

Dielectric studies of solute-solvent interactions in mono-alcohol systems

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Abstract. Kirkwood-Fröhlich's linear correlation factor of dielectric polarisation of propan-2-ol, butan-1-ol, 3-methylbutan-1-ol and phenyl carbinol in solutions with cyclohexane, carbon tetrachloride and benzene as solvents which gives clue on the dipole orientation of the molecular aggregates of the alcohols is reported. The kinetic process responsible for the dielectric behaviour of these alcohols is analysed on the basis of significant structure model of associated liquids. Eyring's interaction parameter G^* is influenced by the nature of the solvent and has been interpreted with regard to the changes in the dipole interaction of the solute domains in the solvent environment.

Keywords. Linear correlation factor ; significant structure theory ; solute-solvent interactions ; mono-alcohol systems.

1. Introduction

The electric dipole moment of a liquid differs from the gaseous phase due to the long-range electrostatic interactions defined by classical macroscopic terms and the short-range specific interactions which are conceived by simplified statistical mechanical models (Böttcher 1973). The Kirkwood-Fröhlich correlation factor g is a measure of local ordering (Fröhlich 1958) in the condensed phase. In the case of alcohols, Oster (1946) theoretically described the dependence of factor on concentration with a graph showing a dip at low concentrations. This was explained by assuming that in dilute solutions multimers of lower order predominate which have a greater tendency to form rings whereas at higher concentrations there is a gradual transition to higher order linear multimers. However, Bellamy and Pace (1966) concluded from bond energy considerations that the multimers of lower order need not be rings whereas the polymers alone should be cyclic with stronger hydrogen bonds. The earlier spectroscopic studies (Kuhn and Bowman 1961; Coburn and Grunwald 1959) on several alcohols could be explained on this basis. Since the formation of a cyclic structure involves greater entropy loss than the formation of an open structure the calorimetric studies of enthalpy and entropy of these systems may be expected to give unambiguous

evidence in favour of or against cyclic structures. A recent review (Marcus 1977) of the thermodynamic studies revealed that such an insight could not be obtained due to the presence of strong solute-solvent interactions.

Solvent effect often masks the g values especially at low concentrations of alcohols due to the presence of the competitive process of non-specific interactions between the solute and the solvent molecules other than the demultimerisation of the alcohols. This implies that the Mecke-Kempter (1939) type of concentration-independent equilibrium constant cannot be assumed for different solvents and hence the exact calculation of the linear correlation factor is rather difficult. In this context the significant structure model proposed by Eyring and Jhon (1969) is useful in understanding the solute-solvent interactions in associated systems.

This theory which is a distinct improvement over the disorder hole theory of Lennard-Jones and Devonshire (1939) recognises the existence of molecular-size holes in liquids as confirmed by x-ray and neutron diffraction experiments and confers a gas-like degree of freedom on $(V - V_s)/V_s$ moles of fluidised vacancies per mol of a liquid where V and V_s are the molar volumes of the liquid and the solid respectively. Making an Einstein-oscillator approximation for the solid-like degrees of freedom for the rest of the molecules one could calculate the thermodynamic properties of a liquid. Introduction of a solvent in an associated liquid increases the relative abundance of the fluidised vacancies and consequently alters the short-range correlations of the dipoles of the solute molecules. Hence according to this model the solvent effect is directly related to the liquid structure of the associated species. In fact the theory is able to reconcile the data obtained from static dielectric measurements with dielectric relaxation measurements (Garg and Smyth 1965).

We report here the dielectric behaviour of several alcohols in non-polar solvents with a view to study the variation of the linear correlation factor with composition and the solute-solvent interactions on the basis of the significant structure theory.

2. Materials and methods

2.1. Experimental details

As detailed in our earlier publication (Sabesan *et al* 1979) dielectric constant (ϵ) measurements were carried out using a Toshniwal RL09 dipolemeter at a frequency of 300 KHz with the cell temperature controlled at $35 \pm 0.01^\circ\text{C}$ by means of a precision thermostat GL15 of Toshniwal Instruments. Refractive indices (n) were measured with an Abbe's refractometer at the same temperature. Densities (d) were determined using a 10 ml specific gravity bottle and a semi-microbalance. The compounds used were of AnalaR BDH grade. The uncertainties in the measurements of ϵ , n and d are ± 0.0025 , ± 0.0002 and ± 0.002 gm/cc respectively.

2.2. Calculation of linear correlation factor

The linear correlation factor (g) of alcohols in different non-polar solvents were determined by considering each kind of multimer as a separate entity and

assuming that the total dipole moment of the cluster of one type of multimer has no specific correlation with the other.

$$g = \frac{9kT(2\varepsilon + \varepsilon_\infty)^2}{4\pi N\mu^2 X_2(\varepsilon_\infty + 2)^2(2\varepsilon + 1)} \left[V \frac{\varepsilon - 1}{\varepsilon} - \frac{3X_1 V_1(\varepsilon_1 - 1)}{2\varepsilon + \varepsilon_1} - \frac{3X_2 V_2(\varepsilon_\infty - 1)}{2\varepsilon + \varepsilon_\infty} \right] \quad (1)$$

where μ is the dipole moment of the monomer of the solute; ε_∞ , the dielectric constant characteristic of electronic polarisation of the polar component in the pure state; ε , the dielectric constant and V , the molar volume of the solution; X_1 and X_2 are the mole fractions of the solvent and solute; ε_1 is the dielectric constant and V_1 , the molar volume of the solvent; V_2 is the molar volume of the solute; N is the Avogadro number; k is the Boltzmann constant and T , the absolute temperature at which the measurements were made.

2.3. Significant structure theory and dipolar interactions

According to this theory the associated liquids are considered to be formed of mosaics with domains of dipoles having an average resultant moment $\mu \cos \theta$ with respect to the direction of maximum polarisation for the domain. This direction of maximum polarisation will tend to orient in an electric field with the dipoles either parallel or antiparallel with the field direction by the growth of favourably oriented molecules in the domains till a steady state is attained. The resulting mean dipole moment of solid-like structure is given (Jhon and Eyring 1968) to be $\mu^2 GF/kT$ where $G = \cos^2 \theta$ and F is the local field. In the case of gas-like holes, the Kirkwood's factor of $\mu^2/3kT$ is retained since free orientation of the molecules in the local field is possible for the gaseous part. Hence the Kirkwood's statistical relation for the associated liquids becomes

$$\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{3\varepsilon} = \frac{4\pi N}{V} \left(\frac{\varepsilon_\infty + 2}{3} \right)^2 \left[\frac{V_s \mu^2 G}{VkT} + \frac{V - V_s}{V} \cdot \frac{\mu^2}{3kT} \right] \quad (2)$$

G , the only adjustable parameter could be easily calculated for pure liquids and it is a measure of the dipolar interaction between like molecules due to the angular correlation of the molecules in a given domain. The addition of a non-polar solvent should alter the liquid structure and hence the dielectric behaviour. Then one has to consider the dielectric polarisation P_s^* of the domains of the solute species in the solvent environment. The number of such domains will increase as the solvent concentration increases. P_s^* is now given by $\mu^2 G^*/kT$ where G^* replaces G to account for the solute-solvent contact interactions, the occurrence of which is proportional to $X_1 X_2$. Equation (2) could be modified to accommodate such interactions and written as

$$\frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{3\varepsilon(\varepsilon_\infty + 2)^2} = \frac{4\pi N}{3kT} \cdot \frac{\mu^2}{3V} \cdot X_2 \times \left[\frac{V_s}{V} (X_2 G + X_1 G^*) + \frac{1}{3} \left(\frac{V - V_s}{V} \right) \right] \quad (3)$$

The data for G for pure liquids and g and G^* for varying compositions of the alcohols in non-polar solvents calculated by using expressions (1), (2) and (3) are presented in table 1.

Table 1. Variation of g and G^* with concentration at 35°C

Cyclohexane				Carbon tetrachloride				Benzene				
X_2	ϵ	d gm/cc	g	X_2	ϵ	d gm/cc	g	X_2	ϵ	d gm/cc	g	G^*
Propan-2-ol ($G = 1.103$)												
0.054	2.0832	0.7670	0.51	0.008	2.2184	1.5663	0.44	0.046	2.3068	0.8622	0.35	0.024
0.114	2.1820	0.7672	0.51	0.022	2.2340	1.5645	0.37	0.098	2.5356	0.8564	0.78	0.154
0.184	2.4004	0.7674	0.67	0.040	2.2652	1.5484	0.44	0.136	2.6708	0.8554	0.81	0.125
0.209	2.4628	0.7675	0.67	0.060	2.2912	1.5344	0.43	0.179	2.8580	0.8511	0.87	0.100
0.310	3.0400	0.7678	0.93	0.076	2.3432	1.5219	0.54	0.261	3.4040	0.8394	1.07	0.102
0.388	3.8044	0.7684	1.20	0.098	2.4056	1.5116	0.60	0.346	4.1476	0.8357	1.25	0.080
0.545	6.0404	0.7696	1.67	0.144	2.5096	1.4774	0.61	0.501	6.0612	0.8242	1.58	0.030
0.698	9.0356	0.7702	2.04	0.193	2.7384	1.4440	0.76	0.657	8.4552	0.8092	1.84	-0.144
Butan-1-ol ($G = 1.647$)												
0.022	2.0364	0.7674	0.68	0.010	2.2288	1.5705	0.75	0.017	2.2912	0.8667	0.78	0.224
0.055	2.0520	0.7683	0.37	0.022	2.2548	1.5581	0.83	0.045	2.3903	0.8654	1.03	0.282
0.112	2.2736	0.7700	0.79	0.048	2.3120	1.5404	0.81	0.093	2.5668	0.8607	1.13	0.257
0.164	2.3796	0.7704	0.89	0.060	2.3380	1.5296	0.81	0.139	2.7748	0.8567	1.23	0.223
0.216	2.5720	0.7726	0.99	0.098	2.4368	1.5013	0.86	0.196	3.0868	0.8534	1.35	0.187
0.264	2.8320	0.7740	1.14	0.102	2.4472	1.4992	0.86	0.227	3.2220	0.8506	1.34	0.126
0.321	3.3520	0.7752	1.46	0.110	2.4680	1.4919	0.86	0.274	3.5912	0.8475	1.50	0.114
0.508	5.7440	0.7805	2.24	0.116	2.4784	1.4895	0.85	0.459	5.5984	0.8355	2.05	0.010
0.690	8.8640	0.7878	2.77	0.139	2.5564	1.4679	0.91	0.644	8.6612	0.8219	2.66	-0.128
				0.161	2.6396	1.4553	0.95					
				0.194	2.7956	1.4309	1.06					
				0.289	3.4.44	1.3591	1.36					
				0.474	5.5308	1.2206	2.05					
				0.664	8.8432	1.0754	2.70					

3-Methyl butan-1-ol ($G = 1.158$)

0.023	2.0416	0.7686	0.55	0.146	0.010	2.2392	1.5523	0.85	0.267	0.020	2.2808	0.8676	0.33	0.045
0.062	2.0936	0.7707	0.43	0.055	0.018	2.2548	1.5376	0.68	0.194	0.048	2.3640	0.8651	0.55	0.102
0.111	2.2028	0.7721	0.50	0.022	0.037	2.2912	1.5240	0.59	0.138	0.101	2.5512	0.8612	0.65	0.087
0.172	2.3380	0.7746	0.51	-0.059	0.077	2.3874	1.4940	0.58	0.091	0.144	2.7592	0.8579	0.73	0.068
0.221	2.4888	0.7767	0.55	-0.118	0.096	2.4212	1.4773	0.55	0.056	0.201	3.0088	0.8540	0.73	-0.009
0.326	3.0140	0.7808	0.67	-0.255	0.143	2.5460	1.4368	0.57	0.002	0.286	3.5028	0.8503	0.75	-0.139
0.441	3.9240	0.7851	0.75	-0.494	0.195	2.7072	1.3936	0.59	-0.068	0.387	4.1892	0.8417	0.75	-0.355
0.548	5.1720	0.7905	0.77	-0.867	0.240	2.8736	1.3548	0.61	-0.133	0.482	5.1564	0.8361	0.76	-0.629
					0.287	3.0868	1.3188	0.63	-0.205					
					0.343	3.4092	1.2762	0.66	-0.303					
					0.392	3.7862	1.2357	0.70	-0.400					
					0.520	5.1876	1.1602	0.74	-0.775					

Phenyl carbinol ($G = 0.663$)

0.058	2.1404	0.7834	0.56	0.143	0.011	2.2392	1.5678	0.60	0.178	0.020	2.3536	0.8734	1.01	0.330
0.117	2.3484	0.7957	0.68	0.159	0.020	2.2912	1.5649	0.94	0.304	0.050	2.4420	0.8770	0.74	0.207
0.165	2.5356	0.8084	0.72	0.148	0.042	2.3744	1.5532	0.87	0.268	0.091	2.6292	0.8854	0.81	0.216
0.227	2.7956	0.8260	0.76	0.122	0.059	2.3900	1.5438	0.65	0.175	0.139	2.8320	0.8987	0.80	0.188
0.322	3.4560	0.8504	0.94	0.143	0.082	2.4784	1.5313	0.69	0.180	0.187	3.1336	0.9063	0.89	0.204
0.429	4.3088	0.8793	1.06	0.123	0.103	2.5876	1.5198	0.77	0.199	0.281	3.6900	0.9232	0.93	0.170
0.638	6.5188	0.9369	1.28	0.037	0.124	2.6344	1.5083	0.71	0.163	0.379	4.4596	0.9407	1.03	0.153
0.809	9.0382	0.9930	1.47	-0.140	0.142	2.7020	1.4939	0.71	0.153	0.586	6.4512	0.9751	1.23	0.080
					0.147	2.7540	1.4905	0.76	0.172	0.810	9.0668	1.0106	1.42	-0.228
					0.165	2.8112	1.4830	0.74	0.152					
					0.299	3.6224	1.4110	0.92	0.148					
					0.406	4.4596	1.3504	1.03	0.130					
					0.612	6.6332	1.2423	1.27	0.075					
					0.818	9.2020	1.1373	1.44	-0.235					

3. Conclusion

The value of g of a mono-alcohol in solution depends on the fractions of the aggregates of alcohol molecules with parallel alignment of dipoles and of antiparallel alignment of dipoles. If the Oster-Kirkwood (1943) model of linear chain association for large multimers is assumed, one is led to the conclusion that linear association might increase with increase of chain length as it was generally found that at room temperatures the experimental values of g increase with increase of chain length of alcohols. However, we find that the g value decreases with the central positioning of the O-H group (as in the case of propan-2-ol) or with the increase of the side chain (as in the case of 3-methyl butan-1-ol when compared to butan-1-ol). The complexity of the alcohol molecules render hydrogen bonding more difficult. This is obviously seen in the case of phenyl carbinol where the hindered rotation of the O-H group due to steric factors is responsible for the low value of g . Nevertheless value of $g < 1$ is found even in mixtures of alcohol with inert solvents where the component alcohol in the pure state possesses a value of $g > 1$.

This is generally attributed to the progressive formation of ring dimers or trimers with low g values (Huyskens and Cracco 1960; Huyskens *et al* 1962, 1963; Clerboux and Huyskens 1966). Then the assumption of the Mecke-Kempton model of concentration-independent equilibrium loses its significance. In this context the model of cyclic tetramers with out-of-plane oxygen and hydrogen atoms for large dipole moment multimers proposed by Bordewijk (1968) seems to be more favourable. At low concentrations of alcohols such multimers might break into cyclic dimers with anti-parallel dipole alignment. Tjia (1974) after a thorough analysis of various other models commends this model as one consistent with both relaxation and static dielectric data. Yet an exact calculation of g seems to be impossible due to non-ideality of solutions.

Eyring on the other hand proposed that a significant modification to the calculation of the short-range correlation factor is essential to understand the fluid structure. The space averaging of the moment $\mu \cos \theta$ of a dipole of a liquid over all possible values of the angle θ through the introduction of the g -factor and the assumption that the central dipole is free to orient in a local field in the Kirkwood's model is questioned and the significant structure theory proposed by Eyring is free from such assumptions. The solute-solute interactions and the interaction of the solute molecules in an environment of solvent molecules are reflected by the values of the parameters G and G^* respectively. The progressive shift in equilibrium between the various multimers of the solute species on dilution with various solvents significantly changes the G^* value. The realignment of solute molecules due to the short-range dipole correlation between the solute and the solvent molecules does occur continuously and this angular correlation is found a better description by the G^* values (Dwivedi and Srivastava 1980). Generally, the trend of G^* value is such that it decreases in the order benzene > carbon tetrachloride > cyclohexane. The dipolar excess free energy reported earlier exhibited such a solvent effect (Sabesan *et al* 1980). This is due to a favourable interaction energy between the hydroxyl group and the π -electrons in the aromatic ring of benzene molecules. This interaction, though less demanding in its geometrical configuration, leads to an interacting environ-

ment around the solute species and gives a favourable alignment of dipoles of the solute species albeit the progressive demolition of the fluid structure by the solvent (benzene) molecules. This effect is marginal in carbon tetrachloride.

While the spectroscopic manifestations of solvent effect are interpreted in terms of bulk dielectric effect and dispersion effects in a most general way, the significant structure model treats the solvent effect in terms of liquid structure and hence possesses a great potential in its application to the solute-solvent interactions.

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