



CORRELATION OF EXCESS FREE ENERGY AND EXCESS MOLAR POLARIZATION IN BINARY MIXTURES USING POLAR-POLAR AND POLAR-NON POLAR INTERACTION

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ABSTRACT

Excess free energy of mixing and excess molar polarization in the binary mixtures of alcohols in non polar solvents like n-pentane, n-hexane, n-heptane and cyclohexane are evaluated considering polar-polar interaction only and polar-polar interaction with polar-non polar interaction. The important observation obtained from the calculation of excess free energy and excess molar polarization clearly indicates that polar-non polar interaction in comparison to polar-polar interaction bears a major role. The decrease in excess free energy after 0.2 mole fraction of polar liquids is due to the formation of domain barriers of non polar molecules in polar molecules which prevents the induced spontaneous polarization in polar liquids. The excess free energy and excess molar polarization is more in n-pentane and n-heptane as induced polarization plays a vital role due to the presence of an odd number of carbon atoms in n-pentane and n-heptane.

KEYWORDS: Binary mixtures; Excess free energy; Excess molar polarization; Induced polarization.



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INTRODUCTION

The emergent technology of the today's world demands the stringent requirement of a process that should be environmentally safe and less expensive. Thus environmentally viable chemical products and processes are more required for the green industry. A lot of effort has been undertaken since from last few decades to study on binary liquid mixtures. Emphasis has been given for the study of dielectric behavior, refractive index and thermodynamic behavior of polar-polar and polar-non polar liquid mixtures¹⁻⁷. However, still yet no linear behavior has been observed in the binary liquid mixtures even the molar concentration of the liquid mixtures varies linearly. The deviation from linearity of these parameters is occurred due to some of the excess parameters which are helpful to understand the nature of bonding between the two liquids^{3,8,9}. Especially, excess free energy and excess molar polarization are two important parameters which are needed to be evaluated. To evaluate the above two parameters, the interaction between like-like and or like-unlike molecules are needed to be established. As experimental evidence for the establishment of such parameters is limited, hence theoretical calculation and proper mathematical equations considering all type of interaction between molecules/solvents is necessary^{10,11}. Excess free energy of mixing evaluated through dielectric measurements is used by many authors to study the interaction in hydrogen bonded systems¹²⁻¹⁴. Haskell's¹⁵ equation for excess free energy of mixing

used by Sabesan¹⁶ takes into account the long range interaction between similar and dissimilar molecules without considering short range interactions among them. The excess free energy of mixing equation for polar and non polar liquids used by Swain¹⁷ based on Winkelmann and Quitzsch theory¹⁸ refers to an ideal case as revealed from proposed theory. On the other hand, Ray and others¹⁹ have developed an equation for excess free energy which involves estimation of separate free energy of mixing due to similar molecules (i.e. polar-polar and non polar-non polar molecules) and due to dissimilar molecules (i.e. polar and non polar molecules). The consideration of interaction between polar-polar and polar-non polar solvents by Ray et al is the advantage to establish the excess free energy and excess molar polarization in the binary liquid mixtures. To establish the fruitfulness of the developed theory of Ray et al, effort has been made to evaluate excess free energy and excess molar polarization in the binary mixtures of n-butanol, n-propanol, i-butanol and i-propanol in the non polar solvents like n-pentane, n-hexane, n-heptane and cyclohexane. A comparative picture has been drawn on both the parameters using WQ equation and Ray et al equation.

THEORY

With the concept of Onsagar's dielectric continuum theory Kirkwood Correlation factor¹⁶ for the binary mixture of polar and non polar liquids can be expressed as

$$g = \left[\frac{9KT(2\epsilon_m + \epsilon_{\infty b})^2}{4\pi N\mu_b^2 X_b (\epsilon_{\infty b} + 2)^2 (2\epsilon_m + 1)} \right] \left[\left(\frac{\epsilon_m - 1}{\epsilon_m} \right) V_m - \left\{ \frac{3X_a V_a (\epsilon_{\infty a} - 1)}{(2\epsilon_m + \epsilon_{\infty a})} \right\} - \left\{ \frac{3X_b V_b (\epsilon_{\infty b} - 1)}{(2\epsilon_m + \epsilon_{\infty b})} \right\} \right] \quad (1)$$

Where a, b and m represent the non polar liquid, polar liquid and mixture respectively. X_b , X_a denote the mole fraction of polar and non polar liquids respectively. The other parameters are dielectric constant (ϵ), square of refractive index (ϵ_{∞}), dipole moment (μ), molar volume (V), Boltzmann constant (K), Temperature (T) in Kelvin and Avogadro's

number (N). From equation-1 it is observed that g increases with decrease of X_B . But in case of amines g is found to decrease with the decrease of mole fraction of polar solute. In view of this we have utilized the concept of Davis and Douheret²⁰ to define a new parameter δg known as excess correlation factor as

$$\delta g = g - g_{\text{ideal}} = g - (X_a g_a + X_b g_b) \quad (2)$$

g_a and g_b represent the correlation factor for pure non polar and polar liquids respectively. In the binary mixture of polar and non polar liquids the non polar molecules are slightly polarized. So the effective dipole moments as well as the gas phase dipole moment of non polar liquids are negligibly small. According to Oster and Kirkwood²¹ the correlation factor for non polar liquid in the mixture can be expressed as

$$g = \lim_{\mu_{\text{eff}} \rightarrow 0, \mu_g \rightarrow 0} (\mu_{\text{eff}}/\mu_g) = 1 \quad (3)$$

In reality, the molecules of non polar liquids and very weakly polar liquids lack of correlation for which correlation factor approaches 1. Hence equation-(2) reduces to

$$\delta g = g - (X_a + X_b g_b) \quad (4)$$

The excess free energy of mixing of binary mixture of a polar liquid in a non polar solvent is given by¹⁶.

$$\Delta F_{W.Q.} = -\left(\frac{N}{2}\right) \left[X_b \mu_b^2 (R_{fb} - R_{fb}^0) \{ X_b (g_b - 1) + 1 \} \right] \quad (5)$$

$$R_{fb} = \left(\frac{8\pi N}{9V_b} \right) \left\{ \frac{(\epsilon_m - 1)(\epsilon_{\infty b} + 2)}{(2\epsilon_m + \epsilon_{\infty b})} \right\}, \quad R_{fb}^0 = \left(\frac{8\pi N}{9V_b} \right) \left\{ \frac{(\epsilon_b - 1)(\epsilon_{\infty b} + 2)}{(2\epsilon_b + \epsilon_{\infty b})} \right\}$$

While deriving this equation Winkelmann and Quitzsch have assumed that the arrangement of the identical molecules will remain unaltered in this mixture, which probably refers to an ideal case. Furthermore, the terms in the curly bracket in equation (5) correspond to g ideal expression. It indicates that the expression for excess free energy of mixing for polar and non polar liquid mixture derived by Winkelmann and Quitzsch refers to an ideal case which is revealed from the experimental observations¹⁷ as the maxima occurs at equimolar

concentration. When a binary mixture is formed, the expected properties such as thermo dynamical properties, dielectric properties, refractive index do not vary linearly²². So the deviation of the parameters from the linear behavior is termed as excess parameter and is considered to be very important and helpful to find the nature of interaction between two liquids. Hence Ray and others¹⁹ have substituted excess correlation factor δg in place of g_b in equation (5).

$$\Delta F_{ab} = -\left(\frac{N}{2}\right) \left[X_b \mu_b^2 (R_{fb} - R_{fb}^0) \{ X_b (\delta g - 1) + 1 \} \right] \quad (6)$$

The expression for molar polarization for binary mixture of polar and non polar liquids given by Winkelmann and Quitzsch is

$$P_{W.Q.} = \left\{ \frac{\epsilon_m}{\epsilon_m + 2} \right\} \left[\left\{ \frac{3X_a V_a (\epsilon_{\infty a} - 1)}{(2\epsilon_m + \epsilon_{\infty a})} \right\} + \left\{ \frac{3X_b V_b (\epsilon_{\infty b} - 1)}{(2\epsilon_m + \epsilon_{\infty b})} \right\} + \left\{ \frac{(\epsilon_{\infty b} + 2)^2}{(2\epsilon_m + \epsilon_{\infty b})^2} \right\} \left\{ \frac{(2\epsilon_m + 1) 4\pi N \mu_{gb}^2 X_b g_b}{9KT} \right\} \right] \quad (7)$$

The above expression for molar polarization also refers to an ideal case as it includes the correlation factor for polar liquid. Hence Dwivedy et al²³ have modified the equation by substituting g in place of g_b .

$$P_{ab} = \left\{ \frac{\epsilon_m}{\epsilon_m + 2} \right\} \left[\left\{ \frac{3X_a V_a (\epsilon_{\infty a} - 1)}{(2\epsilon_m + \epsilon_{\infty a})} \right\} + \left\{ \frac{3X_b V_b (\epsilon_{\infty b} - 1)}{(2\epsilon_m + \epsilon_{\infty b})} \right\} + \left\{ \frac{(\epsilon_{\infty b} + 2)^2}{(2\epsilon_m + \epsilon_{\infty b})^2} \right\} \left\{ \frac{(2\epsilon_m + 1)4\pi N \mu_{gb}^2 X_b g}{9KT} \right\} \right] \quad (8)$$

The excess molar polarization in the binary mixture of polar and non polar liquids is given by

$$\Delta P = P - \sum_{r=a,b} X_r P_r \quad (9)$$

Where P is the molar polarization of the liquid mixture and P_r is the molar polarization of the pure liquid.

EXPERIMENTAL

To have a comparative picture of excess free energy and excess molar polarization in a polar and nonpolar liquids, n-butanol, n-propanol, i-butanol and i-propanol were considered as polar solvents whereas n-pentane, n-hexane, n-heptane, and cyclohexane were considered as nonpolar solvents. Spec pure anal grade chemical were used for the mixture. The chemicals were purified and redistilled before taken for the experimental purpose. The purity of the liquids was checked by comparing the experimental data of density, viscosity and velocity of sound at 313 K with those reported in the literature. The accuracy of the measurement of relative permittivity and density were ± 0.003 and ± 0.002 gm/cm³ respectively. Then the mole amount of polar solvent was varied from 0.1 (approximately) to 0.7 (approximately) in the non polar solvents. The mixed solutions were stirred for 30 minutes to have a homogeneity mixture. Then it was placed in a hot bath and the temperature was kept fixed at 30 °C. The dielectric cell was dipped in the liquid to measure the dielectric constant using Dielectric constant instrument supplied by Mittal Enterprises. The cell temperature was controlled with an electronically regulated thermostat arrangement with temperature variation of ± 0.1 °C. The refractive index of the liquids was measured by Abbes refractometer. The excess free energy and excess molar polarization of all the mixtures were evaluated using the Winklemann-Quitze equation and Ray et al equation given in theoretical section.

RESULTS AND DISCUSSION

Table 1 represents the relevant data for $\Delta F_{W,Q}$, ΔF_{ab} , $\Delta P_{W,Q}$ and ΔP_{ab} at 303K in the binary mixtures of polar liquids n-butanol with the non polar solvents (n-pentane, n-hexane, n-heptane and cyclohexane). All the above parameters were calculated using WQ equation and Ray et al equation considering the dielectric constant and Kirkood correlation factor as raw data. The dielectric constant values were measured experimentally at room temperature and the Kirkood correlation factor is estimated using equation 3 and equation 4. It is observed from our calculation that the $\Delta F_{W,Q}$, ΔF_{ab} increases with the increase of molar concentration of polar solvents and after a critical point, it decreases. It is well observed from our calculations using the WQ and Ray et al equation. The excess free energy $\Delta F_{W,Q}$ increases upto 0.4 mole fraction of polar solvents whereas ΔF_{ab} increases upto 0.2-0.3 mole fraction (approximately) of polar liquids. The reason behind such discrepancy is due to the non consideration of non polar and polar interaction by WQ. WQ considered the interaction between polar-polar molecules and polar-non polar interactions is not taken care of. So the excess free energy is maximum at 0.4-0.5 mole fraction of polar liquids, which is evident from literature in the case of binary mixture of polar-polar liquids^{8,11}. The polar-non polar interaction has a great credential in the calculation whenever two such types of liquids were considered. Hence the excess free energy increases up to 0.2 mole fraction of polar solvents and then it decreases. This is probably due to the formation of domain barrier by the non polar molecules at lower

concentration of polar liquids which prevents the spontaneous polarization in the polar molecules. However, at the same time the non polar molecules become polarized (induced polarization) and form β -clusters (anti parallel orientation of dipoles). With the increase of molar concentration of polar molecules, the spontaneous polarization in polar molecules increases with the increase of induced polarization in non polar molecules. So α -clusters (parallel orientation of dipoles) are formed. Hence excess free energy decreases. This phenomenon is also well interpreted with the result given by Rao et al¹². The surprising

feature is that the excess free energy calculated using WQ is much greater than the excess free energy calculated using Ray et al. Similar type of results is obtained for excess molar polarization by WQ. However the excess molar polarization does not change much due to the higher concentration of non-polar solvents. As polar-non polar solvents intermix properly, so non-polar solvents act as a domain barrier for spontaneous polarization. Hence the excess molar polarization is obtained within a variation of (6-7) $10^{-6} \text{ m}^3/\text{mole}$ and is maximum at 0.5-0.6 mole fraction of polar liquids.

Table 1
Variation of $\Delta F_{W,Q}$, ΔF_{ab} , $\Delta P_{W,Q}$, ΔP_{ab} with mole fraction of n-butanol .

X_b	ϵ_m	$\Delta F_{W,Q}$ in J/mole	ΔF_{ab} in J/mole	$\Delta P_{W,Q}$ in $10^{-6} \text{ m}^3/\text{mole}$	ΔP_{ab} in $10^{-6} \text{ m}^3/\text{mole}$	g
n-butanol + n-pentane						
0.102	1.843	217.656	136.016	37.276	16.771	-0.03447
0.199	2.198	432.925	190.984	47.473	15.922	0.638444
0.301	2.782	613.303	184.828	55.571	16.638	1.040292
0.400	3.924	645.967	159.913	56.035	20.767	1.582365
0.496	5.227	627.439	121.748	52.012	21.556	1.934567
0.599	6.804	570.496	76.699	44.734	19.566	2.212579
0.699	8.779	454.366	45.548	34.018	16.333	2.51909
n-butanol + n-hexane						
0.122	1.622	297.552	138.532	43.841	11.741	-1.05264
0.237	1.942	605.337	164.483	56.001	10.112	0.076803
0.302	2.286	737.084	149.729	62.027	11.883	0.502992
0.381	3.076	779.359	136.515	64.305	17.330	1.092004
0.504	4.352	810.585	72.238	62.744	18.866	1.533143
0.602	6.183	667.980	59.584	48.709	18.632	2.049157
0.703	8.122	537.593	30.794	38.120	16.166	2.377239
n-butanol + n-heptane						
0.097	1.623	225.997	115.909	45.633	16.719	-1.64353
0.200	1.904	490.746	168.460	56.152	15.701	-0.05584
0.298	2.434	684.382	170.793	63.897	18.679	0.719218
0.400	3.107	828.716	124.786	68.471	19.939	1.120749
0.498	4.005	877.145	65.637	67.824	20.479	1.436828
0.600	5.328	821.675	17.157	60.893	19.909	1.771323
0.698	7.412	629.633	16.191	45.975	18.853	2.239773
n-butanol + cyclohexane						
0.100	1.592	237.636	117.752	39.658	9.406	-1.69813
0.201	1.822	511.478	152.924	51.134	6.763	-0.35765
0.300	2.516	670.447	145.237	59.228	11.041	0.556363
0.400	3.607	709.126	118.041	60.450	15.729	1.196348
0.500	4.956	681.243	81.845	55.927	17.461	1.641966
0.600	6.902	558.735	63.439	44.777	17.935	2.135224
0.666	8.257	477.119	48.033	37.147	16.364	2.382449

Considering the above consequences, the calculation has been done for n-propanol, i-butanol and iso-propanol. The mole fractions of polar liquids were varied as above with the similar conditions. The results were tabulated in Table 2, Table 3 and Table 4 for n-propanol,

i-butanol and iso-propanol respectively. Similar type of results has been obtained for the excess free energy ($\Delta F_{W,Q}$, ΔF_{ab}). However the $\Delta F_{W,Q}$ is larger in n-propanol mixture in consideration to the other polar solvents.

Table 2
Variation of $\Delta F_{W,Q}$, ΔF_{ab} , $\Delta P_{W,Q}$, ΔP_{ab} with the mole fraction of n-propanol.

X_b	ϵ_m	$\Delta F_{W,Q}$ J/mole	in	ΔF_{ab} J/mole	in	$\Delta P_{W,Q}$ in $10^6 \text{ m}^3/\text{mole}$	ΔP_{ab} in $10^6 \text{ m}^3/\text{mole}$	g
n-propanol +n-pentane								
0.102	1.907	277.6718		179.1826		38.26532	19.20561	0.218963
0.206	2.442	546.6548		258.2387		50.14245	21.38862	0.978791
0.300	3.029	751.844		250.8015		58.03738	22.16819	1.216838
0.400	3.993	864.6847		197.8256		61.20993	23.52991	1.499298
0.501	5.598	825.0438		145.7248		56.3309	24.95022	1.894754
0.597	7.446	737.6153		95.91076		48.24125	23.39476	2.193115
0.700	9.567	632.0792		40.53656		38.93734	18.93268	2.397625
n-propanol + n-hexane								
0.099	1.608	304.1299		161.2616		42.92896	14.73088	-1.31665
0.199	1.945	628.9221		230.7776		55.00399	15.76671	0.103531
0.281	2.389	847.8852		227.9325		63.2217	18.15981	0.646352
0.399	3.208	1073.586		147.4768		70.67249	20.0293	1.055572
0.501	4.469	1074.117		80.12695		68.54027	22.48333	1.459498
0.605	5.997	1014.247		3.695706		61.95393	21.1898	1.734751
0.709	8.243	830.7362		-28.5887		49.05619	18.30098	2.072339
n-propanol + n-heptane								
0.099	1.708	291.1504		159.6655		47.20124	20.30434	-1.09208
0.200	2.078	600.9278		238.2633		58.45022	22.04835	0.336567
0.304	2.524	902.9227		223.0525		68.33132	22.35464	0.773985
0.402	3.122	1114.03		145.3719		74.36311	22.71759	1.045802
0.497	4.008	1193.627		55.38598		74.90027	23.28071	1.314811
0.600	5.609	1089.316		0.876249		66.635	23.7374	1.698649
0.699	7.887	869.8903		-12.0526		52.10315	21.75019	2.104843
n-propanol + cyclohexane								
0.099	1.606	304.3998		154.6538		41.17393	11.29098	-1.59105
0.200	1.965	628.0507		212.2081		53.62221	11.79983	-0.08959
0.298	2.443	903.0039		181.0861		63.83169	12.62019	0.448921
0.397	3.534	969.3037		136.2049		66.60004	17.70538	1.055225
0.499	4.998	939.8843		79.9514		62.6507	19.87	1.492292
0.600	6.554	890.2822		12.77189		56.27153	18.2544	1.751809
0.700	8.996	704.5103		-2.80825		43.09112	16.19732	2.145687

Table 3
Variation of $\Delta F_{W,Q}$, ΔF_{ab} , $\Delta P_{W,Q}$, ΔP_{ab} with the mole fraction of isobutanol.

X_b	ϵ_m	$\Delta F_{W,Q}$ J/mole	in	ΔF_{ab} J/mole	in	$\Delta P_{W,Q}$ in $10^6 \text{ m}^3/\text{mole}$	ΔP_{ab} in $10^6 \text{ m}^3/\text{mole}$	g
i-butanol +n-pentane								
0.105	1.961	213.665		136.199		38.515	19.152	0.42544
0.205	2.400	422.273		190.786		49.439	19.051	0.987606
0.303	3.389	522.311		198.568		54.265	24.130	1.68279
0.399	4.328	598.175		168.049		55.989	24.354	1.918075
0.503	5.631	612.313		120.539		52.915	23.318	2.173937
0.603	7.730	501.601		93.845		41.804	22.672	2.650826
0.704	10.612	328.800		70.734		26.687	20.140	3.210523
i-butanol+n-hexane								
0.085	1.691	186.269		109.593		40.775	17.202	-1.13926
0.201	2.014	477.052		172.990		54.295	15.242	0.254945
0.305	2.647	671.032		168.509		63.193	18.097	0.951634
0.403	3.462	776.919		127.909		66.811	20.114	1.363255
0.509	4.791	769.020		83.404		63.025	21.878	1.810597
0.604	6.403	681.193		53.733		53.908	21.494	2.202659
0.707	9.003	486.104		46.736		37.550	19.624	2.753517
i-butanol+n-heptane								
0.098	1.697	220.005		127.819		46.744	19.005	-1.23497
0.199	2.080	458.503		175.262		57.591	20.311	0.36629
0.310	2.686	677.655		173.411		66.561	22.274	1.031523
0.399	3.334	795.543		134.922		70.136	23.228	1.357466
0.499	4.293	850.286		75.103		69.292	23.212	1.658937
0.601	5.954	750.953		47.705		59.244	23.637	2.123058
0.700	7.609	656.560		5.960		48.970	19.588	2.378361
i-butanol+ cyclohexane								
0.110	1.942	227.848		128.067		41.712	16.806	-0.2806
0.200	2.288	425.919		168.080		51.622	15.801	0.477563
0.305	3.034	589.380		161.566		59.157	17.711	1.085291
0.402	3.922	676.702		123.010		61.496	18.534	1.441588
0.501	5.430	639.038		93.173		55.680	20.264	1.931419
0.603	7.287	554.561		63.610		45.947	19.253	2.347634
0.670	8.457	504.357		39.247		39.956	16.814	2.515581

Table 4
Variation of $\Delta F_{W,Q}$, ΔF_{ab} , $\Delta P_{W,Q}$, ΔP_{ab} with the mole fraction of isopropanol .

X_b	ϵ_m	$\Delta F_{W,Q}$ in J/mole	ΔF_{ab} in J/mole	$\Delta P_{W,Q}$ in $10^6 \text{ m}^3/\text{mole}$	ΔP_{ab} in $10^6 \text{ m}^3/\text{mole}$	g
Isopropanol + n-pentane						
0.108	1.795	231.057	140.1257	37.148	16.120	-0.194
0.207	2.637	346.5987	189.4465	44.404	24.114	1.339
0.305	3.330	432.4588	180.5542	49.495	24.988	1.557
0.401	4.415	406.476	139.4716	49.273	26.529	1.872
0.507	6.143	262.0579	78.95289	43.014	26.879	2.263
0.607	7.966	83.85553	21.09065	35.262	24.078	2.510
0.714	10.154	-150.142	-28.9187	25.812	18.947	2.710
Isopropanol + n-hexane						
0.101	1.602	236.1371	125.5997	40.87487	14.22764	-1.34995
0.201	1.889	472.013	173.711	50.67698	14.04401	0.002086
0.308	2.432	647.0064	158.6293	59.06605	16.32886	0.672211
0.402	3.108	701.9841	110.4073	62.78805	18.21521	1.039015
0.507	4.223	622.6385	54.42476	60.93098	19.82027	1.406671
0.603	5.569	453.0508	16.15313	54.42369	19.25007	1.69722
0.713	7.6754	152.0864	-0.11621	41.98042	16.4379	2.042244
Isopropanol + n-heptane						
0.097	1.7065	213.1891	120.317	44.72116	20.24861	-1.14848
0.197	2.096	416.9765	181.1582	53.3862	22.45316	0.4114
0.307	2.5903	599.8041	173.6731	61.03716	22.94215	0.8974
0.403	3.356	634.7099	136.2188	63.14446	25.31786	1.304917
0.503	4.3329	587.8511	79.41715	61.41023	25.27353	1.575849
0.606	5.9007	389.3552	36.80873	52.85103	24.52245	1.927929
0.708	7.9871	103.737	7.243252	40.27926	21.13669	2.265172
Isopropanol + cyclohexane						
0.093	1.654	208.6685	114.8817	38.24804	12.68546	-1.52644
0.200	2.007	444.7335	163.5437	48.8396	12.28463	-0.00348
0.301	2.5802	586.303	145.7727	56.28325	14.03352	0.619504
0.402	3.454	607.1091	98.57208	58.91345	16.27059	1.061983
0.505	4.887	468.2364	56.44617	54.04814	18.58972	1.528384
0.608	6.895	223.1805	24.15435	43.34386	18.76635	1.987212
0.712	10.006	-135.292	-21.2895	26.99507	17.30729	2.581317

The variation of excess free energy with the variation of mole fractions n-butanol, n-propanol, i-butanol and i-propanol with the non polar solvents is shown in Fig. 1.

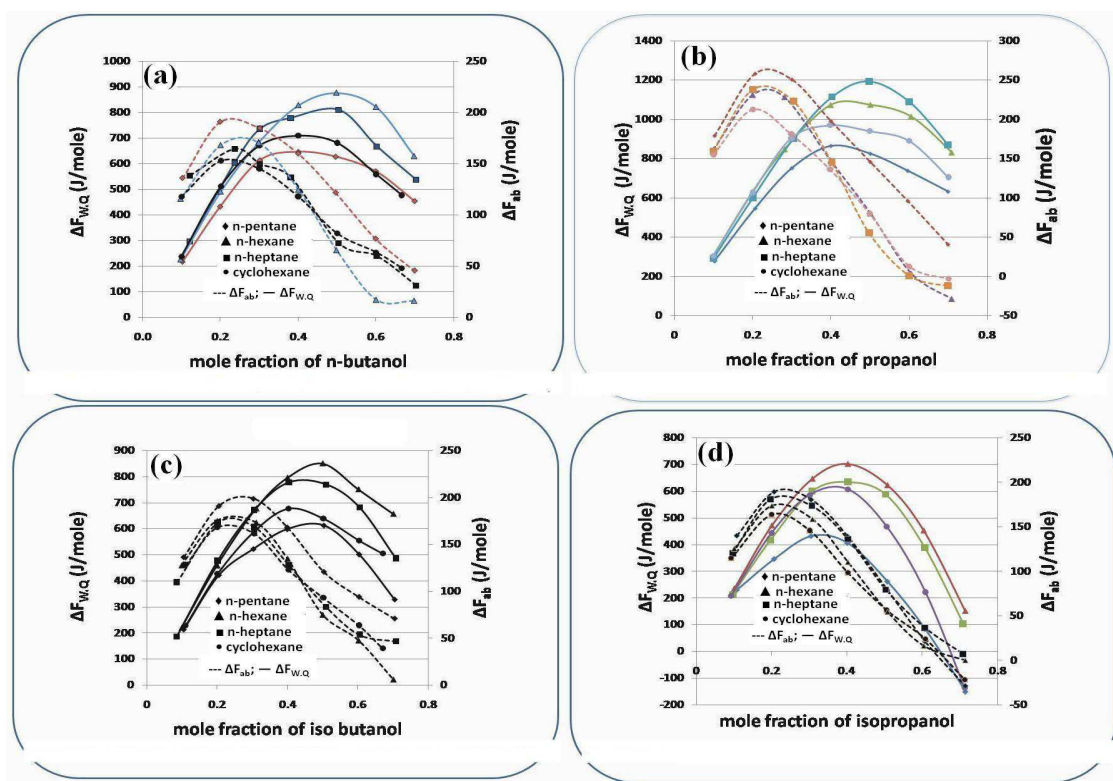


Figure 1
variation of ΔF_{ab} and $\Delta F_{W,Q}$ with the mole fraction of (a) n-butanol;
(b) n-propanol; (c) iso-butanol; and (d) isopropanol.

It is observed from the Table 1-4 and from Figure 1 that both ΔF_{ab} and $\Delta F_{W,Q}$ remain positive for most of the concentrations of alcohols. The gradual increase of ΔF_{ab} and $\Delta F_{W,Q}$ with the increase of mole fraction of the solute is an indication of pre-dominance of β -clusters¹⁷. After certain mole fraction of solute is reached, both ΔF_{ab} and $\Delta F_{W,Q}$ starts to decrease. This decrease in both ΔF_{ab} and $\Delta F_{W,Q}$ is characterized by the parallel orientation of the molecular dipoles (α -clusters). It is also observed that the peak values of ΔF_{ab} in the binary mixture of polar and non polar liquids occurs in the lower concentration region where as the peak values of $\Delta F_{W,Q}$ occurs in the higher concentration region of polar liquids in the mixture. In reality the conversion of β -clusters to α -clusters in the lower concentration region of polar liquids agree with the spontaneous polarization in dilute solutions. In the binary mixture of polar and non polar liquids, there exists an interaction between polar and induced non polar molecules which arises due to formation of α -clusters and β -clusters.

The important feature observed in the binary mixture of all alcohols in non polar solvents is that the peak values of $\Delta F_{W,Q}$ are not same order in all the mixtures. The peak values of ΔF_{ab} in the binary mixture of all alcohols in non polar solvents are in the order n-pentane > n-heptane > n-hexane > cyclohexane. As the alcohols are strongly associated liquids, the induced polarization plays a vital role. n-pentane and n-heptane contain an odd number of carbon atoms. The smaller chain n-pentane gets itself more induced and the zigzag structure of n-heptane favours more induction effect than the n-hexane. So the mixture containing n-heptane favors the formation of more β -clusters than n-hexane. But in cyclohexane, molecules are characterized by boat and chair structure. For low concentration of associated liquid, few of cyclohexane molecules are likely to be trapped in the fold of boat and chair structure and as such correlation is small²⁴. So ΔF_{ab} is least in case of the binary mixture of alcohols with cyclohexane. The variation of excess molar polarization $\Delta P_{W,Q}$ and ΔP_{ab} with the mole

fraction of alcohols is shown in Fig. 2 for n-butanol, n-propanol, i-butanol and i-propanol respectively. It is observed that the peak values of $\Delta P_{W,Q}$ have shown different trends of variation in different binary mixtures. But the peaks of ΔP_{ab} are in the same order that of ΔF_{ab} which has been discussed above. The consideration of polar-polar interaction and

polar-non polar interaction is fruitful for the calculation of excess free energy and excess molar polarization which matches well with the results obtained by other groups. Hence it can be concluded that the contribution of polar-non polar interaction cannot be ruled out when binary mixtures of polar and non-polar solvents will be considered.

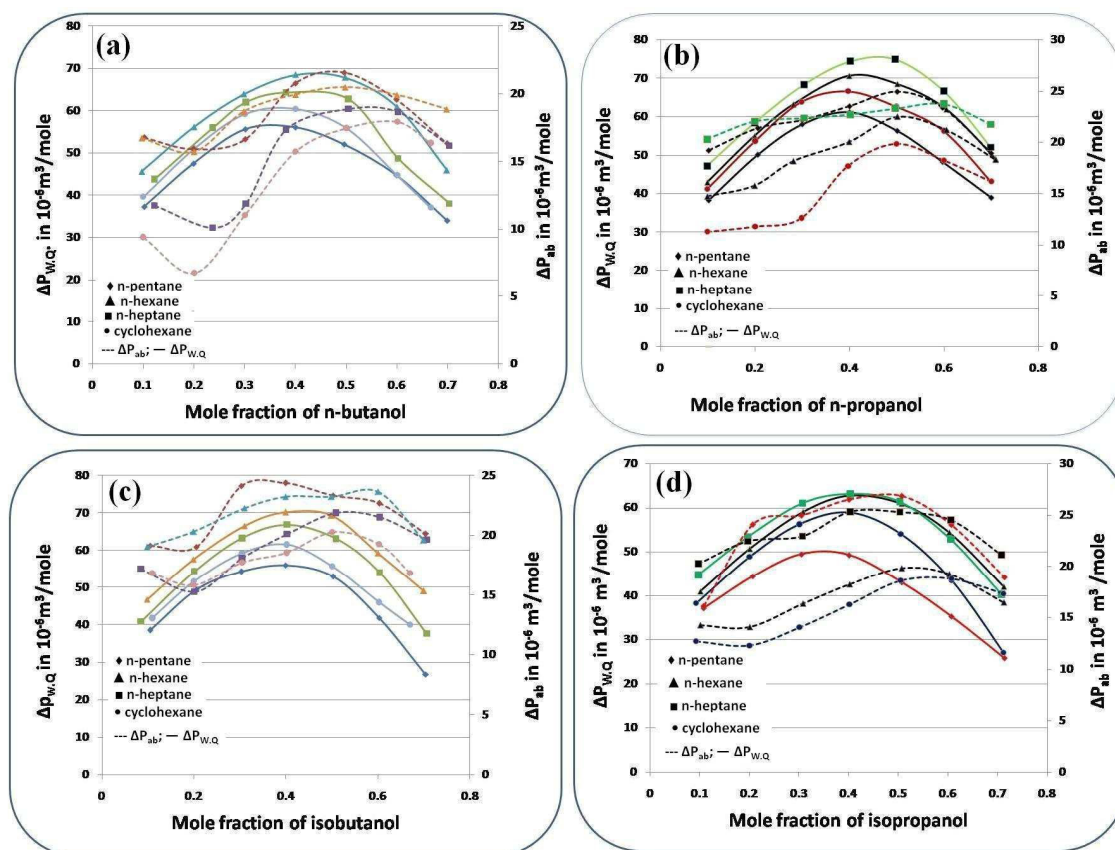


Figure 2
Variation of ΔP_{ab} and $\Delta P_{W,Q}$ with the mole fraction of (a) n-butanol; (b) n-propanol; (c) isobutanol; and (d) isopropanol.

CONCLUSION

In conclusion, polar-non polar interaction in comparison to polar-polar interaction bears a major role in the calculation of excess free energy and excess molar polarization. The decrease in excess free energy at 0.2 mole fraction of polar liquids may be due to the formation of domain barriers of non polar molecules in polar molecules. This is the reason why the spontaneous polarization does

not change drastically even the molar concentration of polar solvents increases in the binary mixtures. The excess free energy and excess molar polarization is more in n-pentane and n-heptane as induced polarization plays a vital role due to presence of an odd number of carbon atoms in n-pentane and n-heptane.

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