

Studies of linear correlation factor of dielectric polarization and excess dipolar free energies of amides in apolar solvents

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MS received 29 May 2004; revised 18 April 2005; accepted 25 April 2005

Abstract. The Kirkwood–Frohlich correlation factor (g), Eyring’s parameters G and G^* and the dipolar excess free energies of dilute solutions of formamide, acetamide, N -methyl acetamide, N,N -dimethyl formamide and N,N -dimethyl acetamide in 1,4-dioxan/benzene were obtained from a measurement of their static dielectric permittivities at 308 K. The fluid structure of these amides is discussed. Both in formamide and acetamide a dimeric linear chain with the individual dipoles more or less parallelly oriented is preferred. In N -methyl acetamide, the antiparallel orientation of dipoles at lower concentrations turns into a parallel orientation with increase of concentration. In tertiary amides, with increase of concentration, parallel orientation of dipoles with global value of g tending to unity is observed. The dipolar excess free energy of mixing in a given solvent is of the order primary amide > secondary amide > tertiary amide.

Keywords. Dielectric constants; amides; Kirkwood–Frohlich correlation factor; Eyring’s significant structure theory; dipolar excess free energies.

PACS Nos 42.25.Ja; 61.20.Ne; 61.25.Em

1. Introduction

Amides are the simplest molecules containing a peptide linkage and a study of their hydrogen bonding ability yields insight into the nature of protein structure. The role of non-covalent interactions in stabilizing polypeptide structure was studied by LCAO–MO–SCF method [1], X-ray diffraction [2] and NMR methods [3]. Amides are associated through inter-molecular hydrogen bonding and also show strong dependence on solvent environment, temperature and concentration [4,5].

To understand the molecular behaviour of associating molecules it is necessary to determine the various dielectric parameters which are related to inter- and intramolecular association and internal rotations with temperature variation [6]. The Kirkwood–Frohlich theory of dipolar liquids [7] defines the short-range dipolar interactions through a dimensionless parameter g . An extensive review of the early

work on the variation of g in liquids with concentration, temperature and solute environment was done by Bottcher [8]. Later work in the field was recently reviewed by Smyth [9]. Cyclic or linear multimerization of amides are easily detected by a measurement of concentration dependence of Kirkwood correlation factor. An increase in g is expected on linearization and a decrease in g on cyclization. However, there is a profound influence on g due to solvent–solute interactions which is not clearly established for substituted amides. The elucidation of the structure of the amide chains in different solvent environment is very important in the context of biological systems and the measured values of g reflects very much, the statistically averaged macroscopic fluid properties of these amides. Hence we have taken up the study of Kirkwood correlation factor and the related parameters of several primary, secondary and tertiary amides in the solution state in two different solvents.

2. Materials and methods

Acetamide, *N*-methyl acetamide and *N,N*-dimethyl acetamide were obtained from E Merck, Germany and used without further purification. AnalarR grade formamide, *N,N*-dimethyl formamide, dioxan and benzene were purified and used.

In the binary mixture of a dipolar liquid and an inert solvent, the Kirkwood correlation factor is obtained using the relation [8]

$$g = \frac{9kT(2\varepsilon_0 + \varepsilon_\infty)^2}{4\pi N_A \mu_2^2 X_2 (\varepsilon_\infty + 2)^2 (2\varepsilon_0 + 1)} \times \left[V \frac{\varepsilon_0 - 1}{\varepsilon_0} - 3X_1 V_1 \frac{(\varepsilon_1 - 1)}{(2\varepsilon_0 + \varepsilon_1)} - 3X_2 V_2 \frac{(\varepsilon_\infty - 1)}{(2\varepsilon_0 + \varepsilon_\infty)} \right],$$

where X_1 , V_1 , ε_1 are the mole fraction, molar volume and static dielectric constant of the solvent, X_2 , V_2 , ε_2 are that of the dipolar solute, ε_0 is the dielectric constant of the solution and N_A is the Avogadro's number. The high frequency limiting permittivity ε_∞ may be set equal to $1.1 n_D^2$, where n_D is the refractive index of the solution, allowing a 10% contribution of atomic polarization. μ_2 , the dipole moment of the solute in the gaseous state, is obtained from bond angle data available in [10]. Dielectric constants and refractive indices were measured using WTW dipolemeter DM01 at 2 MHz and Abbe's refractometer respectively at temperature 308 K.

Eyring's significant structure theory (SST) [11] based on lattice model, takes the short-range correlations in proportion to the relative population of domains oriented with a particular dipole vector. The term $\mu^2/3KT$ in Frohlich equation is replaced by $\mu^2 G/KT$. The values of G indicate the angular correlation parameter for the maximum polarization of domains and increase with increasing short-range correlations. In the case of mixtures of polar solute and non-polar solute, the domain theory is extended and a dimensionless parameter G^* is introduced. The change in value of G^* reflects the angular correlation of the islands of solute in the solvent environment [12].

The values for relative density ρ , the static dielectric constant ε_0 , the Kirkwood correlation factor g and Eyring's correlation parameters G and G^* for various concentrations of amides in dioxan/benzene are given in table 1.

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Table 1. Dielectric data for dilute solutions of various amides in non-polar solvents at 308 K.

Mole fraction of amides	Density ρ (g/cc)	ϵ_0	ϵ_∞	g	G^*	ΔF_0^E (J mole ⁻¹)
Formamide + 1,4-dioxan; $G = 0.659$						
0.017	1.025	2.479	2.006	0.8	0.51	346.1
0.025	1.026	2.663	2.008	0.9	0.46	489.3
0.033	1.026	2.831	2.008	0.9	0.42	618.6
0.041	1.027	3.021	2.008	1.0	0.41	731.4
0.049	1.029	3.221	2.008	1.0	0.40	830.3
0.057	1.029	3.435	2.009	1.0	0.39	915.9
0.064	1.029	3.662	2.009	1.0	0.39	990.1
0.072	1.030	3.864	2.011	1.1	0.39	1059.9
Acetamide +1,4-dioxan; $G = 0.654$						
0.025	1.021	2.655	1.911	1.1	0.67	257.8
0.033	1.022	2.786	1.911	1.1	0.58	328.8
0.041	1.023	2.923	1.913	1.1	0.52	391.8
0.049	1.024	3.050	1.915	1.0	0.48	451.5
0.057	1.025	3.173	1.915	1.0	0.45	506.5
0.064	1.026	3.315	1.915	1.0	0.43	554.0
0.072	1.027	3.426	1.917	0.98	0.40	601.9
0.079	1.028	3.577	1.918	0.98	0.39	639.9
<i>N</i> -Methyl acetamide + benzene; $G = 1.705$						
0.009	0.869	2.410	2.217	0.70	0.25	130.0
0.011	0.870	2.476	2.216	0.76	0.27	160.0
0.019	0.870	2.819	2.216	1.11	0.37	240.8
0.022	0.871	3.052	2.215	1.28	0.43	270.5
0.037	0.872	4.042	2.211	1.62	0.53	355.5
<i>N,N</i> -dimethyl formamide + benzene; $G = 0.383$						
0.009	0.869	2.421	2.222	0.8	0.37	91.1
0.011	0.870	2.456	2.222	0.8	0.36	108.2
0.018	0.870	2.602	2.222	0.9	0.34	169.7
0.021	0.870	2.673	2.221	0.9	0.34	197.7
0.026	0.870	2.778	2.219	0.9	0.33	239.4
0.035	0.871	2.963	2.217	0.9	0.33	298.5
0.051	0.872	3.252	2.214	0.9	0.30	402.7
0.067	0.874	3.654	2.211	0.9	0.31	472.5
0.083	0.875	4.148	2.207	1.0	0.33	514.0
0.083	0.876	4.290	2.205	1.0	0.33	524.6
<i>N,N</i> -dimethyl formamide + 1,4-dioxan; $G = 0.383$						
0.017	1.015	2.535	1.910	1.0	0.69	173.5
0.025	1.016	2.721	1.910	1.0	0.58	244.2
0.033	1.017	2.868	1.910	1.0	0.50	309.3
0.041	1.018	3.032	1.910	1.0	0.47	366.8
0.049	1.019	3.186	1.911	1.0	0.44	419.1
0.057	1.020	3.376	1.913	1.0	0.42	462.6
0.064	1.021	3.570	1.914	1.0	0.42	500.9
0.072	1.023	3.723	1.914	1.0	0.40	539.2

Table 1. Continued.

Mole fraction of amides	Density ρ (g/cc)	ϵ_0	ϵ_∞	g	G^*	ΔF_0^E (J mole ⁻¹)
<i>N,N</i> -dimethyl acetamide + benzene; $G = 0.515$						
0.005	0.869	2.320	2.223	0.6	0.36	39.6
0.010	0.869	2.414	2.223	0.8	0.36	76.1
0.019	0.870	2.591	2.222	0.9	0.34	142.7
0.037	0.871	2.982	2.219	1.0	0.34	247.8
0.055	0.873	3.383	2.215	1.0	0.34	326.3
0.071	0.874	3.783	2.213	1.0	0.34	383.9
0.088	0.875	4.119	2.208	1.0	0.32	432.9
<i>N,N</i> -dimethyl acetamide + 1,4-dioxan; $G = 0.515$						
0.016	1.014	2.476	1.996	1.0	0.54	128.2
0.035	1.017	2.858	1.998	1.0	0.40	254.4
0.052	1.018	3.260	2.001	1.0	0.38	337.1
0.068	1.021	3.699	2.002	1.1	0.38	397.4
0.076	1.022	3.947	2.002	1.1	0.38	420.8
0.084	1.022	4.178	2.003	1.1	0.38	441.9

3. Discussion

The dielectric constants of primary, secondary and tertiary amides differ widely in pure liquids and is largely attributed to the varied nature of short-range interactions leading to various types of multimerization. On dilution with non-polar solvents, one would expect the ‘structure breaking’ mechanism to dominate which is very similar to that of alcohols.

In formamide and acetamide the early *ab initio* SCF calculations [13] showed that the dominant species in the liquid phase is a cyclic dimer. We find that the Kirkwood correlation factor g is almost unity in dilute solutions of formamide and acetamide, which precludes the cyclic structure. It is obvious that a planar linear dimer is favourable as the energy difference between the two is extremely small [14]. (linear – 67.8 kJ mole⁻¹; cyclic – 63.2 kJ mole⁻¹). Further, entropy effects are more in open chain structure than in ring structure due to easier bond rupture between molecules in open chain structure. This structure makes open chain structure more favourable. Trimers and higher order multimers seem to be less important as the stabilization energies are lesser in them. It is clear that in both formamide and acetamide the nature of association is that the individual dipoles are more or less parallelly directed as can be seen from the large orientation polarization. Yet, there is a difference in polarization on going from formamide to acetamide. The computer simulation studies of Richardi *et al* [15] shows that the parallel orientation is dominating in formamide.

In secondary amides, g increases with increase of its concentration. The antiparallel orientation of dipoles are dominant ($g < 1$) in dilute solutions of *N*-methyl acetamide. As the concentration of the amide is increased, a parallel orientation of dipolar results ($g > 1$). The infra-red studies of this compound [16] showed that the absorption maximum of C=O at 1700 cm⁻¹ in dilute benzene solutions shifts to 1640 cm⁻¹ with increase of its concentration owing to H-bond between solute molecules. This is in agreement with our observation of the large increase in g . The

electron diffraction data [17] suggest a planar structure with a *trans* configuration with the methyl group rotating freely about the C–N bond axis due to this linear intramolecular dimerization with a consequent increase in g .

In N,N -dimethyl formamide and N,N -dimethyl acetamide, with increase of concentration, parallel configuration with a global value of g tending to unity is obtained. Raman and infra-red spectral studies of DMF by Fini and Mirone [18] showed that they form clusters oriented in a partially ordered way. However, the *ab initio* SCF studies of Vassiler and Dimitrov [19] indicated no such cluster formation in the liquid state and the dimer stabilization energy was found to be much smaller than that of formamide. This is in agreement with our observed values of g .

We have calculated the Eyring's parameter G and G^* . In primary and tertiary amides $G < 1$, it indicates the anti-parallel alignment of dipole is dominating and in the case of secondary amide $G > 1$, and hence the domains of linear multimers seems to be predominant. Our results G^* show that if benzene is used as the solvent the tertiary amides do not show any progressive realignment of dipoles and G^* is independent of the concentration of the solute. However when dioxan is used as a solvent, the values of G^* show an increasing trend on dilution, for all amides. Even in tertiary amides, where self-association is minimal, compared to primary and secondary amides, G^* progressively increases. This may perhaps be due to the interaction between the fractional positive charge of the nitrogen in DMF and DMA with dioxan. This interaction is less demanding in its geometrical environment around the solute species [20] than in benzene.

3.1 *The dipolar thermodynamic excess free energy of amides in dilute solutions*

In general, the breaking of H-bonds of liquids which are extensively self-associated produces positive contributions to enthalpies of mixing. The dipole–dipole interaction would add to this positive contribution [21]. The dipolar cohesive energy of a polar liquid consists of an interaction energy of the dipole, an interaction energy due to the surrounding molecule and an energy due to the polarization of the molecules. Hence the Helmholtz free energy $F = -KT \ln Z$, where Z is the canonical partition function. Hence dipolar energy change on mixing (ΔF^E) can be obtained by a proper choice of the partition function. The excess dipolar energy due to long-range electrostatic interaction is given by the reaction field R_f

$$\Delta F^E = -\frac{N}{2} \sum_{i=1,2} X_i \mu_i^2 (R_{fi} - R_{fi}^0) + \sum_{i=1,2} X_i^2 (g_{ii} - 1) (R_{fi} - R_{fi}^0).$$

The second term gives excess dipolar energy due to short-range interaction between similar molecules. g_{ii} is the Kirkwood's correlation factor. In amides, at dilute concentrations, g_{ii} tends to unity and hence major contribution to excess free energy is due to long-range interactions only. We have obtained ΔF^E for all the systems studied using Winklemann and Quitzsch [22] method. The reaction field factor of the pure liquids (R_{fi}^0) and that of the solution (R_{fi}) were obtained.

$$R_{fi}^0 = \left(\frac{8\pi N_A}{9V_i} \right) \frac{(\epsilon_i - 1)(\epsilon_{\infty i} + 2)}{(2\epsilon_i + \epsilon_{\infty i})}, \quad R_{fi} = \left(\frac{8\pi N_A}{9V_i} \right) \frac{(\epsilon_m - 1)(\epsilon_{\infty i} + 2)}{(2\epsilon_m + \epsilon_{\infty i})},$$

where ε_i and ε_m are the dielectric constants of the pure liquids and solution respectively and V_i is the molar volume. The results are given in table 1.

Even though the dielectric constants show a wide variation between primary, secondary and tertiary amides, the dipole moments do not differ much. Hence, contrary to alcohols, it can be safely presumed that in amides, the dipolar contribution would be similar to all these amides and the changes in the free energies on mixing with non-polar solvents can be attributed to the breaking of hydrogen bonds. The hydrogen bond breaking is more in low concentration of amides in non-polar solvents. So excess free energy increases with increase in the concentration of amides. It is also found that the positive dipolar excess free energy of mixing in a given solvent is in the order, primary amide > secondary amide > tertiary amide and agrees with the results of Kiyohara and Benson [23] from their calorimetric studies.

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