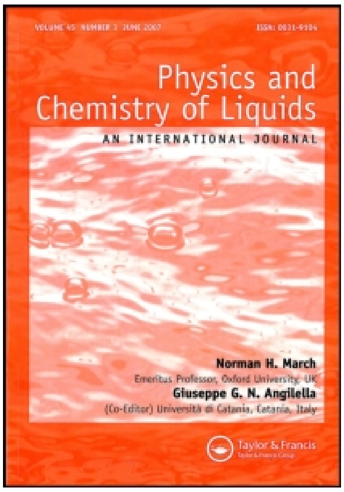

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Garabadu, Kalpana and Swain, Bipin Behari(1996) 'Dipolar Interaction in a Bipolar System-Long-Chain Aliphatic Alcohols with Carboxylic Acids', Physics and Chemistry of Liquids, 31: 1, 63 — 70
To link to this Article: DOI: 10.1080/00319109608029558
URL: http://dx.doi.org/10.1080/00319109608029558

Phys. Chem. Liq., 1996, Vol. 31, pp. 63–70
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DIPOLAR INTERACTION IN A BIPOLAR SYSTEM–LONG-CHAIN ALIPHATIC ALCOHOLS WITH CARBOXYLIC ACIDS

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(Received 5 July 1995)

Dielectric constant of binary mixtures of some long-chain aliphatic alcohols i.e. *n*-propanol, *n*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol with propionic acid and butyric acid measured at 455 kHz and at 303.16 K are utilised to calculate mutual correlation factor g_{ab}, excess molar polarization Δp and excess free energy of mixing ΔF_{ab} in those binary mixtures. The results indicate that acid-alcohol interaction is stronger in butyric acid system than in the propionic acid system.

KEY WORDS: Dielectric constant, binary mixture, WQ equation, mutual correlation factor, excess polarization and free energy.

1. INTRODUCTION

Literature abounds with reports on dieletric properties of binary mixtures of smaller alcohols with both polar and nonpolar solvents. In an earlier study[1], we reported the dielectric response of some long-chain alcohols in their binary mixtures with non-polar solvents. Panigrahi *et al.*,[2] and Sabesan *et al.*,[3] also investigated the dielectric properties of binary mixtures of acetic acid and non-polar solvents. But we have not come across any such report for dielectric study of long-chain alcohol–Carboxylic acid system. The purpose of the present study is, therefore, to investigate some aspects in the binary mixtures of some long-chain alcohols with propionic acid and butyric acid.

We have used the Winkelmann and Quitzsch equations to study mutual correlation factor g_{ab} between the unlike polar molecules in the binary mixtures, and also excess free energy ΔF_{ab} which reflect upon the short-range dipolar interaction between the unlike molecules. Excess molar polarization is also evaluated adopting the WQ equation.

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2. THEORY

Winkelmann and Quitzsch[4] developed the mixture equation written as,

$$\frac{\varepsilon-1}{\varepsilon}V=\sum_{r=a,b}\frac{3X_rV_r(\varepsilon_{\infty r}-1)}{2\varepsilon+\varepsilon_{\infty r}}$$
$$+\sum_{r=a,b}\frac{(\varepsilon_{\infty r}+2)^2(2\varepsilon+1)}{(2\varepsilon+\varepsilon_{\infty r})^2}\frac{4\pi N}{9kT}\cdot X_r\mu_r^2 g_{rr}$$
$$+\frac{(\varepsilon_{\infty a}+2)(\varepsilon_{\infty b}+2)(2\varepsilon+1)}{(2\varepsilon+\varepsilon_{\infty a})(2\varepsilon+\varepsilon_{\infty b})}\frac{4\pi N}{9kT}\mu_a\mu_b(g_{ab}-1) \tag{1}$$

where a and b refer to molecules of two varieties.

X_r – mole fraction of the component in the mixture.
V_r and V – molar volume of the component and mixture, respectively.
ε – dielectric constant of the mixture.
ε_r – dielectric constant of the component.
$\varepsilon_{\infty r}$ – is taken as the square of the refractive index of the component.
μ_r – dipole moment of the component.
g_{rr} – linear correlation factor between the similar molecules.
g_{ab} – mutual correlation factor between the dissimilar molecules.
N – Avogadro's number
T – Temperature Kelvin
k – Boltzmann constant

The molar Polarization of the binary mixture[5]

$$P_m=\frac{\varepsilon}{\varepsilon+2}\left(\sum_{r=a,b}\frac{3X_rV_r(\varepsilon_{\infty r}-1)^2}{(2\varepsilon+\varepsilon_{\infty r})(\varepsilon_{\infty r}+2)}+\sum_{r=a,b}\frac{2\pi N g_{rr}X_r{}_r^2}{9kT}\cdot\frac{(\varepsilon_{\infty r}+2)^2(2\varepsilon+1)}{(2\varepsilon+\varepsilon_{\infty r})^2}\right.$$
$$\left.+\frac{(\varepsilon_{\infty a}+2)(\varepsilon_{\infty b}+2)(2\varepsilon+1)4\pi N\mu_a\mu_b(g_{ab}-1)}{9kT(2\varepsilon+\varepsilon_{\infty a})(2\varepsilon+\varepsilon_{\infty b})}\right) \tag{2}$$

The excess Polarization

$$\Delta P=P_m-\sum X_rP_r \tag{3}$$

where P_r is the molar polarization of the component.

The excess free energy ΔF is given by Winkelmann and Quitzsch

$$\Delta F=-\frac{N}{2}\Bigg[\sum_{r=a,b}\{X_r\mu_r^2(R_{fr}-R^o_{fr})+X_r^2\mu_r^2(g_{rr}-1)(R_{fr}-R^o_{fr})\}$$

$$+X_aX_b\mu_a\mu_b(g_{ab}-1)(R_{fa}+R_{fb}-R^o_{fa}-R^o_{fb})\Big] \tag{4}$$

$$=\Delta F_0+\Delta F_{rr}+\Delta F_{ab}$$

ΔF_0 represents the excess dipolar energy due to long range electrostatic interaction, the term ΔF_{rr} gives the excess dipolar energy due to short-range interaction between identical molecules and ΔF_{ab} gives the excess dipolar energy due to short-range interaction between dissimilar molecules.

The interaction terms are

$$R_{fr}=\frac{8\pi N(\varepsilon-1)(\varepsilon_{\infty r}+2)}{9V_r(2\varepsilon+\varepsilon_{\infty r})} \tag{5a}$$

$$R^o_{fr}=\frac{8\pi N(\varepsilon_r-1)(\varepsilon_{\infty r}+2)}{9V_r(2\varepsilon_r+\varepsilon_{\infty r})} \tag{5b}$$

where, V_r is the molar volume of the component, ε_r is the dielectric constant of the pure liquid.

3. EXPERIMENTAL

The dielectric constant was measured by a wavemeter-oscillator combination at 455 kHz, developed and designed in this laboratory, used earlier by one of the authors[6]. The experimental accuracy was also the same.

4. RESULTS AND DISCUSSION

Relative permittivity of the binary mixtures of long-chain alcohols namely *n*-pentanol, *n*-hexanol, *n*-heptanol and *n*-octanol with two polar solvents viz. propionic acid and butyric acid was measured at 455 kHz at 303.16 K. the experimental data are used to calculate the value of g_{ab}, ΔP and ΔF_{ab} in these mixtures. Some of the relevant data are displayed graphically in Fig. 1, 2 and presented in the Table 1. For comparison all these parameters pertaining to *n*-propanol–a small alcohol–are also used.

The Kirkwood-Fröhlich linear correlation factor g in the pure propanol, pentanol, hexanol, heptanol and octanol are 3.27, 3.25, 3.92, 2.43, 3.08, respectively indicating predominance of α-multimers with parallel orientation. On the other hand, the carboxylic acid molecules exist mostly in the form of closed dimers with antiparallel orientation[7]. The value of g in pure propionic acid and butyric acid are 0.289 and 0.222, respectively.

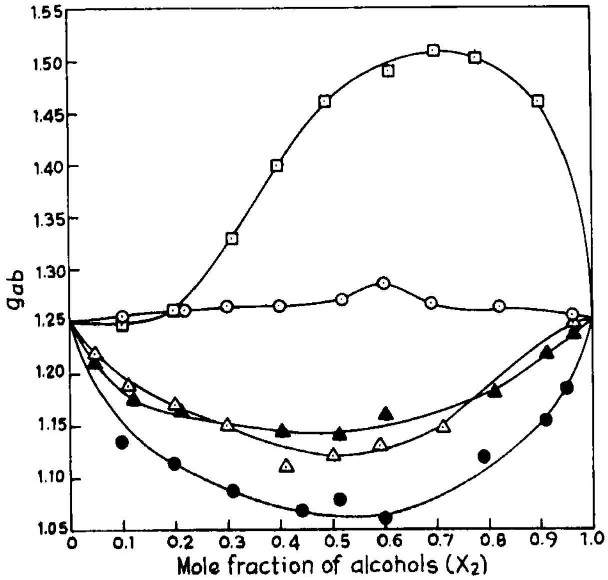

Figure 1 Variation of g_{ab} with concentration X_2 of alcohol in propionic acid. Plots: □ Propionic acid + *n*-propanol, ○ Propionic acid + *n*-pentanol, △ Propionic acid + *n*-hexanol, ▲ Propionic acid + *n*-heptanol, ● Propionic acid + *n*-octanol.

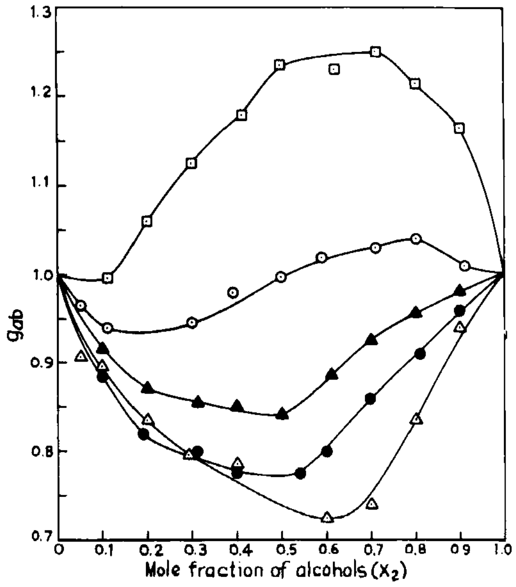

Figure 2 Variation of g_{ab} with concentration X_2 of alcohols in Butyric acid. Plots: □ Butyric acid + *n*-propanol, ○ Butyric acid + *n*-pentanol, △ Butyric acid + *n*-hexanol, ▲ Butyric acid + *n*-heptanol, ● Butyric acid + *n*-octanol.

Table 1 Variation of ε, g_{ab}, ΔP, ΔF_{ab} with concentration in different solvents at 303.16 K.

Solvent-propionic acid					*Solvent-butyric acid*				
X_2	ε	g_{ab}	ΔP cm^3 $mole^{-1}$	ΔF_{ab} J $mole^{-1}$	X_2	ε	g_{ab}	ΔP cm^3 $mole^{-1}$	ΔF_{ab} J $mole^{-1}$
				Alcohol-*n*-Propanol					
0.105	4.862	0.97	7.34	0.98	0.110	4.413	0.99	10.07	0.02
0.200	6.612	1.01	12.09	−0.26	0.199	6.000	1.06	16.50	−5.03
0.312	8.925	1.08	14.86	−11.22	0.300	8.621	1.12	22.09	−29.25
0.399	10.798	1.15	15.36	−31.14	0.412	10.023	1.18	20.27	−32.57
0.493	12.723	1.21	14.66	−54.17	0.501	11.893	1.24	19.37	−56.29
0.611	14.935	1.24	12.48	−68.25	0.625	14.100	1.23	16.04	−61.69
0.700	16.601	1.26	10.39	−71.88	0.710	16.060	1.25	13.55	−74.70
0.789	18.059	1.25	7.79	−57.50	0.800	17.613	1.21	9.84	−53.81
0.902	19.713	1.21	4.05	−26.39	0.902	19.110	1.16	5.12	−20.18
				Alcohol-*n*-Pentanol					
0.123	5.205	1.00	8.13	−0.08	0.051	3.402	0.96	2.49	1.30
0.221	6.401	1.01	10.21	−1.54	0.112	4.005	0.94	5.74	2.36
0.299	7.313	1.01	10.91	−2.14	0.299	6.198	0.94	12.43	3.69
0.405	8.501	1.01	10.88	−2.08	0.395	7.455	0.98	13.83	2.68
0.523	9.799	1.02	10.08	−4.80	0.502	8.701	0.99	13.30	1.77
0.602	10.656	1.03	9.17	−8.69	0.598	9.889	1.02	12.20	−4.61
0.697	11.452	1.01	7.33	−3.94	0.713	11.146	1.03	9.62	−6.34
0.821	12.576	1.01	4.67	−2.37	0.800	12.093	1.04	7.22	−7.16
0.961	13.600	1.00	1.08	−0.00	0.916	13.104	1.01	3.16	−0.01
				Alcohol-*n*-Hexanol					
0.055	4.033	0.97	3.00	−0.47	0.058	3.299	0.90	0.54	−3.47
0.115	4.732	0.94	5.13	−0.36	0.103	3.811	0.89	3.74	−3.54
0.214	5.592	0.92	5.91	5.31	0.199	4.705	0.83	6.72	−0.51
0.300	6.913	0.90	8.77	10.08	0.288	5.581	0.79	8.44	10.15
0.412	8.013	0.87	8.60	22.14	0.403	6.869	0.78	10.03	26.18
0.507	8.997	0.86	8.26	26.03	0.603	8.700	0.72	7.85	51.66
0.598	9.911	0.88	7.46	24.81	0.699	9.712	0.74	6.41	48.42
0.713	10.899	0.89	5.71	21.92	0.800	11.012	0.83	5.09	26.08
0.960	13.100	1.01	1.17	0.04	0.895	12.225	0.94	3.19	6.12
				Alcohol-*n*-Heptanol					
0.052	3.821	0.96	1.48	−0.67	0.113	3.799	0.91	3.12	−2.48
0.123	4.500	0.92	3.39	−0.38	0.201	4.502	0.87	5.18	0.41
0.219	5.513	0.91	5.81	4.20	0.311	5.516	0.86	7.62	10.76
0.400	7.104	0.89	7.00	16.77	0.400	6.317	0.85	8.46	19.32
0.515	8.001	0.89	6.64	21.80	0.498	7.098	0.84	8.14	28.03
0.600	8.699	0.91	6.32	17.73	0.613	8.197	0.88	7.98	23.41
0.811	10.003	0.93	3.32	12.81	0.702	9.003	0.92	7.13	14.76
0.914	10.688	0.96	1.82	10.77	0.799	9.778	0.95	5.35	7.06
0.971	11.002	0.98	0.67	1.45	0.910	10.553	0.98	2.63	1.53
				Alcohol-*n*-Octanol					
0.109	4.112	0.88	0.96	−1.5	0.102	3.559	0.88	0.84	−3.38
0.200	5.001	0.86	3.33	4.1	0.196	4.201	0.81	2.35	−0.76
0.312	5.914	0.83	4.49	15.7	0.311	5.199	0.80	5.17	13.28
0.440	6.932	0.81	5.22	26.42	0.400	5.878	0.77	5.37	26.18
0.514	7.410	0.82	4.87	31.83	0.559	7.399	0.80	5.72	37.57
0.605	7.903	0.81	3.92	37.21	0.704	8.305	0.86	5.45	25.75
0.798	9.101	0.86	2.35	20.48	0.815	9.097	0.91	3.88	13.50
0.913	9.700	0.90	0.71	7.72	0.900	9.613	0.96	2.06	6.27
0.951	9.921	0.93	0.25	3.38	0.960	9.779	0.99	0.21	4.29

The value of mutual correlation factor g_{ab} in the mixture of propionic acid with octanol, hexanol, heptanol is found to be less than unity over the entire range of concentration. For Pentanol, $g_{ab} > 1$, but very close to unity. On the other hand, in the Propanol-Propionic acid mixture it is mostly greater than unity except in the acid-rich region (X alcohol $= 0.1$) where it is slightly lower than unity.

In the mixture with butyric acid $g_{ab} < 1$ in the three higher alcohols while $g_{ab} > 1$ for propanol over the entire compositional range. But for pentanol, it is less than unity in the acid-rich region. The departure of g_{ab} from unity which reflects upon degree of interaction is in the decreasing order octanol > hexanol > heptanol in propionic acid systems while in the butyric acid systems it is in the order hexanol > heptanol > octanol. For octanol, its magnitude is nearly equal in both the systems while for hexanol and heptanol, it is greater in butyric acid systems.

On addition of an alcohol to the carboxylic acid the acid dimers as well as alcohol multimers break and monomers of both species form association due to hydrogen bonding between $O^{\delta-}$ of acid and $H^{\delta+}$ of alcohol. Rajendran *et al.*, also reported similar type of bond breaking from ultrasonic studies[8]. Owing to greater steric hindrance and high viscosity, it is probable that molecules of higher alcohols find it convenient to have more stable structure with end to end linear linkage resulting in microheterogeneous β-clusters with antiparallel orientation (Fig. 3a). On the other hand, a relatively small molecule like propanol could establish strained linkage due to switching mechanism[9,10] prevalent in alcohols and form α-clusters with parallel orientation (Fig. 3b). Pentanol probably represents the dividing line. It is worth noting here that similar differential response was also noticed in our earlier study on long-chain alcohol in nonpolar solvents[1]. The terms α and β-clusters for unlike molecules are adopted analogous to α-multimers and β-multimers in a pure associated liquid.

The departure of g_{ab} from unity which reflects upon the degree of interaction is found to be maximum in nearly equimolar concentration range in the three higher alcohols. As the alcohol concentration increases more of the acid dimers break into multimers and get trapped in the voids of alcohol and thereby correlation is

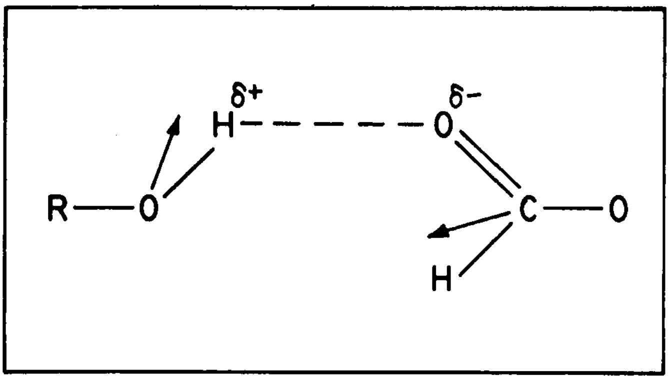

Figure 3(a) Linear linkage-β-clusters.

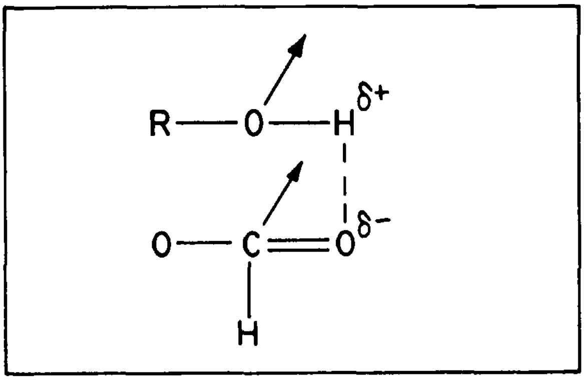

Figure 3(b) Strained linkage-α-clusters.

gradually increased to a maximum value. With further increase in alcohol the environment alters and the acid molecules becomes scarce in a sea of alcohol molecules thereby reducing the degree of interaction. Furthermore, the interaction between acid-alcohol molecules seems to be relatively stronger in butyric acid system probably because the bonds break more easily in bigger butyric acid molecules than the propionic acid molecules and therefore more clusters of unlike molecules come into existence.

The molar polarization ΔP is found to be positive in both the systems decreasing in the order propanol > pentanol > hexanol > heptanol > octanol. It corroborates our findings that multimers break to monomers and align to increase polarization and ΔP being highest in propanol system agrees with the findings that α-clusters are predominant in them. Also in octanol system, the lowest value of ΔP, corroborates our findings on g_{ab} showing dominance of β-clusters compared to other alcohols.

Formation of β-clusters are expected to result in reduced internal energy while α-clusters are associated with increased internal energy. As such, ΔF_{ab} being +ve corresponding to $g_{ab} < 1$ and being −ve when $g_{ab} > 1$ in propionic acid systems agrees with our earlier conclusion. The results for butyric acid system is also identical.

Acknowledgments

The authors express their gratitude to Dr. G. S. Roy and S. C. Dash for many helpful discussions during the progress of the work.

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