

A POSSIBLE MECHANISM UNDERLYING THE ANOMALOUS DIELECTRIC RESPONSE IN CONCENTRATED METHANOL-IN- CARBON TETRACHLORIDE MIXTURES

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(Nota presentata dal Socio Ordinario Cirino Vasi)

ABSTRACT. The association of CCl_4 with the non-donating ends of open (chain-like) methanol aggregates, is shown to be relevant in the occurrence of positive deviations of the static dielectric constant with respect to ideality in methanol/ CCl_4 mixtures. This interaction tends to reduce in fact the fraction of methanol aggregated in cyclic clusters. This hypothesis is suggested by the comparison with the data of lattice calculations for the equilibrium distribution of methanol clusters.

1. Introduction

Methanol/Carbon tetrachloride mixtures are interesting model systems for the study of the effects of molecular association due to H-bonding [1]. Very recently a simple lattice model has been developed in order to analyze experimental data pointing out deviations of these solutions from regular ones. In particular, it has been shown that the static dielectric response [2] and the Raman spectral features in the OH stretching region [3], both at moderate-to-high alcohol dilutions, reflect complementary aspects of the same methanol cluster distribution. More specifically, the depletion of the static dielectric constant ε with respect to ideality in this dilution range is mainly due to the presence of a non-zero fraction η of methanol molecules aggregated in cyclic clusters (in fact a non-polar component made of polar molecules). The lattice calculations indicate a well defined energy E_h to be assigned to the H-bonds, in order to recover the η values consistent with the data.

On the other hand, the same E_h is yielded by the analysis of the Raman data, which probe the fraction ψ of non H-bond accepting methanol molecules (i.e. either non H-bonded ones or open-chain end ones). Indeed, the fractions of ψ and η are related by:

$$(1) \quad \psi \simeq \frac{1 - \eta}{\langle n_{open} \rangle},$$

where $\langle n_{open} \rangle$ is the average aggregation number of the open chains. It is a considerable proof of consistency the fact that the same cluster distribution is able to fit the data of such different responses like dielectric and Raman at one time.

In a first version of the model, the non-polar component (i.e. CCl_4) was treated as a non-structured filler of the voids left empty by the volume fraction ϕ of methanol contained

in a given volume V of the solution. In this approximation the H-bonding energy was found to be $E_h \simeq 3.2$ kcal/mol, which however differs from the results of both numerical simulation [4] ($E_h \simeq 5.5$ kcal/mol) and calorimetric analysis [5] ($E_h \simeq 4 - 5.5$ kcal/mol). More recently, the effect of a relatively strong interaction between CCl_4 and the non-bonding lone pairs of the methanol oxygen has been accounted for in an improved version of the model [6]. The main effect of this sort of “heterogeneous association” is of introducing a correction term in the configurational entropy, which is associated to the number of ways a fraction of CCl_4 molecules can be chosen to couple with methanol. By using the new version of the model for a further analysis of both dielectric and Raman data, a unique value of $E_h \simeq 6$ kcal/mol was obtained [6], in better agreement with calorimetry and simulation.

In the present article we put forward the possibility that the heterogeneous association process may also underlie another anomaly in the dielectric response of these systems, namely, the positive excess dielectric constant of high- ϕ mixtures with respect to ideality.

2. Main features of the dielectric behavior and theoretical backgrounds

The details of the experiment are reported in Ref. [2]; here we limit ourselves to reproduce the dielectric response data in Fig. 1. The solid straight line represents what we mean here by ideal behaviour:

$$(2) \quad \varepsilon_{id} \equiv \phi \varepsilon_a + (1 - \phi) \varepsilon_s,$$

where $\varepsilon_a = 32.5$ and $\varepsilon_s = 2.2$ are the bulk (relative) dielectric constants at room temperature of methanol and CCl_4 , respectively. This linear dependence is indeed almost indistinguishable from what is found by Onsager theory [7] for a mixture of a non-polar solvent (solute) with a polar, non-associating solute (solvent). In the present case the Onsager prediction for the ε vs. ϕ dependence can be fairly well approximated by the solution of the equation

$$(3) \quad \frac{(\varepsilon - \varepsilon_\infty)(2\varepsilon + \varepsilon_\infty)}{\varepsilon(\varepsilon_\infty + 2)^2} = \frac{4\pi\mu_{\text{eff}}^2}{9k_B T v_a} \phi,$$

where v_a is the molecular volume of methanol, T is the temperature and k_B is the Boltzmann constant; the dielectric constant at optical frequencies ε_∞ has been considered to be the same for both the components and equal to ε_s . The quantity μ_{eff} is an effective dipole moment associated to each polar molecule in the mixture. Every significant deviation from ideality (linearity) in the actual ε vs. ϕ dependence is attributed here to the association mechanism.

Following Kirkwood [8] the explicit form of μ_{eff}^2 is

$$(4) \quad \mu_{\text{eff}}^2 = \mu_0^2 g_K$$

where μ_0 is the dipole moment of a single methanol molecule and g_K is the so-called Kirkwood correlation factor. For methanol $\mu_0 = 1.7$ D in its gas phase; but in the liquid phase a larger value of ~ 2.4 D is indicated by simulations [9]. Only recently an appropriate analysis of the temperature dependence of ε in pure methanol allowed for the deduction of $\mu_0 = 2.2/2.4$ D entirely from experimental data. Last result was rendered possible by expressing g_K in terms of the single-H-bond conformational partition function Z_c , whose

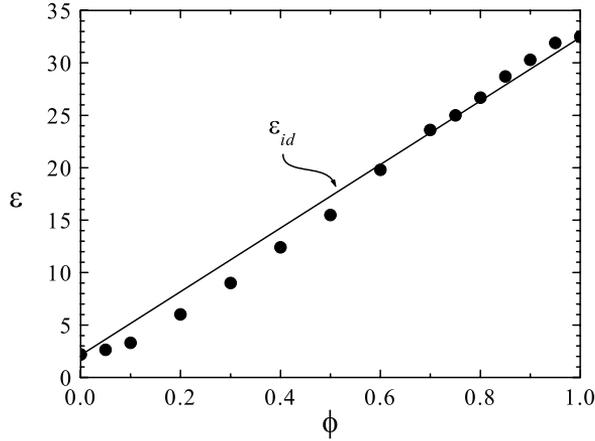


FIGURE 1. Static dielectric constant ε for selected values of the methanol volume fraction ϕ at room temperature. The solid line represents the ideal behavior described by eq. 2. The error bars are of the same size of the markers or smaller.

T -dependence is known [10]. For a methanol molecule being part of a virtually infinite open chain, the approximate form of g_K is:

$$(5) \quad g_K \simeq \frac{Z_c + 1}{Z_c - 1}$$

In order to generalize eq. 3 to the case of an associating polar component we simply consider that the Kirkwood factor is zero for all methanol molecules belonging to cyclic clusters. Thus any methanol molecule whatsoever has a correlation factor given by g_K times the probability p that *it is not* part of a cyclic cluster. Since the fraction of cyclic methanol is η , we have $p = (1 - \eta)$ and the term

$$(6) \quad \mu_{\text{eff}}^2 = \mu_0^2 g_K (1 - \eta)$$

has to be substituted in eq. 3 to account for the association of methanol.

Figure 2 reports the η vs. ϕ dependence as predicted by the model in its former version [2, 3] (dashed line), i.e. without accounting for the heterogeneous association mechanism. This calculation has been carried out for $E_h \simeq 3.2$ kcal/mol, which is appropriate to fit the low- ϕ dielectric data [2] (the value $E_h \simeq 4.2$ kcal/mol is reported in ref. [2], but an improved calculation procedure yields ~ 3.2 kcal/mol from the analysis of the same data). Note the rather pronounced increase of η as ϕ approaches the low- ϕ region from above, as only an effect of a balance between entropy loss and energetic stability gain in aggregation. (For $\phi \rightarrow 0$ of course η will tend to zero eventually, since the methanol molecules are then too much dispersed to form clusters.)

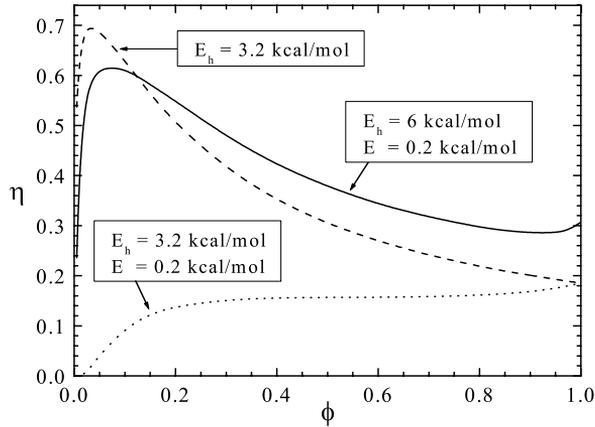


FIGURE 2. Fraction η of methanol aggregated in cyclic clusters as a function of the methanol volume fraction ϕ . The dashed line refers to the calculation carried out without including heterogeneous association, but with an H-bonding energy appropriate to fit both dielectric and Raman data at low- ϕ [2, 3]. The solid line is obtained accounting for heterogeneous association (to which an interaction energy $E = 0.2$ kcal/mol is assigned), along the lines described in ref. [6]; $E_h = 6$ kcal/mol is appropriate to the dielectric and Raman data. Note the inversion of $d\eta/d\phi$ at high- ϕ in the latter case. The dotted line shows the result of accounting for heterogeneous association, but with the H-bonding energy appropriate to fit the data with the former version of the model [2, 3].

3. The high- ϕ anomaly

Figure 1 shows that $\varepsilon > \varepsilon_{id}$ in the $0.8 < \phi < 1$ range. In a first attempt to explain this behavior [11], it was assumed that a quasi-static dipole moment could be gained by the CCl_4 molecules interacting with the terminal methanol molecules of open chains. Indeed, a perturbation of the charge distribution in these CCl_4 molecules was thought to accompany the rather strong interaction with methanol observed by calorimetry [5]. The problem of this assumption is, however, the exceedingly high value to be assigned to the CCl_4 dipole in order to recover the observed deviation in ε . Even after developing the lattice model in its first version [2, 3], this was the only available picture, because $d\eta/d\phi < 0$ in the high- ϕ region (dashed line of Fig.2). In other words, the formation of cyclic clusters would cause again negative deviations from ε_{id} at high ϕ , in contrast with the observations.

4. Role of heterogeneous association

As mentioned in the Introduction, the mechanism of heterogeneous association affects the equilibrium cluster distribution through a configurational entropy contribution associated to CCl_4 . What is the effect to be expected at the outset? Consider initially the case where heterogeneous association is disregarded and only homogeneous association (i.e. between just methanol molecules) is effective. When two independent methanol molecules undergo mutual association, both loose translational entropy. If N_t is the number of lattice sites in which the volume V is ideally partitioned, the configurational entropy associated to the molecules before association (state I) is

$$(7) \quad S_a^{\text{I}} = k_B \ln N_t^2 z^2,$$

where z is the lattice coordination number. On the other hand, after association (state II) the entropy of this two-molecule cluster reduces to

$$(8) \quad S_a^{\text{II}} = k_B \ln N_t z^2,$$

assuming no hindering effect of the H-bond on the mutual orientations of the molecules. Thus, the entropy change $\Delta S_a \equiv S_a^{\text{II}} - S_a^{\text{I}}$ is negative and the association process takes place only if the energy of this two-molecule system suitably drops. This is in fact the role of the H-bonding. The aggregation process proceeds following the same pathway until an appropriate balance between entropy loss and energy drop is reached. The same mechanism controls the balancing of the population of open and closed clusters. Indeed, the number of chain conformations decreases drastically in passing from open to closed configurations. Again this entropy loss, which increases with the number m of molecules forming the cluster, may or may not be compensated by a corresponding drop in energy (E_h in this case).

Consider now heterogeneous association. When a cyclic chain made of m molecules opens at one point, then both its configurational entropy $S_a(m)$ and the overall energy E increase by $\Delta S_a(m)$ and $\Delta E = E_h$, respectively. However, if at the same time, say, one CCl_4 molecule also associates to the appropriate chain end, then there is not a unique physically distinguishable state for the CCl_4 population anymore. Conversely, the possibility to chose which CCl_4 molecule actually associates, increases the number of physically distinguishable settlements of the non polar component of the mixture. Thus, a further entropy contribution $\delta S_s (> 0)$ must be added to $\Delta S_a(m)$, and an E_h value larger than before is needed to balance the actual entropy changes accompanying aggregation in general.

Now, in the balancing of open and cyclic clusters' population established by E_h at $\phi = 1$, no such entropy δS_s even exists. But when small amounts of CCl_4 are introduced, then the δS_s does exist and starts to increase. The distribution of methanol between the classes of open and cyclic aggregates consequently deviates from the case where δS_s was assumed to be zero, i.e. in the hypothesis that no heterogeneous association is effective.

It is not possible to draw a simple picture of the effect on the whole aggregate distribution just on the basis of single-cluster arguments, because of the different pathways the system has to compensate the variation due to the CCl_4 association on the configurational entropy changes connected to aggregation. The final result, however, is the necessity to increase E_h in order to maintain given values of η when δS_s is introduced. This is best

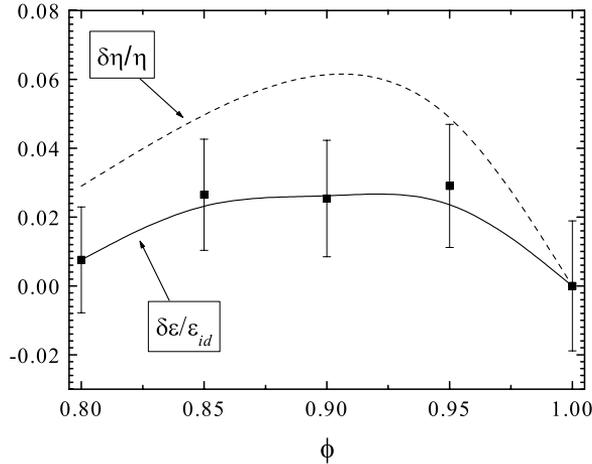


FIGURE 3. Relative deviations of ε and η with respect to the $\phi = 1$ values in the high- ϕ concentration region. Note that the error bars have been drawn considering as standard deviation the size of the symbols of Fig. 1

seen in Fig. 2, where the calculations of similar η vs. ϕ behaviors derived by either including CCl_4 association or not (solid and dashed lines respectively), are compared. The case where heterogeneous association is considered, but with an energy appropriate to fit the data with the former version of the model ($\delta S_s = 0$) is plotted by a dotted line. The necessity to increase E_h in order to recover the η values implied by the data, is evident from the comparison of the solid and dotted lines.

Note that when heterogeneous association is accounted for, $d\eta/d\phi > 0$ on approaching $\phi = 1$. This reflects the fact that heterogeneous association favours the rupture of cyclic clusters, as was pointed out above considering the increase of E_h necessary to obtain the two similar η vs. ϕ profiles of Fig.2 (solid and dashed lines).

In conclusion, the fraction of methanol aggregating in *open* clusters at ϕ slightly less than 1, is actually larger than in the occurrence of an ideal behavior at high- ϕ , that is, if η had remained constant after mixing.

From the data of Fig.1, and the calculation carried out in Fig.2, we find the ϕ dependencies of $\delta\varepsilon/\varepsilon_{id}$ and $\delta\eta/\eta$ reported in Fig.3, where $\delta\varepsilon \equiv \varepsilon - \varepsilon_{id}$, and $\delta\eta \equiv \eta|_{\phi=1} - \eta(\phi)$

If we assume that the contributions to ε of the polar and non-polar components in the liquid are simply additive (*i.e.* in the same spirit of eq. 2), then the fact that $\delta\varepsilon/\varepsilon_{id}$ and $\delta\eta/\eta$ are of the same order suggest that the fractional increase of polar component, due to the rupture of cyclic clusters caused by heterogeneous association (*i.e.* $\delta\eta/\eta$), may well be the major responsible of the observed $\delta\varepsilon/\varepsilon_{id}$.

5. Conclusion

The analysis carried out above points out the relevance of the heterogeneous association mechanism in determining the non-ideal behavior of the dielectric response of concentrated methanol-in- CCl_4 mixtures. Probably the gain of a dipole moment by associated CCl_4 molecules is also effective, but the influence of heterogeneous association on the cluster distribution seems to be even more important. Certainly, the rather impressive consistency between $\delta\varepsilon/\varepsilon_{id}$ and $\delta\eta/\eta$ confers to the mechanism of rupture of cyclic cluster a larger margin of confidence in the explanation of the $\varepsilon > 0$ anomaly.

As a further check of the present hypothesis it would be important to see whether the model is able to follow the changes of the ε vs. ϕ dependence on T . Although it is known that g_k decreases with increasing T (see eqs. 6 and 13 of [10]) and that the η convexity in the high- ϕ region can be calculated [6], sets of measurements at different temperatures are not available at present, so we leave this point open.

The conclusion is that both the above mechanisms, and possibly also the dependence of g_K on the average aggregation number, need be investigated more deeply if a definitive answer to the question has to be found. Preliminary account on this subject will be found in Ref. [12]. In this respect, however, also the effect of the alcohol alkyl tail length deserves being considered. Indeed, methanol is the only case, among n -alcohol/ CCl_4 mixtures, where a positive $\delta\varepsilon$ is observed [2], and since the alkyl tail does in fact influence the cluster distribution because of its steric hindrance effects, it is worth considering also this aspect in more detail.

References

- [1] V. A. Durov, *J. Mol. Liquids* **103-104**, 41 (2003).
- [2] M. Pieruccini, F. Saija, R. Ponterio and C. Vasi, *J. Chem. Phys.* **119**, 10771 (2003).
- [3] B. Fazio, M. Pieruccini, C. Vasi, *J. Phys. Chem B* **109**, 16075 (2005).
- [4] R. Veldhuizen and S. W. de Leeuw, *J. Chem. Phys.* **105**, 2828 (1996).
- [5] J.-E. A. Otterstedt and R. W. Missen, *Trans. Faraday Soc.* **57**, 879 (1962).
- [6] M. Pieruccini, *J. Phys. Chem. B* **110**, 18521 (2006).
- [7] L. Onsager, *J. Am. Chem. Soc.* **58** 1486 (1936).
- [8] J. G. Kirkwood, *J. Chem. Phys.* **7**, 911 (1939).
- [9] M. Haughney, M. Ferrario, and I. R. McDonald, *J. Phys. Chem.* **91**, 4934 (1987); T. Fonseca and B. M. Ladanyi, *J. Chem. Phys.* **93**, 8148 (1990); J. Gao, D. Habibollazadeh, and L. Shao, *J. Phys. Chem.* **99**, 16460 (1995); M. E. Martin, M. L. Sanchez, F. J. Olivares del Valle, and M. A. Aguilar, *J. Chem. Phys.* **116**, 1613 (2002); M. Pagliai, G. Cardini, R. Righini, and V. Schettino, *J. Chem. Phys.* **119**, 6655 (2003).
- [10] M. Pieruccini, F. Saija, *J. Chem. Phys.* **121**, 3191 (2004).
- [11] M. Pieruccini, F. Saija, C. Vasi and M. Musso, *Chem. Phys. Lett.* **382**, 523 (2003).
- [12] M. Pieruccini, F. Saija, *in preparation*.

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Presented: May 15, 2006
Published on line on January 17, 2007