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Short Communication

Ultrasonic Study of Binary Liquid Mixtures of Methyl Methacrylate with Alcohols

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Abstract

MMA is an important monomer which has a wide range of applications in the field of medicine and industries, while tert-butanol and iso-butanol are widely used as a solvent in chemical reactions, as well as being a useful starting material for organic synthesis. Therefore, physico-chemical properties on such mixtures will be useful in process engineering. Ultrasonic velocity and density have been experimentally determined for binary liquid mixtures of Methyl methacrylate (MMA) with tert-butanol and iso-butanol at three different temperatures. The measured velocities are compared with those obtained from various theoretical models of liquid mixtures. Relative merits and interrelation in these mixing rules have been discussed. Good agreement has been found between the experimental values with the respective values obtained from the mixing rules.

Key words: MMA, alcohols, ultrasonic velocity, mixing rules.

Introduction

During the last two decades, ultrasonic study of liquid mixtures has gained much importance in assessing the nature of molecular interactions present in the mixtures. The deviation from linearity in the values of ultrasound velocity when studied as a function of concentration is found to exhibit interesting variations in the case of liquid mixtures[1]. A number of existing empirical, semi-empirical and statistical mechanical theories proved mixing rules for theoretically predicting the viscosity and ultrasonic velocity of binary liquid mixtures. These parameters give better insight in understanding various intermolecular interactions taking place within the mixtures. This in turn helps us in bringing out the facts, which can have positive implication of both industry as well as the theory building process. Thus, one verifies and modifies the already existing theories and formulations and can lay a solid ground work for the emergence of new theories and formulations of various psysico-chemical phenomena associated with liquid mixtures[2]. A researcher pointed out the theoretical basis and the pertinent relations in the mixing rules (Free Length theory and Collision factor theory)[3]. Molecular interactions of MMA with several organic solvents and alcohols[4-10] have been studied by several workers through excess property and thermo dynamical calculations. For examining the validity of various mixing rules for predicting the values of ultrasonic velocity, We have applied five mixing rules, Nomoto's relation, VanDael and Vangeel's relation, Collision factor theory (CFT), Impedance Dependence relation (IDR) and Junjie's relation, and based relation for the theoretical prediction of ultrasonic velocity for binary mixtures of MMA with tert-butanol and iso-butanol.

Material and Methods

Experimental Section: The chemicals 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 brown bottles to minimize evaporation losses and light effects. Density measurements were made with a (single pan) mettler balance. The experimentally determined values of densities and velocities agreed well with literature data. Ultrasonic velocities were determined using a crystal controlled variable path ultrasonic interferometer operating at a frequency of 1 MHz In all, the accuracy of the determined values of density, viscosity and ultrasonic velocity work out to be ±0.0001 gm/cm^3, ±0.0001mpa and ±0.2m/s respectively. Ultrasonic Velocities were measured by using multi frequency ultrasonic interferometer (Model – 3, Mittal Enterprises).

Theory: Mixing hpgRules for Ultrasonic Velocity

Nomoto's relation[11]

$$U = (\sum x_i R_i / \sum x_i V_{i)}^3 \quad \ldots(1)$$

VanDael and Vangeel's relation (VDV) [12,13]

$$U = (\sum x_i M_i) / (x_i / \sum M_i U_i^2)^{-1/2} \quad \ldots(2)$$

Collision Factor Theory (CFT) [1 4]

$$U = U_\infty (\sum x_i S_i) (\sum x_i B_i) / (\sum x_i V_i) \quad \ldots(3)$$

Impedance Dependence relation (IDR) [15]

$$U = (\sum x_i Z_i / \sum x_i d_i) \quad \ldots(4)$$

Junjie's equation[16]

$$U = (\sum x_i V_i / \sum x_i M_i)^{1/2} [\sum x_i V_i / d_i U_i^2)]^{-1/2} \quad \ldots(5)$$

Where x_i is the mole fraction, U_i is ultrasonic velocity, R_i is molar sound velocity, V_i is molar volume, M_i is molecular weight, S_i collision factor, Z_i is acoustic impedance and B_i is the actual volume of i^{th} component in the mixture. Collision factors are calculated using $S_i = U/U_\infty$ r_f, where r_f is the space filling factor which in turn is given by $B/V = r_f = V_0/V$, V_0 is the specific volume of a mol of molecules and V is the molar volume of the liquid. The constant $U_\infty = 1600$ m/s.

Results and Discussion

Ultrasonic Velocity: The experimentally measured values of density and ultrasonic velocity of the pure liquids are agreed well with the literature are given in table-1. The measured values of ultrasonic velocities of the MMA + tert - butanol and MMA + iso - butanol mixtures are given in table-2.

The validity of the different theoretical formulae is checked in terms of average percentage deviation (APD). APD values for all five mixing rules are given in table-3. Examining the validity of mixing rules has been already done [20]. The values of the ultrasonic velocity (U), which are predicted by the mixing rules for all the binary mixtures at three different temperatures at 303K, 313K and 323K, are not shown here. But they have deviations from the respective measured values which is very small in magnitude. The approximation and assumption incorporated in the theories on which these mixing rules are based, may have a bearing on the deviations. The five mixing rules holds good at all temperatures. Out of the two binary mixtures, MMA + iso - butanol mixture gives comparatively highest value of all, for Impedance Dependence relation at 313 K.

Table-1
Densities and velocities of sound for the components of mixtures

System	Temperature (K)	Density 'ρ'(gm m^{-3})		Ultrasonic Velocity 'U' (ms^{-1})	
		Exp.	Lit.	Exp.	Lit.
MMA	303	0.9323	0.9317[4]	1165	1179[18]
			0.9323[10]		
	313	0.9215	0.9209[18]	1133	1136[18]
	323	0.9092	0.9084[18]	1108	---
tert-butanol	303	0.7734	0.7757[17]	1110	1114[17]
			0.7762[19]		1104[11]
	313	0.7637	---	1068	---
	323	0.7529	---	1031	---
iso-butanol	303	0.7935	0.7942[17]	1177	1179[17]
					1172[18]
	313	0.7756	---	1152	---
	323	0.7529	---	1127	---

Table-2
The experimental values of ultrasonic velocity of MMA + tert-butanol and MMA + iso-butanol mixture

Mole fraction of MMA 'X_1'	Ultrasonic Velocity 'U' (ms^{-1}) for MMA + tert-butanol mixture			Mole fraction of MMA 'X_1'	Ultrasonic Velocity 'U' (ms^{-1}) for MMA + iso-butanol mixture		
	303 K	313 K	323 K		303 K	313 K	323 K
0.0000	1110	1068	1031	0.0000	1177	1152	1127
0.0902	1112	1079	1037	0.0881	1175	1149	1126
0.1824	1119	1089	1049	0.1786	1174	1148	1125
0.2767	1122	1091	1052	0.2715	1172	1146	1123
0.3730	1125	1093	1054	0.3670	1169	1143	1121
0.4716	1127	1108	1067	0.4652	1169	1141	1120
0.5724	1129	1116	1077	0.5661	1169	1139	1118
0.6756	1134	1120	1081	0.6699	1168	1137	1114
0.7812	1141	1123	1082	0.7767	1166	1135	1112
0.8893	1145	1127	1095	0.8867	1165	1134	1110
1.0000	1165	1133	1108	1.0000	1165	1133	1108

Table-3
Average Percentage deviation (APD) *of various theoretical mixing rules at different temperatures

System	Temperature (K)	VDV	IDR	Junji's	CFT	Nomoto
MMA + tert-butanol	303	-0.197	-0.716	-0.529	-1.154	0.494
	313	1.475	0.277	0.846	0.628	1.509
	323	0.976	-0.347	-0.091	-0.371	3.104
MMA +iso-butanol	303	0.515	-0.067	0.075	1.723	1.050
	313	0.494	-4.739	0.102	2.792	1.078
	323	0.668	0.107	-0.076	-0.271	3.390

Where *APD = $[(U_{theory}-U_{exp.})/U_{theory}]*100$

Nomoto based his mixing rules on the assumptions of the linearity of the molar sound velocity and the additivity of the molar volumes in the liquid mixture[21]. Van Dael and Vangeel method is most suitable for mixtures in which the component molecules are of the same size, it assumes the mixture to be ideal with components having molar specific heat ratios equal to that of the mixture. Also their molar volumes are assumed to be equal. This assumption holds very well for the two binary mixtures. Thus, in terms of relative merits of the mixing rules for ultrasonic velocity, it appears that the Junji's method is best suited for predicting the ultrasonic velocity, as it gives an overall smaller APD than that given by rest of the mixing rules. One of the researcher also stated that the calculated values are in agreement with the literature values as both Nomotto's relation and ideal ideal mixing relations gives identical values., but the Collision Factor Theory proves to be better than both of these[22].

Conclusions

The study indicates that almost all the mixing rules employed here, give reasonably good results with allowed error less than 5%. The presence of dipole-dipole interactions is observed in both the systems due to the polar nature of alcohols.

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