Evaluation of Excess Free Volume and Internal Pressure in Binary Mixtures of Methyl Methacrylate(MMA) with Alcohols

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Abstract: Methyl methacrylate (MMA) is an important monomer attracting the attention of industrialists and scientists because of its various applications and reactivity. The knowledge of thermodynamic and transport properties of MMA in alcohols and other organic solvents is useful in industrial processes. Ultrasonic and viscometric parameters offer simple, easy and accurate ways for calculating several physical parameters which throw light on molecular interactions in solutions. In this paper, the interactions of two alcohols; *tert*-butanol and *iso*-butanol with MMA are reported for the first time. Comparison has been made on the interactive nature of the two alcohols. Computation of free volume, internal pressure and excess free volume has been made for the entire concentration range. Existence of mesomeric effects of MMA is clearly seen and the role of structure of alcohols is observed.

Keywords: MMA, Ultrasonic velocity, Free volume, Internal pressure.

Introduction

Many engineering problems require quantitative data of the viscosity and density of the liquid mixtures. The physical properties and thermodynamic behaviour of polar and non polar mixtures have been studied for many reasons, one of the most important of which is that these properties provide information about molecular interactions. Methyl methacrylate (MMA) monomer is an excellent base material used in dentistry, ophthalmology and other

industries. It has been studied widely by several researchers because of its varied applications, structure and its reactivity with organic solvents. From the structure point of view, ^{13}C NMR and FTIR studies have been made by several workers¹⁻⁶. Molecular interactions of MMA with several organic solvents⁷⁻¹⁰, alkanes^{11,12} hydrocarbons¹³⁻¹⁵, alcohols¹⁶⁻¹⁸ and alkylamines and haloalkanes¹⁹ have been studied by several workers through excess property and thermo dynamical calculations. The free volume²⁰ has been found to be an important property of liquid state and has been extensively applied to liquid and liquid mixtures. Several workers^{11,12,21-24} evaluated the free volume and internal pressure using different relations and discussed the intermolecular interactions on the basis of these parameters. In this report we have evaluated the free volume (V_f), Internal pressure (π_i) and excess free volume (V_f^E) at three different temperatures (303, 313, 323 K) in MMA + *tert*-butanol and MMA + *iso*-butanol systems.

Experimental

The MMA and alcohols were purchased from Lobochem, and were of Analar grade (purity greater than 99%). The mixtures were prepared by mixing the measured volumes of the components in airtight stoppered brown bottles to minimize evaporation losses and light effects. Density measurements were made with an electronic balance (Mettler). The experimentally determined values of densities agreed well with literature data. The kinematic viscosities were measured by means of an Ubbelohde viscometer in a water bath with temperature stabilization (tolerance of ± 0.15 K) provided with a thermostat. The viscometer was calibrated with double-distilled water. Ultrasonic velocities were measured using a crystal controlled variable path ultrasonic interferometer (Mittal Enterprises, New Delhi) operating at a frequency of 1 MHz. In all, the accuracy of the determined values of density, viscosity and ultrasonic velocity works out to be ± 0.0001 gm/cm³, ± 0.0001 mPa-s and ± 0.2 m/s respectively.

Theory

The standard relationship for finding the internal pressure (π_i) and free volume (V_f) and the excess free volume (V_f^E) respectively²⁵ are given in Eqs. (1), (2) and (3) respectively. Eq. (1) is based on one dimensional analysis of the situation when an ultrasonic wave passes through a liquid medium.

$$\pi_i = bRT (K\eta/U)^{1/2} (\rho^{2/3}/M_{\text{eff}}^{7/6}) \quad (1)$$

where η is the viscosity of the mixture which is to be found (m Pa-s), 'b' is the packing factor (1.78), T is the temperature of the mixture (K), ρ is the density of the mixture (gm/cm³), M_{eff} is effective mass of the mixture ($M_1X_1 + M_2X_2$), U is the ultrasonic velocity of the mixture (m/s), R is gas constant given as 8.314 Joule/mole K and K is the constant of value 4.28×10^9 independent of temperature. The free volume is given by:

$$V_f = (MU/k\eta)^{3/2} \quad (2)$$

Where M is the molecular weight (gm), U is the ultrasonic velocity (m/sec), H is the viscosity (m Pas-s), K is a constant equal to 4.28×10^9 independent of temperature, and V_f is free volume, in millilitre per mole. The excess free volume is given by:

$$V_f^E = V_{\text{fm}} - (X_1V_{f1} + X_2V_{f2}) \quad (3)$$

where V_f^E is the excess free volume, V_{fm} is the free volume of mixture, V_{f1} and V_{f2} are the free volumes of the pure components. X_1 and X_2 are the mole fractions of the components. All the three equations have been very widely used for liquids, mixtures and solutions. These equations have been used in this paper too.

Results and Discussion

The measured values of ρ , η and u of the pure components are given in Table 1. As seen, the density of MMA is greater than those of the alcohols. The velocity is found to follow the order

$$U_{\text{Isobutanol}} > U_{\text{MMA}} > U_{\text{tert-Butanol}}$$

The alcohols are more viscous than MMA. The variations of the quantities of all the components with the temperature follow the usual trend. All the three parameters ρ , η and u decrease with rise in temperature.

Table 1. Densities, viscosities and speeds of sound of the components of mixtures.

System	T K	ρ gm m ⁻³		η m Pa-s		u ms ⁻¹	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
MMA	303	0.9323	0.9317 ⁷ 0.9323 ¹⁸	0.5311	0.5290 ²⁶	1165	
	313	0.9215	0.9209 ²⁸	0.4501	0.453 ¹⁸	1133	1136 ²⁸
	323	0.9092	0.9084 ²⁸	0.4331		1108	
<i>tert</i> -Butanol	303	0.7734	0.7757 ³¹ 0.7762 ²⁹	4.324	4.312 ²⁶	1110	1114 ^a 1104 ²⁹
	313	0.7637		2.6261		1068	
	323	0.7529		1.417	1.421 ²⁶	1031	
<i>iso</i> -Butanol	303	0.7935	0.7942 ³¹	3.4342		1177	1179 ³¹ 1172 ²⁷
	313	0.7756		2.6848		1152	
	323	0.7529		2.0098		1127	

Internal pressure

Table 2 gives the values of internal pressure of the two binary mixtures for different temperatures. The internal pressure is a sensitive parameter to solute-solvent interactions, and reflects both the attractive and repulsive molecular interactions.

Table 2. Internal pressure of MMA + alcohols.

Mole fraction of MMA X_1	Internal Pressure, atm		
	Temperature, K		
	303	313	323
MMA + <i>tert</i> -Butanol			
0.0000	10171	8279	6331
0.0902	7755	7335	6201
0.1824	5623	5075	4853
0.2767	5201	4522	4320
0.3730	4418	3789	3881
0.4716	3975	3662	3525
0.5724	3736	3397	3420
0.6756	3547	3211	3216
0.7812	3354	3059	3064
0.8893	3144	2889	2905
1.0000	2830	2806	2819

MMA + <i>iso</i> -Butanol			
0.0000	8955	8144	7209
0.0881	7739	7325	6734
0.1786	4809	4837	4718
0.2715	4667	4561	4536
0.3670	4433	4359	4419
0.4652	3944	3910	4300
0.5661	3560	3549	3733
0.6699	3589	3378	3463
0.7767	3545	3212	3290
0.8867	3307	2981	3030
1.0000	2830	2806	2819

The internal pressure of the solutions decreases with concentration. The decrease in internal pressure of the solutions indicates that the addition of monomer (solute) decreases the cohesive forces of the solvent (alcohols) at all temperatures. The decrease is more prominent at lower concentrations of MMA for both the mixtures. The magnitude of π_i follows the order

$$\text{MMA} + \textit{iso}\text{-butanol} > \text{MMA} + \textit{tert}\text{-butanol}$$

The internal pressure of all the solutions decreases with temperature at all concentrations. As the temperature increases, the cohesive forces weaken and hence there is a fall in internal pressure. (Figure 1 & 2)

Figure 1. Internal pressure vs mole fraction of MMA + *tert*-Butanol.

Figure 2. Internal pressure vs mole fraction of MMA + *iso*-butanol.

Volumetric behaviour

The computed values of free volume for the mixtures over the entire composition range at temperatures 303, 313 and 323 K are given in Table 3, along with the excess values (V_f^E). The free volume and the excess free volumes have been calculated using equations (2) and (3) respectively.

Table 3. Free volume (V_f) and excess free volume (V_f^E) of MMA + alcohols.

Mole fraction MMA X_1	Free volume (V_f) mL/mole			Excess free volume (V_f^E) mL/mole		
	303 K	313 K	323 K	303 K	313 K	323 K
MMA + <i>tert</i> -Butanol						
0.0000	0.0094	0.0187	0.0447	0.0000	0.0000	0.0000
0.0902	0.0207	0.0269	0.0480	-0.0210	-0.0309	-0.0345
0.1824	0.0538	0.0795	0.0989	-0.0209	-0.0182	-0.0222
0.2767	0.0671	0.1082	0.1340	-0.0413	-0.0304	-0.0266
0.3730	0.1042	0.1788	0.1819	-0.0388	-0.0016	-0.0190
0.4716	0.1410	0.1973	0.2367	-0.0373	-0.0258	-0.0054
0.5724	0.1670	0.2365	0.2505	-0.0474	-0.0302	-0.0338
0.6756	0.1965	0.2703	0.2887	-0.0548	-0.0411	-0.0388
0.7812	0.2239	0.3021	0.3230	-0.0652	-0.0550	-0.0486
0.8893	0.2689	0.3410	0.3642	-0.0591	-0.0629	-0.0525
1.0000	0.3676	0.4519	0.4630	0.0000	0.0000	0.0000
MMA + <i>iso</i> -Butanol						
0.0000	0.0145	0.0203	0.0303	0.0000	0.0000	0.0000
0.0881	0.0212	0.0268	0.0375	-0.0243	-0.0319	-0.0310
0.1786	0.0841	0.0901	0.1078	0.0066	-0.0080	0.0001
0.2715	0.0867	0.1023	0.1169	-0.0236	-0.0361	-0.0312
0.3670	0.0970	0.1120	0.1236	-0.0471	-0.0678	-0.0659
0.4652	0.1315	0.1475	0.1308	-0.0472	-0.0748	-0.1012
0.5661	0.1811	0.1882	0.1932	-0.0333	-0.0776	-0.0824
0.6699	0.1797	0.2127	0.2319	-0.0713	-0.0978	-0.0886
0.7767	0.1944	0.2477	0.2613	-0.0943	-0.1087	-0.1054
0.8867	0.2362	0.3020	0.3217	-0.0914	-0.1014	-0.0924
1.0000	0.3676	0.4519	0.4630	0.0000	0.0000	0.0000

It is clear that the value of free volume of the both the mixtures (MMA + *tert*-Butanol, and MMA + *iso*-butanol) increases in a non linear manner as the temperature increases. Such behaviour of alcohols has also been observed by Arul *et al*³⁰. It implies that when the temperature is increased, there is a tendency for the component molecules to move away from each other. This results in the reduction of cohesive forces leading to an increase in free volume. This may depend on the hydrogen bonding and size of the molecules, which in turn depend on the concentration of the hydroxyl solvent size and structure of the alcohol. As the concentration of alcohol decreases the hydrogen bonding also decreases. Therefore the solvent molecule occupies lesser volume and hence, an increase in free volume is observed for both the systems. However, as the temperature increases, hydrogen bonds break and hence the free volume increases with temperature. The increase in free volume of the mixtures is due to the breaking of hydrogen bonds in both MMA and hydroxyl groups

present in alcohols. MMA is a conjugated system of single and double bonds, leading to polarisation. This gives a dipolar structure. Hence dipole-dipole attractions are possible between its molecules. While increasing temperature, the force of attraction between the molecules decreases, and therefore the free volume increases. This may be visualized as shown in the following scheme 1.

Scheme 1

The variations in V_f and π_i are almost similar for the entire concentration range for both the mixtures. Only a small variation is observed due to the isomeric forms of butanol system. At lower mole fractions of MMA (up to ≈ 0.40), lower values of free volume are observed for MMA + *tert*-butanol mixture and higher values for MMA + *iso*-butanol mixture. In contrast, at higher mole fractions, an inverse trend are observed, *i.e.*, the free volume is lower for MMA + *iso*-butanol mixture. This is due to the number of branches present in the *iso*-butanol chain isomer. The same trend was also observed by Arul *et al.*²⁶ for the binary mixtures of benzene with *tert*-butanol and *iso*-butanol.

The excess free volume (V_f^E) values for both MMA + *tert*-Butanol, and MMA + *iso*-butanol are completely negative which indicates that the intermolecular interactions present in both the systems are strong (Figure 3). However with rise in temperature, intermolecular interactions become weak when the solute and solvent are almost equal in concentration and for further increase in temperature the intermolecular interactions become totally weak for the whole range of concentration.

Figure 3. Excess free volume vs mole fraction of MMA for MMA + *tert*-butanol and MMA + *iso*-butanol.

-○- *iso*-butanol-303 K, -□- *iso*-butanol-313K, -△- *iso*-butanol-323K,
 -●- *tert*-butanol-303 K, -■- *tert*-butanol-313 K, -▲- *tert*-butanol-323 K.

Similar observations - presence of weak interactions between the component molecules were found in benzene + *iso*, *sec*, *tert*-butanol systems by Anwar Ali *et al*³¹. Dharmalingam *et al*⁴. reported that the strength of the hydrogen bonding depends on the alkyl chain length of both the esters and the alcohols when they studied the hydrogen bond interaction between alkyl methacrylates (MMA,EMA,BMA) and six primary alcohols by FTIR and dielectric methods.

Figure 4. Plot of $\log(\pi_i)$ vs $\log(1/V_{fi})$ for MMA + *tert*-butanol.

Figure 5. Plot of $\log(\pi_i)$ vs $\log(1/V_{fi})$ for MMA + *iso*-butanol.

Lalitha *et al.*³² studied the relation between V_f and π_i at different temperatures and found that it obeys the equation $\pi_i V_f^X = K$ where X and k are constants. The same quantitative relationship between V_f and π_i was verified for the present systems of study. Plots of $\log(\pi_i)$ vs $\log(1/V_f)$ were perfectly linear for both mixtures at all three temperatures (Figures 4 & 5). This proves that the relation, $\pi_i V_f^X = K$ is true for MMA + alcohol mixtures too. The slope of the lines obtained is found to be close to 1/3. The values of K are nearly the same for both the alcohols. There is a marginal increase in the K values with temperature at all concentrations. The values of K are given in Table 4

Table 4. Values of 'K' from the equation $\pi_i V_f^X = K$ for binary mixtures at three different temperatures.

X_1	'K'		
	303 K	313 K	323 K
MMA + <i>tert</i> -butanol			
0.0000	1965	1984	2017
0.0902	1981	2004	2028
0.1824	2010	2045	2071
0.2767	2010	2035	2061
0.3730	1993	2043	2073
0.4716	1994	2045	2074
0.5724	1989	2024	2055
0.6756	2000	2008	2036
0.7812	1981	1990	2021
0.8893	1980	1963	2003
1.0000	1951	1991	2032
MMA + <i>iso</i> -butanol			
0.0000	1957	1939	2004
0.0881	1941	1933	2025
0.1786	1978	1995	2088
0.2715	1940	1971	2068
0.3670	1918	1948	2056
0.4652	1904	1933	2042
0.5661	1928	1920	2045
0.6699	1938	1911	2028
0.7767	1969	1922	2013
0.8867	1970	1919	2001
1.0000	1940	1985	2026

Conclusions

The present study on MMA + alcohol mixtures indicates the following conclusions:

1. Existence of specific interactions of strong magnitude is noticed in both the systems.
2. Mesomeric effects are predominantly noticed in the systems due to the presence of MMA molecules.
3. The nature of *isomeric* chain and the placement of the alcoholic group have sharp variations in the interaction mechanism.
4. The effects of the concentration of MMA as a solute and the temperature effects on hydrogen bonds in the system are clearly seen.
5. The role of hydrogen bonds and the structure of alcohols in interactions are observed.

6. The negative excess values of free volume show specific interactions among unlike molecules. The lower values in the MMA + *tert*-butanol system indicate ideal mixing.

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