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Deviation in Some Thermodynamic Properties of Fluorocarbon Mixtures

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Abstract : Deviations in thermodynamic properties (molar volume, molar compressibility and molar sound velocity) from ideal values have been computed for six binary fluorocarbon liquid mixtures. Computed results show the applicability of the relations for fluorocarbons. The deviations in these properties show the interaction among the component molecules of the system under investigation.

1. Introduction

Fluorocarbons have gained enormous significance in industrial applications owing their high thermal and chemical stability. They have been used as coolants, sealing liquids, high temperature lubricants and dielectric media.

It has been found that liquids with a very low ultrasound propagation velocity (below 900 ms^{-1}) find extensive applications in sound lenses, cavity resonators and ultrasonic light modulators. Narayana et al[1]. investigated low ultrasonic propagation velocity in liquid fluoropentanes (Flutec PP 50) at 298.15 K. Molar compressibility, molar sound velocity and molar volume provide a measure of studying interaction among the molecules of liquid mixture. The relation for molar sound velocity was proposed by Rao et al[2-3]. and has been applied by various workers[4-7]. Wada[8] proposed the relation for molar compressibility.

In the present investigation, deviations in some of the properties (ultrasonic velocity, molar volume, molar compressibility and molar sound velocity) from their ideal values have been computed and analysed for six binary liquid mixtures involving fluorocarbons.

2. Theory

Molar volume, V, for liquid mixture can be calculated as

$$V_{mix} = \frac{\sum M_i x_i}{\rho_{mix}} \quad (1)$$

where M_i and x_i are molar mass and mole fraction of i^{th} component respectively and ρ_{mix} is the density of liquid mixture. The deviation in molar volume from ideal values in liquid mixture can be computed as

$$\Delta V = V_{idl} - V_{mix} \quad (2)$$

where V_{idl} is ideal molar volume, given by $V_{idl} = \sum x_i V_i$, V_i being molar volume of i^{th} component. Molar sound velocity or Rao constant, R, for liquid mixture can be calculated as

$$R_{mix} = V_{mix} u_{mix}^{1/3} \quad (3)$$

where u_{mix} is ultrasonic velocity of liquid mixture. The deviation in sound velocity from ideal value of mixture can be computed as

$$\Delta R = R_{idl} - R_{mix} \quad (4)$$

where R_{idl} is ideal molar sound velocity, given by $R_{idl} = \sum x_i R_i$, R_i being molar sound velocity of i^{th} component.

Molar compressibility, W, for liquid mixture can be calculated as

$$W_{mix} = \frac{\sum M_i x_i}{\rho_{mix}} \beta_s^{-1/7}. \quad (5)$$

The deviation in molar compressibility from the ideal value of mixture can be computed as

$$\Delta W = W_{idl} - W_{mix} \quad (6)$$

where W_{idl} is ideal molar compressibility given by $W_{idl} = \sum x_i W_i$, W_i being molar compressibility of i^{th} component.

Ultrasonic velocity, u, for liquid mixture has been taken from the work of Narayana et al[1]. and ideal ultrasonic velocity, u_{idl} can be evaluated using the relation

$$u_{idl} = \frac{R_{idl}}{V_{idl}}. \quad (7)$$

The deviation in ultrasonic velocity from ideal values of mixture can be computed as

$$\Delta u = u_{idl} - u_{\exp}. \quad (8)$$

Table 1

Deviation in thermodynamic properties in various flurocarbon liquid mixtures [molar volume (V), molar sound velocity (R) and molar compressibility (W)]

x_1	V_{mix} $m^3\ mol^{-1}$	$\Delta V / V_{idl}$	R_{mix} $m^{10/3} s^{-1/3}\ mol^{-1}$	$\Delta R / R_{idl}$	W_{mix} $N^{1/7} m^{19/7}\ mol^{-1}$	$\Delta W / W_{idl}$	u_{mix} $m\ s^{-1}$	$\Delta u / u_{idl}$
1. Perfluorohexane + perfluoropentane (flutec PP1 + flutec PP50)								
0.0000	179.112	0.0000	1399.471	0.0000	57.830	0.0000	477.0	0.0000
0.1828	182.314	0.0035	1419.495	0.0163	58.802	0.0140	472.0	0.0381
0.3737	186.387	0.0031	1471.422	0.0115	60.921	0.0098	492.0	0.0250
0.4723	188.422	0.0033	1493.509	0.0123	61.840	0.0105	498.0	0.0267
0.5731	190.469	0.0036	1521.765	0.0093	62.987	0.0079	510.0	0.0170
0.7816	194.645	0.0046	1567.232	0.0117	64.898	0.0099	522.0	0.0211
1.0000	200.144	0.0000	1637.832	0.0000	67.708	0.0000	548.0	0.0000
2. Perfluoromethylcyclohexane + perfluoropentane (flutec PP2 + flutec PP50)								
0.0000	179.112	0.0000	1399.471	0.0000	57.830	0.0000	477.0	0.0000
0.1858	181.548	0.0041	1451.437	− 0.0009	60.004	− 0.0002	511.0	− 0.0027
0.3784	184.636	0.0051	1499.815	0.0019	62.060	0.0016	536.0	− 0.0097
0.4771	186.048	0.0065	1521.554	0.0052	63.003	0.0045	547.0	− 0.0038
0.5779	187.774	0.0064	1542.192	0.0096	63.914	0.0082	554.0	0.0093
0.7850	191.950	0.0030	1609.014	0.0028	66.645	0.0025	589.0	− 0.0007
1.0000	196.208	0.0000	1672.169	0.0000	69.269	0.0000	619.0	0.0000
3. Perfluorodecalin + perfluoropentane (flutec PP5 + flutec PP50)								
0.0000	179.112	0.0000	1399.471	0.0000	57.830	0.0000	477.0	0.0000
0.1571	186.214	0.0132	1509.429	0.0049	62.513	0.0040	532.6	− 0.0255
0.3322	196.806	0.0129	1647.288	0.0002	68.266	0.0001	586.4	− 0.0393
0.4273	202.006	0.0155	1714.881	0.0022	71.136	0.0017	611.8	− 0.0412
0.4279	208.591	0.0130	1796.177	− 0.0014	74.506	− 0.0011	638.5	− 0.0441
0.7429	222.657	0.0080	1956.048	− 0.0009	81.246	− 0.0008	678.0	− 0.0271
1.0000	240.138	0.0000	2146.315	0.0000	89.260	0.0000	714.0	0.0000

Table *contd.*

x_1	V_{mix} $m^3\ mol^{-1}$	$\Delta V / V_{idl}$	R_{mix} $m^{10/3} s^{1/3}\ mol^{-1}$	$\Delta R / R_{idl}$	W_{mix} $N^{1/7} m^{19/7}\ mol^{-1}$	$\Delta W / W_{idl}$	umix $m\ s^{-1}$	$\Delta u / u_{idl}$
4. Perfluoromethylcyclohexane + perfluorohexane (flutec PP2 + flutec PP1)								
0.0000	200.144	0.0000	1637.832	0.0000	67.708	0.0000	548.0	0.0000
0.2032	198.579	0.0038	1634.655	0.0062	67.669	0.0052	557.8	0.0070
0.4047	197.479	0.0054	1636.408	0.0093	67.796	0.0079	569.0	0.0116
0.5049	196.858	0.0066	1635.075	0.0121	67.781	0.0104	573.0	0.0168
0.6046	196.631	0.0057	1641.320	0.0104	68.037	0.0089	581.6	0.0141
0.8037	196.206	0.0039	1654.681	0.0065	68.579	0.0056	599.8	0.0076
1.0000	196.208	0.0000	1672.169	0.0000	69.269	0.0000	619.0	0.0000
5. Perfluorodecalin + perfluorohexane (flutec PP5 + flutec PP1)								
0.0000	200.144	0.0000	1637.832	0.0000	67.708	0.0000	548.0	0.0000
0.1724	204.591	0.0118	1692.556	0.0191	70.261	0.0163	566.2	0.0219
0.3572	212.132	0.0107	1789.190	0.0166	74.399	0.0134	600.0	0.0178
0.4543	215.513	0.0128	1831.835	0.0198	76.136	0.0176	614.1	0.0210
0.5555	219.387	0.0134	1891.335	0.0151	78.666	0.0127	636.8	0.0113
0.7690	229.215	0.0073	2002.510	0.0130	83.344	0.0111	666.8	0.0171
1.0000	240.138	0.0000	2146.315	0.0000	89.260	0.0000	714.8	– 0.0011
6. Perfluorodecalin + perfluoromethylcyclohexane (flutec PP5 + flutec PP2)								
0.0000	196.208	0.0000	1672.169	0.0000	69.269	0.0000	619.0	0.0000
0.1729	202.224	0.0077	1702.205	0.0296	70.878	0.0254	596.4	0.0647
0.3526	209.763	0.0091	1789.614	0.0270	74.552	0.0231	621.0	0.0532
0.4495	213.721	0.0103	1837.464	0.0254	76.552	0.0217	635..5	0.0449
0.5505	218.165	0.0101	1887.696	0.0529	78.655	0.0163	647.8	0.0458
0.7654	227.758	0.0090	2011.428	0.0116	83.729	0.0099	688.8	0.0345
1.0000	240.138	0.0000	2146.315	0.0000	89.260	0.0000	714.0	0.0000

3. Results and Discussion

The calculated values of deviations in the properties ($\Delta V/V_{idl}$, $\Delta R/R_{idl}$, $\Delta W/W_{idl}$, $\Delta u/u_{idl}$) for six binary liquids including fluorocarbons are displayed in Table 1. From the results, it is clear that there exists interaction between molecules of component liquids. Deviation in molar volume mostly shows highest value at a mole fraction of 0.4 to 0.6 showing strong interaction in this region, whereas deviations in molar sound velocity, molar compressibility and ultrasonic velocity show little bit irregular trend. The obvious deviation patterns show the applicability of the relations for the mixtures of fluorocarbons.

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