Enterprises, India) and a measuring cell. The measuring cell was a specially designed cell in which water was circulated through the cell to maintain the desired temperature.

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The speeds of sound values for the purified liquids at (298.15±0.01) K (recorded in Table1) compare well with their corresponding experimental values [14, 26]. The uncertainties in the measured speed of sound values are ±1 ms^{-1}.

Results

Excess molar volumes, V^E and speeds of sound, u data of W (1) + P12D or P13D (2) mixtures measured as a function of composition at 298.15 and 308.15K are recorded in Tables 2-3. The isentropic compressibility's, κ_S for (1+2) mixtures were determined from their speeds of sound data using relation:

$$\kappa_S = (\rho_{12} \, u^2)^{-1} \tag{1}$$

The densities, ρ_{12} of binary mixtures were evaluated from their excess molar volumes data by employing eq 2

$$V^E = \sum_{1=1}^{2} x_1 M_1 (\rho_{12})^{-1} - \sum_{1=1}^{2} x_1 M_1 (\rho_1)^{-1} \tag{2}$$

Where x_1, M_1 and ρ_1 are the mole fraction, molar mass and density of component (1) of (1+2) binary mixture. Isentropic compressibilities changes of mixing, κ_S^E for the investigated mixtures were determined using

$$\kappa_S^E = \kappa_S - \kappa_S^{id} \tag{3}$$

κ_S^{id} values were obtained as suggested by Benson and Kiyohara [16]

$$\kappa_S^{id} = \sum_{1=1}^{2} \phi_1 \left[\kappa_{S,1} + \frac{T v_1 \alpha_1^2}{C_{p,1}} \right] - T \left(\sum_{1=1}^{2} x_1 v_1 \right) \frac{\left(\sum_{1=1}^{2} \phi_1 \alpha_1 \right)^2}{\left(\sum_{1=1}^{2} x_1 C_{p,1} \right)} \tag{4}$$

Where ϕ_1 is the volume fraction of component (1) in the mixed state $\kappa_{S,1}$ and v_1 are isentropic compressibility and molar volume respectively of the pure component (1). Such κ_S^E values for the investigated mixtures are recorded in Table 3. V^E and κ_S^E values for the studied (1 + 2) mixtures are plotted in Figures 1-2

Excess molar volumes V^E and isentropc compressibility changes of mixing, κ_S^E data were fitted to eq 5

$$X^E (X = V \, or \, \kappa_S) = x_1 x_2 [X^{(0)} + X^{(1)} (2x_1 - 1) + X^{(2)} (2x_2 - 1)^2] \tag{5}$$

Where

$$X^{(n)} (n = 0 - 2)$$

etc. are the parameters characteristic of (1 + 2) mixtures. These parameters were evaluated by fitting $X^E (X = V$ or κ_S) data to eq 5 by least squares methods and are recorded along with standard deviations, $\sigma (X^E)(X = V$ or κ_S) defined by eq 6

$$\sigma(X^E) = [\sum (X_{exptl}^E - X_{calc.Eq.(6)}^E)^2 / (m - n)]^{0.5} \tag{6}$$

[Where m is the number of data points and n is the number of adjustable parameters in eq 6] in Tables 2-3.

Discussion

We are unaware of any V^E and κ_S^E data of the studied mixtures with which to compare our results V^E and κ_S^E data of these mixtures are negative over entire mole fraction range. While V^E data for an equimolar composition vary as P13D > P12D.

The sign of molar excess volumes provides information about the molecular arrangement and molecular interactions among the components of mixtures. The negative sign of molar excess volumes suggests strong interaction between unlike molecules in the mixtures and qualitatively be interpreted in terms of unlike molecules leading to reduction in volume. Further, dissociation of molecular entity of a component of a mixtures makes a positive contribution to the molar excess volumes. Negative values of V^E for W(1) + P12D or P13D (2) mixtures suggest that addition of P12D or P13D (2) to W(1) results in enhancing the liquid structures in (1+2) mixtures as compared to pure water. Further V^E values for these mixtures suggest that P12D or P13D give least packed arrangement.

The negative values of κ_S^E are the commutative effect of several contributions like those from (i) W(1) and P12D or P13D (2) are associated molecular entities (ii) establishment of unlike 1-2 contacts (iii) formation of unlike contacts between 1 and 2 then leads to depolymerization of associated molecular entities to yield their respective monomer, and (iv) monomers of 1 and 2 undergo interaction to form 1:2 molecular complex.

The negative values of κ_S^E for these mixtures suggest net contribution due to factors (i), (ii) and (iv) far outweigh the contribution due to (iii) factor. So that overall κ_S^E for (1+2) mixtures are negative. Further less negative values of W(1) and P12D(2) mixtures than those for W(1) and P13D (2) mixtures is due to the presence of bulky –CH$_3$ groups at the adjacent carbon atomsof P12D which restricts the approach of W(1) molecules. Thus, contribution to κ_S^E for W(1) and P12D (2) mixtures due to factor (iii) should be less than those for W(1) and P13D (2) mixtures. Hence κ_S^E for W(1) and P12D (2) must be less negative than those for W(1) and P13D (2) mixture.

Graph theory and results

Excess molar volumes. Excess molar volumes, V^E for a binary (1 + 2) mixture is a packing effect and influenced by the change in topology of the constituents in mixed state. Thus it was worthwhile to analyze V^E data of the studied

mixtures in terms of Graph theory. According to this theory, V^E is given by [17]

$$V^E = \alpha_{12}\{[\sum x_1 ({}^3\xi_1)_m]^{-1} - [\sum x_1 ({}^3\xi_1)]^{-1}\} \quad (7)$$

Where α_{ij} is a constant characteristics of (1+2) mixtures. $({}^3\xi_1)$, $({}^3\xi_1)_m$ (1 = 1 or 2) etc are the connectivity parameters of the third degree of components (1) and (2) in pure and mixed state and are defined by relation:

$$\sum_{{}^3\xi = m<n<o<p} (\delta_m^v \, \delta_n^v \, \delta_o^v \, \delta_p^v)^{-0.5} \quad (8)$$

Where δ_m^v etc. have the same significance as described elsewhere[18]. ${}^3\xi$ etc. parameters were determined by fitting experimental V^E data to eq 7 and only those values of $({}^3\xi_1)$, $({}^3\xi_1)_m$ (1 = 1 or 2) parameters were retained that best describe the experimental V^E data. These parameters, along with V^E values [predicted by employing eq 7] at various x_1 are recorded in Table 4. Examination of data in Table 4 reveals that V^E values compare well with their experimental values.

 A number of structures were then assumed for (1) and (2) components in pure and mixed state and their ${}^3\xi'$ values were evaluated from their structural consideration (via. eq 8). These ${}^3\xi'$ values were then compared with ${}^3\xi'$ obtained via eq 7. Any structure or combination of structures which provided ${}^3\xi'$ values comparing with ${}^3\xi$ value was taken to be representative structure of that component. For W(1) and P12D or P13D (2) mixtures, it was assumed that W, P12D and P13D exist as molecular entitites I-VI, ${}^3\xi'$ VII-VIII, IX-X respectively. The P12D and P13D (2) for molecular entities I-X were then calculated to be 0.426, 1.379, 1.462, 1.229, 1.328, 1.072, 0.264, 1.754, 0.258 and 1.923 respectively. ${}^3\xi$ values of (1.01-1.03) for W suggests that water in pure state exist as an equilibrium mixtures of molecular entities I, IV and V (average ${}^3\xi' = 1.088$). Our analysis of V^E data has yielded information that is consistent with the more involved studies[19-21] on the state of aggregation of water. Further ${}^3\xi$ values of 1.502 and 1.250 suggest that P12D and P13D exist as an mixture of associated molecular entitites VII-VIII (${}^3\xi' = 1.658$) and IX-X(${}^3\xi' = 1.498$) respectively.

$({}^3\xi'_2)_m$ values were then calculated and utilized to understand the state in which P12D and P13D (2) exist in W(1). For this purpose, we assumed that W(1) exist in P12D and P13D (2) as molecular entities XIII and XIV respectively (Scheme-II). While evaluating ${}^3\xi'$ values it was assumed that these molecular entities are characterized by interaction between hydrogen/oxygen atom of alcohol and oxygen / hydrogen atom of water. $({}^3\xi'_2)_m$ values for molecular entities XIII-XIV were then calculated to 1.155 and 1.239 respectively. $({}^3\xi'_2)_m$ values of 1.502 and 1.251 (Table 4) suggest that W(1) and P12D or P13D (2) binary mixtures are characterized by the presence of molecular entities XIII and XIV respectively. The present analysis thus suggests that W P12D and P13D are associated entities and that all these moieties are characterized by the presence of molecular entities XIII and XIV.

.Isentropic compressibility's changes of mixing

κ_S^E data of studied (1+2) mixtures were then analyzed in terms of Graph theory. For this purpose, it was assumed that W (1) + P12D or P13D (2) binary mixtures formation involve processes (i) formation of unlike contact between 1_n and 2_n molecules; (ii) unlike contact 1_n-2_n formation then weakens

1_n-2_n interactions and leads to the depolmerization of 1_n and 2_n; (iii) the monomers of 1 and 2 then undergo specific interactions to form 1:2 molecular complex. If $\chi_{12}, \chi_{11}, \chi_{22}$ and χ_{12}^* are molar interactions and molar compressibility interactions parameters for 1-2, 1-1, 2-2 contacts and specific interactions respectively, then change in molar thermodynamic properties, ΔX ($X = \kappa_S$) due to processes (i)-(iii)} would be given[22-24] by relations

$$\Delta X_1 = \frac{x_1 x_2 \chi_{12} v_2}{\sum x_1 v_1} \quad (9)$$

$$\Delta X_2 = \frac{x_1^2 x_2 \chi_{11} v_2}{\sum x_1 v_1} \quad (10)$$

$$\Delta X_3 = \frac{x_1^2 x_2 \chi_{22} v_2}{\sum x_1 v_1} \quad (11)$$

$$\Delta X_4 = \frac{x_1 x_2^2 \chi_{12}^* \, v_2}{\sum x_1 v_1} \quad (12)$$

Where v_1 is the molar volume of component (1). The overall excess thermodynamic properties, X^E ($X = \kappa_S$) for the investigated (1+2) mixtures can, therefore, be expressed by eq 12

$$X^E = \sum_{1=1}^{4} \Delta X_1 = [x_1 x_2 v_2 / \sum x_1 v_1][\chi_{12} + x_1 \chi_{11} + x_1 \chi_{22} + x_2 \chi_{12}^*] \quad (13)$$

Singh *et al.* [25] have suggested $v_2/v_1 = {}^3\xi_1 / {}^3\xi_2$ consequently eq 13 redues to

$$X^E = \left[\frac{x_1 x_2 ({}^3\xi_1/{}^3\xi_2)}{x_1 + x_2 ({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12} + x_1 \chi_{11} + x_1 \chi_{22} + x_2 \chi_{12}^*] \quad (14)$$

For the studied mixtures, it is reasonable to assume that $\chi_{12} = \chi_{12}^* = \chi_{12}'$ and $\chi_{11} = \chi_{22} = \chi^*$, the eq 14 can be expressed by

$$X^E = \left[\frac{x_1 x_2 ({}^3\xi_1/{}^3\xi_2)}{x_1 + x_2 ({}^3\xi_1/{}^3\xi_2)}\right][(1 + x_2)\chi_{12}' + 2x_1 \, \chi^*] \quad (15)$$

Eq. 15 contains two unknown parameters and these parameters were calculated by employing κ_S^E data of the investigated (1+2) binary mixtures at two compositions. These parameters were then employed to predict κ_S^E values at other values of x_1. Such κ_S^E data along with χ_{12}' and χ^*

parameters are recorded in Table 4 and are also compared with their corresponding experimental values. An examination of Table 4 reveals that calculated K_S^E values for various (1+2) mixtures compare well with their corresponding experimental values. This lends additional support to the assumptions made in deriving eq 15.

Table 1: Comparison of densities and speeds of sound, u of pure liquids with their literature values at 298.15 K

| Liquids | ρ | | u | |
| | kg.m^{-3} | | m.s^{-1} | |
	Exp.	Lit.	Exp.	Lit.
W	997.05	997.08[a]	1498	1496.7[c]
P12D	1032.7	1032.8[b]	1500	1500.1[d]
P13D	1050.1	1050.1[b]	1638	1636.1[d]

[a] Ref 11. [b]Ref 12. [c]Ref 13. [d]Ref 14

Table 2: Measured excess molar volumes, V^E data for the various (1+2) mixtures as a function of mole fraction, x_1, of component (1) at 298.15 and 308.15 K.

x_1	V^E cm^3.mol^{-1}	x_1	V^E cm^3.mol^{-1}
W(1) + P12D (2) [a] T = 298.15 K			
0.1352	-0.208	0.6211	-0.642
0.2011	-0.295	0.6899	-0.630
0.2599	-0.369	0.7115	-0.621
0.3217	-0.430	0.7510	-0.592
0.3750	-0.490	0.8516	-0.450
0.4352	-0.556	0.9215	-0.285
0.5211	-0.618	0.9370	-0.239
0.5517	-0.624	0.9811	-0.085
W(1) + P12D (2) [b] T = 308.15 K			
0.0692	-0.095	0.4050	-0.505
0.1171	-0.152	0.4617	-0.540
0.1552	-0.205	0.5254	-0.574
0.1917	-0.252	0.6265	-0.586
0.2161	-0.285	0.7011	-0.555
0.2411	-0.325	0.7517	-0.513
0.3215	-0.414	0.8215	-0.423
0.3812	-0.476	0.9517	-0.142
W(1) + P13D (2) [c] T = 298.15 K			
0.1025	-0.201	0.5786	-0.490
0.2119	-0.363	0.6139	-0.487
0.2810	-0.421	0.6570	-0.456
0.3019	-0.436	0.7001	-0.437
0.3911	-0.493	0.7889	-0.344
0.4109	-0.501	0.8239	-0.311
0.4831	-0.511	0.8699	-0.239
0.5069	-0.500	0.9036	-0.198
W(1) + P12D (2) [d] T = 308.15 K			
0.0567	-0.083	0.4612	-0.467
0.1791	-0.240	0.4952	-0.480
0.1921	-0.256	0.5317	-0.475
0.2310	-0.301	0.5819	-0.472
0.2699	-0.342	0.6315	-0.450
0.3292	-0.396	0.7919	-0.312
0.3816	-0.432	0.8516	-0.244
0.4352	-0.464	0.9210	-0.140

Also included are various V$^{(n)}$ (n=0-2) parameters along with standard deviations, σ(V^E)
[a] $V^{(0)}$= -2.404, $V^{(1)}$= -1.312, $V^{(2)}$= -0.533 ; σ($V^{(E)}$)= 0.006 cm^{3}mol^{-1}
[b]$V^{(0)}$= -2.269, $V^{(1)}$= -0.990, $V^{(2)}$= -0.004 ; σ($V^{(E)}$)= 0.004 cm^{3}mol^{-1}
[c]$V^{(0)}$= -2.031, $V^{(1)}$= 0.042, $V^{(2)}$= -0.292 ; σ($V^{(E)}$)= 0.001 cm^{3}mol^{-1}
[d]$V^{(0)}$= -1.919, $V^{(1)}$= -0.203, $V^{(2)}$= 0.299 ; σ($V^{(E)}$)= 0.003 cm^{3}mol^{-1}

Table 3: Speeds of sound, u, isentropic compressibilities, κ_S, and isentropic compressibilities changes of mixing, κ_S^E for the various (1 + 2) mixtures as a function of mole fraction, x_1 of component (1) at 308.15 K.

x_1	u	κ_S	κ_S^E
	m.s^{-1}	TPa^{-1}	TPa^{-1}
W (1) + P12D (2) [a] T=298.15K			
0.0742	1535	410.6	-9.6
0.1746	1538	408.6	-13.0
0.2788	1540	406.8	-15.7
0.3212	1550	400.3	-18.9
0.3723	1554	399.0	-24.5
0.4344	1572	389.8	-34.9
0.5742	1636	359.4	-67.8
0.6362	1670	345.1	-83.4
0.7143	1705	324.5	-99.3
0.8640	1682	343.6	-93.8
0.8956	1653	357.6	-81.5
0.9001	1648	360.2	-79.4
0.9160	1611	369.4	-70.0
0.9310	1609	379.9	-61.9
W (1) + P12D (2) [b] T=30815K			
0.0342	1523	421.9	-3.0
0.0984	1528	418.9	-6.0
0.1734	1530	417.1	-8.5
0.2319	1538	425.6	-10.5
0.2911	1540	411.2	-14.6
0.3642	1554	403.2	-22.9
0.4464	1580	391.2	-37.1
04989	1602	379.1	-47.8
0.5764	1639	361.9	-65.5
0.6301	1665	350.5	-77.6
0.6984	1694	339.1	-89.7
0.7643	1706	334.5	-95.0
0.8992	1651	361.7	-70.3
0.9580	1583	397.6	-36.4
W (1) + P13D (2) [c] T=298.15K			
0.0862	1651	349.6	-8.6
0.1326	1651	349.3	-10.2
0.1937	1649	350.1	-11.0
0.2306	1651	349.1	-13.1
0.2964	1653	348.4	-16.7
0.3624	1659	345.7	-21.8
0.4203	1643	339.6	-30.6
0.5106	1703	328.5	-46.6
0.5964	1765	306.6	-74.3
0.6514	1798	295.6	-89.7
0.7204	1824	291.9	-100.2
08964	1699	339.2	-79.8
0.9362	1628	372.1	-56.4
0.9610	1683	395.9	-39.4
W (1) + P13D (2) [d] T=308.15K			
0.0462	1619	370.9	-2.5
0.1309	1622	369.1	-5.9
0.1966	1624	367.7	-8.4
0.2341	1625	367.1	-9.9
0.2965	1635	362.4	-16.1
0.3435	1622	368.3	-11.5
0.4340	1664	349.7	-32.8
0.5108	1707	332.4	-53.1
0.5964	1757	314.3	-75.0
0.6345	1776	307.6	-83.8
0.7442	1801	300.4	-98.4
0.8643	1733	327.0	-83.9
0.9102	1675	352.3	-65.2
0.9344	1639	369.9	-51.5

Also included are various κ_S^n (n=0-2) parameters along with standard deviations, σ (κ_S^E)

[a] $\kappa_S^{(0)}$ = -195.8, $\kappa_S^{(1)}$ = -475.5, $\kappa_S^{(2)}$ = -480.8; $\sigma\left(\kappa_S^E\right)$ = 0.8 TPa⁻¹

[b] $\kappa_S^{(0)}$ = -192.7, $\kappa_S^{(1)}$ = -443.5, $\kappa_S^{(2)}$ = -362.2; $\sigma\left(\kappa_S^E\right)$ = 0.9 TPa⁻¹

[c] $\kappa_S^{(0)}$ = -189.2, $\kappa_S^{(1)}$ = -476.6, $\kappa_S^{(2)}$ = -477.4; $\sigma\left(\kappa_S^E\right)$ = 1.0 TPa⁻¹

[d] $\kappa_S^{(0)}$ = -206.4, $\kappa_S^{(1)}$ = -455.5, $\kappa_S^{(2)}$ = -315.7; $\sigma\left(\kappa_S^E\right)$ = 0.9 TPa⁻¹

Table 4: Comparison of V^E, κ_S^E values calculated from eqs 7 and 15 with their corresponding experimental values at 298.15 and 308.15K for the various (1+2) mixtures as a function of x_1 , mole fraction of component (1).

Properties	Mole fraction of component (1), x_1								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
W (1) + P12D (2) T=298.15K[a]									
V^E(Exptl)	-0.150	-0.295	-0.419	-0.515	-0.650	-0.635	-0.549	-0.335	
V^E(Graph)	-0.189	-0.348	-0.473	-0.562	-0.610	-0.556	-0.443	-0.261	
κ_S^E (Exptl)	-10.5	-13.2	-15.9	-	-73.9	-96.1	-104.1	-78.9	
κ_S^E (Graph)	14.6	9.8	-6.6	-	-63.9	-70.0	-63.3	-40.8	
T=308.15K[b]									
V^E(Exptl)	-0.130	-0.265	-0.388	-0.490	-0.595	-0.560	-0.454	-0.270	
V^E(Graph)	-0.173	-0.320	-0.435	-0.516	-0.560	-0.511	-0.407	-0.240	
κ_S^E (Exptl)	-6.2	-10.1	-15.2	-	-70.5	-89.4	-93.9	-70.4	
κ_S^E (Graph)	13.0	7.8	-8.0	-	-62.4	-67.8	-61.0	-39.2	
W (1) + P13D (2) T=298.15K[c]									
V^E(Exptl)	-0.203	-0.346	-0.441	-0.492	-	-0.488	-0.433	-0.338	-0.197
V^E(Graph)	-0.136	-0.249	-0.330	-0.401	-	-0.431	-0.393	-0.311	-0.183
κ_S^E (Exptl)	-10.2	-11.1	-16.7	-	-44.3	-	-97.0	-100.4	-79.8
κ_S^E (Graph)	17.1	12.9	-5.1	-	-54.6	-	-83.4	-76.9	-50.5
T=308.15K[d]									
V^E(Exptl)	-0.143	-0.270	-0.371	-0.448	-	-0.462	-0.410	-0.310	-0.165
V^E(Graph)	-0.157	-0.285	-0.382	-0.446	-	-0.466	-0.418	-0.326	-0.187
κ_S^E (Exptl)	-3.9	-8.4	-16.1	-	-51.4	-	-95.2	-94.1	-69.3
κ_S^E (Graph)	20.0	6.8	-1.4	-	-53.8	-	-85.2	-79.2	-52.3

Also included are various $(^3\xi_l)$ and $(^3\xi_l)_m$ (1=1 or 2) ; α_{12} and $\chi_{12}^{/}$ etc parameters.

[a] $(^3\xi_1)= (^3\xi_1)_m=1.030$; $(^3\xi_2)=(^3\xi_2)_m=1.502$; $\alpha_{12}=18.270$ cm³mol⁻¹;

$\chi_{12}^{/}$ = -380.3 TPa⁻¹; χ^*_{12} = 654.3 TPa⁻¹

[b] $(^3\xi_1)=(^3\xi_1)_m=1.030$; $(^3\xi_2)= (^3\xi_2)_m=1.502$; α_{12} =-16.802 cm³mol⁻¹;

$\chi_{12}^{/}$ = -350.0 TPa⁻¹; χ^*_{12} = -615.0 TPa⁻¹

[c] $(^3\xi_1) = (^3\xi_1)_m = 1.021$; $(^3\xi_2) = (^3\xi_2)_m = 1.251$; $\alpha_{12} = 15.202$ cm³mol⁻¹ ;

$\chi_{12}^{/}$ = 152.7 ; χ^*_{12} = -474.9 TPa⁻¹

[d] $(^3\xi_1) = (^3\xi_1)_m = 1.021$; $(^3\xi_2) = (^3\xi_2)_m = 1.251$; $\alpha_{12} = 42.750$ cm³mol⁻¹ ;

$\chi_{12}^{/}$ = 172.6 ; χ^*_{12} = -500.9 TPa⁻¹
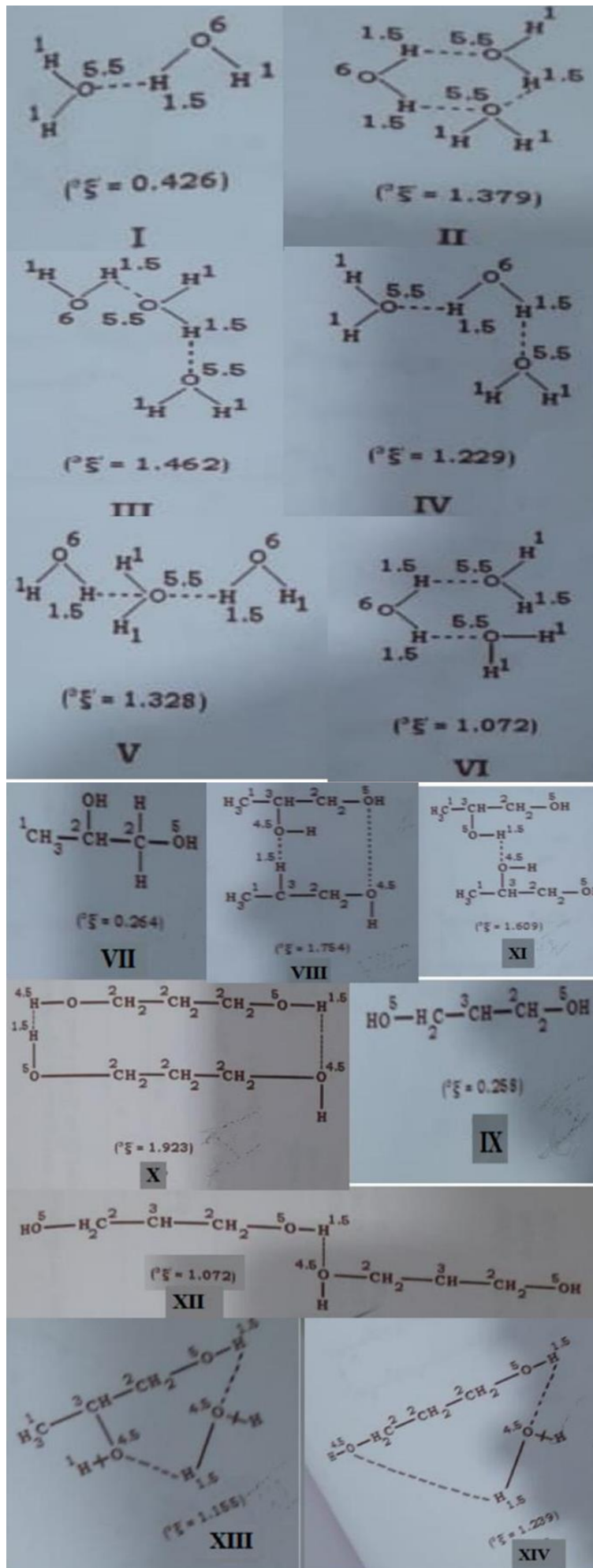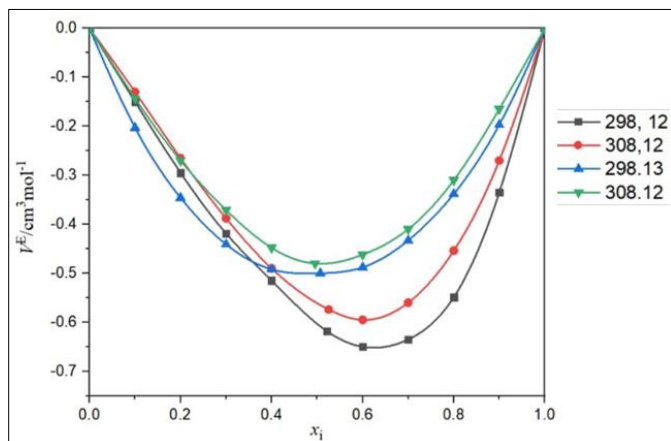
Fig 1: Excess molar volumes, V^E at 298.15K and 308.15K: W (1) + P12D (2); and W (1) + P13D (2);
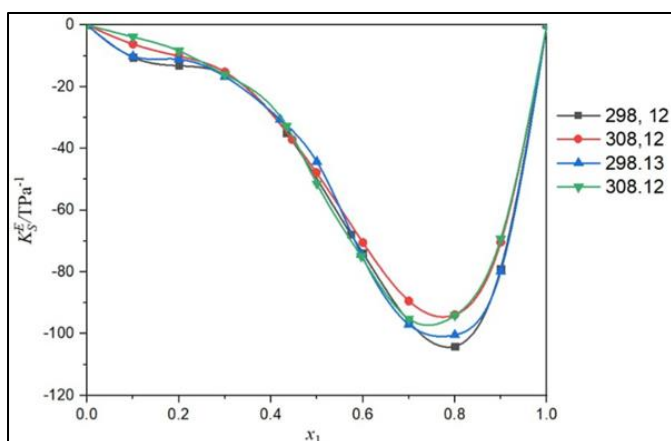

Fig 2: Isentropic compressibilities changes of mixing, κ_S^E at 298.15K and 308.15K: W (1) + P12D (2); and W (1) + P13D (2);

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