

Excess Isentropic Compressibilities for 1,3-Dioxolane or 1,4-Dioxane + Water + Formamide or N,N-Dimethylformamide Ternary Mixtures at 308.15 K

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Speeds of sound, u_{ijk} , of 1,3-dioxolane or 1,4-dioxane (i) + water (j) + formamide or dimethylformamide (k) ternary mixtures and of their binary subsystems, u_{ij} , of 1,3-dioxolane or 1,4-dioxane (i) + formamide or dimethylformamide (j), and water (i) + formamide or dimethylformamide (j) have been measured over the entire composition range at 308.15 K. The experimental data have been used to evaluate the excess isentropic compressibilities of binary $(\kappa_s^E)_{ij}$ and ternary $(\kappa_s^E)_{ijk}$ mixtures using their densities calculated from molar excess volume data. The Moelwyn-Huggins concept [M. L. Huggins, *Polymer* **12**, 389 (1971)] of interaction between the surfaces of components of a binary mixture has been employed to evaluate the excess isentropic compressibilities (using the concept of connectivity parameter of third degree of a molecule, $^3\xi$, which in turn depends on its topology) of binary mixtures, and this method has been extended to predict excess compressibilities of ternary mixtures. Values of $(\kappa_s^E)_{ij}$ and $(\kappa_s^E)_{ijk}$ have also been calculated by the Flory theory. It was observed that $(\kappa_s^E)_{ij}$ and $(\kappa_s^E)_{ijk}$ predicted by the Moelwyn-Huggins approach compare well with calculated and experimental values.

KEY WORDS: Speed of sound; isentropic compressibility; organic mixtures; 1,3-dioxolane; 1,4-dioxane; formamide; di-methylformamide; water.

1. INTRODUCTION

Molecular structure and intermolecular forces play important roles in determining the bulk properties of liquids.⁽²⁾ The idea that molecular properties originate from structural characteristics of molecules is one of the fundamental concepts in chemistry. The structural formula of compounds can be viewed as

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molecular graphs, where atoms are represented by dots and bonds joining them are represented by lines. The topology of the molecule then describes the total information contained in that molecule.^(3,4,5) In our earlier publications,^(6,7) we extended the Moelwyn-Huggins concepts⁽¹⁾ of interactions between the molecular surfaces for the binary mixtures to include ternary mixtures, by employing the connectivity parameter of third degree, ${}^3\xi$, of the mixture constituents (based upon the topology of molecule) to evaluate excess isentropic compressibilities of ternary mixtures. In the present study we report speed of sound data for 1,3-dioxolane (*i*) or 1,4-dioxane (*i*) + water (*j*) + formamide or + dimethylformamide (*k*) mixtures and their binary subsystems 1,3-dioxolane or 1,4-dioxane (*i*) + water or + formamide or + dimethylformamide (*j*) mixtures. It is of interest to see how well the extension of Moelwyn-Huggins concepts of interactions from binary mixtures to ternary mixtures describes the excess isentropic compressibilities of the studied ternary mixtures.

2. EXPERIMENTAL

1,3-dioxolane (Fluka, 99% USA), 1,4-dioxane (AR Grade, 99%), formamide (FD) (AR Grade, 99%), and N,N-dimethylformamide (DMF) (AR Grade, 99.5%) were purified by standard methods.^(8,9) Deionized water (w) was doubly distilled from water containing a small amount of KMnO_4 and 2 to 3 pellets of NaOH. The water used had a specific conductance of $2.05 \times 10^{-6} \text{ S}^{-1}\text{-cm}^{-1}$. The purities of the purified liquids were checked by measuring their densities (recorded in Table I) at $(298.15 \pm 0.01) \text{ K}$, and these densities agreed to within $\pm 5 \times 10^{-3} \text{ kg-m}^{-3}$ of their corresponding literature values.^(10,11,12,13)

Speeds of sound in various binary and ternary mixtures were measured at $(308.15 \pm 0.01) \text{ K}$ using a variable path interferometer (Model M 81, Mittal

Table I. Comparison of Densities, ρ , and Speeds of Sound, u , of Pure Liquids, Along with Their Literature Values at (298.15 and 308.15) K

Liquids	<i>T</i> /K	ρ (g-cm ⁻³)		u (m-s ⁻¹)	
		Expt.	Lit.	Expt.	Lit.
1,3-dioxolane	298.15	1.05885	1.05881 ⁽¹⁰⁾	1388	1388.8 ⁽¹⁴⁾
1,4-dioxane	298.15	1.02792	1.02797 ⁽¹⁰⁾		
	308.15			1324	1325 ⁽¹⁵⁾
Water	298.15	0.99708	0.99704 ⁽¹¹⁾		
	308.15			1520	1519.8 ⁽¹⁶⁾
Formamide	298.15	1.12926	1.12918 ⁽¹²⁾		
	308.15			1580	1580.5 ⁽¹⁷⁾
Dimethylformamide	298.15	0.94445	0.94447 ⁽¹³⁾		
	308.15			1464	1465 ⁽¹³⁾

Enterprises, India) and a measuring cell. Water from the thermostat was circulated through the cell to maintain the desired temperature. The speeds of sound values for the purified liquids at (308.15 ± 0.01) K (recorded in Table I) compare well with their corresponding experimental values.^(14,15,16,17) The uncertainties in the measured speed of sound values are $\pm 1 \text{ m}\cdot\text{s}^{-1}$.

3. RESULTS AND DISCUSSION

The speeds of sound, u_{ijk} , of ternary 1,3-dioxolane or 1,4-dioxane (i) + W (j) + FD or DMF (k) mixtures and u_{ij} data of their binary subsystems 1,3-dioxolane or 1,4-dioxane (i) + FD or DMF (j), and W (i) + FD or DMF (j) have been measured over the entire composition range at 308.15 K. The isentropic compressibilities for binary, $(\kappa_s^E)_{ij}$, and ternary, $(\kappa_s^E)_{ijk}$, mixtures were calculated using Eqs. (1) and (2)

$$(\kappa_s)_{ij} = (\rho_{ij} u_{ij}^2)^{-1} \quad (1)$$

$$(\kappa_s)_{ijk} = (\rho_{ijk} u_{ijk}^2)^{-1} \quad (2)$$

The densities, ρ_{ij} and ρ_{ijk} , of the binary and ternary mixtures, respectively, were calculated from their excess molar volume data,^(18,19,20,21,22) by employing Eqs. (3) and (4).

$$V_{ij}^E = \sum_{i=i}^j x_i M_i (\rho_{ij})^{-1} - \sum_{i=i}^j (x_i M_i) (\rho_i)^{-1} \quad (3)$$

$$V_{ijk}^E = \sum_{i=i}^k x_i M_i (\rho_{ijk})^{-1} - \sum_{i=i}^k x_i M_i (\rho_i)^{-1} \quad (4)$$

where the x_i , M_i , and ρ_i are the mole fraction, molar mass, and density, respectively, of component (i) in their binary or ternary mixtures. Excess isentropic compressibilities, $(\kappa_s^E)_{ij}$ and $(\kappa_s^E)_{ijk}$, for the binary and ternary mixtures were calculated using Eqs. (5) and (6).

$$(\kappa_s^E)_{ij} = \kappa_s - \sum_{i=i}^j \phi_i (\kappa_s)_i \quad (5)$$

$$(\kappa_s^E)_{ijk} = \kappa_s - \sum_{i=i}^k \phi_i (\kappa_s)_i \quad (6)$$

where ϕ_i and $(\kappa_s)_i$ are the volume fraction and isentropic compressibility of component i . The resulting $(\kappa_s^E)_{ij}$ and $(\kappa_s^E)_{ijk}$ values for the binary and ternary mixtures are recorded in Tables II and III, and are plotted in Figs. 1–4. Values of

$(\kappa_s^E)_{ij}$ for binary mixtures were fitted to Eq. (7)

$$(\kappa_s^E)_{ij} = x_i x_j \left[\sum_{n=0}^2 \kappa_s^{(n)} (2x_i - 1)^n \right] \quad (7)$$

The $\kappa_s^{(n)}$ ($n = 0, 1, 2$) are parameters characteristic of a binary mixture that were evaluated by the least-squares method, and the parameter values along with their standard deviations, $\sigma(\kappa_s^E)_{ij}$, are recorded in Table II. The values of $(\kappa_s^E)_{ijk}$ for ternary mixtures were fitted to the Redlich-Kister equation, Eq. (8)

$$\begin{aligned} (\kappa_s^E)_{ijk} = & x_i x_j \left[\sum_{n=0}^2 (\kappa_s^{(n)})_{ij} (x_i - x_j)^n \right] + x_j x_k \left[\sum_{n=0}^2 (\kappa_s^{(n)})_{jk} (x_j - x_k)^n \right] \\ & + x_i x_k \left[\sum_{n=0}^2 (\kappa_s^{(n)})_{ik} (x_k - x_i)^n \right] + x_i x_j x_k \left[\sum_{n=0}^2 (\kappa_s^{(n)})_{ijk} (x_j - x_k)^n x_i^n \right] \end{aligned} \quad (8)$$

where $(\kappa_s^{(n)})_{ijk}$ ($n = 0, 1, 2$) are parameters characteristics of the ternary mixtures. The $(\kappa_s^{(n)})_{ij}$ parameters characteristic of the $(i + k)$, $(j + k)$, and $(i + k)$ binary mixtures, and for the 1,3-dioxolane or 1,4-dioxane (i) + water (j) binary mixtures, were taken from literature.⁽²²⁾ The $(\kappa_s^{(n)})_{ijk}$ parameters were calculated by fitting the parameters of Eq. (9) to the $(\kappa_s^E)_{ijk}$ data by the least-squares method

$$\begin{aligned} & \left(\begin{array}{l} (\kappa_s^E)_{ijk} - x_i x_j \left[\sum_{n=0}^2 (\kappa_s^{(n)})_{ij} (x_i - x_j)^n \right] \\ - x_j x_k \left[\sum_{n=0}^2 (\kappa_s^{(n)})_{jk} (x_j - x_k)^n \right] \\ - x_i x_k \left[\sum_{n=0}^2 (\kappa_s^{(n)})_{ik} (x_k - x_i)^n \right] \end{array} \right) [x_i x_j x_k]^{-1} \\ & = \left(\sum_{n=0}^2 (\kappa_s^{(n)})_{ijk} (x_j - x_k)^n x_i^n \right) \end{aligned} \quad (9)$$

and their values are reported along with their standard deviations $\sigma(\kappa_s^E)_{ijk}$ in Table II.

We are unaware of any published $(\kappa_s^E)_{ij}$ and $(\kappa_s^E)_{ijk}$ data for the studied binary and ternary mixtures at 308.15 K with which to compare our results.

The $(\kappa_s^E)_{ij}$ values for 1,3-dioxolane (i) + FD or DMF (j) and 1,4 dioxane (i) + DMF (j) binary mixtures are negative over the entire composition range. However, for the 1,4-dioxane (i) + DMF (j) mixtures, the $(\kappa_s^E)_{ij}$ values are positive over entire composition range.

The negative values of $(\kappa_s^E)_{ij}$ for 1,3-dioxolane + FD or DMF mixtures suggest that molecular interactions⁽²⁰⁾ occur between the ether oxygen atom of

Table II. Speeds of Sound, u_{ij} , and Excess Isentropic Compressibilities, $(\kappa_s^E)_{ij}$, for Various $(i + j)$ Mixtures as a Function of x_i , the Mole Fraction of Component i , at 305.15 K^a

x_i	u_{ij}	$(\kappa_s)_{ij}$	$(\kappa_s^E)_{ij}$ (TPa ⁻¹)
1,3-dioxolane (i) + formamide (j)			
0.0987	1528	387.0	-6.8
0.1716	1497	407.0	-10.4
0.2010	1485	415.0	-11.5
0.2680	1462	431.0	-14.4
0.2970	1452	438.2	-15.0
0.3284	1443	445.0	-16.3
0.3750	1429	456.6	-17.0
0.4010	1423	460.7	-18.0
0.4687	1406	474.8	-18.9
0.4990	1399	480.5	-19.5
0.5460	1388	489.6	-19.9
0.5720	1383	494.4	-20.0
0.6510	1365	509.6	-19.2
0.7462	1346	527.9	-16.7
0.8912	1316	536.3	-9.6
0.9119	1311	560.8	-8.0
$\kappa_s^{(0)} = -77.2$, $\kappa_s^{(1)} = -77.1$, $\kappa_s^{(2)} = -17.3$, and $\sigma(\kappa_s^E) = 0.2$			
1,3-dioxolane(i) + di-methylformamide (j)			
0.1250	1450	507.8	-8.7
0.1520	1448	508.4	-9.9
0.1988	1443	509.8	-11.7
0.2374	1437	511.5	-12.6
0.2840	1430	513.8	-13.5
0.3784	1415	519.3	-14.6
0.4110	1410	521.3	-14.8
0.4385	1405	523.8	-14.3
0.4910	1395	527.8	-14.0
0.5120	1391	529.4	-13.9
0.5538	1383	533.0	-13.4
0.6714	1361	543.5	-11.5
0.7010	1355	546.3	-10.9
0.7712	1341	553.2	-9.3
0.8385	1327	560.6	-7.0
0.9010	1314	567.9	-4.5
$\kappa_s^{(0)} = -56.8$, $\kappa_s^{(1)} = 17.4$, $\kappa_s^{(2)} = -16.2$, and $\sigma(\kappa_s^E) = 0.2$			
1,4-dioxane (i) + formamide (j)			
0.1550	1544	384.0	-31.2
0.1912	1536	389.8	-36.4
0.2090	1533	392.4	-39.0
0.2413	1525	397.9	-42.4
0.2790	1517	404.0	-46.1
0.3185	1508	410.6	-49.1
0.3517	1501	416.0	-51.3
0.3740	1496	419.8	-52.3

Table II. Continued

x_i	u_{ij}	$(\kappa_s)_{ij}$	$(\kappa_s^E)_{ij}$ (TPa ⁻¹)
0.4050	1490	424.0	-54.5
0.4714	1475	435.7	-55.7
0.5210	1461	445.8	-54.4
0.5681	1449	454.8	-53.2
0.6510	1430	470.6	-50.0
0.6880	1418	479.4	-46.3
0.7917	1390	502.3	-36.7
0.8889	1361	527.5	-22.5
$\kappa_s^{(0)} = -220.7$, $\kappa_s^{(1)} = -15.0$, $\kappa_s^{(2)} = -23.1$, and $\sigma(\kappa_s^E) = 0.5$			
1,4-dioxane (<i>i</i>) + dimethylformamide (<i>j</i>)			
0.0234	1455	510.7	1.1
0.0984	1439	517.7	3.8
0.1456	1430	522.0	5.4
0.2301	1414	528.9	7.6
0.2703	1407	532.0	8.5
0.3540	1340	538.0	9.9
0.4104	1385	541.2	10.1
0.4746	1376	545.0	10.4
0.5340	1369	547.8	10.1
0.5964	1362	550.3	9.4
0.6463	1356	551.9	8.4
0.7208	1349	554.4	7.1
0.8102	1341	556.5	4.7
0.9634	1327	560.4	1.0
$\kappa_s^{(0)} = 41.2$, $\kappa_s^{(1)} = -9.0$, $\kappa_s^{(2)} = -11.2$, and $\sigma(\kappa_s^E) = 0.1$			
water (<i>i</i>) + formamide (<i>j</i>)			
0.0750	1600.2	349.3	-10.9
0.1119	1606.4	347.1	-14.5
0.1885	1616.0	344.2	-20.6
0.2251	1618.3	344.0	-22.5
0.2417	1618.9	344.0	-23.2
0.2912	1620.5	344.4	-25.2
0.3470	1618.4	346.7	-25.8
0.3999	1616.1	349.1	-26.3
0.4320	1613.4	351.3	-26.0
0.4790	1608.8	354.9	-25.4
0.5510	1599.7	361.7	-23.5
0.5881	1595.1	365.4	-22.6
0.6312	1589.0	370.1	-21.2
0.7090	1577.9	379.6	-18.6
0.8598	1550.9	403.8	-10.9
0.9217	1537.4	416.7	-6.3
$\kappa_s^{(0)} = -99.8$, $\kappa_s^{(1)} = 37.9$, $\kappa_s^{(2)} = -32.2$, and $\sigma(\kappa_s^E) = 0.3$			
water (<i>i</i>) + dimethylformamide (<i>j</i>)			
0.0770	1503	476.8	-30.1
0.1298	1526	460.9	-45.0

Table II. Continued

x_i	u_{ij}	$(\kappa_s)_{ij}$	$(\kappa_s^E)_{ij}$ (TPa ⁻¹)
0.1669	1539	452.0	-53.0
0.1967	1548	446.0	-58.4
0.2515	1560	437.0	-66.0
0.2710	1563	434.6	-68.0
0.3001	1566	431.8	-70.0
0.3599	1571	427.0	-73.0
0.3901	1573	424.9	-74.1
0.4109	1575	423.3	-74.9
0.4712	1574	421.9	-74.0
0.5010	1573	421.2	-73.4
0.5370	1573	420.6	-72.4
0.6715	1565	420.8	-64.2
0.7351	1567	418.0	-62.0
0.8999	1539	428.8	-30.4

$\kappa_s^{(0)} = -295.9$, $\kappa_s^{(1)} = 51.5$, $\kappa_s^{(2)} = -13.8$, and $\sigma(\kappa_s^E)_{ij} = 0.6$

^aUnits: $(\kappa_s^{(n)})_{ij}$ and $\sigma(\kappa_s^E)$: TPa⁻¹; u_{ij} : m-s⁻¹.

1,3-dioxolane and a hydrogen atom of FD or DMF. Furthermore, the $(\kappa_s^E)_{ij}$ values for 1,3-dioxolane or 1,4-dioxane (i) + FD or DMF (j) mixtures suggest that the addition of 1,3-dioxolane or 1,4-dioxane to FD or DMF results in a relatively more packed structure in FD as compared to DMF. This is due to the presence of -CH₃ groups in DMF, which restrict the approach of 1,3-dioxolane molecules to the DMF molecules.

Values of $(\kappa_s^E)_{ijk}$ for the studied ternary mixtures are negative over the entire composition range. The more negative values of $(\kappa_s^E)_{ijk}$ for 1,3-dioxolane (i) + W (j) + FD or DMF (k) mixtures, compared to those for 1,4-dioxane (i) + water (j) + FD or DMF (k) ternary mixtures, suggest that the addition of 1,3-dioxolane to a water (j) + FD or DMF (k) binary mixture gives more densely packed structures compared to the 1,4-dioxane in FD or DMF (k).

4. CONCEPTUAL ASPECTS OF THE GRAPH THEORETICAL APPROACH AND RESULTS

According to the mathematical discipline of graph theory, if atoms in a structural formula of a molecule are represented by points, and the edges represent the chemical bonds between them, then the resulting graph describes the total information contained in that molecule. Kier⁽²³⁾ has suggested that the effects from branching in molecules can be examined by evaluating the connecting parameter

Table III. Speeds of Sound, u_{ijk} , Excess Isentropic Compressibilities, $(\kappa_s^E)_{ijk}$, for Various $(i + j + k)$ Ternary Mixtures at 308.15 K, with Values Evaluated from Graph Theory and Flory's theory; Also Included are Various Parameters $(\kappa_s^{(n)})_{ijk}$ ($n = 0, 1, 2$) Along with their Standard Deviation $\sigma(\kappa_s^E)_{ijk}$, and the Interaction Parameters χ_{ij} and $({}^3\xi_i)^d$

x_i	x_j	u_{ijk} (m-s ⁻¹)	$(\kappa_s)_{ijk}$	$(\kappa_s^E)_{ijk}$ (TPa ⁻¹)		
				(Exptl.)	(Graph)	(Flory)
1,3-dioxolane (<i>i</i>) + water (<i>j</i>) + formamide (<i>k</i>)						
0.0608	0.7221	1583	381.3	-52.2	-42.0	21.1
0.0822	0.6528	1604	369.1	-67.0	-54.5	28.5
0.1079	0.5705	1622	358.6	-80.4	-66.3	36.1
0.1231	0.6254	1625	360.2	-91.4	-80.7	12.9
0.2108	0.3703	1553	388.9	-69.0	-91.4	28.9
0.5028	0.3501	1551	397.8	-136.0	-136.0	-84.6
0.5318	0.4652	1422	477.4	-76.0	-198.6	-117.9
0.5710	0.3659	1446	459.3	-90.4	-156.1	-109.7
0.6208	0.2103	1460	449.6	-93.0	-89.3	-92.2
0.6427	0.3210	1413	482.2	-76.1	-148.5	-121.4
0.7827	0.1102	1371	511.8	-48.4	-48.4	-115.8
0.7912	0.0902	1355	524.3	-35.3	-38.0	-114.0
0.8345	0.0521	1330	543.6	-18.9	-18.9	-117.0
$(\kappa_s^{(0)})_{ijk} = -1024.5$, $(\kappa_s^{(1)})_{ijk} = -35963.0$, $(\kappa_s^{(2)})_{ijk} = 188162.9$, $\sigma(\kappa_s^E)_{ijk} = 0.8$, $\chi_{ij}^* = -600.1$; $\chi_{jk}^* = 41.4$; $\chi_{ik}^* = 70.3$; $\chi^* = -401.5$, $({}^3\xi_i) = 0.601$, $({}^3\xi_j) = 1.010$, and $({}^3\xi_k) = 0.440$						
1,3-dioxolane (<i>i</i>) + water (<i>j</i>) + dimethylformamide (<i>k</i>)						
0.0282	0.8949	1534	428.5	-37.2	-31.2	-5.6
0.0680	0.8085	1551	420.7	-63.0	-66.8	3.5
0.1309	0.6910	1566	415.5	-86.2	-95.4	5.6
0.1960	0.5819	1508	443.8	-99.0	-99.0	-2.4
0.3696	0.4501	1477	462.5	-79.6	-93.8	-48.4
0.4401	0.4010	1477	462.5	-79.6	-79.6	-65.2
0.4800	0.2714	1494	444.9	-99.2	-50.0	-47.3
0.5102	0.3615	1444	479.6	-69.1	-62.6	-82.0
0.5638	0.1206	1351	515.4	-33.6	-33.6	-42.5
0.5961	0.3010	1420	491.7	-64.0	-38.0	-96.9
0.6320	0.2516	1425	488.5	-69.3	-33.3	-96.8
0.7110	0.1525	1399	501.7	-60.3	-35.2	-97.9
0.8120	0.0821	1355	531.3	-36.9	-36.9	-110.5
$(\kappa_s^{(0)})_{ijk} = -1025.3$, $(\kappa_s^{(1)})_{ijk} = -2100.2$, $(\kappa_s^{(2)})_{ijk} = 102050.2$, $\sigma(\kappa_s^E)_{ijk} = 0.7$, $\chi_{ij}^* = -708.8$; $\chi_{jk}^* = 92.1$; $\chi_{ik}^* = -492.8$; $\chi^* = 1610.4$, $({}^3\xi_i) = 0.601$, $({}^3\xi_j) = 1.010$, and $({}^3\xi_k) = 0.589$						
1,4-dioxane (<i>i</i>) + water (<i>j</i>) + formamide (<i>k</i>)						
0.1040	0.6395	1534	405.5	-43.6	-45.6	-2.5
0.1736	0.3689	1557	384.7	-62.0	-62.0	12.0
0.1876	0.4484	1542	395.3	-63.2	-64.1	6.6
0.1916	0.5830	1516	414.5	-59.0	-60.0	-27.9
0.2753	0.4050	1528	405.0	-75.7	-74.6	-31.4
0.3430	0.2343	1531	404.1	-78.6	-77.0	-29.0

Table III. Continued

x_i	x_j	u_{ijk} (m-s ⁻¹)	$(\kappa_s)_{ijk}$	$(\kappa_s^E)_{ijk}$ (TPa ⁻¹)		
				(Exptl.)	(Graph)	(Flory)
0.3812	0.4505	1493	433.7	-77.3	-78.1	-73.7
0.4102	0.3624	1499	426.6	-82.0	-82.0	-69.1
0.5321	0.2269	1481	438.5	-81.0	-80.1	-82.9
0.6210	0.1542	1456	456.3	-72.1	-72.1	-94.1
0.6408	0.1248	1450	460.3	-68.0	-68.6	-94.4
0.6918	0.1012	1433	472.6	-61.0	-62.0	-102.3
0.7712	0.1326	1408	491.8	-54.4	-54.2	-123.1
0.8610	0.0851	1376	516.6	-36.4	-36.4	-133.0
$(\kappa_s^{(0)})_{ijk} = -115.3$, $(\kappa_s^{(1)})_{ijk} = 1810.2$, $(\kappa_s^{(2)})_{ijk} = 9950.3$, $\sigma(\kappa_s^E)_{ijk} = 0.8$, $\chi_{ij}^* = -91.6$; $\chi_{jk}^* = -53.1$; $\chi_{ik}^* = -115.8$; $\chi^* = -299.8$, $({}^3\xi_i) = 0.801$, $({}^3\xi_j) = 1.010$, and $({}^3\xi_k) = 0.440$						
1,4-dioxane (i) + water (j) + dimethylformamide (k)						
0.0386	0.8626	1542	423.2	-49.2	-33.4	60.0
0.0798	0.7630	1576	405.3	-83.6	-53.5	10.4
0.1087	0.6929	1603	392.2	-105.0	-65.5	17.8
0.1190	0.7320	1564	409.3	-87.1	-57.9	-4.9
0.1827	0.8006	1462	457.2	-44.1	-44.1	-54.7
0.2155	0.6557	1473	457.5	-53.7	-67.7	-37.6
0.2916	0.5216	1507	439.9	-81.4	-81.4	-36.7
0.3712	0.4515	1487	451.5	-77.0	-82.6	-55.0
0.3267	0.4806	1524	430.3	-94.5	-83.0	-42.2
0.4502	0.1856	1465	474.6	-59.2	-59.2	-18.2
0.5320	0.1020	1487	460.1	-78.0	-32.3	-31.0
0.7260	0.1620	1464	462.8	-87.0	-45.0	-111.3
0.8510	0.1251	1381	515.8	-40.4	-40.4	-138.0
$(\kappa_s^{(0)})_{ijk} = -3500.3$, $(\kappa_s^{(1)})_{ijk} = -5179.3$, $(\kappa_s^{(2)})_{ijk} = 402353.5$, $\sigma(\kappa_s^E)_{ijk} = 0.5$, $\chi_{ij}^* = -125.1$; $\chi_{jk}^* = -170.3$; $\chi_{ik}^* = 127.1$; $\chi^* = -366.7$, $({}^3\xi_i) = 0.801$, $({}^3\xi_j) = 1.010$, and $({}^3\xi_k) = 0.589$						

^aUnits: χ^* , χ_{ij}^* , χ_{ik}^* , $(\kappa_s^{(n)})_{ijk}$ ($n = 0, 1, 2$), and $\sigma(\kappa_s^E)$: TPa⁻¹.

of third degree, ${}^3\xi$, of a molecule. Singh⁽²⁴⁾ defined ${}^3\xi$ by

$${}^3\xi = \sum_{m < n < o < p} (\delta_m^v \delta_n^v \delta_o^v \delta_p^v)^{-0.5} \quad (10)$$

where the δ_m^v reflect explicitly the valency for forming bonds of the mth vertex in the molecular graph, and it is related to the maximum valency, Z_m , and the number of hydrogen atoms attached to the mth vertex, by the relation $\delta_m^v = Z_m - h_m$.⁽²³⁾ Furthermore, Singh *et al.*⁽²⁵⁾ postulated that the value of $1/{}^3\xi$ of a molecule provides a measure of the probability that the surface of one molecule interacts effectively with the surface of another molecule, and the values can be utilized

to predict molar excess volumes, molar excess enthalpies, and excess isentropic compressibilities of binary and ternary mixtures.

5. EXCESS ISENTROPIC COMPRESSIBILITIES OF BINARY MIXTURES

An analysis of the V^E and H^E results for the W (i) + FD or DMF (j) mixtures by the graph theoretical approach⁽²⁶⁾ has revealed that W (i) and FD or DMF (j) exist as associated molecular entities, and that ($i + j$) mixture formation involves the following processes: (1) establishment of unlike i_n-j_n interactions between the (i) and (j) components; (2) formation of unlike contacts between i and j leads to the depolymerization of (a) i_n and (b) j_n entities to give their respective monomers; and (3) monomers of i and j then undergo specific interactions to yield the $i;j$ molecular complex. If χ_{ij} , χ_{ii} , χ_{jj} , and χ_{12} are the molar interaction parameters for unlike $i-j$ and like $i-i$ or $j-j$ contact formation, and specific interactions occur between (i) and (j), then changes in the isentropic compressibility due to processes 1, 2 (a), 2 (b), and 3 are given by^(1,27,28)

$$\Delta X_1(X = k_s) = \left[x_i x_j V_j \chi_{ij} / \sum x_i V_i \right] \quad (11)$$

$$\Delta X_2(X = k_s) = x_i^2 x_j V_j \chi_{ii} / \sum x_i V_i \quad (12)$$

$$\Delta X_3(X = k_s) = x_i^2 x_j V_j \chi_{jj} / \sum x_i V_i \quad (13)$$

$$\Delta X_4(X = k_s) = x_i x_j^2 V_j \chi_{12} / \sum x_i V_i \quad (14)$$

where V_i is the molar volume of component (i). The overall changes in the thermodynamic property, $(\kappa_s^E)_{ij}$, for ($i + j$) mixture formation are then given by Eq. (15)

$$\begin{aligned} (\kappa_s^E)_{ij} &= \sum_{i=1}^4 \Delta X_i \\ &= \left[x_i x_j V_j / \sum x_i V_i \right] [\chi_{ij} + x_i \chi_{ii} + x_i \chi_{jj} + x_j \chi_{12}] \end{aligned} \quad (15)$$

Since $V_j/V_i = ({}^3\xi_i/{}^3\xi_j)$,⁽²⁵⁾ then Eq. (15) reduces to Eq. (16)

$$(\kappa_s^E)_{ij} = [x_i x_j ({}^3\xi_i/{}^3\xi_j) / x_i + x_j ({}^3\xi_i/{}^3\xi_j)] [\chi_{ij} + x_i \chi_{ii} + x_i \chi_{jj} + x_j \chi_{12}] \quad (16)$$

If it is also assumed that $\chi_{ij} \cong \chi_{12} = \chi'_{ij}$ and $\chi_{ii} \cong \chi_{jj} = \chi^*$, then Eq. (16) can be rewritten as Eq. (17)

$$(\kappa_s^E)_{ij} = [x_i x_j ({}^3\xi_i/{}^3\xi_j) / x_i + x_j ({}^3\xi_i/{}^3\xi_j)] [(1 + x_j) \chi'_{ij} + 2x_i \chi^*] \quad (17)$$

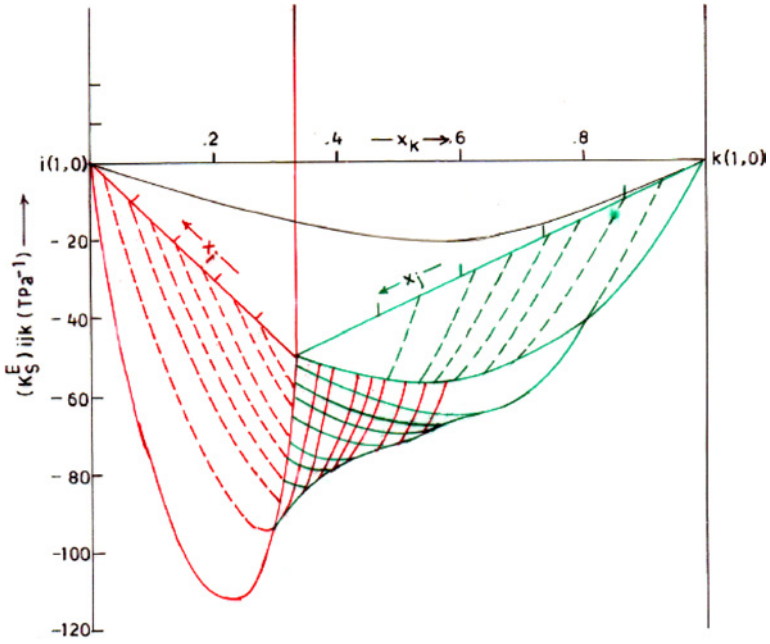


Fig. 1. Excess isentropic compressibilities of 1,3-dioxolane (i) + water (j) + Formamide (k) at 308.15 K.

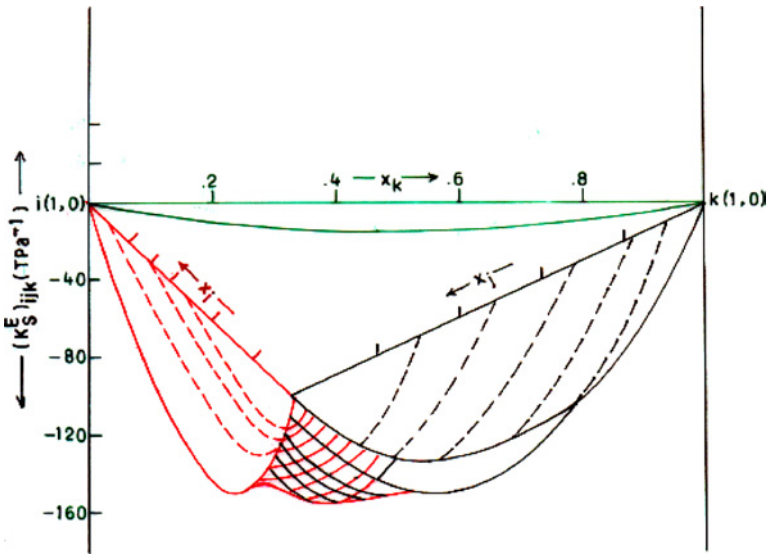


Fig. 2. Excess isentropic compressibilities of 1,3-dioxolane (i) + water (j) + DMK (k) at 308.15 K.

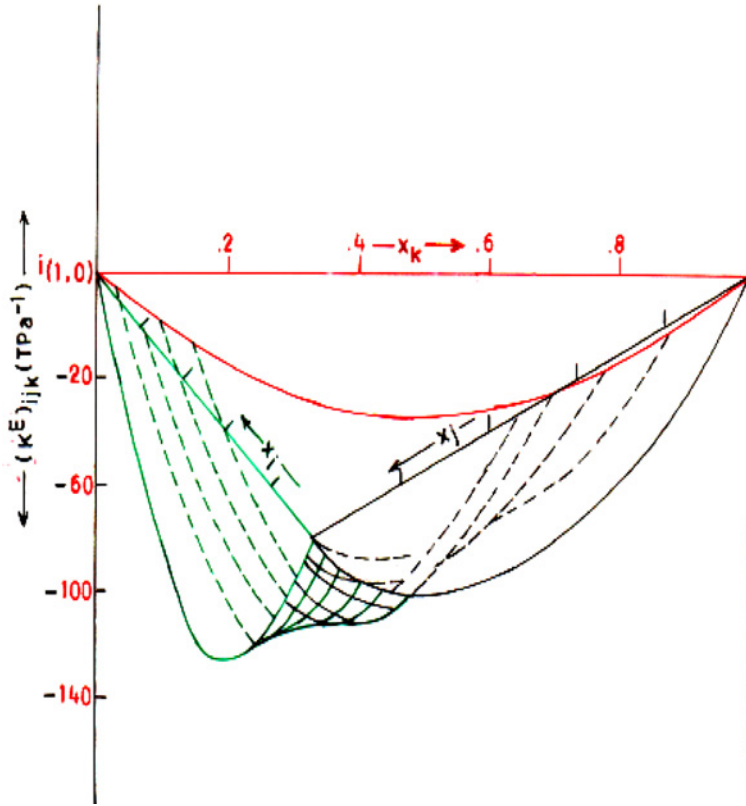


Fig. 3. Excess isentropic compressibilities of 1,4-dioxolane (*i*) + water (*j*) + formamide (*k*) at 308.15 K.

A thermodynamic analysis of the V^E and H^E data for 1,3-dioxolane (*i*) + FD or NND (*j*) and 1,4-dioxane + W (*j*) mixtures has shown⁽²⁰⁾ that 1,3-dioxolane and 1,4-dioxane exist as monomers, whereas FD or NND are associated in molecular entities. Consequently, $\chi_{ii} = 0$ for 1,3-dioxolane or 1,4-dioxane (*i*) + FD or DMF (*j*) mixtures. If it is assumed that $\chi_{ij} \cong \chi_{ii} = \chi'_{ij}$, then for 1,3-dioxolane or 1,4-dioxane (*i*) + FD or DMF (*j*) binary mixtures, Eq. (16) reduces to Eq. (18)

$$(\kappa_s^E)_{ij} = [x_i x_j ({}^3\xi_i / {}^3\xi_j)] / x_i + x_j ({}^3\xi_i / {}^3\xi_j) [(1 + x_i)\chi'_{ij} + x_j \chi_{12}] \quad (18)$$

Equations (17) and (18) contain two unknown parameters whose values were calculated by employing $(\kappa_s^E)_{ij}$ data at two compositions ($x_i = 0.4$ and 0.5) of the various binary mixtures. These parameters were subsequently utilized to predict $(\kappa_s^E)_{ij}$ values at other values of x_i . The resulting $(\kappa_s^E)_{ij}$ values for binary mixtures, along with the χ'_{ij} , χ_{12} parameters, are recorded in Table IV, where they are also compared with their corresponding experimental values.

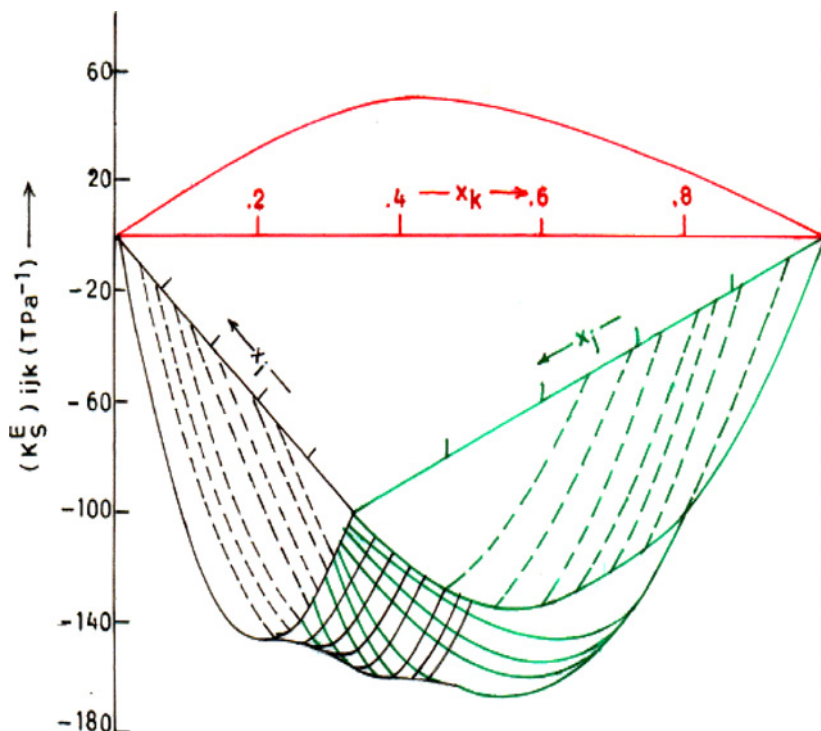


Fig. 4. Excess isentropic compressibilities of 1,4-dioxolane (*i*) + water (*j*) + DMF (*k*) at 308.15 K.

Examination of the data in Table IV reveals that the $(\kappa_s^E)_{ij}$ values compare well with their corresponding experimental values. This lends additional support to the various assumptions made in deriving Eqs. (17) and (18), and also to the validity of the assumption that $V_i/V_j = {}^3\xi_j/{}^3\xi_i$.

6. EXCESS ISENTROPIC COMPRESSIBILITIES OF TERNARY MIXTURES

If a third component such as FD or NND (*k*) is added to 1,3-dioxolane or 1,4-dioxane (*i*) + W (*j*) binary mixtures, then ternary mixture formation involve the processes: (1) the establishment of unlike (a) $i-j_n$, (b), j_n-k_n , and (c) $i-k_n$ contacts; (2) unlike molecular contact formation between the *i*, *j* and *k* components of the mixture results in depolymerization of (a) j_n and (b) k_n to yield their respective monomers; (3) monomers of *i*, *j* and *k* then undergo specific interaction to give (a) $i:j$ (b) $j:k$ and (c) $i:k$ molecular associations. Consequently, if χ_{ij} , χ_{jk} , and χ_{ik} are interaction energies for unlike $i-j$, $j-k$, and $i-k$ contacts, then changes in the

Table IV. Comparison of Excess Isentropic Compressibility Values, κ_s^E , for Various ($i+j$) Mixtures as a Function of Mole Fraction, x_i , of Component i , at 308.15 K with Values Evaluated from Graph Theory and Flory's Theory; Also Included are the Energy Interaction Parameters χ_{ij} , χ_{12} , and χ_{ij}^{**a}

	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
1,3-dioxolane (i) + formamide (j)									
κ_s^E (exptl)	-6.7	-11.7	-15.4	—	—	-19.5	-18.2	-14.9	-9.2
κ_s^E (graph)	-6.0	-11.2	-15.1	—	—	-19.2	-17.4	-17.6	-8.0
κ_s^E (Flory)	-19.2	-22.9	-25.0	-26.3	—	-28.0	-28.6	-29.0	-29.3
(ξ_i) = 0.601, (ξ_j) = 0.440, χ'_{ij} = -34.2, χ_{12} = -31.1, and χ_{ij}^{**} = 208.7									
1,3-dioxolane (i) + dimethylformamide (j)									
κ_s^E (exptl)	-7.3	-11.7	-14.0	—	—	-12.9	-11.0	-8.4	-4.8
κ_s^E (graph)	-6.6	-11.0	-13.6	—	—	-12.6	-10.2	-7.1	-3.6
κ_s^E (Flory)	-6.8	-5.1	-4.3	-3.9	—	-3.4	-3.4	-3.1	-3.0
(ξ_i) = 0.601, (ξ_j) = 0.589, χ'_{ij} = -17.8, χ_{12} = -58.9, and χ_{ij}^{**} = 14.1									
1,4-dioxane (i) + formamide (j)									
κ_s^E (exptl)	-22.2	-38.0	-48.3	—	—	-52.4	-45.8	-35.1	-20.1
κ_s^E (graph)	-21.1	-37.0	-47.9	—	—	-51.8	-44.2	-32.7	-17.8
κ_s^E (Flory)	-13.8	-15.3	-15.9	-16.4	—	-16.9	-17.0	-17.2	-17.3
(ξ_i) = 0.801, (ξ_j) = 0.440, χ'_{ij} = -52.0, χ_{12} = -185.5, and χ_{ij}^{**} = 32.7									
1,4-dioxane (i) + dimethylformamide (j)									
κ_s^E (exptl)	3.7	6.8	9.0	—	—	9.3	7.5	5.0	2.4
κ_s^E (graph)	4.1	7.2	9.2	—	—	9.5	8.0	5.9	3.1
κ_s^E (Flory)	-5.1	-3.7	-3.0	-2.6	—	-2.1	-2.0	-1.9	-1.8
(ξ_i) = 0.801, (ξ_j) = 0.589, χ'_{ij} = 12.24, χ_{12} = 34.8, and χ_{ij}^{**} = 9.6									
water (i) + formamide (j)									
κ_s^E (exptl)	-13.5	-21.4	-25.2	—	—	-22.4	-18.6	-14.1	-8.1
κ_s^E (graph)	-11.7	-19.7	-24.5	—	—	-21.3	-16.0	-9.8	-3.4
κ_s^E (Flory)	-9.3	-9.4	-9.3	-9.5	—	-9.3	-9.2	-9.1	-9.0
(ξ_i) = 1.000, (ξ_j) = 0.440, χ_{ij} = -67.55, χ' = 29.6, and χ_{ij}^{**} = 63.7									
water (i) + dimethylformamide (j)									
κ_s^E (exptl)	-37.5	-59.4	-70.6	—	—	-69.8	-62.0	-49.5	-30.0
κ_s^E (graph)	-31.4	-54.0	-68.3	—	—	-67.0	-54.6	-38.2	-19.4
κ_s^E (Flory)	-16.3	-14.6	-13.3	-12.3	—	-10.9	-10.4	-10.0	-9.6
(ξ_i) = 1.000, (ξ_j) = 0.589, χ_{ij} = -55.3, χ_{12} = -304.4, and χ_{ij}^{**} = 233.9									

^aUnits: χ_{ij}^{**} : J-mol⁻¹.

molar isentropic compressibility due to processes 1(a)–(c) are given by^(1,27,28)

$$\Delta X_1 = \left[x_i x_j V_j / \sum x_i V_i \right] \chi_{ij} + \left[x_j x_k V_k / \sum x_j V_j \right] \chi_{jk} + \left[x_i x_k / \sum x_k V_k \right] \chi_{ik} \quad (19)$$

Furthermore, if χ_{ii} , χ_{kk} , χ_{12} , χ'_{12} , and χ''_{12} are molar interaction energies for like (i - i , k - k) contacts and specific interactions occur between the i , j and k components

of the ternary mixtures, then changes in the thermodynamic property $(\kappa_s^E)_{ijk}$, due to processes 2(a)–(b) and 3(a)–(c), can be expressed^(1,27,28) by Eq. (20).

$$\Delta X_2 = x_i^2 x_j V_j \chi'_{ii} / \sum x_i V_i + x_k^2 x_i V_k \chi'_{kk} / \sum x_k V_k \quad (20)$$

$$\Delta X_3 = x_i x_j^2 V_j \chi_{12} / \sum x_i V_i + x_j x_k^2 V_k \chi'_{12} / \sum x_k x_i \chi''_{12} V_i / \sum x_k V_k \quad (21)$$

The overall change in the thermodynamic property, $(\kappa_s^E)_{ijk}$, due to processes 1(a)–(c), 2 (a)–(b), and 3 (a)–(c) would then be expressed by Eq. (22)

$$\begin{aligned} \kappa_s^E &= \sum_{i=1}^3 \Delta X_i \\ (\kappa_s^E)_{ijk} &= \left[x_i x_j V_j / \sum x_i V_i \right] [\chi_{ij} + x_i \chi'_{ii} + x_j \chi_{12}] \\ &+ \left[x_j x_k V_k / \sum x_j V_j \right] [\chi_{jk} + x_k \chi'_{12}] \\ &+ \left[x_i x_k V_i / \sum x_k V_k \right] [\chi_{ik} + x_k \chi'_{kk} + x_i \chi''_{12}] \end{aligned} \quad (22)$$

Because $V_j/V_i = ({}^3\xi_i/{}^3\xi_j)$,⁽²⁵⁾ Eq. (22) reduces to Eq. (23).

$$\begin{aligned} (\kappa_s^E)_{ijk} &= [x_i x_j ({}^3\xi_i/{}^3\xi_j) / x_i + x_j ({}^3\xi_i/{}^3\xi_j)] [\chi_{ij} + x_i \chi'_{ii} + x_j \chi_{12}] \\ &+ [x_j x_k ({}^3\xi_j/{}^3\xi_k) / x_j + x_k ({}^3\xi_j/{}^3\xi_k)] [\chi_{jk} + x_k \chi'_{12}] \\ &+ [x_i x_k ({}^3\xi_k/{}^3\xi_i) / x_k + x_i ({}^3\xi_k/{}^3\xi_i)] [\chi_{ik} + x_k \chi'_{kk} + x_i \chi''_{12}] \end{aligned} \quad (23)$$

If it is assumed that $\chi_{ij} \cong \chi_{12} = \chi_{ij}^*$, $\chi_{jk} \cong \chi'_{12} = \chi_{jk}^*$, $\chi_{ik} \cong \chi'_{12} = \chi_{ik}^*$, and $\chi'_{ii} = \chi'_{kk} = \chi^*$, then Eq. (23) reduces to

$$\begin{aligned} (\kappa_s^E)_{ijk} &= [x_i x_j ({}^3\xi_i/{}^3\xi_j) / x_i + x_j ({}^3\xi_i/{}^3\xi_j)] [(1 + x_j) \chi_{ij}^* + x_i \chi^*] \\ &+ [x_j x_k ({}^3\xi_j/{}^3\xi_k) / x_j + x_k ({}^3\xi_j/{}^3\xi_k)] [(1 + x_k) \chi_{jk}^*] \\ &+ [x_i x_k ({}^3\xi_k/{}^3\xi_i) / x_k + x_i ({}^3\xi_k/{}^3\xi_i)] [(1 + x_i) \chi_{ik}^* + x_k \chi^*] \end{aligned} \quad (24)$$

Equation (24) contains four unknown parameters, and the values of these parameters were evaluated by employing $(\kappa_s^E)_{ijk}$ data for the studied mixtures at four compositions. The resulting parameters were then utilized to predict $(\kappa_s^E)_{ijk}$ values over the entire composition range. These $(\kappa_s^E)_{ijk}$ values, along with χ_{ij}^* parameters, are recorded in Table III where they are also compared with their corresponding experimental values.

7. FLORY'S THEORY

The κ_s^E values for the various binary and ternary mixtures have also been calculated in terms of Flory's theory.^(29,30) According to this theory, κ_s^E is given by

$$\kappa_s^E = \kappa_s - \kappa_s^{id} \quad (25)$$

The isentropic compressibility, κ_s , of a mixture at effectively zero pressure is given by Eq. (26).

$$\kappa_s = K_T - T v_m^* \alpha_p^2 / C_{p,m} \quad (26)$$

The isothermal compressibility, K_T , of a mixture at effectively zero pressure is given by relation:

$$K_T = [(3\bar{v}_m^2/p^*)(\bar{v}_m^{1/3} - 1)/(4 - 3(\bar{v}_m^{1/3}))] \quad (27)$$

where

$$v_m^* = \sum_{i=i}^{j \text{ or } k} \phi_i v_i^* \quad (28)$$

$$\alpha_p = 3((\bar{v}_m^{1/3} - 1)/T(4 - 3\bar{v}_m^{1/3})) \quad (29)$$

$$p^* = \sum_{i=i}^k \phi_i p_i^* - \sum_{i=i}^k \phi_i \theta_j \chi_{ij}^{**} \quad (30)$$

$$\bar{v} = v/v^* \quad (31)$$

$$\bar{v}_m = \sum_{i=i}^{j \text{ or } k} \phi_i v_i^* \quad (32)$$

$$C_{p,m} = (\partial H^E/\partial T) + \sum_{i=i}^{j \text{ or } k} x_i C_{p,i} \quad (33)$$

where \bar{v} , v^* , and $c_{p,i}^*$ represent the reduced volume, the characteristic volume, and the molar heat capacity of component (i) in binary or ternary mixtures, and all other terms have the same significance as described by Flory.^(29,30) The values of $(\partial H^E/\partial T)$ for binary mixtures were calculated from their experimental data available in the literature.^(19,20,21,26) The $(\partial H_{ijk}^E/\partial T)$ values for ternary mixtures at 308.15 K were assumed to be related by⁽³¹⁾ $H_{ij}^E + H_{jk}^E + H_{ik}^E$, and the H_{ijk}^E values at 298.15 K were determined in the manner described elsewhere.⁽³²⁾ The interaction energy parameters, χ_{ij}^{**} , were determined by employing H_{ij}^E data for binary ($i + j$) mixtures at $x_i = 0.5$. Values of κ_s^{id} for the corresponding ideal mixtures were calculated using Eq. (26). Although α_p^{id} and $c_{p,m}^{id}$ were assumed to be equal

to their mole fraction averages, for κ^{id} volume fraction averages were taken. The parameters of the pure components were determined using isothermal compressibility (K_T) values reported in the literature.⁽³²⁾ Liquids for which (K_T) values are available have been calculated in the manner described by Hildebrand.⁽³³⁾

The $(\kappa_s^E)_{ij}$ and $(\kappa_s^E)_{ijk}$ values calculated for the present binary and ternary mixtures are recorded in Tables III and IV, where they are also compared with their corresponding experimental values.

Examination of the data in Tables III and IV reveals that $(\kappa_s^E)_{ij}$ and $(\kappa_s^E)_{ijk}$ values predicted by Flory's theory are of same sign as the experimental values, but the quantitative agreement is poor. The failure of Flory's theory to predict correctly the magnitude of $(\kappa_s^E)_{ij}$ and $(\kappa_s^E)_{ijk}$ may be due to the use of various parameters that were not available in the literature, but whose values have been estimated.

In conclusion, the $(\kappa_s^E)_{ij}$ and $(\kappa_s^E)_{ijk}$ values predicted by graph theory and Flory's theory, for the studied binary and ternary mixtures, have revealed that $(\kappa_s^E)_{ij}$ and $(\kappa_s^E)_{ijk}$ values predicted by graph theory compare well with their corresponding experimental values relative to the values predicted by Flory's theory. Even where the quantitative agreement between theoretical and experimental values is not impressive, the values predicted by the graph theory approach are closer to the experimental values than those predicted by Flory's theory.

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