

## Volume and Transport Properties of Binary Liquid Systems of N,N-Dimethylformamide with Aromatic Ketones at 308.15 K

SAVITHA JYOTSNA TANGEDA and SATYANARAYANA NALLANI\*

*Department of Chemistry, Kakatiya University, Warangal-506 009, India.*

*Fax: (91)(870)2438800; E-mail: ns\_narayana@yahoo.com*

The densities of binary mixtures of N,N-dimethylformamide with 1-phenyl-ethanone, 1-phenyl-propan-1-one, 1-*p*-tolyl-ethanone and 1-(4-chloro-phenyl)ethanone have been determined and used to calculate the excess molar volumes. Flow times of the mixtures have also been determined. Using densities and flow times, values of the deviations in viscosity have been calculated. All  $V^E$  vs.  $x_1$  isotherms are sigmoidal whereas all  $\Delta\eta$  vs.  $x_1$  isotherms are not sigmoidal. This trend indicates that both specific and non-specific interactions are operative between unlike molecules of the mixtures.

**Key Words:** Density, Viscosity, Aromatic ketones, DMF, Binary solvent mixtures.

### INTRODUCTION

N,N-Dimethylformamide<sup>1</sup> is used as a solvent in industrial process. It is also used as crystallization medium for vitamins, hormones and sulfonamides. The mixture of dimethylformamide with propylene carbonate has potential use in lithium batteries. Acetophenone and other aromatic ketones have industrial importance as they are used in perfumery. A survey of literature indicates that no transport and volume data on these mixtures have been produced.

Transport properties generally yield a valuable information regarding the molecular interactions in pure liquids as well as in liquid mixtures. The viscosity of liquid mixtures plays an important role in finding their heat content, mass transport, fluid flow, molecular structure, etc. The study of excess parameters such as excess molar volume  $V^E$ , deviation in viscosity  $\Delta\eta$ , excess Gibbs free energy of activation of viscous flow ( $G^{*E}$ ) and Grunberg-Nissan interaction parameter ( $d'$ ) of binary liquid mixtures is useful in understanding the nature of intermolecular interactions between two liquids.

### EXPERIMENTAL

N,N-Dimethylformamide (DMF) was purchased from Merck (GR) and kept overnight over freshly ignited quicklime and distilled at reduced pressure. The middle fraction of the distillate was collected and kept over solid potassium hydroxide pellets for 24 h. It was then distilled under reduced pressure and stored

over 0.3 nm molecular sieves for a few weeks. All the four phenones<sup>2,3</sup> (1-phenylethanone, 1-phenylpropan-1-one, 1-*p*-tolylethanone and 1-(4-chloro-phenyl)ethanone purchased from SISCO Company were dried over anhydrous potassium carbonate for 3 d. After 3 d they were filtered and distilled. The middle fractions of the distillate were retained and stored over 0.4 nm molecular sieves.

Binary mixtures were prepared by mixing appropriate volumes of the liquid components in specially designed glass bottles with airtight teflon coated caps and the mass measurements were performed on a Dhona 100 DS (India) single pan analytical balance with a precision of  $\pm 0.01$  mg. The required properties were measured on the same day immediately after preparing each composition. The uncertainty in the mole fraction was  $\pm 0.0001$ . Experimental values of density for the pure liquids were compared with the literature values at 298.15 K in Table-1.

TABLE-1  
COMPARISON OF EXPERIMENTAL DENSITIES AND VISCOSITIES OF PURE LIQUIDS WITH LITERATURE VALUES AT 298.15 K AND MOLAR VOLUMES

Component	$\rho/\text{g cm}^{-3}$		$\eta/\text{mPa s}$		Molar volume ( $V^{\circ}$ ) at 293.15 K $\text{cm}^3 \text{mol}^{-1}$
	This work	Lit.	This work	Lit.	
1-Phenylethanone	1.0231	1.0225 <sup>18</sup>	1.652	1.670 <sup>3</sup>	120.9 <sup>21</sup>
1-Phenylpropan-1-one	1.0092	1.0087 <sup>19</sup>	1.468*	—	137.4 <sup>21</sup>
1- <i>p</i> -Tolylethanone	0.9963*	—	1.536*	—	137.2 <sup>21</sup>
1-(4-Chloro-phenyl)ethanone	1.1889	1.1880 <sup>19</sup>	2.293*	—	132.9 <sup>21</sup>
N,N-Dimethylformamide	0.9454	0.9445 <sup>20</sup>	0.802	0.792 <sup>20</sup>	67.6 <sup>21</sup>

\*Values at 308.15 K

A double-arm pycnometer<sup>4</sup> with a bulb of  $10 \text{ cm}^3$  and a capillary of an internal diameter of about 1 mm was used to measure the densities ( $\rho$ ) of pure liquids and binary mixtures. The pycnometer was calibrated by using conductivity water (conductivity less than  $1 \times 10^{-6}$  mho  $\text{cm}^{-1}$ ) with 0.9970 and 0.9940  $\text{g cm}^{-3}$  as its densities at 298.15 and 308.15 K, respectively. The pycnometer filled with air bubble free liquids was kept in a thermostat (INSREF model IRI-017C, India) with a thermal stability of  $\pm 0.01$  K, for 25 to 30 min to attain thermal equilibrium. The uncertainty in the density values was  $\pm 1 \times 10^{-4}$   $\text{g cm}^{-3}$ .

Ubbelohde viscometer<sup>5</sup> with the bulb between etched lines having a capacity of about 4 mL and a capillary tube having a length of about 90 and 0.5 mm internal diameter was used to measure the flow times of pure liquids and liquid mixtures. The viscometer was filled with the sample liquid by tilting the viscometer to about  $30^\circ$  from the vertical and its limbs were closed with teflon caps. The viscometer was kept vertically in the above said thermostat for about 30 min. The efflux time was measured between the marks on either side of the bulb with a stop watch of  $\pm 0.1$  second precision. The uncertainty in viscosity values was  $\pm 0.005$  mPa s.

## RESULTS AND DISCUSSION

## Solvent Parameters and Excess Parameters of the Mixtures

The densities and flow times of the mixtures of DMF with 1-phenylethanone, 1-phenylpropan-1-one, 1-*p*-tolylethanone and 1-(4-chloro-phenyl)ethanone and their corresponding excess molar volumes, deviation in viscosities, excess free energy of activation of viscous flow and Grunberg-Nissan interaction parameter as a function of mole fraction of ketone at 308.15 K are presented in Table-2.

TABLE-2  
EXPERIMENTAL DENSITIES ( $\rho$ ), VISCOSITIES ( $\eta$ ), EXCESS MOLAR VOLUMES ( $V^E$ ), DEVIATIONS IN VISCOSITIES ( $\Delta\eta$ ), GIBBS FREE ENERGY OF ACTIVATION OF VISCOUS FLOW ( $G^{*E}$ ) AND GRUNBERG-NISSAN INTERACTION PARAMETERS ( $d'$ ) AT 308.15 K

$x_1$	$\rho$ ( $\text{g cm}^{-3}$ )	$\eta$ ( $\text{mPa s}$ )	$V^E$ ( $\text{cm}^3 \text{mol}^{-1}$ )	$\Delta\eta$ ( $\text{mPa s}$ )	$G^{*E}$ ( $\text{kJ mol}^{-1}$ )	$d'$
1-Phenylethanone (1) + N,N-dimethyl formamide (2)						
0.0000	0.9394	0.7181	—	—	—	—
0.0683	0.9480	0.7599	-0.0510	-0.0015	11.58	0.2100
0.1426	0.9565	0.8055	-0.0794	-0.0029	21.63	0.2020
0.2206	0.9647	0.8534	-0.1030	-0.0044	29.29	0.1927
0.3059	0.9729	0.9088	-0.1166	-0.0030	36.75	0.1986
0.3978	0.9810	0.9720	-0.1311	0.0020	43.42	0.2139
0.4979	0.9892	1.0390	-0.1374	0.0057	45.72	0.2189
0.6056	0.9968	1.1081	-0.1049	0.0066	42.72	0.2134
0.7230	1.0041	1.1823	-0.0326	0.0064	35.12	0.2075
0.8529	1.0113	1.2627	0.0540	0.0046	21.73	0.2011
1.0000	1.0200	1.3512	—	—	—	—
1-Phenyl-propan-1-one (1) + N,N-dimethyl formamide (2)						
0.0000	0.9394	0.7181	—	—	—	—
0.0599	0.9461	0.7574	-0.0562	-0.0057	11.95	0.1846
0.1308	0.9528	0.8048	-0.0782	-0.0114	23.72	0.1799
0.1963	0.9583	0.8501	-0.0778	-0.0153	32.70	0.1797
0.2796	0.9644	0.9089	-0.0459	-0.0189	66.10	0.1771
0.3693	0.9703	0.9754	-0.0145	-0.0209	47.59	0.1808
0.4665	0.9760	1.0469	0.0188	-0.0211	49.22	0.1742
0.5765	0.9820	1.1318	0.0385	-0.0188	47.60	0.1746
0.6689	0.9866	1.2049	0.0473	-0.0150	42.94	0.1767
0.8383	0.9941	1.3413	0.0440	-0.0056	26.54	0.1863
1.0000	1.0006	1.4682	—	—	—	—

$x_1$	$\rho$ (g cm <sup>-3</sup> )	$\eta$ (mPa s)	$V^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\Delta\eta$ (mPa s)	$G^{*E}$ (kJ mol <sup>-1</sup> )	$d'$
1- <i>p</i> -Tolyethanone (1) + N,N-dimethyl formamide (2)						
0.0000	0.9394	0.7181	—	—	—	—
0.0611	0.9473	0.7882	-0.1909	0.0210	359.30	0.8139
0.1254	0.9537	0.8572	-0.2730	0.0364	529.36	0.7439
0.1971	0.9599	0.9199	-0.3319	0.0406	612.53	0.6181
0.2754	0.9653	0.9729	-0.3195	0.0295	634.42	0.4722
0.3624	0.9703	1.0202	-0.2726	0.0056	610.50	0.3269
0.4654	0.9754	1.0768	-0.1920	-0.0221	546.45	0.2058
0.5714	0.9800	1.1536	-0.1052	-0.0321	464.29	0.1609
0.6951	0.9850	1.2487	-0.0202	-0.0382	346.13	0.1160
0.8390	0.9901	1.3664	-0.0651	-0.0383	186.98	0.0384
1.0000	0.9963	1.5364	—	—	—	—
1-(4-Chloro-phenyl)ethanone (1) + N,N-dimethyl formamide (2)						
0.0000	0.9394	0.7181	—	—	—	—
0.0648	0.9640	0.7962	0.0622	-0.0240	23.40	0.4622
0.1294	0.9864	0.8756	0.1037	-0.0463	40.85	0.4269
0.2052	1.0022	0.9728	0.0921	-0.0684	61.21	0.4007
0.2823	1.0372	1.0770	-0.1399	-0.0857	64.51	0.3829
0.3721	1.0638	1.1992	-0.3398	-0.1049	67.33	0.3458
0.4702	1.0880	1.3460	-0.3509	-0.1126	68.94	0.3307
0.5812	1.1120	1.5209	-0.3152	-0.1125	63.95	0.3110
0.7050	1.1351	1.7328	-0.2012	-0.0955	53.06	0.3001
0.8398	1.1573	1.9766	-0.0709	-0.0640	07.99	0.2792
1.0000	1.1813	2.2929	—	—	—	—

The excess molar volumes ( $V^E$ ) have been evaluated from density using the equations

$$V^E = V - (V_1x_1 + V_2x_2) \quad (1)$$

$$V = (x_1m_1 + x_2m_2)/\rho \quad (2)$$

where  $V$  and  $\rho$  are the molar volume and density of the mixture,  $x_1$ ,  $V_1$ ,  $m_1$ ,  $x_2$ ,  $V_2$  and  $m_2$  are the mole fraction, molar volume and molecular weight of pure components 1 and 2, respectively.

From the values of density and efflux time the dynamic viscosity ( $\eta$ ) of the sample liquid is calculated using the equation<sup>6</sup>

$$\frac{\eta}{\eta_w} = \frac{\rho t}{\rho_w t_w} \quad (3)$$

where  $\rho$ ,  $\rho_w$  and  $t$ ,  $t_w$  are the density and flow time of the liquid and water respectively. At 308.15 K, the viscosity of water ( $\eta_w$ ) is 0.72 mPa s<sup>4,5</sup>.

The deviation in viscosity is calculated using the equation

$$\Delta\eta = \eta - (x_1\eta_1 + x_2\eta_2) \quad (4)$$

where  $\eta$ ,  $\eta_1$  and  $\eta_2$  are viscosities of the liquid mixture and of the pure components 1 and 2 respectively;  $x_1$  and  $x_2$  are the mole fractions of the pure components 1 and 2 in the liquid state. The excess Gibbs free energy of activation of viscous flow ( $G^{*E}$ ) is obtained by the equation

$$G^{*E} = RT [\ln \eta V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \quad (5)$$

where  $V$  is the molar volume of the mixture,  $R$  and  $T$  have their usual meaning.

Grunberg and Nissan formulated the following equation to assess the molecular interactions leading to viscosity changes.

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d' \quad (6)$$

where  $d'$  is a constant.

The excess properties  $y^E$  are fitted by the method of least squares to the Redlich-Kister equation<sup>7</sup>

$$y^E = x_1 x_2 [a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \quad (7)$$

where  $a_0$ ,  $a_1$  and  $a_2$  are the polynomial coefficients. The values of the coefficients and standard deviations  $\sigma$  are listed in Table-3. The standard deviations are calculated by using the equation

$$\sigma(y^E) = [\Sigma (y_{obs}^E - y_{cal}^E)/(n - m)]^{1/2} \quad (8)$$

where  $n$  is the total number of experimental points and  $m$  is the number of coefficients. The plots of excess molar volume and deviation in viscosity vs. mole fraction  $x_1$  are shown in Figs. 1, 2a and 2b respectively.

TABLE-3  
POLYNOMIAL COEFFICIENTS AND STANDARD DEVIATIONS OF KETONES  
+ N,N-DIMETHYLFORMAMIDE SYSTEMS AT 308.15 K

Binary system	Property	Coefficients			Deviations $\sigma$
		$a_0$	$a_1$	$a_2$	
1-Phenylethanone (1) + N,N-dimethylformamide (2)	$V^E \text{ cm}^3 \text{ mol}^{-1}$	-0.0680	0.8290	0.8597	0.3051
	$\Delta\eta \text{ mPa s}$	0.0088	0.0459	-0.0125	0.0040
1-Phenylpropan-1-one (1) + N,N-dimethylformamide (2)	$V^E \text{ cm}^3 \text{ mol}^{-1}$	-0.4248	0.2664	-0.4471	0.1856
	$\Delta\eta \text{ mPa s}$	-0.0604	0.0506	0.0460	0.0163
1- <i>p</i> -Tolylethanone (1) + N,N-dimethylformamide	$V^E \text{ cm}^3 \text{ mol}^{-1}$	-1.0734	1.8766	-0.3025	0.1619
	$\Delta\eta \text{ mPa s}$	-0.1646	-0.5530	-0.3424	0.1102
1-(4-Chloro-phenyl)ethanone (1) + N,N-dimethylformamide	$V^E \text{ cm}^3 \text{ mol}^{-1}$	-0.9022	-1.5293	-0.6323	0.0901
	$\Delta\eta \text{ mPa s}$	-0.4271	-0.0319	0.0654	0.0221

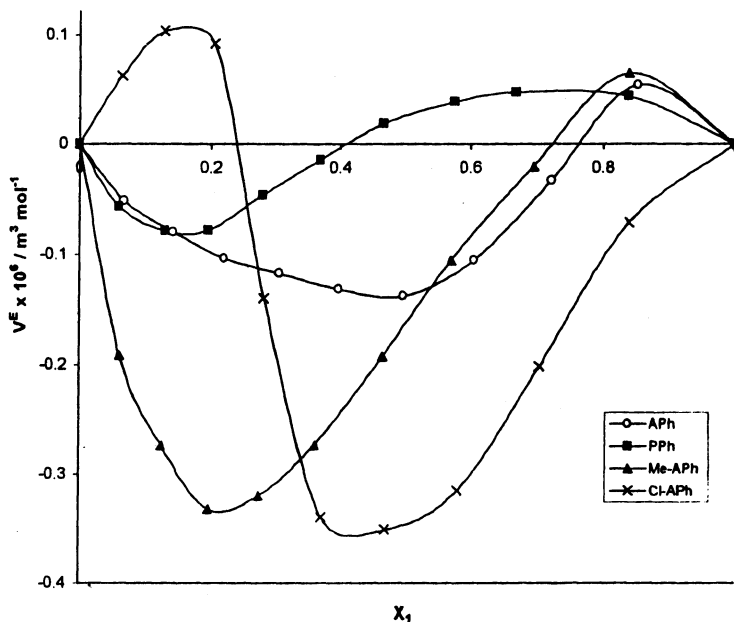


Fig. 1. Variation of  $V^E$  of the binary liquid mixtures of N,N-dimethylformamide (2) with 1-phenylethanone (1), 1-phenylpropan-1-one (1), 1-*p*-tolylethanone (1) and 1-(4-chlorophenyl)ethanone (1) at 308.15 K

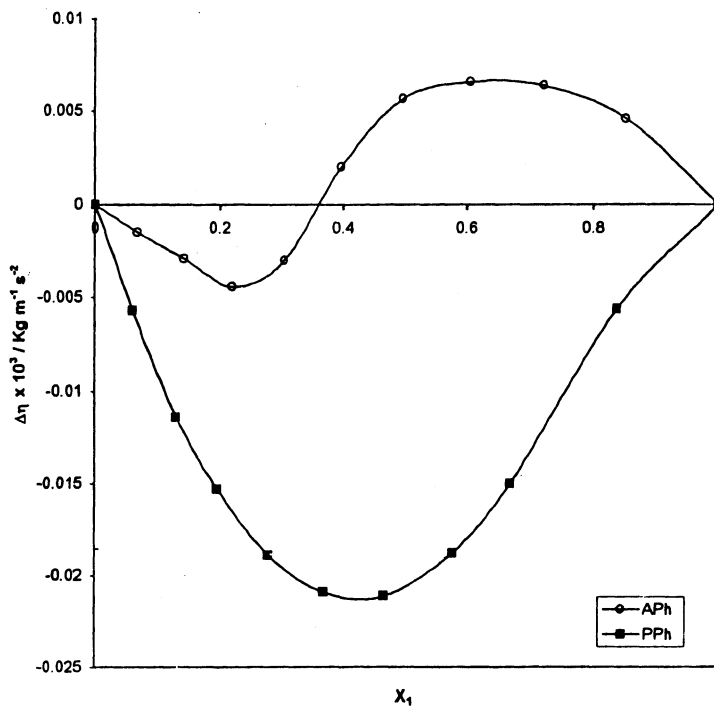


Fig. 2a. Variation of  $\Delta\eta$  of the binary liquid mixtures of N,N-dimethylformamide (2) with 1-phenylethanone (1) and 1-phenylpropan-1-one (1) at 308.15 K

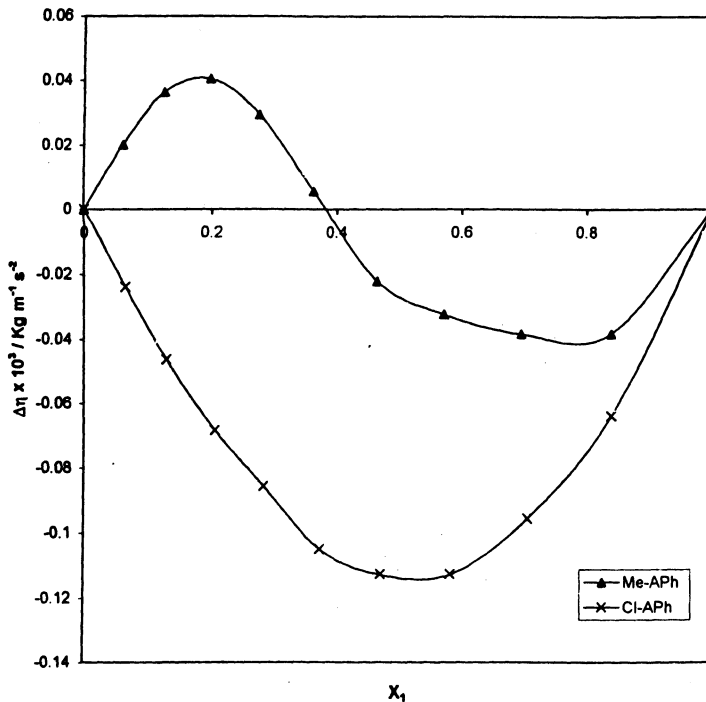


Fig. 2b. Variation of  $\Delta\eta$  of the binary liquid mixtures of N,N-dimethylformamide (2) with 1-*p*-tolylethanone (1) and 1-(4-chloro-phenyl)ethanone (1) at 308.15 K

All the systems of DMF with ketones show sigmoidal nature in  $V^E$  values (Fig. 1). Such sigmoidal behaviour is also observed by Reddy and Rao<sup>8</sup> in their work of DMF with branched alcohols. All the ketone molecules are normal polar molecules with strong dipole-dipole interaction exhibiting self-association<sup>9</sup>. Because of its large tendency to provide hydrogen bonds *via* acceptor sites of the amido group  $-\text{C}(\text{O})\text{N}=\text{}$ , DMF has weak self-association<sup>10</sup>. The positive contribution to  $V^E$  would be due to the breaking of two kinds of interactions: (i) The intermolecular dipolar forces in ketones and (ii) The hydrogen bonds present in self-associated DMF molecules.

The positive deviation can also be ascribed to the inefficient packing in the mixture of these components as a result of their incompatible structure.

The negative  $V^E$  values may be due to the existence of hydrogen bonds<sup>11</sup>, dipole-dipole interactions and formation of donor-acceptor complexes<sup>12</sup> between unlike molecules.

A correlation between the sign of  $\Delta\eta$  and  $V^E$  has been observed for a number of binary solvent systems,  $\Delta\eta$  being positive where  $V^E$  is negative or *vice-versa*. In general, for the systems, where dispersion and dipolar interactions are operating  $\Delta\eta$  values are found to be negative, whereas charge transfer, hydrogen bonding interactions and other chemical forces leading to the formation of complex species between unlike molecules result in positive values of  $\Delta\eta$ . The actual values depend upon the dominant factor as stated by Fort and Moore<sup>13</sup>.

Figs. 1, 2a and 2b clearly indicate that the isotherms of  $V^E$  and  $\Delta\eta$  do not obey the general rule of Fort and Moore<sup>13</sup>. Therefore, the strength of the specific/dispersion forces is not the only factor influencing the viscosity deviation of liquid mixtures. The molecular sizes and shapes of the components are equally important factors.

It is observed in many systems that there is no simple correlation between the strength of the interactions and the observed properties. Rastogi *et al.*<sup>14</sup>, therefore, suggested that the observed excess property is a combination of an interaction and a non-interaction part. Thus, we may write

$$X_{(\text{observed})}^E = X_{(\text{interaction})}^E + X_{(\text{size effect})}^E \quad (9)$$

where  $X^E$  refers to the excess or deviation in the property. The non-interaction part in the form of the size effect can be comparable to the interaction part and may be sufficient to reverse the trend set by the latter. Based on this theory the observed incongruity in the isotherms may be due to smaller size of DMF compared to ketones and their molar volume difference (Table-1).

In order to elucidate the forces that are acting between unlike molecules, it is resorted to free energy of activation of viscous flow,  $G^{*E}$  and Grunberg-Nissan interaction parameter  $d'$ . According to Reed and Taylor<sup>15</sup> and Meyer *et al.*<sup>16</sup>, the positive  $G^{*E}$  values indicate specific interactions while negative values indicate the dominance of dispersion forces. If  $d'$  is positive, the interactions between the components in the liquid mixture are strong and if it is negative the molecular interactions are weak. From Table-2, it is clear that the  $G^{*E}$  and  $d'$  values for all the systems are positive over the entire range of mole fraction. Hence, a conjectural conclusion can be drawn that the chemical/specific interactions are having edge over the physical/dispersion forces.

When the isotherms of excess properties are exhibiting a sigmoidal character, the comparison between the experimental results and strength of the molecular interactions is highly difficult at any composition. A flawless verdict cannot be given. But, an appropriate termination at equimolar composition  $x = 0.5$  can be sighted. Hence, the molecular interaction strength among the four ketone molecules at the mole fraction  $x = 0.5$  based on the absolute values of  $V^E$  and  $\Delta\eta$  is given as

$V^E$ : 1-phenylpropan-1-one > 1-phenylethanone > 1-*p*-tolylethanone  
> 1-(4-chloro-phenyl)ethanone

$\Delta\eta$ : 1-phenylethanone > 1-phenylpropan-1-one > 1-*p*-tolylethanone  
> 1-(4-chloro-phenyl)ethanone

The above order in two properties ( $V^E$  and  $\Delta\eta$ ) is differing only in 1-phenylethanone and 1-phenylpropan-1-one barring other compounds. An inter-comparison of  $V^E$  and  $\Delta\eta$  supports the contention of Kaulqud<sup>17</sup> that the two properties are determined by different factors. A mere knowledge of expansion and contraction is not sufficient to predict the deviations correctly but the magnitude and sign of excess entropy has to be taken into account. Finally, the orders indicate that the factors which are responsible for  $V^E$  and  $\Delta\eta$  are not the same in these mixtures<sup>8</sup>.



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Contact:

Professor Fabio Augusto

IQ Unicamp

CP 6154, 13084-971

Campinas-SP, Brazil

Tel.: (+55-19) 3788-3057

Fax: (+55-19) 3788-3023

E-mail: [augusto@iqm.unicamp.br](mailto:augusto@iqm.unicamp.br)