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Advances in Applied Science Research, 2011, 2 (4):338-347



Molecular Interactions of Acrylonitrile and Methylmethacrylate in Methanol, Cyclohexane & P-dioxane

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ABSTRACT

The Velocity of ultrasonic waves (10 MHz) for different compositions of mixtures of methanol, Cyclohexane and p-dioxane with acrylonitrile and methylmethacrylate has been measured in the temperature range 10 - 40^o C. The excess compressibility β_a^E and excess molar volume V^E parameters have been discussed in the light of inter-molecular AB interactions and resulting disorder in these mixtures. It is observed that excess parameters β_a^E and V^E can be used for classification of all types of molecular interactions in binary liquid mixtures.

Keywords: Ultrasonic waves, Binary liquid mixtures, Methanol, Cyclohexane, p-dioxane, Acrylonitrile, Methylmethacrylate, Excess compressibility, Excess molar Volume.

INTRODUCTION

Ultrasonic parameters are being used extensively to study molecular interaction in pure liquid [1-4] binary and ternary liquid mixtures [5,6], and Ionic interactions in single mixed salt solution [5-7]. A departure from linearity in the velocity versus composition behaviour in liquid mixtures is taken as an indication of the existence of interaction between the different species. However, it is seen that a representation in terms of the observed parameters, such as velocity of ultrasonic waves, has a limited utility. Such representation does not provide any information about the nature and the relative strength of the various inter-molecular interactions. On the other hand, a number of theoretical and experimental investigations [8-13] have shown that a representation in terms of the derived parameters, such as adiabatic compressibility (β_a), vander waal`s parameters (b) and their derivatives such as β_a^E , b^E etc from those obtained from the additive rule provide a better insight into the intermolecular processes. This paper presents the results of an ultrasonic study of mixtures of methanol Cyclohexane and p-dioxane with acrylonitrile and methylmethacrylate. Though a few investigations are available in the preparation of some of liquids studied here, no comprehensive ultrasonic study has yet been reported.

Methylmethacrylate + Methanol						Acrylonitrile + Methanol				
Χ	uo	du₀/ dT	ρο	dp/dT	uo	du _o /dT	ρ _o	dp/dT		
(Cm)	m/s	ms ⁻¹ / K	*10 ³ kg/m ³	kgm ⁻³ /K	m/s	ms ⁻¹ / K	*10 ³ kg/m ³	kgm ⁻³ /K		
0.0	1215	-2.4970	1.002	-2.520	1550	-4.0050	0.893	-2.900		
0.1	1213	-2.5000	0.989	-2.400	1425	-3.0000	0.882	-2.250		
0.2	1211	-2.6000	0.968	-2.300	1525	-3.9000	0.979	-2.350		
0.3	1207	-2.7000	0.947	-1.850	1465	-4.4500	0.868	-2.200		
0.4	1205	-2.8000	0.924	-1.900	1411	-4.3500	0.860	-2.050		
0.5	1203	-2.8330	0.904	-1.700	1350	-3.9750	0.850	-1.900		
0.6	1198	-2.8660	0.885	-1.550	1292	-3.3750	0.843	-1.800		
0.7	1193	-3.0000	0.875	-1.600	1268	-3.6250	0.830	-1.400		
0.8	1189	-2.9330	0.840	-1.200	1230	-3.2500	0.820	-1.200		
0.9	1183	-2.9330	0.819	-1.000	1195	-3.0000	0.816	-1.200		
1.0	1180	-3.1400	0.803	-0.950	1180	-3.1400	0.803	-0.950		

 Table 1-The observed ultrasonic velocities and densities of methylmethacrylate+ methanol & acrylonitrile + methanol.

 Table 2-The observed ultrasonic velocities and densities of methylmethacrylate+cyclohexane & acrylonitrile

 + cyclohexane.

Methylmethacrylate + Cyclohexane				Acry	Acrylonitrile + Cyclohexane			
Х	uo	du₀/ dT	ρο	dp/dT	uo	du₀/dT	ρο	dp/dT
(Cm)	m/s	ms ⁻¹ / K	*10 ³ kg/m ³	kgm ⁻³ /K	m/s	ms ⁻¹ / K	*10 ³ kg/m ³	kgm ⁻³ /K
0.0	1216	-2.6667	1.002	-2.520	1545	-4.0000	0.893	-2.900
0.1	1234	-2.7040	0.979	-2.240	1533	-4.0720	0.873	-2.690
0.2	1266	-3.6925	0.957	-2.110	1515	-4.1240	0.879	-2.490
0.3	1269	-3.5000	0.947	-1.990	1498	-4.1760	0.866	-2.280
0.4	1280	-3.3200	0.918	-1.780	1480	-4.2280	0.856	-2.080
0.5	1293	-3.5220	0.894	-1.610	1462	-4.2820	0.841	-1.800
0.6	1310	-3.7500	0.889	-1.390	1447	-4.3360	0.839	-1.670
0.7	1324	-3.9320	0.868	-1.400	1429	-4.3880	0.826	-1.390
0.8	1343	-4.1380	0.837	-1.180	1411	-4.4400	0.818	-1.380
0.9	1360	-4.3420	0.818	-1.100	1393	-4.4920	0.807	-1.000
1.0	1372	-4.4000	0.798	-0.860	1372	-4.4000	0.798	-0.860

 Table 3-The observed ultrasonic velocities and densities of methylmethacrylate+ p-dioxane & acrylonitrile + p-dioxane.

Methylmethacrylate + P-dioxane				Acry	Acrylonitrile + P-dioxane			
Χ	uo	du ₀ /dT	ρ _o	dp/dT	uo	du ₀ /dT	ρο	dp/dT
(Cm)	m/s	ms ⁻¹ / K	*10° kg/m°	kgm ⁻³ /K	m/s	ms ⁻¹ / K	*10° kg/m°	kgm ⁻³ /K
0.0	1216	-2.6670	1.002	-2.520	545	-4.0000	0.893	-2.900
0.1	1232	-3.0425	1.003	-2.190	1533	-4.0720	0.915	-2.600
0.2	1234	-2.4000	1.008	-2.190	1515	-3.5460	0.924	-2.500
0.3	1220	-1.6600	1.012	-2.970	1498	-3.3526	0.943	-2.380
0.4	1258	-2.4660	1.018	-1.830	1480	-3.1100	0.958	-2.170
0.5	1305	-3.1800	1.022	-1.690	1462	-2.8653	0.973	-2.000
0.6	1312	-3.2500	1.028	-1.550	1447	-2.7206	0.998	-1.790
0.7	1398	-5.6000	1.034	-1.390	1429	-2.3446	1.005	-1.580
0.8	1429	-5.8300	1.038	-1.290	1411	-2.1330	1.022	-1.410
0.9	1450	-5.4730	1.045	-1.130	1393	-2.9886	1.032	-1.180
1.0	1450	-4.2420	1.057	-0.986	1450	-2.2420	1.057	-0.986

MATERIALS AND METHODS

The liquids used were of BDH Analar grade distilled thrice before use, the middle fraction being taken in each case. The mixture was measured at 25^oC, immediately before use, by mixing

appropriate volumes of the constituent liquids taken correct to 0.1 ml, the total volume being about 100ml. The Ultrasonic velocity was measured at 10 MHz by the Ultrasonic Time Intervelometer UTI - 101 (Innovative Instruments, Hyderabad) in the temperature range 10 - 40° C for acrylonitrile + methanol, acrylonitrile + cyclohexane, acrylonitrile + p-dioxane, methylmethacrylate + methanol, methylmethacrylate + cyclohexane, methylmethacrylate + p-dioxane, respectively.

The consistency of the Oscillator frequency was checked using a digital frequency meter and was found to be 4 in 10^4 . The density of solutions was measured by hydrostatic sinker method in the temperature range $10 - 40^{\circ}$ C and had an accuracy of 1 in 10^4 . A specially designed and fabricated doubled walled, metallic ultrasonic cell and glass cell along with 6 digit monopan balance achieved an accuracy 1 in 10^4 g. in density measurement. The temperature of the solution was maintained constant to 0.1° C Using an ultra thermostat U - 10. The solutions were stirred by moving the reflector and the sinker up and down.

Parameters β_a^E and V^E were obtained using standard relations. The excess parameters β_a^E and V^E are given by the difference between the observed and the theoretical (simple additive rule) values of respective parameters. The error for each of the excess parameters was estimated and the deviations from additive law were found outside the limit of error (≈ 3 %).

RESULT AND DISCUSSION

The observed ultrasonic velocity and densities of pure liquids and binary mixtures with methanol solute are given in Table 1, cyclohexane solute in Table 2 and p-dioxane solute in Table 3. Fig. 1 shows variation of percentage excess compressibility and excess volume of cyclohexane + methylmethacrylate and cyclohexane + acrylonitrile. Fig. 2 shows variation for p-dioxane + acrylonitrile, methanol + methylmethacrylate and methanol + acrylonitril and Fig. 3 shows the variation for p-dioxane + methylmethacrylate.

The observed ultrasonic velocity and density variation with composition is found to be nonlinear and this indicates the presence of hetero-molecular weak AB interaction. This presence of hetero-molecular AB interactions is reflected through the excess molar parameters such as, excess compressibility β_a^{E} excess molar volume V^{E} and excess v.d.w. parameter b^{E} . Excess b^{E} has been found to have the same variation as V^{E} and so the plots are not included. Hence for understanding the nature and strength of the intermolecular interactions, only two parameters β_a^{E} and V^{E} are considered simultaneously.

4. Broad classification of molecular Interactions:

A broad classification of molecular interactions is presented below :

Sr. No.	β_{a}^{E}	$\mathbf{V}^{\mathbf{E}}$
1	Negative	Negative
2	Positive	Positive
3	Negative	Positive
4	Positive	Negative

4.1 Case - I: $\beta_a{}^E$ <0 and V^E <0

As velocity of ultrasonic waves is a sensitive function of space-filling factor, small, changes in volume cause significant changes in velocity of ultrasonic waves. The volume of the liquid

mixtures depends upon the structure arrangement in liquid as well as on inter molecular interactions. The forces between the molecules and also their geometry would decide the structural arrangement. Thus the geometry of molecules has a vital role in deciding the volume of a liquid. In a mixture of two liquids, the shapes of the molecules i.e. cluster geometry or macro-geometry, would therefore, predominantly, decide an excess of molar volume. An increase in the strength of the hetero-molecular forces manifesting in a decrease in adiabatic compressibility β_a of the mixture would tend to reduce the size of the cluster, hence decrease in total volume of the mixture.

The variation of both $\beta_a^{\ E}$ and V^E is non-linear with at least one minimum. Such smooth variation with minimum of certain composition is known to indicate an attractive hetero-molecular AB interaction, leading to association of the molecules.

Let the pure liquid A and B be represented as A) Liq = (A, A.A, A.A.A, - - -)

B) Liq = (B, B.B, B.B.B, - - -)

i.e. a set of monomers, dimmers, trimmers, etc. Due to an associative hetero-molecular AB interaction, the mixture can be :

(AB) mix = (A.B, A.B.B, A.A.B, - - -)

Two minima will be obtained for two relatively stable clusters. The process leading to the stable clusters would be in equilibrium at these concentrations, respectively.

The above association would occur due to the presence of an active subgroup in A type and an active subgroup in B type molecules. If minima is closer to higher concentration of A then, AA>BB, while a symmetrical variation would indicate AB>AA as well as AB>BB as the relative strength of interactions.

4.2 Case- II: $\beta_a^E > 0$ and $V^E > 0$

An increase in β_a^E denotes the weakening of the intermolecular interactions. The heteromolecular AB interaction not only disturb the homo-molecular AA, BB interactions in components liquids, but also cause a rearrangement in the geometry of the clusters. If the geometry were such that, the volume of the cluster increases, it would lead to an increase in volume of the mixture, i.e. excess molar volume would be positive. The dissociation taking place in component liquid would be represented as:

n. Ai - - - - - > m.Aj, i > j

The dissociation would predominantly occur in one of the component liquids in which homomolecular interaction is extremely weak as compared to the hetero-molecular interactions. One may be in a position to identify the dissociating component from the β_a^E and V^E variation with composition of liquid A and B, the maximum occurring for the higher concentration of the component.

The dissociation is maximum where there is maxima in β_a^E function, and the dissociated component takes maximum inter-cluster spacing at that concentration. For two maxima the total is a sum of two dissociate process. These processes are exactly an inverse of associative processes, but here, it is the A or B type of molecular cluster, which dissociates and not Aj Bj type.

4.3 Case - III: $\beta_a{}^E < 0$ and $V^E > 0$

In this case, an observed decrees in β_a^{E} indicate an attractive hetero-molecular interaction, leading to an association between these moleculs. An observed increase in V^E (along with negative β_a^{E}) shows, using schaaff's relation, an increase in b the occupied molar volume. This may be due to presence of clusters of type AB....AB over AB. The reason for increase in volume may be due to the larger size of the molecular cluster. The size of the cluster AB....AB would however depends upon whether the hetero-molecular interactions are of short range or relatively long range.

Interaction of short range would lead to cluster of smaller size, while long range interactions producing, ordering in cluster would lead to large size of clusters. An observed increase in volume would also be due to ordering in cluster. The relative importance of the above processes in mixture depends upon the nature of the component molecules and would show themselves in shapes of the excess adiabatic compressibility and excess molar volume variations.

4.4 Case - IV: $\beta_a^{E} > and V^{E} < 0$ An observed β_a^{E} indicates a hetero-molecular interaction tending to destroy the weak AA and BB interactions. The loosening of homo-molecular interactions does not lead to an increase in size of the respective cluster, but its complete destruction. The negative V^{E} shows the molecules, which are set free from the original clusters now occupy interstitial, free space in the clusters, which are not broken, without appreciably increasing their size, The concealment of one type of molecules (of one component) in the clusters of the other types may be imagined to occur, leading to a decrease in the total volume of the mixture. The rate of breaking upto the weaker clusters would be reflected in the shape of β_a^E and V^E variations with compositions.

The broad discussion given above regarding the variation of β_a^{E} and V^{E} show that, these variations not only indicate the presence of hetero-molecular AB interaction in liquid mixtures, but also provide information on the relative strengths of homo molecular AA and BB interactions. When the AB interactions are comparable or slightly stronger than both AA and BB cluster forming AB clusters as indicated by a decrease in adiabatic compressibility and diminished volume of the mixtures. When AB interaction is much stronger than AA and BB interaction, it may not lead to formation of AB cluster but also ordering in the clusters, giving rise to ABAB...... of larger size giving an increase in volume of the mixtures.

When AB and BB interactions in component liquids are of comparable strength and AB interaction is slightly weaker then it does not lead to a disruption of AA and BB cluster, but only gets loosened. AA and BB interactions leading to an increase in the size of the respective clusters result in increase in volume of the mixtures. However, when AB interactions are stronger than the other, it causes a complete disruption of the weaker clusters but stronger clusters remain intact. Molecules released from the disrupted cluster may occupy interstitial spaces in the intact clusters leading to a concealment of free molecules, resulting in the reduction of total volume of the liquid. Thus the observed excess compressibility β_a^{E} considered along with observed excess volume V^E provide an insight into the relative strength of the inter molecular interactions in liquid mixtures.

5. Discussion of the System:

The system cyclohexane + methylmethacrylate & Cyclohexane + acrylonitrile fall under the Case - I of broad classification where both β_a^E and V^E are negative. In the system cyclohexane + methylmethacrylate β_a^E and V^E curves are symmetrical (Fig. 1), and AB interactions are greater than AA and BB.



 $\label{eq:Fig.1:Variation of \ \% \ of \ V^E \ \& \ \beta_a{}^E \ with \ respect \ to \ composition \ (c_m) \ of \ cyclohexane \ + \ Methylmethacrylate \ \& Cyclohexane \ + \ Acrylonitrile$

Cyclohexane is non polar liquid having dipole moment zero, while methylmethacrylate is polar liquid having dipole moment 1.68 D. Therefore AB interaction in this system are dipole-induced dipole type. The other system cyclohexane + acrylonitrile, β_a^E and V^E plots are symmetrical and its relative depth is greater than above system. Therefore strength as compared to the system, Cyclohexane + methylmethacrylate is relatively greater.



Fig. 2: Variation of % of V^E & $\beta_a^{\ E}$ with respect to composition (c_m) of p – dioxane + Acrylonitrile, Methanol + Methylmethacrylate & Methanol + Acrylonitrile .





It is also greater than AA and BB interaction due to symmetricity of curve. Cyclohexane is a non polar liquid while acrylonitrile is a polar liquid with dipole moment 3.87D. The AB interaction is therefore dipole-induced dipole type. The relative strength of AB interaction in this case is in the order cyclohexane + acrylonitrile, cyclohexane + methylmethacrylate.

The system p-dioxane + acrylonitrile, methanol + methylmethacrylate and methanol + acrylonitrile falls under the case III of broad classification, where $V^E > 0$ and $\beta_a^E < 0$. The β_a^E variation with composition in all the system is negative .This indicates the presence of AB interaction in the system resulting in formation of clusters. The relative strength of AB interaction is different in these systems indicated by the change in relative depth of β_a^E curve. In p-dioxane and acrylonitrile the strength of AB interaction is stronger than AA and BB in p-dioxane and acrylonitrile mixtures. In high concentrations of nearly equal strengths but different natures.

The relative strength of AB interaction in the above systems is found to be decrease in the order methanol + acrylonitrile, methanol + methylmethacrylate, p-dioxane + acrylonitrile. The velocity verses composition plots for the systems methanol + acrylonitrile exhibits a peak at molar ratio 2:8. The compressibility verses composition plots for the above system exhibits a dip at the same molar ratio.

This confirms the formation of complex molecule at above molar ratio. The strength of a AB interaction at higher concentration of B is found to be greater as compared to the other system. Methanol and acrylonitrile both being polar liquid with dipole moment 1.70 D and 3.87 D, AB interaction is of the types dipole- dipole interactions which is greater than methanol + methylmethacrylate as is expected, because dipole moment of methylmethacrylate is of the order 1.68 D which is small. Hence the AB interaction in the systems methanol + methylmethacrylate will be small as compared to methanol + acrylonitrile. The AB interaction in all the systems are such that they increase the volume of resulting polymolecules, indicated by positive V^E variation. The system p-dioxane + methylmethacrylate falls under the case IV, where $\beta_a^{E} > 0$ and $V^{E} < 0$. The hetero molecular AA interaction are strong which disturbs the homomolecular AA, BB interaction and cause dissociation. New cluster may be form in case of methylmethacrylate as is known from its properties. The nature of β_a^{E} curve is symmetrical indicating more AB interaction than AA and BB and volume of cluster decrease which cause decrease in volume making V^E negative.

CONCLUSION

1. Molecular interactions in any binary liquid system can be interpreted under the broad classification out lined in this paper.

2. The hetero-molecular AB interaction is present in all the system investigated.

3. The dipole - induced dipole and dipole -dipole interactions are found to be responsible for the observed hetero - molecular interaction in the system.

4. The AB interaction in the system methanol + acrylonitrile leads to complex formation at molar ratio of 2:8 of the type 1 (CH3OH) : 4 (CH2=CH - CN).

5. The systems investigated are classified in three categories of broad classification namely the system in which,

a) β_{-}^{E} and V^{E} both are nagative,

b) β^{E} is nagative and V^E is positive, and

c) β^{E} is positive and V^E is nagative.

Acknowledgement

The authors (VDB and GRB) acknowledges the financial assistance from the UGC, New Delhi, in the form of minor research project grant. They are are also grateful to Professor Dr.V. A. Tabhane, Department of Physics ,Pune University, Pune for his guidance.

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