Associating Behaviour of Pure Polar Liquids: Dielectric Properties of Pelargonic Acid

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The associating behaviour of pelargonic acid has been studied by the determination of its dielectric properties. A high degree of dimerisation in the liquid phase is suggested, with the number of dimers decreasing with increasing temperature.

1. Introduction

The theory of dielectrics brought in by Onsager [1], which takes into account the interaction between molecules and their environment, though applicable to pure polar liquids, is inadequate to justify the behaviour of some liquids whose molecules exhibit associating properties, such as acids, alcohols, amides and cyanides. This inadequacy led Kirkwood [2] to hypothesize an orientational correlation of neighbouring molecules as the result of short-range specific interactions. Kirkwood's theory, extended by Fröhlich [3, 4] to the case of polarisable molecules with permanent dipole moment, affords, through the introduction of a correlation factor, a useful tool for obtaining, from static permittivity measurements, information about the interactions among molecules in dependence on the liquid structure. The results are, as yet, not confirmable through comparison with otherwise gained determinations.

In the present work the static permittivity of pelargonic acid has been measured as a function of temperature, and the results are discussed on the basis of the Kirkwood-Fröhlich theory.

2. The Correlation Factor

The Kirkwood-Fröhlich equation

$$g = \frac{9\,kT}{4\pi N \mu^2} \, \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2}, \qquad (1)$$

where N is the number of molecules per unit volume of the polar fluid, relates the correlation factor g to the static permittivity ε of the fluid, the high frequency permittivity ε_∞ and the permanent dipole moment μ of the molecules. The g factor is indicative of the correlation among the orientations of the molecules.

The introduction in (1) of an apparent molecular dipole moment μ_{eff}, defined as

$$\mu_{\text{eff}}^2 = g\,\mu^2, \qquad (2)$$

points out the analogy of (1) with the expression obtained by Onsager [1] for polar fluids neglecting short-range interactions.

From considerations of statistical mechanics it follows that $g > 1$ when the molecular interaction favours parallel orientation between dipoles of neighbouring molecules while, when $g < 1$ these interactions favour antiparallel orientation. Clearly, $g = 1$ is indicative of the lack of any correlation among the molecular dipoles.

If one considers that in the carboxylic acids the presence of the hydrogen bond between terminal carboxylic groups leads to the formation of complexes which are dimer when the number of carbon atoms in the chain is $n \geqq 3$, while for $n < 3$ formation of multimers has been found [5, 6], it is expected, from thermodynamic considerations [7], that the permittivity must increase with the temperature.

3. Properties of Pelargonic Acid

3.1 General

Pelargonic acid $CH_3(CH_2)_7COOH$, also referred to as nonanoic acid, is a saturated monocarboxylic fatty acid, molecular weight $M = 158.24$, MP 12 °C. The total chain length is about 12 Å and, as occurs

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for all saturated fatty acids, the molecule is rod-like and the molecular dipole moment is located in the acid group. The crystalline structure shows two enantiotropic forms with carboxyl groups of two molecules in juxtaposition. The arrangement of carboxyl groups is unsymmetrical in the α form and symmetrical in the β form. This is typical for all odd acids [8].

Pelargonic acid of purity greater than 97% was obtained from Fluka AG and employed without further treatments.

3.2 Density

The temperature dependence of the density of pelargonic acid in the liquid phase was obtained from literature data [9–13].

The inverse of the density d was found to depend linearly on the absolute temperature:

$$d^{-1} = A + BT \tag{3}$$

with $A = 8.08 \times 10^{-1}\ \mathrm{g^{-1}\,cm^3}$ and $B = 1.01 \times 10^{-3}\ \mathrm{g^{-1}\,cm^3\,K^{-1}}$.

N is calculated by

$$N = N_A\, d/M, \tag{4}$$

where N_A is the Avogadro number.

4. Experimental Details

4.1 Refractive Index and High Frequency Permittivity

The refractive index n_D of pelargonic acid, for the sodium D-line, was measured with an Abbe refractometer (Officine Galileo) to an accuracy of ± 0.0005. The results are reported in Table 1 together with data taken from literature, which are in very good agreement with our data. For $283 < T/\mathrm{K} < 353$ the refractive index n_D depends linearly on T:

$$n_D = C + DT. \tag{5}$$

$C = 1.5469$ and $D = -3.9 \times 10^{-4}\ \mathrm{K^{-1}}$ were obtained from a best fit of the data reported in Table 1.

For the high frequency permittivity ε_∞, i.e. the permittivity due to induced polarisation we used $\varepsilon_\infty = 1.05\, n_D^2$ [7].

Table 1. Refractive index of pelargonic acid. Data are from the present work unless a reference is given.

T (K)	n_D	Reference
283.65	1.4362	
284.65	1.4358	
287.15	1.4346	
288.15	1.43446	[14]
293.15	1.43220	[15]
293.15	1.4322	[16]
293.65	1.4313	
298.15	1.4301	[16]
298.15	1.4296	
302.15	1.4281	
303.15	1.4287	[16]
308.15	1.4258	
313.15	1.4250	[16]
313.15	1.4249	
318.15	1.4235	
321.15	1.4212	
323.15	1.4210	[16]
323.15	1.4205	
327.15	1.4182	
329.15	1.4177	
333.15	1.4171	[16]
333.15	1.4162	
336.65	1.4149	
338.15	1.4145	
341.15	1.4132	
343.15	1.4132	[16]
343.15	1.4130	[17]
343.15	1.4122	
345.15	1.4115	
348.15	1.4104	
353.15	1.4092	[16]

4.2 The Static Permittivity

The permittivity of pelargonic acid was measured from the MP to 365 K by a General Radio bridge mod. 1616. A three-terminal cell for measurements on liquids, with platinum electrodes, was used. The permittivity measurements were done in a field of $50\ \mathrm{V\,m^{-1}}$ and were found to be independent of field intensity and frequency. The values reported in Table 2, from about 10 K above the MP to 365 K, were obtained from measurements done at 1 kHz. At this frequency the permittivity values can be considered as static for pelargonic acid.

Permittivity measurements just above the MP were not taken into account because, in this temperature region, the physical properties of the liquid may deviate considerably from those at higher temperature. The conductivity was found to be frequency independent and increasing with temperature. At room temperature the conductivity was found to be less than $10^{-12}\ \Omega^{-1}\,\mathrm{cm}^{-1}$.

Table 2. Static permittivity of pelargonic acid, values of μ_{eff} obtained with (1) and (2) and correlation factors evaluated for $\mu = 1.5$ D.

T (K)	ε	μ_{eff} (D)	g
294.85	2.475	0.675	0.203
296.92	2.488	0.694	0.214
302.76	2.498	0.720	0.230
308.31	2.491	0.729	0.236
314.52	2.485	0.741	0.244
319.70	2.479	0.750	0.250
326.09	2.465	0.754	0.253
330.92	2.457	0.760	0.257
336.35	2.448	0.766	0.261
342.02	2.444	0.779	0.269
347.43	2.441	0.791	0.278
352.65	2.439	0.805	0.288
359.05	2.436	0.820	0.299
364.73	2.435	0.839	0.313

5. Discussion

Through the Kirkwood-Fröhlich relation (1) it is possible to evaluate the dependence of the correlation factor g on the permittivity, the refraction index n_D and the density, all as a function of the temperature, when the permanent dipole moment μ of the molecule is known.

For a molecule containing several dipoles in fixed positions an approximate calculation of μ can be carried out by the vector sum of the various dipole moments with respect to a set of reference axes in the molecule. In the saturated fatty acids the greater contribution to the molecular dipole moment is furnished by the acid group COOH, whose moment can be calculated as the resultant of the bond moments of the C−O, C=O, H−O bonds. On the basis of such considerations, values of 1.4 D for the planar "cis" configuration and of 1.7 D for the non-planar configuration of this group have been obtained [18]. The inductive effect of the molecular radical CH_3, located at the opposite end of the molecule, should, as observed by Smyth [18], be negligible on the COOH group. Otherwise, the few dipole moments as yet known for some low molecular weight monocarboxylic acids exhibit values between 1.35 and 1.7 D.

Owing to the foregoing considerations we found it reasonable to assign the value 1.5 D to the permanent dipole moment of the pelargonic acid.

In Table 2 the values of μ_{eff}, obtained with (2) and (3), are reported at several temperatures, together with the corresponding correlation factor g.

The extrapolation of the μ_{eff} values of Table 2 for the liquid phase towards low temperatures gives, just below the MP, effective dipole moments not in contrast with the coexistence of two enantiotropic forms in the crystalline phase with calculated dipole moments $\mu_\alpha = 0.36$ D for the α form and $\mu_\beta = 0$ for the β form.

In the whole temperature range explored the g values are quite small, and this corresponds to a high degree of association. Therefore it can be deduced that, in the liquid phase, pelargonic acid consists mainly of dimer molecules. This is in agreement with evidence from IR spectra of low molecular weight fatty acids [19].

The g values in Table 2 increase roughly linearly with increasing temperature, with a mean slope of $0.012\ \mathrm{K}^{-1}$. This small rate of increase corresponds to a slight decrease of dimerisation as the temperature increases.

A comparison of the g values of pelargonic acid ($n = 9$) with those of ***n***-valeric acid ($n = 5$) [20] shows that, at temperatures at which g values are available for both acids, i.e. from 295 K to 343 K, the g values of pelargonic acid are lower than the corresponding values for ***n***-valeric acid. This could be indicative of a greater degree of correlation between molecular orientations as the length of the molecules increases. On the contrary, this behaviour is just the opposite of what is expected considering only the dependence of g on the number N of molecules (and hence the number of dipoles) per unit volume which, in turn, is a decreasing function of the number n of carbon atoms per molecule. At, say, 300 K one has $N = 6.3 \times 10^{21}\ \mathrm{cm}^{-3}$ for ***n***-valeric acid and $N = 4.2 \times 10^{21}\ \mathrm{cm}^{-3}$ for pelargonic acid. Assuming that the dipole moment μ is, in first approximation, the same for both molecules, it then follows that the g factor should increase, due to the lower concentration of dipoles, instead of decrease as observed.

Finally, as concerns the temperature dependence of the permittivity, one can observe from the data reported in Table 2 that it increases in the interval from 295 K to 303 K and then decreases above 303 K. This could be explained by assuming that the liquid has a high degree of association, as discussed before, but is not fully associated, i.e. that there exists a ratio between the number of dimers $\boldsymbol{d}$ and that of monomers $\boldsymbol{m}$ per unit volume (with $2\boldsymbol{d} + \boldsymbol{m} = N$) which is temperature dependent. In the condition of $\boldsymbol{d} \gg \boldsymbol{m}$, found for pelargonic acid just above the MP, the external electric field could tend to destroy the dimers thus creating disorder with a consequent increase of entropy and hence a positive slope for ε vs. T. At higher temperatures the number of dimers is decreased and, correspondingly, the number of monomers is increased. The external electric field creates order in the system of randomly distributed dipoles, thus involving a decrease of entropy as evidenced by the negative slope for ε vs. T.

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