

SHORT COMMUNICATIONS

DIFFUSION TENSOR OF A PLASMA

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THE knowledge of diffusion tensor is useful to study thermonuclear controlled fusion. Here expressions have been derived for the components of diffusion tensor of a weakly ionised plasma in the presence of steady electric and magnetic fields using the Grad 13-moment method. This method has already been applied to study viscosity tensor, electrical conductivity and thermal conductivity of a plasma¹⁻⁴. Calculations have been done using the algebra of irreducible spherical tensors. Unless otherwise specified, notations of paper⁴ (hereafter referred to as I) have been used.

Consider a weakly ionised plasma in the presence of steady electric field **E** and magnetic field **B**. The simplified Boltzmann equation for electrons⁵ is

$$\frac{\partial f}{\partial t} + \mathbf{c} \cdot \nabla f - \frac{e}{m} \mathbf{E} \cdot \frac{\partial f}{\partial \mathbf{c}} - (\mathbf{c} \times \boldsymbol{\Omega}) \cdot \frac{\partial f}{\partial \mathbf{c}} = -\nu(f - f_0) \quad (1)$$

where ν is the collision frequency assumed to be independent of velocity $\boldsymbol{\Omega}$ is the cyclotron frequency defined by

$$\boldsymbol{\Omega} = \frac{e}{m} \mathbf{B}.$$

As in paper I, the distribution function $f(\mathbf{r}, \mathbf{c}, t)$ is expanded as

$$f(\mathbf{r}, \mathbf{c}, t) = n w(\alpha \mathbf{c}) \sum_{\nu=0}^{\infty} \sum_{l=0}^{\infty} \sum_{m=-l}^l \times f_m^{(\nu l)}(\alpha \mathbf{r} t) \phi_m^{(\nu l)}(\alpha \mathbf{c}) \quad (2)$$

where $f_m^{(\nu l)}$'s are the moments of the distribution function, $\phi_m^{(\nu l)}$'s are the spherical harmonics and are related to the Grad Hermite polynomials³. The Grad thirteen moments correspond to the following values of $\nu = (\nu, l, m) = (000), (01m), (100), (02m)$ and $(11m)$.

Proceeding on the same lines as in paper I, the equation for the moment $f_m^{(01)}$ in the first approximation is

$$-\sqrt{2}[\boldsymbol{\Omega}^{(1)} \times f_m^{(01)}]^{(1)} + \nu f_m^{(01)} + d_m^{(1)} - \frac{2}{\alpha^2} c_m^{(1)} \alpha + \alpha(\mathbf{c} \times \boldsymbol{\Omega})_m^{(1)} + \frac{\alpha e}{m} E_m^{(1)} = 0. \quad (3)$$

The diffusion tensor D_{ij} is defined as

$$\sum_{j=1}^3 D_{ij} d_j = -\frac{1}{\alpha^2} \sum_{i=1}^3 (i/lm) \langle \mathbf{c}_m^{(1)} \rangle \quad (4)$$

where $\alpha^2 = m/KT$, (i/lm) is the transformation matrix.

Taking the magnetic field along z-axis and using (3) and (4) the expressions for the components of diffusion tensor in cartesian notation are

$$D_{11} = D_{22} = \frac{\nu KT}{m(\nu^2 + \Omega^2)}$$

$$D_{12} = -D_{21} = \frac{\Omega KT}{m(\nu^2 + \Omega^2)}$$

$$D_{33} = \frac{KT}{m\nu}$$

$$D_{13} = D_{31} = D_{23} = D_{32} = 0$$

The results are in complete agreement with those available in literature⁶ using different formulations.

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MUTUAL CORRELATION FACTOR IN BINARY MIXTURES OF ALCOHOLS AND TOLUENE

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SABESAN *et al*¹ in a study of Kirkwood-Fröhlich linear correlation factor², g , of mixtures of alcohols in

nonpolar solvents reported the existence of a solvent effect. Quantitatively they expressed this effect by introducing a parameter G^* whose value changes with the solute-solvent pair. Furthermore, the G^* value also changes as the concentration of alcohol in the mixture is varied. This probably suggests that alcohol molecules which are characterized by distinct local order have weak short-range dipolar interaction even with a nonpolar molecule having induced moment. In the present study, therefore, such interactions have been evaluated in the binary mixtures of some alcohols with a weak polar liquid, toluene (dipole moment = 0.36 D).

Considering both long-range and short-range dipolar interaction between identical and dissimilar molecules in a binary mixture, Winkelmann *et al*³ developed a relation linking the dielectric constant of a binary mixture with those of the components in the mixture. The mixture equation is given as,

$$\frac{\epsilon_m - 1}{\epsilon_m} V_m = \sum_{r=a,b} \frac{3\chi_r V_r (\epsilon_{\infty r} - 1)}{2\epsilon_m + \epsilon_{\infty r}} + \sum_{r=a,b} \left(\frac{\epsilon_{\infty r} + 2}{2\epsilon_m + \epsilon_{\infty r}} \right)^2 (2\epsilon_m + 1)$$

$$\frac{4\pi N}{9KT} \chi_r m_r^2 g_{rr} + \frac{(\epsilon_{\infty a} + 2)(\epsilon_{\infty b} + 2)(2\epsilon_m + 1)}{(2\epsilon_m + \epsilon_{\infty a})(2\epsilon_m + \epsilon_{\infty b})} \frac{4\pi N}{9KT} m_a m_b [g_{ab} - 1] \quad (1)$$

where a and b refer to the molecules of variety a and b . χ_r denotes the respective mole fraction of the component in the mixture, V_r and V_m denote the molar volumes of the components and the mixture respectively, N is the Avogadro number, K is the Boltzmann constant, T denotes temperature (K), m_r denotes the gas phase dipole moment of the component, ϵ_m is the dielectric constant of the mixture, $\epsilon_{\infty r}$ is taken as the square of the refractive index of the component, g_{rr} refers to the linear correlation factor between identical molecules, g_{ab} is the mutual correlation factor between dissimilar molecules.

The Kirkwood equation for pure material and also the Onsager's mixture equation⁴ where only long-range dipolar interactions are considered are found to be special cases of this equation. All but three terms in (1), i.e. g_{aa} , g_{bb} and g_{ab} are experimentally assessable. In the model proposed by Winkelmann *et al*³, it is presumed that g_{aa} and g_{bb} in the mixture are identical with their values in the pure liquids. Reducing (1) to the form of Kirkwood equation we have calculated the value of linear correlation factor for alcohols as well as for toluene, though its value in case of the latter is

usually taken as unity in the literature. Thus, the mutual correlation factor g_{ab} between the alcohol molecules and toluene molecules are calculated over the entire concentration range. The results are presented in table 1. The gas-phase dipole moment values have been taken from the Handbook of Chemistry & Physics—58th edn., CRC Press.

The dielectric constants have been measured at 455 kHz by an oscillator-wavemeter combination for low-loss mixtures. For medium and high-loss mixtures a device similar to the one used by Davies *et al*⁵ has been used. All measurements were done at 34°C and the temperature was controlled by electronic thermostatic arrangement with temperature variation of $\pm 0.1^\circ\text{C}$. The density was measured with a semi-

Table 1 Mutual Correlation factor in binary mixture at 307 K.

| Mole fraction of the alcohol in the mixture | ϵ_m | V_m cc | g_{ab} |
|---|--------------|----------|----------|
| (1) <i>n</i> -butanol + Toluene | | | |
| 0.115 | 2.751 | 106.18 | -0.04 |
| 0.226 | 3.409 | 104.28 | -0.73 |
| 0.334 | 4.687 | 102.41 | -0.72 |
| 0.438 | 5.536 | 100.75 | -1.24 |
| 0.539 | 7.210 | 99.03 | -0.86 |
| 0.637 | 8.887 | 97.32 | -0.59 |
| 0.732 | 10.889 | 95.02 | -0.07 |
| 0.824 | 12.957 | 94.80 | +0.73 |
| (2) Methanol + Toluene | | | |
| 0.220 | 3.560 | 93.20 | -0.54 |
| 0.389 | 5.050 | 82.18 | -1.44 |
| 0.522 | 7.416 | 73.22 | -1.60 |
| 0.629 | 10.217 | 66.32 | -1.38 |
| 0.718 | 12.375 | 60.60 | -1.62 |
| 0.793 | 16.122 | 55.73 | -0.90 |
| 0.856 | 20.781 | 51.65 | -0.79 |
| (3) <i>n</i> -propanol + Toluene | | | |
| 0.039 | 2.416 | 106.72 | +0.55 |
| 0.091 | 2.557 | 104.97 | +0.02 |
| 0.220 | 3.281 | 100.74 | -0.85 |
| 0.331 | 4.449 | 97.25 | -1.07 |
| 0.429 | 5.512 | 94.03 | -1.37 |
| 0.503 | 6.831 | 91.65 | -1.15 |
| 0.549 | 7.864 | 90.15 | -0.85 |
| 0.601 | 9.065 | 88.46 | -0.52 |
| 0.642 | 10.011 | 87.13 | -0.31 |
| 0.730 | 12.474 | 84.33 | +0.44 |
| 0.827 | 14.755 | 81.15 | +0.71 |
| 0.869 | 15.817 | 79.10 | +0.74 |
| 0.914 | 17.000 | 78.41 | +1.00 |

microbalance with a pycnometer of 25 ml capacity. The refractive indices were measured by a Pulfrich refractometer for sodium-D line. Chemicals used were of reputed make, purified and redistilled before use. The experimental values were reproducible within limits of reasonable experimental error so as not to affect the calculated values of g_{ab} (table 1).

It is expected that the two dissimilar molecules in the mixture form microheterogeneous clusters that vary in composition over the entire concentration range of the components in the mixture. The magnitude of g_{ab} reflects at least qualitatively the relative arrangement of these dissimilar molecules in those clusters. When the dissimilar molecules align in the same direction (co-operative angular correlation) they are said to form α -clusters and the value of g_{ab} comes out to be greater than unity. Alignment in opposition (destruction of angular correlation) results in formation of β -clusters for which the value of g_{ab} is less than unity. A perusal of table 1 indicates that β -clusters appear to be predominant in all the mixtures studied. The alcohol molecules in the pure state are arranged in homogeneous clusters of at least three molecules⁶. There are molecular size holes or voids^{7,8} in such structures. But the toluene molecules have no such clustering tendency. As the concentration of alcohol increases, some of the toluene molecules go to fill the voids in alcohol structure while maintaining anti-parallel alignment. This is manifested by gradual decrease in the value of g_{ab} reaching a minimum somewhere in the mid-range. Apparently, the α -clusters are predominant over clusters in these cases.

In mixtures (not reported here) of toluene with non-associated liquids such as chlorobenzene, methylbenzoate, ethyl benzoate, the value of g_{ab} comes out close to unity indicating no tendency for clustering of dissimilar molecules in such binary mixtures.

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EXTRACTIVE SPECTROPHOTOMETRIC DETERMINATION OF TRACE AMOUNTS OF PALLADIUM WITH BENZYLDIMETHYLPHENYLAMMONIUM CHLORIDE

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BENZYLDIMETHYLPHENYLAMMONIUM chloride, a quaternary ammonium salt possesses considerable potentiality to find application as a reagent for the determination of a number of metal ions when present in trace amounts in solution. Use of this reagent for detection of large anions, viz CrO_4^{2-} , $\text{S}_4\text{O}_6^{2-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, and I^- and for the spectrophotometric determination of Co(II), Fe(III), Cu(II), Mo(V) and Bi(III) has been reported¹⁻³. In this paper, we present a method for the extractive spectrophotometric determination of palladium in microamounts using benzyldimethylphenylammonium chloride as the reagent and 1,2-dichloroethane as the solvent for extraction.

Absorbance was measured with a Hilger Uvispek photoelectric spectrophotometer in matched quartz cells of 1 cm optical path.

Standard solution

A stock solution was prepared by dissolving Palladium(II) chloride (Johnson Matthey, London) in distilled water containing a few drops of HCl and was standardized by the known method⁴. Test solutions of lower concentration were prepared by appropriate dilution of the stock.

Reagents

The reagent, benzyldimethylphenylammonium chloride was prepared by mixing equimolar amounts of benzyl chloride and dimethylaniline and allowing the mixture to stand until a crystallisation was effected. The solid after washing with acetone was recrystallized from alcohol.

A 0.01 M (0.24%) aqueous solution of benzyldi-