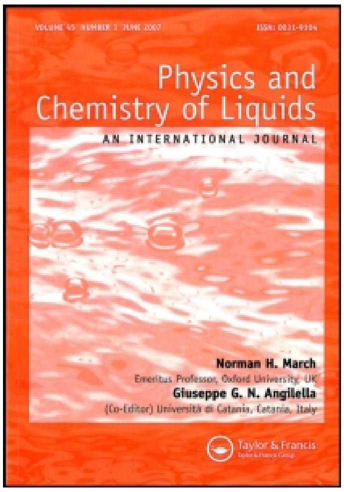

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Dielectric Relaxations of Binary Mixtures—a Correlation of the Component Relaxations with the Binary Systems

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The permittivity data, ε' and ε'' have been used to evaluate the dielectric relaxation times τ_F (Fröhlich's relation) for six polar molecules and their binary mixtures in dilute solutions. The τ_F so obtained have been compared with the τ_G (G. Krishna relation) values reported earlier. The two parameters have been found in good agreement, showing that Fröhlich's equation is equally applicable for determining the relaxation times of simple molecules in dilute solutions at a fixed frequency. The behaviour of individual molecules in relation to their binary mixtures have widely been investigated. A correlation between the relaxation times of the component molecules and their mixtures has been proposed recently by Madan. The proposed relation has been applied to a few rigid systems to yield satisfactory results. However, with a view to explore the applicability of the proposed relation further, six polar molecules and their mixtures were examined for their relaxation behaviour using the above relation. The enthalpies associated with the mechanism were also determined. Comparison of the experimental and theoretically calculated parameters, exhibit an excellent agreement.

INTRODUCTION

It is well known that single frequency method for determining the dielectric relaxation times gives an average effect representing an over all relaxation for simple systems. However, if the molecules under investigation are of rigid type, the method provides quite an accurate data. Many systems having small polar groups attached to it, have been investigated using the fixed frequency method and overall relaxation parameters have been reported. It has been observed that the assessment based on afforesaid technique gives valuable information which describes the behaviour of the molecules under applied field in a qualitative manner. We have used G. Krishna's[1] fixed frequency method for determining the relaxation time τ and the thermodynamical parameters for a number of systems and their mixtures in dilute solutions. Earlier investigation by Schallamach[2] on binary mixtures as a function of temperature at a single frequency reveals that the dielectric relaxation involves relatively large regions in the liquid indicating a single relaxation time for the system provided that the polar components of the binary mixtures are both associative or both nonassociative in nature. Since his initial work, only a few investigations have been made on the mixture of simple polar molecules. In contrast investigations by Kadaba,[3] Smyth,[4] Kilp[5] and Baba[6] on binary mixtures yielded two separate relaxation processes, provided the component molecules in the mixture has sufficiently different relaxation times. Results similar to that reported by Shallamach[2] were also supported by Denney[7] and Bos,[8] the latter work on the binary mixture of chlorobenzene and nitrobenzene. These studies have indicated either a broader dispersion giving rise to a single absorption or in some cases, two separate absorptions suggesting the dipolar rotations of the individual molecules comprising the system. Studies correlating the relaxation behaviour of the component molecules and that of mixtures have not been reported earlier.

Recently Madan[9] has proposed an empirical relation representing the relaxation behaviour of a system of two Debye type polar components in a non-polar solvent. This has been tested for a few rigid molecules in solutions. Comparison of the experimental relaxation times of the binary mixtures with those calculated using the proposed relation show an agreement for the rigid systems. However this empirical relation needs much further verification by a number of systems where the data exist.

We have investigated a number of molecules and their mixtures for dielectric dispersion behaviour in dilute solutions. The dielectric relaxation times were calculated using G. Krishna's method. Fröhlich's equation may also be used for determining the dielectric relaxation time of the rigid systems in dilute solutions at a single frequency. Since all the single frequency measurements give rise to an overall effect of relaxation mechanism, we have evaluated the dielectric relaxation times using this method also. The thermodynamical parameters have been determined using these relaxation data and a comparison with the earlier results has been made.

We have applied Madan's relation for the systems studied using G. Krishna's method and presently using Fröhlich's relation on several polar molecules and their binary mixtures in dilute solutions.

THEORY

G. Krishna Method

The dielectric relaxation times of the individual molecules and their mixtures in dilute solutions have been determined using the following equations of G. Krishna[1]

$$\tau = \frac{\lambda}{2\pi c}\frac{\mathrm{d}y}{\mathrm{d}x} \qquad (1)$$

$$x = \frac{\varepsilon'^2 + \varepsilon''^2 + \varepsilon' - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad (2)$$

$$y = \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} \qquad (3)$$

where λ is the free space wavelength, ε' is the dielectric constant and ε'' the loss factor.

Method Based on Fröhlich Equation

The frequency dependence of complex dielectric constant ε^* of the systems having single relaxation process can be described by the Fröhlich's equation

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau} \qquad (4)$$

If the measurements are made in dilute solutions and we consider small molecular systems exhibiting an overall rotation at a fixed frequency, the above relation, on separating into the real and imaginary parts gives

$$\varepsilon' = \varepsilon_\infty + \frac{1}{\omega\tau}\varepsilon'' \qquad (5)$$

Since the measurements are taken for very dilute solutions, ε_∞ may be treated as a constant and if this is the case the plot of ε' vs. ε'' would be a straight line and τ can be evaluated from its slope. This equation has been applied previously for rigid molecules, however, this can be applied to small flexible polar molecules presuming that an average effect of the dielectric dispersion shall be observed. Jai Prakash[10] have used Fröhlich's equation for determining the dielectric relaxation of some rigid systems.

Model Describing the Relaxation Process of Liquid Mixtures

With a view to obtain sufficient information about the relaxation process of liquid mixtures, Madan[9] has suggested a simple relation describing the mechanism. If the liquid mixture comprises of two similar systems, the dielectric behaviour of the mixture tends to be the resultant of the behaviours of each polar solute in the solvent. In general, if the liquid mixture comprises of a number of rigid polar molecules in dilute solutions, the apparent relaxation time of the mixture can be represented by a relation of the type

$$\frac{1}{\tau_a} = \sum_j \frac{A_i}{\tau_i} \tag{6}$$

where A_i is the parameter representing the effect of molecular environment, shape and size, viscosity, fractional volumes, solute-solvent interactions and other factors affecting the dipole reorientation. Since, the measurements are made in sufficiently dilute solutions, the solute-solvent interaction term can be neglected. If we consider that the weight of a particular relaxation process depends upon the square of the associated dipolemoments, the ith constituent of A may be written as

$$A_i = \frac{C_i \mu_i^2}{\sum_i C_i \mu_i^2} \tag{7}$$

Where C_i is the parameter involving effects other than those due to dipole moments μ_i. For a binary system Eq. (6) takes the form

$$\begin{aligned} \frac{1}{\tau_a} &= \frac{1}{\tau_1} \cdot \frac{C_1 \mu_1^2}{(C_1 \mu_1^2 + C_2 \mu_2^2)} + \frac{1}{\tau_2} \cdot \frac{C_2 \mu_2^2}{(C_1 \mu_1^2 + C_2 \mu_2^2)} \\ &= \frac{1}{\tau_1} \cdot \frac{C \mu_1^2}{(C \mu_1^2 + \mu_2^2)} + \frac{1}{\tau_2} \cdot \frac{\mu_2^2}{(C \mu_1^2 + \mu_2^2)} \end{aligned} \tag{8}$$

If $C_1/C_2 = C$, the parameter C_i may be taken approximately equal to the molar volume V_i for the solute systems. For the binary system having similar shape and size, C may be taken as unity and thus Eq. (8) reduces to

$$\frac{1}{\tau_a} = \frac{\mu_1^2/\tau_1 + \mu_2^2/\tau_2}{\mu_1^2 + \mu_2^2} \tag{9}$$

Equations (8) and (9) have been applied for simple systems both rigid and slightly flexible types in dilute solutions. The concept of overall rotation in such systems seems to hold true when measured at a fixed frequency. Madan[9] has applied the relation for the relaxation behaviour of four rigid molecules and their binary mixtures. This has given satisfactory results as the experimental and calculated relaxation time parameters for the binary systems are in good agreement. It however, needs much further testing by applying the relation to the binary mixtures of simple systems. We have applied this relation on six polar molecules and their binary mixtures in dilute solutions, for which the relaxation time data were available and the measurements were made in our laboratory. Further, the relaxation times were calculated using Fröhlich's equation also and a comparison with the reported data using G. Krishna method was made. An agreement between the experimental and calculated parameters using the proposed model has been observed. In order to investigate further, the applicability of the proposed model, the thermodynamical parameters have been evaluated using both the τ_a and τ_F values.

EXPERIMENTAL

The dielectric constant ε' and the losses ε'' for all the six systems and their mixtures were determined using Von-Hippel's[11] technique later modified by Dakin and Works.[12] The G. Krishna relaxation times and thermodynamical parameter were taken from our earlier work.[13–16,17] The dielectric relaxation times (τ_F) using Fröhlich's equation were determined using ε' and ε'' data. Thermodynamical parameters were evaluated using τ_F values also. The dipole moments of the solutes were calculated using the group moments taken from the literature.[18,19]

RESULTS AND DISCUSSION

The dielectric data of *o*-methoxybenzaldehyde yields a relaxation time τ_F of 20.6 ps at 298 K. This is in agreement with the observed τ_G value of 19.9 ps at the same temperature. Similar results have been observed for the relaxation time values at other temperature also.

For *p*-methoxybenzaldehyde, Fröhlich's equation yields a τ_F of 14.8 ps which is in close agreement with the τ_G of 14.9 ps at 298 K. In this case also similar results have been observed at other temperatures under investigation.

It may be seen from Table I that for all the molecular systems, the τ_G and τ_F values are in close agreement. This shows that for simple systems the Fröhlich's equation is equally applicable for determining the relaxation time parameters.

Comparison of τ_F and τ_G Data for Binary Mixtures

The binary mixture, *o*-methoxybenzaldehyde + 3-fluorophenol yields a dielectric relaxation time τ_F of 16.5 ps at 298 K when determined using Fröhlich equation. This value is very close to the τ_G value of 15.0 ps at the abovementioned temperature. A close resemblance between τ_F and τ_G has been observed for the measurements at other temperatures also.

TABLE I

Dielectric relaxation times and enthalpy parameters of component molecules

Temperature K	Dipole moment μ (D)	τ_G ps	τ_F ps	ΔH_ε (τ_G) K cal mol^{-1}	ΔH_F (τ_F) K cal mol^{-1}
		o-methoxybenzaldehyde			
298		19.9	20.6		
303	1.41	17.4	18.9	2.3	2.9
308		16.2	16.5		
313		14.9	14.8		
		p-methoxybenzaldehyde			
298		14.9	14.8		
303	2.03	13.3	14.4	2.2	1.4
313		11.6	13.2		
		3-fluorophenol			
298		14.1	14.1		
303	2.0	13.3	13.7	1.7	1.7
308		12.5	13.3		
313		12.2	12.4		
		2-fluoroanisole			
298		14.9	—		
303	1.32	14.1	—	1.8	—
		1,2,4-trichlorobenzene			
298		17.4	18.3		
308	1.24	15.8	15.4	1.5	1.7
313		14.5	15.0		
		4-fluoroanisole			
293		17.4	17.9		
298	1.92	16.3	—	0.8	0.9
306		15.8	15.4		
314		14.9	14.9		

The τ_F of 14.0 ps for the binary mixture, *p*-methoxybenzaldehyde + 3-fluorophenol is in agreement with the τ_G value of 12.4 ps at 298 K. Similar results have been observed for the liquid mixtures of 2-fluoroanisole + 1,2,4-trichlorobenzene, 4-fluoroanisole + 3-fluorophenol and 4-fluoroanisole + 1,2,4-tri-chlorobenzene.

On the Applicability of the Proposed Relation for the Binary Mixtures

As has been mentioned earlier, if the dielectric relaxation times, dipole-moments and the molar volumes of the component molecules of the mixture

TABLE II

Dielectric relaxation times and enthalpy parameters of the binary mixtures

Temperature K	τ_G ps (exptl.)	τ_F ps (Fröhlich)	τ_a ps (using G. data)	τ_a ps (using Fröhlich data)	ΔH_ε (τ_G) K cal mol^{-1}	ΔH_ε (τ_a G data) K cal mol^{-1}
o-methoxybenzaldehyde + 3-fluorophenol						
298	15.0	16.5	15.9	15.7		
303	14.5	15.7	14.7	15.1	1.6	1.6
308	13.2	14.8	13.7	14.2		
313	12.4	12.4	13.2	13.2		
p-methoxybenzaldehyde + 3-fluorophenol						
298	12.4	14.0	14.6	14.4		
303	11.5	13.2	13.3	14.0	1.6	1.8
308	10.7	12.3	—	—		
313	9.2	—	11.9	—		
o-methoxybenzaldehyde + *p*-methoxybenzaldehyde						
298	18.0	18.9	16.3	16.3		
303	17.2	—	14.4	15.6	1.2	—
308	16.4	17.7	—	—		
313	16.1	16.5	12.5	13.7		
3-fluorophenol + 1,2,4-trichlorobenzene						
298	13.5	13.2	15.1	11.9		
303	12.5	12.2	—	—	1.9	
308	11.6	11.5	13.5	13.8		
2-fluoroanisole + 1,2,4-trichlorobenzene						
298	14.9	11.9	16.1	—		
303	14.5	11.1	14.9		1.2	—
308	13.5	9.9	—	—		
4-fluoroanisole + 3-fluorophenol						
298	15.3	13.2	15.1			
303	14.4	11.9	14.5	—	1.4	1.1
308	13.6	11.1	14.0	14.2		
4-fluoroanisole + 1,2,4-trichlorobenzene						
298	16.6	13.6	16.7	—		
303	16.2	11.9	—	—	3.0	—
308	13.3	11.1	15.8	15.4		
4-fluoroanisole + 2-fluoroanisole						
298	14.6	14.8	15.8	—		
303	13.5	13.6	15.2	—	1.9	—
308	12.6	12.4	—	—		

are known, an estimate of the relaxation time of the mixture (τ_a) can be made using a relation.

$$\frac{1}{\tau_a} = \frac{1}{\tau_1}\,\frac{C\mu_1^2}{C\mu_1^2 + \mu_2^2} + \frac{1}{\tau_2}\,\frac{\mu_2^2}{C\mu_1^2 + \mu_2^2}$$

The equation has been applied for eight systems of binary mixtures.

The experimental relaxation time τ_G of 15.0 ps for the binary mixture of *o*-methoxybenzaldehyde + 3-fluorophenol has been found in close agreement with the calculated τ_a value of 15.9 ps using Eq. (8) at 298 K. Similarly, the τ_a of 14.7, 13.7 and 13.2 ps are comparable to τ_G values of 14.5, 13.2 and 12.4 ps respectively at 303, 308 and 313 K.

The binary system, *p*-methoxybenzaldehyde + 3-fluorophenol yields τ_G of 12.4, 11.5 and 9.2 ps which is in good agreement with the τ_a values of 14.6, 13.3 and 11.9 ps respectively at 298, 303 and 313 K.

The liquid mixture of *o*-methoxybenzaldehyde + *p*-methoxybenzaldehyde, which consists of the molecules of almost similar shape and size gives rise to a τ_a value of 16.3 ps at 298 K, whereas the τ_G obtained experimentally was 18.0 ps. The two parameters are in agreement within the experimental errors.

Similarly, 3-fluorophenol + 1,2,4-trichlorobenzene and 2-fluoroanisole + 1,2,4-trichlorobenzene systems give rise to a τ_G values of 13.5 and 14.9 ps at 298 K. These τ_G values may be compared with the calculated τ_a parameters of 15.1 and 16.1 ps respectively at the same temperature. Similar is the behaviour at all other temperatures under investigation.

The systems, comprising of 4-fluoroanisole + 3-fluorophenol and 4-fluoroanisole + 1,2,4-trichlorobenzene yield an experimental relaxation time (τ_G) of 15.3 and 16.6 ps which are in good agreement with τ_a values of 15.1 and 16.7 ps respectively at 298 K. For other temperatures investigated, the relaxation time data exhibits a good agreement.

Another system 4-fluoroanisole + 2-fluoroanisole, which has similar constituent molecules, gives a τ_G values of 14.6 and 13.5 ps respectively at 298, 303 K. The individual data when applied to the proposed model, yields the relaxation time (τ_a) of 15.8 and 15.2 ps respectively for the above mentioned temperature. The two values of τ_G and τ_a are again fairly in good agreement.

It may be seen from the observed data that in general fairly good agreement is reached in the experimental (τ_G) and theoretically calculated relaxation time (τ_a) for all the eight binary mixtures in the dilute solutions. The τ_a values calculated using Fröhlich's relaxation times also show a close agreement with the experimental relaxation times for the mixtures.

Enthalpy of Activation

The τ_F values calculated from the Fröhlich equation have also been tested for their temperature dependence by the evaluation of enthalpy of activation ΔH_F. The molecule *o*-methoxybenzaldehyde, yields a value of 2.9 K cal/mole for ΔH_F whereas the enthalpy value ΔH_ε for the relaxation times calculated using G. Krishna method, is 2.3 K cal/mole. The two values of enthalpy mentioned above do not exhibit appreciable difference. Similar results have been observed for other polar molecules also.

In order to assess further, the applicability of the proposed relation, the enthalpies associated with τ_G (experimental) and τ_a (calculated) for the mixture were evaluated and compared. It is observed that the first two binary mixtures of *o*-methoxybenzaldehyde + 3-fluorophenol and *p*-methoxybenzaldehyde + 3-fluorophenol yield experimental enthalpies of 1.6 K cal/mole each. This compares well with the enthalpies of 1.6 and 1.8 K cal/mole respectively determined using the corresponding τ_a values. Similarly, for the mixture of 4-fluoroanisole + 3-fluorophenol, $\Delta H_\varepsilon(\tau_G) \sim 1.4$ K cal/mole shows an agreement with the $\Delta H_\varepsilon(\tau_a) \sim 1.1$ K cal/mole. Enthalpies for other systems could not be evaluated due to non-availability of the common temperature data. The agreement exhibited by the observed enthalpy parameters further testifies the applicability of the proposed relation for the mixture.

CONCLUSION

The relaxation times using the Fröhlich equation have been evaluated and compared with those obtained from G. Krishna method. The results show an excellent agreement with the G. Krishna relaxation times both for the individual molecules and their mixtures.

The relation proposed by Madan for determining the relaxation time of the mixture of rigid polar components has been applied on the relaxation times evaluated from both, G. Krishna method and the Fröhlich equation. Equation (9) suggested by Madan has been applied for the molecules of nearly similar size and Eq. (8) on those having slightly different size and it was found that the results calculated were congruous to the relaxation times of the mixture observed experimentally. The results of enthalpy parameters also indicate that the proposed relation gives satisfactory results for simple systems.

Thus it appears that the model can be applied for simple systems where the relaxation of the mixture is exhibited by broadening of the dispersion curve rather than the separate relaxation peaks.

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References

1. K. V. Gopala Krishna, *Trans. Faraday Soc.*, **53**, 767 (1957).
2. A. Schallamach, *Trans. Faraday Soc.*, **42A**, 180 (1946).
3. S. K. Garg and P. K. Kadaba, *J. Physic Chem.*, **69**, 674 (1965).
4. E. Forest and C. P. Smyth, *J. Physic. Chem.*, **69**, 1392 (1965).
5. H. Kilp, S. K. Garg, and C. P. Smyth, *J. Chem. Physics*, **45**, 2799 (1966).
6. K. Baba, T. Fujimura, and K. Kamiyoshi, *J. Physic. Chem.*, **73** 1146 (1969).
7. D. J. Denney and R. H. Cole, *J. Chem. Physics*, **23**, 1767 (1955).
8. F. Bos, Doctoral dissertation, University of Leiden, Holland 1958.
9. M. P. Madan, *Can. J. Phys.*, **58**, 20 (1980).
10. Jai Prakash, *Ind. J. Pure and Appl. Phys.*, **8**, 106 (1970).
11. S. Roberts and A. Von Hippel, *J. Appl. Physics*, **17**, 610 (1946).
12. T. W. Dakin and C. N. Works, *J. Appl. Physics*, **18**, 789 (1947).
13. J. P. Shukla, S. I. Ahmad, D. D. Shukla, and M. C. Saxena, *J. Phys. Chem.*, **72**, 1013 (1968).
14. J. P. Shukla and M. C. Saxena, *Z. Physik. Chem. Neue Folge*, **83**, 205 (1973).
15. J. P. Shukla, R. L. Dhar, G. R. Gurnani, and M. C. Saxena, Z. Physik. Chem. Neue Folge, **85**, 76 (1973).
16. R. L. Dhar and J. P. Shukla, *Z. Physik. Chem. Neue Folge*, **84**, 25 (1973).
17. J. P. Shukla and M. C. Saxena, *Ind. J. Pure and Appl. Phys.*, **6**, 9, 492 (1968).
18. C. P. Smyth, *Dielectric Behaviour and Structure*, McGraw-Hill Book Company, New York 1955.
19. N. E. Hill, W. E. Vaughan, A. H. Price, and M. Davies. *Dielectric Properties and Molecular Behaviour*, Van Nostrand Reinhold Company, London 1969.