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Hetero-molecular associations in different polar and non-polar binary mixtures

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Abstract

Excess molar volumes and viscosity deviations have been studied comparatively for some binary systems involving nitrobenzene, aniline, methanol, benzene, toluene and CCl_4 by experimentally measured values of viscosity and density. These values are interpreted in the light of hetero-molecular associations among the polar and non-polar constituents.

Key Words: Hetero-molecular association, molar excess volume, binary liquids

1. Introduction

Studies on densities, viscosities and molar volumes along with their respective excess properties in liquids and liquid mixtures is essential to understand the molecular interactions between unlike molecules, to develop new theoretical models as well as engineering applications in the process industries.

Considerable scientific and practical interest has been stimulated by the investigation of organic liquids by viscosity. Viscosity is a fundamental characteristic of substances such as adhesive, lubricants, paintings, etc. [1]. Studies involving density and viscosity measurements are important for elucidation of ion-solvent, ion-ion and solvent-solvent interaction in mixed solvent systems [2–4]. The nature and degree of molecular interactions in different solutions depend upon the nature of the medium, the structure of the solute molecule and also the extent of solvation taking place in solution. Thermodynamic properties derived from viscosity and its related parameters [5–9] are also important to designing industrial equipments with better precision. It has been studied by several workers [10, 11] that excess thermodynamic functions are dependent not only on the difference in intermolecular forces but also on the difference in the size of the molecules.

In the present study, different binary mixtures have been studied involving various polar and non-polar liquids such as benzene, carbon tetrachloride, toluene, aniline, nitrobenzene and methanol.

All these components have their extensive applications in various industries, where these chemicals are used either as a single solvent or as a mixture of solvents. Review of literature showed that binary mixtures involving polar and non-polar components have also been studied by a number of workers. Singh and his

group [12] have studied these binary mixtures, where nitrobenzene has been taken as the common component. The excess properties of binary liquid mixtures reflect difference in molecular size, shape and interaction of the two components. Swain et al [13] have studied the thermodynamic properties of polar and polar-like molecules. Therefore, the major attempt of such work is to show a comparative study among different binary liquid mixtures containing various polar and non-polar compounds, and their intermolecular interaction by considering the viscosity measurement and their related excess properties.

2. Materials and methods

The chemicals used were of Analytical grade and were procured from S. D. Fine, Qualigen etc., and were purified by standard procedure [14]. The solutions were prepared on fractional basis (v/v), by mixing known volumes of nitrobenzene, aniline, and methanol in appropriate volumes of benzene, toluene and CCl_4, etc.

The densities of the solutions were measured by a specific gravity bottle calibrated with deionised double distilled water of 0.9968×10^3 kg m^{-3} as its density at 303.15 K. The precision in density measurement was within ± 0.0003 kg m^{-3}. Viscosities of the solutions were measured by an Ostwald viscometer immersed in a constant temperature water bath maintained within ± 0.01 C, and the time of flow was determined.

3. Theoretical aspect

These intermolecular forces of attraction can be determined form different physical measurements. Viscosity measurements are one out of those. Viscosity and its excess properties such as excess viscosity or viscosity deviation, etc, are widely used for determining interaction factors.

The experimental values of density ρ and viscosity η were used to calculate molar volumes [15, 16]. Excess molar volume and viscosity deviations for all the systems were also evaluated. The molar volume of a substance can be evaluated from its molar mass and density by applying the relation

$$V_m = \frac{M}{\rho}.$$

For a sample mixture containing N components, the molar volume is calculated using the relation

$$V_m = \frac{\sum_{i=1}^{N} x_i M_i}{\rho_{\text{mixture}}}.$$

The excess properties A^E that shed light on the deviation from ideality, and thus can help assess the structural variation and the type of molecular interactions. A^E can be computed via the equation

$$A^E = A - [x_i A_1 + (1 - x_i) A_2],$$

where A, A_1 and A_2 correspond to the parameters V_m, and η, for binary mixtures, for component 1 and for component 2, respectively; and x_i is the mole fractions of nitrobenzene, aniline and methanol. The measured values for all the systems are shown in Tables and the excess values are represented in figures.

The sign of the excess properties, plotted in Figures 1–6, plays a vital role in assessing the compactness due to molecular arrangement and the extent of molecular interaction.

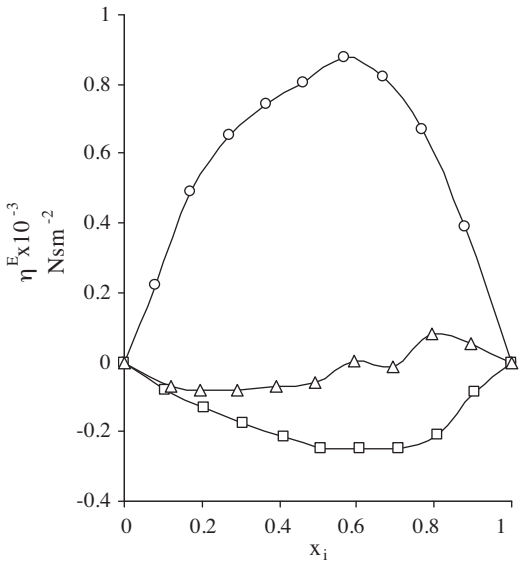

Figure 1. Plot of η^E as a function of mole fraction in binary mixtures nitrobenzene + {benzene (◯), toluene (□), CCl_4 (Δ)}.

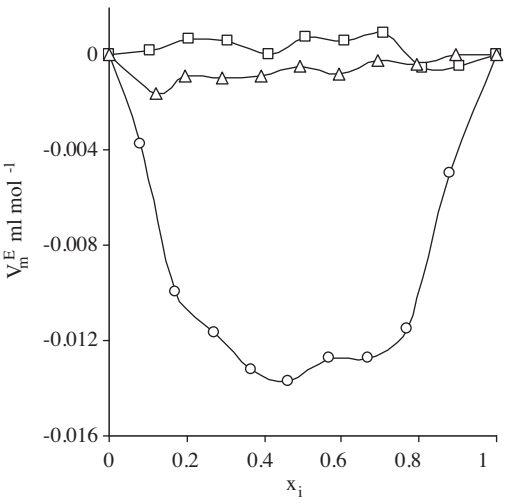

Figure 2. Plot of V_m^E as a function of mole fraction in binary mixtures nitrobenzene + {benzene (◯), toluene (□), CCl_4 (Δ)}.

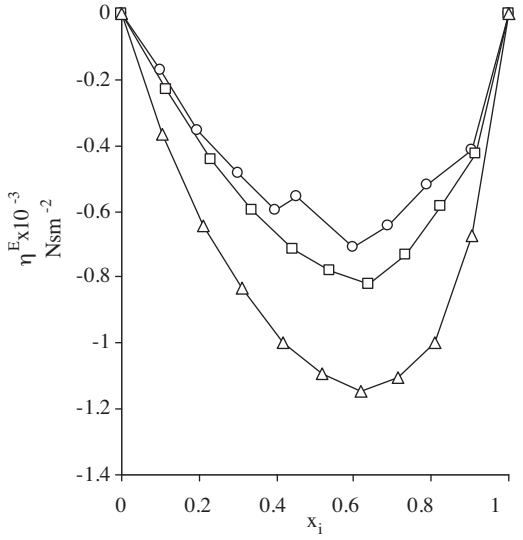

Figure 3. Plot of η^E as a function of mole fraction in the binary mixtures aniline + {benzene (◯), toluene (□), CCl_4 (Δ)}.

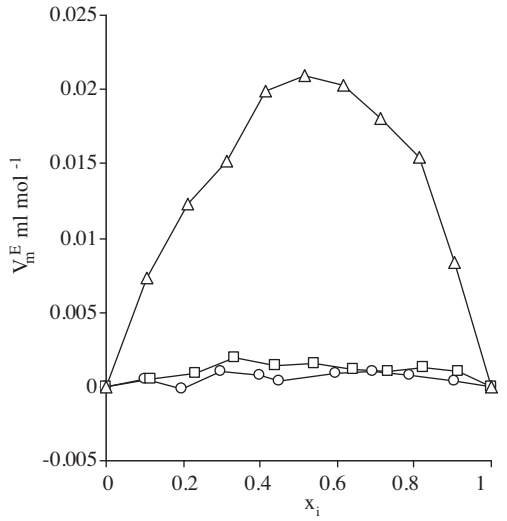

Figure 4. Plot of η^E as a function of mole fraction in the binary mixtures aniline + {benzene (◯), toluene (□), CCl_4 (Δ)}.

4. Results and discussion

Results obtained from the measured densities, viscosities of different binary systems and their excess properties have been studied and discussed comparatively with interpretation invoking intermolecular interaction.

The measured densities, viscosities and the computed properties are shown in Tables 1–3. The excess properties are displayed in Figures 1–6. The interpretations of the hetero-molecular interactions in various binary systems are explained on the basis of the measured and computed values.

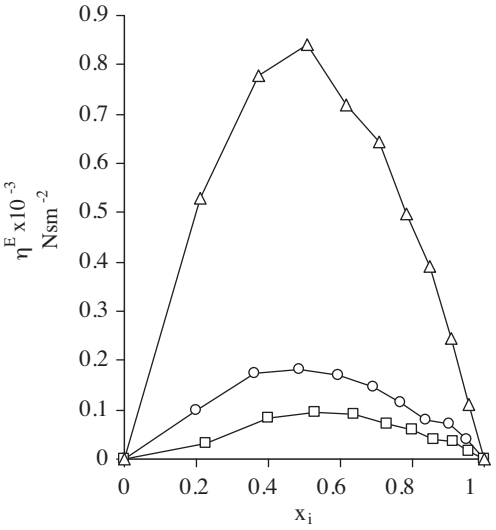

Figure 5. Plot of η^E as a function of mole fraction in the binary mixtures methanol + {benzene (◯), toluene (□), CCl_4 (Δ)}.

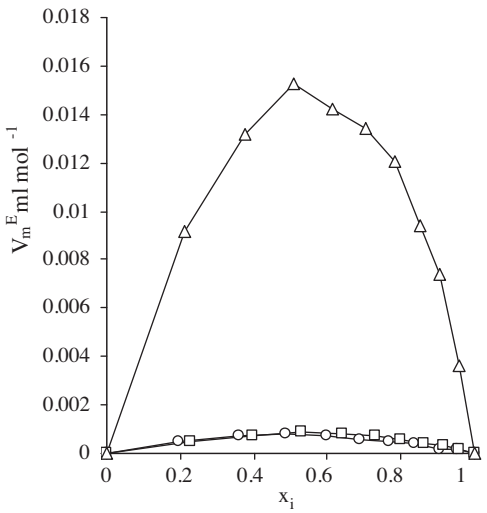

Figure 6. Plot of η^E as a function of methanol mole fraction in binary mixtures methanol + {benzene (◯), toluene (□), CCl_4 (Δ)}.

According to Fort and Moore [17], excess viscosity tends to become more positive as the strength of interaction increases. The variation in excess viscosity gives a quantitative estimation of the strength of intermolecular interactions; and these values can be explained by considering two factors. One is the difference in size, and shape of the component molecules and the loss of dipolar association in pure compound that may lead to a decrease in viscosity. The other factor is the specific interactions between unlike components such as hydrogen bond formation and charge transfer complexes which may cause increase in viscosity in mixtures over that found in pure components. The former effect produces negative deviation in excess viscosity whereas the latter effect produces positive deviation in excess viscosity. Similarly, according to Petek et al [18], the positive excess molar volumes, V_m^E can be explained by the predominance of expansion in volume, caused by the loss of dipolar association and difference in size and shape of component molecules, over contraction in volumes, due to the dipole-dipole and dipole-induced dipole interactions.

4.1. Binary mixtures of nitrobenzene with benzene, toluene and carbon tetrachloride

The measured density and viscosity values for the binary systems nitrobenzene with benzene, toluene and CCl_4 and calculated values of molar volumes V_m are shown in Table 1. The calculated values of excess molar volumes and excess viscosities against the mole fractions are shown in Figures 1 and 2. All these values, which shed light on the type and strength of interaction between the component molecules, are discussed. The negative excess viscosity values indicate easier flow of this mixture compared with the behaviour of the pure liquids (in case of nitrobenzene with toluene, CCl_4), and the positive excess viscosity values indicate the difficulty in flowing of this mixtures as compared with the behaviour of the pure liquids (in nitrobenzene + benzene). The

negative excess values show the absence of any specific interaction. The order of interactions from the studies may be assumed as nitrobenzene + benzene > nitrobenzene + toluene > nitrobenzene + CCl_4.

Table 1. Densities, Viscosities, Excess viscosities and Molar volumes of the binary mixtures of Nitrobenzene +benzene, toluene and CCl_4.

Sl No	x_i	1-x_i	ρ ($\times 10^3$ kg m^{-3})	η ($\times 10^{-3}$ Nsm^{-2})	V_m (ml mol^{-1})
Nitrobenzene +benzene					
1	0.0000	1.0000	0.8661	0.5650	0.09018
2	0.0788	0.9212	0.9341	0.8702	0.08741
3	0.1699	0.8301	1.0410	1.2348	0.08238
4	0.2701	0.7299	1.1021	1.5049	0.08190
5	0.3689	0.6311	1.1599	1.7001	0.08165
6	0.4599	0.5401	1.2001	1.8598	0.08233
7	0.6699	0.3301	1.2601	2.0985	0.08591
8	0.7702	0.2298	1.2750	2.0531	0.08844
9	0.8799	0.1201	1.2215	1.8901	0.09636
10	1.0000	0.0000	1.1970	1.6301	0.10284
Nitrobenzene + toluene					
1	0.0000	1	0.8578	0.5231	0.10741
2	0.1040	0.8960	0.8901	0.5598	0.10714
3	0.2067	0.7933	0.9199	0.6219	0.10712
4	0.3089	0.6911	0.9539	0.6901	0.10662
5	0.4099	0.5901	0.9871	0.7599	0.10620
6	0.5099	0.4901	1.0199	0.8398	0.10583
7	0.7092	0.2908	1.0879	1.0599	0.10488
8	0.8078	0.1922	1.124	1.2090	0.10423
9	0.9041	0.0959	1.1598	1.4390	0.10359
10	1.0000	0.0000	1.1972	1.6301	0.10283
Nitrobenzene + CCl_4					
1	0.0000	1.0000	1.5553	0.8925	0.09890
2	0.1216	0.8784	1.5349	0.9137	0.09778
3	0.1937	0.8063	1.4971	0.9535	0.09877
4	0.2918	0.7082	1.4622	1.0252	0.09907
5	0.3906	0.6094	1.4249	1.1129	0.09953
6	0.4903	0.5097	1.3819	1.1944	0.10041
7	0.6917	0.3083	1.3078	1.3865	0.10137
8	0.7937	0.2063	1.2735	1.5623	0.10165
9	0.8967	0.1033	1.2322	1.6076	0.10249
10	1.0000	0.0000	1.1972	1.6301	0.10283

4.2. Binary mixtures of Aniline with Benzene, toluene and carbon tetrachloride

The interaction studies of binary mixtures of aniline with benzene, and toluene and CCl_4 are reported on the basis of excess viscosity and molar volume. Results are plotted in Figures 3 and 4, with measured values shown in Table 2.

Table 2. Densities, Viscositis, Excess viscosities and Molar volumes of the binary mixtures of Aniline + benzene, toluene and CCl_4.

Sl No	x_i	1-x_i	ρ ($\times 10^3$ kg m^{-3})	η ($\times 10^{-3}$ Nsm^{-2})	V_m (ml mol^{-1})
Aniline + benzene					
1	0.0000	1.0000	0.8660	0.5650	0.09020
2	0.0989	0.9011	0.8763	0.6501	0.09083
3	0.1978	0.8022	0.8988	0.7259	0.09021
4	0.2990	0.7010	0.9019	0.8601	0.09159
5	0.3981	0.6019	0.9201	1.0069	0.09139
6	0.5981	0.4019	0.9501	1.4169	0.09167
7	0.6899	0.3101	0.9619	1.7198	0.09198
8	0.7898	0.2102	0.9802	2.1021	0.09179
9	0.9021	0.0979	1.0012	2.5004	0.09155
10	1.0000	0.0000	1.0210	3.1705	0.09121
Aniline + Toluene					
1	0.0000	1.0000	0.8578	0.5231	0.10741
2	0.1159	0.8841	0.8698	0.6015	0.10606
3	0.2301	0.7699	0.8831	0.6902	0.10459
4	0.3349	0.6651	0.8898	0.8150	0.10392
5	0.4401	0.5599	0.9098	0.9751	0.10175
6	0.6402	0.3598	0.9450	1.3998	0.09817
7	0.7328	0.2672	0.9610	1.7297	0.09663
8	0.8249	0.1751	0.9750	2.1202	0.09534
9	0.9140	0.0860	0.9939	2.5149	0.09362
10	1.0000	0.0000	1.0210	3.1705	0.09121
Aniline + CCl_4					
1	0.0000	1.0000	1.5553	0.8928	0.09890
2	0.1071	0.8929	1.3982	0.7710	0.10536
3	0.2112	0.7888	1.2862	0.7326	0.10963
4	0.3138	0.6862	1.2068	0.7763	0.11168
5	0.4161	0.5839	1.1118	0.8398	0.11564
6	0.6157	0.3843	1.0171	1.1483	0.11450
7	0.7131	0.2869	0.9915	1.4120	0.11149
8	0.8109	0.1891	0.9679	1.7430	0.10808
9	0.9061	0.0939	0.9849	2.2819	0.10034
10	1.0000	0.0000	1.0210	3.1705	0.09121

The intensity of dispersive interactions in carbon tetrachloride mixture is more than that of other mixtures. Among toluene and benzene, toluene is richer in π-electrons than benzene due to the enhanced density of π-electrons by the introduction of -CH_3 group in the benzene ring, improving the probability of $\pi - \pi$ weak interactions in toluene. This results in lowering η^E values in the case of toluene.

In the present systems, the plots are parabolic in shape and are characterized by the presence of well-defined maxima / minima which indicate the presence of complex formation between the mixing components of binary mixtures. It is assumed that the type of interaction may be due to the specific interaction, which is predominant over dispersion forces.

4.3. Binary mixtures of methyl alcohol with benzene, toluene and carbon tetrachloride

Viscosity properties have been measured for binary mixtures of methyl alcohol with benzene, toluene and carbon tetrachloride. The measured values are presented in Table 3 and the excess values are graphically displayed Figures 5 and 6. Positive values for excess viscosity as well as excess molar volume values have been obtained for all the systems. In the above-mentioned binary mixtures, methyl alcohol is a polar liquid while benzene, toluene, and CCl_4 are non-polar liquids.

Table 3. Densities, Viscositis, Excess viscosities and Molar volumes of the binary mixtures of Methanol +benzene, toluene and CCl_4.

Sl No	x_i	1-x_i	ρ ($\times 10^3$ kg m^{-3})	η ($\times 10^{-3}$ Nsm^{-2})	V_m (ml mol^{-1})
Methanol +benzene					
1	0.0000	1.0000	0.8661	0.5650	0.09019
2	0.1982	0.8018	0.8535	0.6599	0.08081
3	0.3621	0.6379	0.8421	0.7328	0.07293
4	0.4872	0.5128	0.8322	0.7398	0.06687
5	0.5968	0.4032	0.8249	0.7241	0.06133
6	0.7689	0.2311	0.8112	0.6657	0.05258
7	0.8379	0.1621	0.8047	0.6309	0.04905
8	0.9051	0.0949	0.7991	0.6217	0.04552
9	0.9519	0.0481	0.7922	0.5865	0.04319
10	1.0000	0.0000	0.7878	0.5478	0.04062
Methanol + toluene					
1	0.0000	1.0000	0.8578	0.5231	0.10741
2	0.2273	0.7727	0.8461	0.5602	0.09274
3	0.3981	0.6019	0.8363	0.6173	0.08155
4	0.5311	0.4689	0.8269	0.6291	0.07280
5	0.6380	0.3620	0.8198	0.6278	0.06559
6	0.7981	0.2019	0.8069	0.6002	0.05471
7	0.8611	0.1389	0.8022	0.5851	0.05030
8	0.9139	0.0861	0.7961	0.5829	0.04670
9	0.9573	0.0427	0.7929	0.5639	0.04360
10	1.0000	0.0000	0.7878	0.5478	0.04062
Methanol + CCl_4					
1	0.0000	1.0000	1.5553	0.8928	0.09890
2	0.2096	0.7904	1.3390	1.3480	0.09581
3	0.3747	0.6253	1.1991	1.5428	0.09021
4	0.5072	0.4928	1.0880	1.5569	0.08459
5	0.6161	0.3839	1.0201	1.3989	0.07721
6	0.7063	0.2937	0.9521	1.2911	0.07119
7	0.8502	0.1498	0.8549	0.9912	0.05878
8	0.9065	0.0935	0.8121	0.8229	0.05343
9	0.9563	0.0437	0.7980	0.6752	0.04677
10	1.0000	0.0000	0.7878	0.5478	0.04062

In these mixtures, the predominance of physical effect may arise due to dipole-induced dipole interaction resulting in disruption in the favourable orientation order of methyl alcohol and the non-polar solvents. This may give rise to an increase in the viscosity of these binary systems resulting in positive excess viscosity values.

The rate of interaction between mixture pairs may be ordered as: methylalcohol + CCl_4 > methyl alcohol + benzene > methyl alcohol + toluene. The effect may be due to disruption of the orientation order of the polar and non-polar solvents.

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