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Study of Molecular Interactions in Ternary Liquid Mixtures of Aliphatic Carboxylic Acids with Polar and Non Polar Solvents

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Abstract

Viscosity of ternary liquid mixture containing aliphatic carboxylic acid with polar and non polar solvents were measured at 25^0C and the excess viscosities were computed. Densities and viscosities of ternary mixtures of Acetic acid with polar and non polar solvents, have been measured at 25^0C from these data, excess molar volume (V^E) data, deviation in viscosity ($\Delta\eta$) have been calculated several empirical equations have been used to predict the excess molar volume and deviations in viscosity of ternary mixtures.

Keywords: Viscosity, Molecular Interactions, Excess molar volume, Excess Gibbs free energy, excess enthalpy.

Introduction

Viscosities of liquid mixtures provide information for the elucidation of fundamental behaviour of liquid mixture. Arrhenius was probably the first who correlated the viscosity of binary liquid mixtures with those of pure components with a view to estimating the strength of molecular interactions between components of binary liquid mixtures, Grunberg and Nissan modified Arrhenius equation.

The organic liquid has been classified into the following three categories depending on their intermolecular interactions in pure form:

1. Simple liquid either non-associated or weakly associated their molecular interactions depending on their molecular weights and the shape of the molecules.
2. The nitrogen containing liquids which involve similar type of interactions, the magnitude of which varies with the presence of functional group as well as the position of nitrogen in the molecular structure; and
3. Hydroxyl group containing liquids in which molecular interactions are very high due to hydrogen bonding.

The above classification can be used to predict the extent and type of molecular interactions in liquid systems.

The excess thermodynamic functions or excess thermodynamic properties (denoted by superscipt^E) is defined as the difference between the thermodynamic function of mixing for an actual system and the value of thermodynamic function corresponding to a perfect solution at the same temperature, pressure and composition. The literature concerning excess properties of liquid mixtures has been exhaustive after the pioneering work of Prigoging. These include the excess molar volume (V^E), the excess Gibbs free energy of activation of flow ($\Delta G^{\#E}$), the excess enthalpy (H^E), the excess entropy (S^E) the excess viscosity (η^E) etc.

However, the studies in regard to the viscosities of ternary organic liquid mixtures vis-a-vis moelcular interactions are rather scanty, Pandey et al. have predicted viscosity of multicomponent liquid mixtures by various models and analysed the data in the light of structures of molecules and the interactions involved. Pandey and co-workers have also studied viscosities of ternary liquid mixtures in relation to significant structure theory of Erying.

Experimental Techniques

Experimental techniques used for the measurement of densities and viscosities of pure organic liquids and their ternary mixtures. IN these ternary liquid mixtures the first component is an aliphatic carboxylic acid

while the second component is a polar solvent and the third component is a non-polar solvent.

Aim of the Study

To Evaluate the thermodynamically parameters and their excess functions to find the molecular interactions between unlike molecules in ternary liquid mixture

Material and Methods

The organic liquids were purified by the standard procedures, and their purities were checked by density determination dialatometrically at 298.15K. All the chemicals were stored and protected against atmospheric moisture and CO_2 as for as possible.

The ternary liquid mixture of different known compositions was prepared volumetrically in stoppered bottles. The heavier components were charged first to minimise the errors in composition due to evaporation during the solution preparation. This led to accuracy of the order of $3x10^{-4}$ in the mole fraction. The change of composition due to vapourisation during measurements was minor.

Before any measurments, the liquid mixtures were placed for about an hour in the thermostate bath which was electrically operated and temperature controlled by electronic relay. The bath also consisted of a heating device, a stirrer, a contact thermometer, a check thermometer and a circulation system for the bath water. The thermostat temperature was set and monitored by a thermometer, calibrated against a platinum resistance thermometer.

Determination of Density

All the density measurements were made by using a dilatometer. It consisted of a bulb of about 10 cm^3 in volume. The liquid maintained at the experimental temperature was introduced into the weighed dilatometer up to a definite mark with the help of a hypodermic syringe set. It consisted of 0.5 mm thick needle fitted with a 20 ml syringe. Both the needle and the syringe were previously cleaned with acetone solvent.

the density (ρ) of the liquid/the ternary liquid mixture was calculated by the following expressions:

$$\rho = \frac{W_3 - W_1}{W_2 - W_1} \times \rho_w \qquad \text{----------(1)}$$

Where W1, W2 and W3 are the weights of the empty dilatometer, weight of the dilatometer with water and weight of the dilatometer with the liquid/the ternary liquid mixture respectively and ρ_w is the density of the water at the experimental temperature.

Determination of Viscosity

Viscosities of the liquid systems were determined with an accuracy of $\pm$ 3 $x10^{-3}$ m Pa.s using Ostwald's Viscometer which was suspended in a thermostate maintained at 298.15 K. By comparing the flow time of the pure liquid or mixture with that of water, the viscosity (η) was calculated from the following relation.

$$\eta = \frac{t}{t_w} \times \frac{\rho}{\rho_w} \times \eta_w \qquad \text{----------(2)}$$

Where η_w is coefficient of viscosity of water, ρ and ρ_w are the densities and t and t_w are the times of flow for the liquid mixture and the water respectively. The value of ρ and ρ_w were measured dilatometricaly.

Determination of Mole Fraction

Mole fraction of a component liquid is the ratio of the molarity of the component liquid to that of the ternary liquid mixture. It is denoted by the symbol, (x) It has no unit.

$$x_1 = \frac{\text{Molarity of componet 1}}{\text{Molarity of component 1} + \text{Molarity of component 2} + \text{Molarity of component 3}} \qquad \text{----- (3)}$$

$$x_2 = \frac{\text{Molarity of componet 2}}{\text{Molarity of component 1} + \text{Molarity of component 2} + \text{Molarity of component 3}} \qquad \text{-----(4)}$$

$$X_3 = 1 - (X_1 + X_2) \qquad \text{--------(5)}$$

Where, the molarity of any componet is defined by the following expression:

$$\text{Molarity} = \frac{\text{Volume of the component} \times \text{Density of the component}}{\text{Molecular weight of the component}} \qquad \text{-------(6)}$$

Determination of Molar Volume (V)

Molar volume may be defined as the volume in milliliters occupied by one mole of a liquid. It is generally denoted by V. It may be calculated by using the relation, $V=M/\rho$ where M is the molecular weight and ρ is the density of the component, If x_1, x_2 and x_2 are the mole fractions and M_1, M_2 and M_3 be the molecular weights of components 1, 2 and 3 respectively, the molar volume (V) of the ternary liquid mixture may be given by the relation.

$$V = \frac{x_1M_1 + x_2M_2 + x_3M_3}{\rho} \qquad \text{-------(7)}$$

Where, ρ is the density of the ternary mixture.

Determination of Excess Thermodynamic Properties

The excess viscosity, ηE of a given ternary liquid mixture has been evaluated from the observed viscosity of the ternary mixture and that of its pure component by using the following relations.

$$\eta^E = \eta - (x_1\eta_1 + x_2\eta_2 + x_3\eta_3) \qquad \text{--------(8)}$$

where η is the viscosity of ternary liquid mixture and η_1, η_2 and η_3 are the viscosities of pure

components 1,2 and 3 respectively; and x_1, x_2 and x_3 are the mole fractions of the components 1,2 and 3.

The excess molar volume (V^E) of the ternary liquid mixtures has been evaluated from the molar volume (V) of the mixtures and that of the pure components V_1, V_2 and V_3 using the following relation:

$$V^E=V-(x_1V_1+x_2V_2+x_3V_3) \quad \text{---------(9)}$$

The excess Gibbs free energy of activation of flow ($\Delta G^{\#E}$) for the ternary liquid mixture has been derived from the Eyring equation. The resulting equation is given below:

$$\Delta G^{\#E}= RT[\ln \eta V-(x_1 \ln V_1 \eta_1+ x_2 \ln V_2\eta_2 +x_3 \ln V_3\eta_3)] \quad \text{-----(10)}$$

Where, the letters have their usual significances. The experimental data in regard to the above mentioned ternary liquid mixtures have been presented in the subsequent Table:

Experimental values of Density (ρ), Viscosity (η) and Excess Thermodynamic Properties of Ternary Liquid Mixtures of Acetic Acid with Polar and Non-Polar Solvents at 298.15K.

Table: 1 Acetic Acid (1) + Methyl alcohol (2) + Benzene (3) System

S.No.	X_1	X_2	X_3	ρ	η	η^E	V	V^E	d	$\Delta G^{\#E}$
				gm.c.c^{-1}	mpa.s	mpa.s	cm^3 mol^{-1}	cm^3 mol^{-1}		J. mol^{-1}
1	0.0000	0.6854	0.3146	0.7914	0.6069	0.0459	58.7991	2.6379	0.3698	487.4931
2	0.0498	0.6293	0.3209	0.8059	0.5517	-0.0402	59.8322	2.5511	-5.3562	145.7331
3	0.1447	0.6074	0.2479	0.8236	0.7307	0.0851	57.6904	2.3978	7.4808	655.3043
4	0.1501	0.5605	0.2894	0.8277	0.6663	0.0149	59.8973	2.5038	2.5619	414.0084
5	0.2417	0.5409	0.2174	0.8450	0.7846	0.0814	57.7818	2.3823	5.7723	640.1215
6.	0.2509	0.4914	0.2577	0.8509	0.7354	0.0242	59.8660	2.3616	2.7759	454.1334
7	0.3387	0.4745	0.1868	0.8673	0.8464	0.0856	57.8034	2.3017	5.6554	633.6793
8.	0.3518	0.4220	0.2263	0.8712	0.7925	0.0214	60.0583	2.4227	2.6812	442.5713

Table: 2 Acetic Acid (1) + Methyl alcohol (2) + Toluene (3) System

S.No.	X_1	X_2	X_3	ρ	η	η^E	V	V^E	d	$\Delta G^{\#E}$
				gm.c.c^{-1}	mpa.s	mpa.s	cm^3 mol^{-1}	cm^3 mol^{-1}		J. mol^{-1}
1	0.0000	0.7231	0.2769	0.8236	0.6245	0.0788	59.1084	-0.0262	0.6740	588.7306
2	0.0526	0.6647	0.2828	0.8338	0.5929	0.0149	60.5814	0.1942	4.3737	363.6185
3	0.1508	0.6333	0.2159	0.8556	0.7253	0.0880	57.5494	-0.0346	8.3415	633.6190
4	0.1576	0.5884	0.2539	0.8581	0.7152	0.0734	60.2617	0.0684	6.4548	603.0459
5	0.2507	0.5611	0.1882	0.8769	0.7878	0.0897	57.4443	0.0502	6.7914	630.9915
6.	0.2620	0.5132	0.2248	0.8789	0.7845	0.0791	60.1765	0.1879	5.5016	616.2692
7	0.3495	0.4897	0.1608	0.9016	0.8611	0.1029	57.1135	-0.0922	7.0755	636.4746
8.	0.3654	0.4384	0.1962	0.9062	0.8541	0.0858	59.6628	-0.1336	5.5303	595.4591

Table: 3 Acetic Acid (1) + Methyl alcohol (2) + Carbon tetrachloride (3) System

S.No.	X_1	X_2	X_3	ρ	η	η^E	V	V^E	d	$\Delta G^{\#E}$
				gm.c.c^{-1}	mpa.s	mpa.s	cm^3 mol^{-1}	cm^3 mol^{-1}		J. mol^{-1}
1	0.0000	0.7047	0.2953	1.1884	0.8191	0.1663	57.2212	-8.0511	1.2367	832.4398
2	0.0512	0.6474	0.3014	1.2000	0.8519	0.1655	58.4822	-0.3906	25.5012	824.1849
3	0.1479	0.6211	0.2309	1.1449	0.9255	0.2063	56.1608	-0.2819	14.2132	912.0952
4	0.1541	0.5753	0.2706	1.1845	0.9095	0.1717	58.5141	-0.2906	10.7805	815.8107
5	0.2465	0.5516	0.2019	1.1335	0.9695	0.2008	56.0493	-0.3614	10.5168	855.0380
6.	0.2568	0.5029	0.2403	1.1738	1.0039	0.2145	58.3547	-0.4071	9.5280	880.7465
7	0.3444	0.4825	0.1731	1.1174	1.0039	0.1860	56.1722	-0.2024	9.2034	781.6046
8.	0.3590	0.4307	0.2103	1.1610	1.0078	0.1671	58.3169	-0.4109	7.3224	715.9744

Table: 4 Acetic Acid (1) + Ethyl alcohol (2) + Benzene (3) System

S.No.	X_1	X_2	X_3	ρ	η	η^E	V	V^E	d	$\Delta G^{\#E}$
				gm.c.c^{-1}	mpa.s	mpa.s	cm^3 mol^{-1}	cm^3 mol^{-1}		J. mol^{-1}
1	0.0000	0.6047	0.3953	0.8412	0.6031	-0.2925	69.7730	-0.8000	-1.4879	-854.3433
2	0.0613	0.5437	0.3951	0.8200	0.5640	-0.3359	72.6250	2.1142	-32.3850	-928.6468
3	0.1767	0.5206	0.3028	0.8566	0.7034	-0.2491	67.9549	0.4344	-9.5904	-595.5324
4	0.1802	0.4725	0.3473	0.8348	0.6325	-0.2985	71.4945	2.5978	-11.7413	-714.1974
5	0.2881	0.4529	0.2591	0.8710	0.8084	-0.1728	67.0173	0.9699	-4.7478	-314.4668
6.	0.2939	0.4042	0.3020	0.8488	0.7497	-0.2110	70.4891	3.1118	-5.8760	-359.2180

Table: 5 Acetic Acid (1) + Ethyl alcohol (2) + Toluene (3) System

S.No.	X_1	X_2	X_3	ρ	η	η^E	V	V^E	d	$\Delta G^{\#E}$
				gm.c.c^{-1}	mpa.s	mpa.s	cm^3 mol^{-1}	cm^3 mol^{-1}		J. mol^{-1}
1	0.0000	0.6471	0.3529	0.8370	0.8319	-0.0677	74.4120	-0.9604	-0.1322	1.9039
2	0.0656	0.5818	0.3527	0.8138	0.5449	-0.3592	77.6602	2.3578	-33.9748	-948.8560
3	0.1859	0.5479	0.2661	0.8526	0.9254	-0.0327	71.4112	0.4400	0.2481	130.7203
4	0.1911	0.5011	0.3078	0.8272	0.6106	-0.3257	76.0238	3.0305	-12.9341	-739.1615
5	0.3010	0.4731	0.2259	0.8618	0.9781	-0.0093	70.3784	1.4663	0.8751	212.0255
6.	0.3093	0.4253	0.2654	0.8424	0.7180	-0.2488	74.3011	3.4825	-7.2990	-413.8865

Table: 6 Acetic Acid (1) + Ethyl alcohol (2) + Carbon Terachloride (3) System

S.No.	X_1	X_2	X_3	ρ	η	η^E	V	V^E	d	$\Delta G^{\#E}$
				gm.c.c^{-1}	mpa.s	mpa.s	cm^3 mol^{-1}	cm^3 mol^{-1}		J. mol^{-1}
1	0.0000	0.6263	0.3737	1.1782	0.7988	-0.2249	73.2408	0.2226	-1.0452	-518.6125
2	0.0635	0.5631	0.3735	1.1985	0.8637	-0.1643	72.7305	-0.2216	-12.7537	-349.7443
3	0.1816	0.5350	0.2834	1.1417	0.8632	-0.1881	69.2894	0.0194	-7.0244	-405.4360
4	0.1859	0.4876	0.3265	1.1778	0.9044	-0.1398	71.1624	0.1952	-4.7175	-261.0656
5	0.2949	0.4636	0.2416	1.1295	0.9074	-0.1587	67.4611	-0.0502	-4.7650	-324.9335
6.	0.3020	0.4153	0.2827	1.1666	0.9547	-0.1047	69.1958	0.0749	-2.8179	-170.9127

Results and Discussion

In all the ternary liquid mixtures the first component is acetic acid, the second component is a polar solvent and the third one is a non-polar solvent.

The values of density (ρ), viscosity (η) and molar volume (V) of the ternary liquid mixtures under discussion have been determined at temperature 298.15 K and presented in Table 1-6. The values of various excess thermodynamic properties viz., the excess volume (V^E), the excess viscosity (η^E) and excess free energy of activation of flow ($\Delta G^{\#E}$) have been calculated from density, viscosity and molar volume data. The results have been presented in table 1-6.

Conclusion

From the literature concerning the viscometric studies of organic liquid mixtures vis-a-vis molecular interactions, it is seen that comprehensive studies of ternary organic liquid mixtures involving aliphatic carboxylic acids are still lacking. Since these compounds are highly polar, it would be worthwhile to determine the excess thermodynamic properties of their ternary mixtures from viscometric data with such organic liquids as are polar and non-polar. To determining the excess thermodynamic properties viz., the excess molar volume (V^E), the excess viscosity (η^E) and the excess Gibbs free energy of activation of flow ($\Delta G^{\#E}$). The main thrust of the present study would be to correlate the excess thermodynamic properties and interaction parameter d of Grunberg and Nissans equation/ with the nature of molecular interactions between the components of the ternary liquid mixture.

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