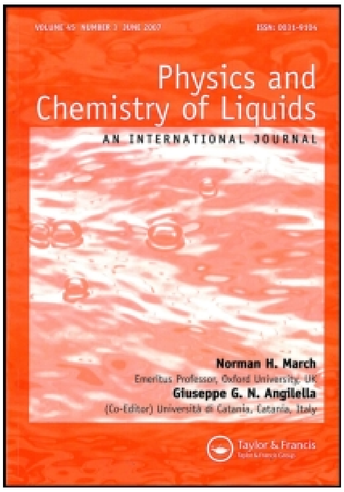

Physics and Chemistry of Liquids

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Kinart, Cezary M. and Kinart, Wojciech J.(1996) 'Physicochemical Properties of Glycerol-Formamide Liquid Mixtures and Their Assumed Internal Structures', Physics and Chemistry of Liquids, 33: 3, 159 — 170
To link to this Article: DOI: 10.1080/00319109608039817
URL: http://dx.doi.org/10.1080/00319109608039817

Phys. Chem. Liq., 1996, Vol. 33, pp. 159–170
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PHYSICOCHEMICAL PROPERTIES OF GLYCEROL-FORMAMIDE LIQUID MIXTURES AND THEIR ASSUMED INTERNAL STRUCTURES

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(Received 3 June 1996)

The ^{1}H-NMR spectra of liquid binary mixtures of glycerol (PT-1,2,3) and formamide (F) were recorded at 298 K over almost the whole range of the mixed solvent compositions. From these data were found the values of the spectral parameter, $\Delta\delta$(F-PT-1, 2, 3). The densities (d_{12}), viscosities (η_{12}) and relative permittivities (ε_{12}) were measured at 288.15 K, 293.15 K, 298.15 K and 303.15 K. From all these data, the molar volumes (V_{12}) and their deviations from ideality were calculated. Additionally, the temperature coefficients of relative permittivity, $\alpha_{12} = (1/\varepsilon_{12})\cdot[d\varepsilon_{12}/d(1/T)]$, were found. These structural parameters of functions of concentration suggest the formation of stable F·PT-1,2,3 and F·2PT-1,2,3 type complexes.

Keywords: Intermolecular interactions, binary liquid mixtures, ^{1}H-NMR spectra

In the present work we have analysed the mutual intermolecular interactions in the liquid mixtures of glycerol and formamide. It is a continuation of series of studies of internal structures of some liquid binary mixtures, in which F or an aliphatic alcohol is one of the two constituents, based on the correlation existing between the ^{1}H-NMR spectral results and some physicochemical intensive properties of the same binary mixtures [1–3].

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X-Ray diffraction investigations [4] on the crystal structure of solid formamide (F) have shown that the structure consists of puckered sheets of the F molecules, separated by about 3.1 Å. Within the sheets, pairs of the associated F molecules form nearly coplanar "bimolecular" units linked together by two types of H-bonds: one type, 2.93 Å long and thus weaker, links monomer together to form the said bimolecular species, the other type, 2.88 Å long, links the bimolecular units to form the sheets. The structure of formamide may be, alternatively, described as consisting of multimetric chains of F molecules cross-linked by H-bonds to form the sheets. Formamide seems to be very strongy chainwise associated by H-bonding [5]. It has been suggested [5] that formation of cyclic dimers by F is less likely, since it would noticeably diminish its relative permittivity values and dipole moment, which is not observed experimentally. On melting of F or upon dilution of F with inert solvent the H-bonded multimetric chain structure is preserved to a great extent. Contrariwise, the association is markedly reduced in "active" solvents ($CHCl_3$, dioxane, ketones and particulary dimethyl sulfoxide) because the aggregates are broken up by solute-solvent H-bonding, although some association persists even in relativey dilute solutions [6].

The internal structure of liquid polyalcohols has already been reviewed in our previous paper [7]. Taking into account the published data concerning the structure of liquid F and PT-1,2,3 seemed quite interesting to extend these studies onto the F-PT-1,2,3 binary mixtures.

EXPERIMENTAL

For the present ^{1}H-NMR spectral studies and all the physicochemical measurements, chemical pure formamide (Fluka) and glycerol (Polskie Odczynniki Chemiczne-Gliwice) were used. These solvents were dried and purified according to the known procedure [8].

^{1}H-NMR spectra were recorded on the Tesla Spectrometer of the type BS 467 (60 MHz), at 298 K. The chemical shift values for proton signals of formamide and glycerol were measured with an accuracy of about ± 0.2 Hz in respect to an external standard HMDS (hexamethyldisiloxane). The viscosities were measured with an accuracy

$\pm 0.1\%$ at 288.15, 293.15, 298.15 and 303.15 K, using Höppler viscometer. Solvent densities were measured at 288.15, 298.15 and 303.15 K, using a glass pycnometer of the Lipkin type. The maximum error in the density measurements was 1.10^{-4} g·cm^{-3}. The dielectric permittivity measurements were performed with an accuracy $\pm 0.1\%$, using a bridge of the type OH-301 (made in Hungary), at 288.15, 293.15, 298.15 and 303.15 K. All the binary mixtures made of F and PT-1,2,3 were prepared by weight.

RESULTS AND DISCUSSION

There is no literature data concerning the analysis of intermolecular interactions and internal structures in liquid mixtures of formamide with glycerol. In this paper, with the aim of analysing these effects in the liquid binary mixtures F-PT-1,2,3, we have measured the values of chemical shift differences δ(F-PT-1,2,3) (in Hz), at 298 K, between the centre of the ^{1}H-NMR signals of the formyl proton of formamide molecules and the centre of the ^{1}H-NMR signals of -OH groups of glycerol molecules over a wide range of solvent compositions, i.e. from 3.04 mol.% to 98.02 mol.% of F.

Subsequently, using the same method as previously [1–3], from these new spectral data the spectral parameter $\Delta\delta$(F-PT-1,2,3) has been found. The values of this parameter, or more precisely, the location of its maximum values, as have been shown in our previous papers [1–3], are located at the composition with the strongest intermolecular interactions between the components of the binary liquid mixtures. The δ(F-PT-1,2,3) values are shown in Table I, whereas the $\Delta\delta$(F-PT-1,2,3) values are visualized in Figure 1 as a function of the mixture compositions.

The analysis of the obtained data indicates the presence of a maximum $\Delta\delta$(F-PT-1,2,3) at ca. 67 mol.% of F. Thus, the conclusion would be drawn that at this composition the strongest interactions between components with involving hydrogen bonds are displayed and that the most stable "complex" is of the 2F·Pt-1,2,3 type.

We have also performed the independent studies of dielectric permittivities (ε_{12}) over a whole range of solvent compositions, at 288.15, 293.15, 298.15 and 303.15 K. The measured values of ε_{12} are summarized inTable II.

TABLE I Relative ^{1}H-NMR chemical shifts, δ(F-PT-1,2,3), measured at 298 K

mol.% of F	δ(F-PT-1,2,3) [Hz]
3.04	168.5
6.51	170.5
11.54	174.5
16.94	178.5
22.48	183.0
28.01	187.5
33.04	191.5
39.50	197.0
44.03	200.5
51.02	206.5
56.50	211.5
60.99	216.0
64.61	219.0
67.10	221.0
70.03	222.0
74.91	223.0
81.08	222.5
84.61	222.0
87.99	222.0
94.29	221.5
98.02	221.0

Using these data, we have calculated values of the temperature coefficients of dielectric permittivities, $\alpha_{12} = (1/\varepsilon_{12})\cdot[d\varepsilon_{12}/d(1/T)]$. As shown in Räetzsch's thermodynamic consideration [11], the composition range of liquid binary mixtures, within which coefficient α_{12} attains the highest value, should be interpreted as a region characterized by maximal intermolecular interactions between two different components of the given liquid mixture. Change in the α_{12} value versus compositions of liquid F-PT-1, 2, 3 mixtures are shown in Figure 2.

As can be seen from Figure 2, α_{12} attains the highest value within the composition range corresponding to about 67 mol.% of F. This would correspond to the formation of a stable intermolecular "complex" with a composition of 2 F•PT-1, 2, 3, which has been confirmed by spectral ^{1}H-NMR measurements. Further interesting results can be obtained by detailed analysis of the function $\alpha_{12} = f$(mol.% of F). It indicates that on increasing addition of F to glycerol up to ca. 11 mol.% of F, where a minimum is reached, causes a rapid drop in

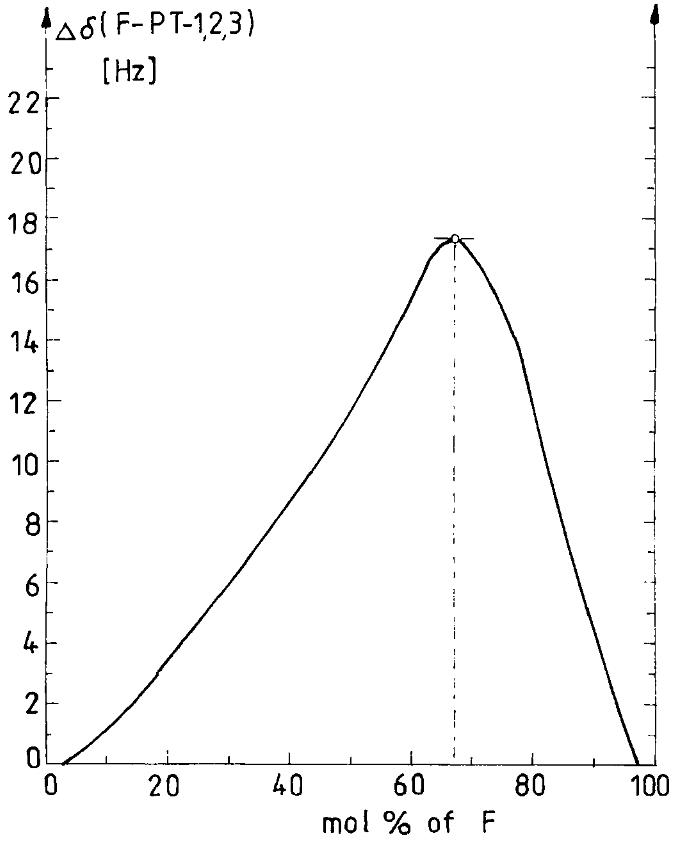


FIGURE 1 Changes in the function Δδ(F-PT-1,2,3) = *f*(mol.%) for the liquid formamide-glycerol mixtures, at 298 K.

the α_{12} values. Further addition of F to the studied mixtures causes an increase in α_{12}, which results in a maximum at ca. 67 mol.% of F. Therefore, it is possible to assume that small amounts of formamide being added to neat glycerol break its internal structure (composition region up to 11 mol.% of F), whereas further addition of formamide, up to ca. 67 mol.% of F, makes the internal structure of the mixed solvent more and more stabilized by hydrogen bonds formed between molecules of its components. The same analysis made for the formam-

TABLE II Dielectric permittivities (ε_{12}) for binary liquid mixtures F-PT-1, 2, 3, measured at 288.15 K, 293.15 K, 298.15 K and 303.15 K

mol.% of F	ε_{12}			
	288.15 K	293.15 K	298.15 K	303.15 K
0.00	43.52	42.95	42.54	41.81
6.51	47.61	47.01	46.25	45.62
11.54	50.69	50.04	49.27	48.51
16.94	53.99	53.26	52.48	51.36
25.12	59.21	58.47	57.58	56.45
30.52	62.80	61.98	60.91	59.78
35.99	68.48	66.18	64.22	63.12
44.03	71.49	70.49	69.42	68.05
49.25	74.06	73.51	72.37	70.83
51.02	75.18	74.36	73.36	71.87
56.50	78.51	77.75	76.41	74.75
59.47	80.35	79.51	78.06	76.24
64.61	83.20	82.24	80.67	78.49
70.03	87.64	86.48	84.81	82.82
74.91	91.36	90.76	89.32	87.23
81.08	96.97	96.04	95.04	93.52
87.99	101.98	101.31	100.54	99.17
94.29	106.27	105.38	104.88	103.78
100.00	110.80	110.26	109.70	109.44

ide-rich composition region shows a permanent increase of values of the α_{12} coefficient down to ca. 67 mol.% of F. Therefore, it seems that molecules of glycerol in the studied mixture, within the composition range between 100 to 67 mol.% of F, play a role of "structure-makers" in respect to molecules of formamide in the neat solvent. As has been shown in this paper, solid formamide has a structure of layers formed by crossing chains of molecules linked by hydrogen bonds [4, 5]. This layer arrangement, according to Ladell and Post is partly disturbed on melting [4]. Probably the addition of small quantities of PT-1, 2, 3 to F causes the alcohol molecules to become an additional bonding element in the disarranged formamide structure.

Within the composition range corresponding to ca. 67 mol.% of F, it means in the composition where maximum values of structural parameters are located [$\Delta\delta$(F-PT-1, 2, 3) and α_{12}], we also observe maximum deviations from ideality in viscosity [$\Delta(\eta_{12})^{x}_{\text{ideal}}$] and dielectric permittivity as a function of the composition of a binary liquid

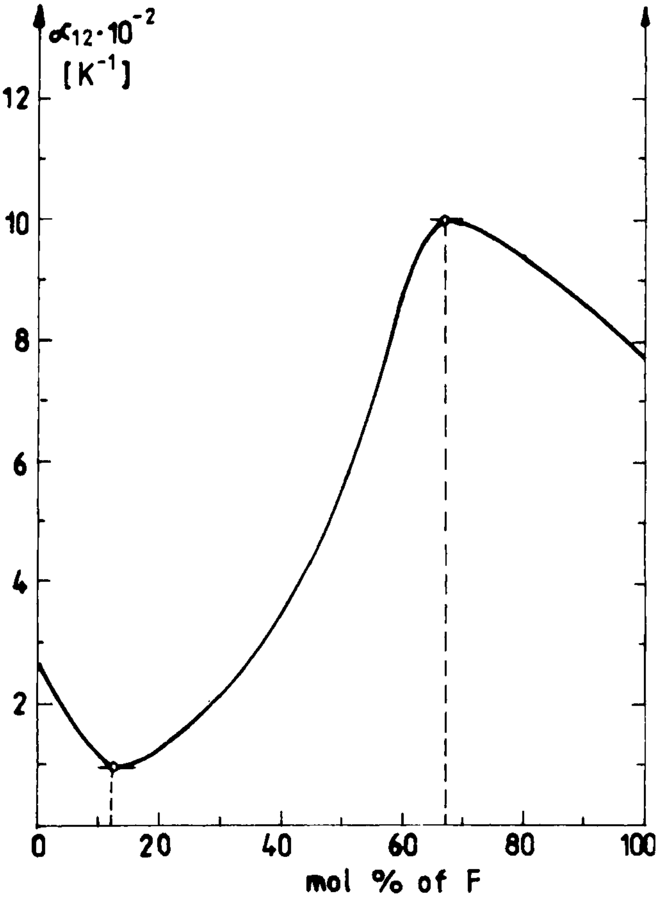


FIGURE 2 Changes in the temperature coefficient of dielectric permittivity drawn as a function of composition for the liquid formamide-glycerol mixtures, at 298.15 K.

mixture at 298.15 K (see Fig. 3). Values of analysed functions were calculated from experimental data of viscosity (η_{12}) and dielectric permittivity (ε_{12}) (see Table II and III) from the equations discussed in the previous works [1–3]. Therefore, it is necessary to assume that intermolecular "complexes" of the 2F•PT-1,2,3 type are linear and they are similar to these of solid F. The deviations from ideality of

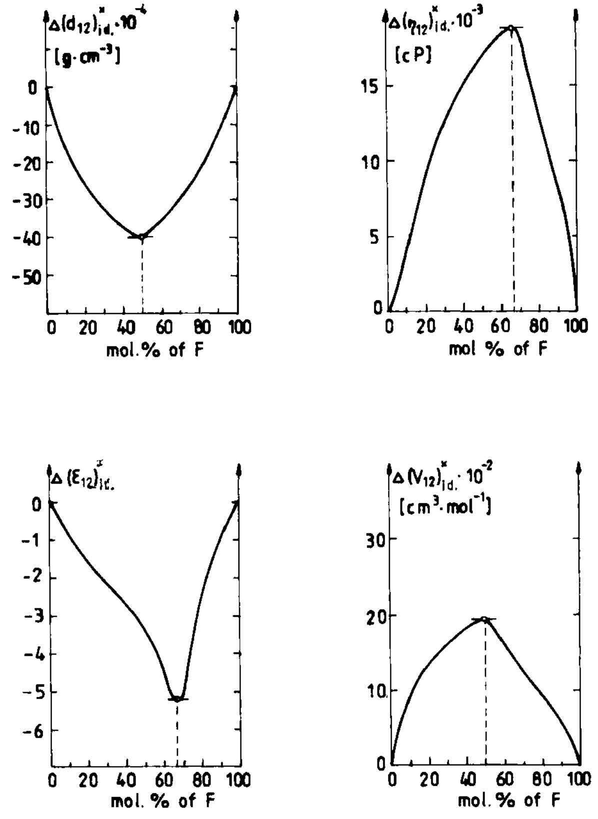


FIGURE 3 The course of changes of deviations from "ideality" of density, viscosity, dielectric permittivity and molar volume as a function of composition for the liquid formamide-glycerol mixtures, at 298.15 K.

density $[\Delta(d_{12})^{x}_{\text{ideal.}}]$ and molar volume $[\Delta(V_{12})^{x}_{\text{ideal.}}]$ were calculated from equations discussed previously [1–3] from the experimental data of density (see Tab. IV) over almost the whole range of the mixed solvent composition at 298.15 K (see Fig. 3). A maximum value of $\Delta(d_{12})^{x}_{\text{ideal.}}$ and a minimum value $\Delta(V_{12})^{x}_{\text{ideal.}}$ were observed for this system for ca. 50 mol.% of F. It corresponds to the formation of the intermolecular "complex" of the type F•PT-1, 2, 3.

TABLE III Viscosities (η_{12}) for binary liquid mixtures F-PT-1, 2, 3, measured at 288.15 K, 293.15 K, 298.15 K and 303.15 K

mol.% of F	η_{12}			
	288.15 K	293.15 K	298.15 K	303.15 K
0.00	2335.610	1499.120	945.640	623.860
16.94	817.710	522.010	366.240	241.480
25.12	561.140	373.630	258.360	158.420
30.52	427.810	290.840	198.430	118.630
44.03	147.210	102.010	74.850	48.480
49.25	94.630	72.750	53.750	38.782
51.02	84.490	65.980	48.570	35.613
53.88	69.970	54.620	40.891	30.694
59.47	50.880	38.891	29.712	23.198
64.61	38.552	28.016	22.202	17.428
67.10	35.011	25.342	19.982	15.593
74.91	22.254	17.008	13.691	10.119
81.08	13.739	10.994	9.241	7.699
94.29	6.264	5.365	4.544	3.965
100.00	4.329	3.718	3.393	2.994

TABLE IV Densities (d_{12}) for liquid binary mixtures F-PT-1, 2, 3, measured at 288.15 K, 298.15 K and 303.15 K

mol.% of F	d_{12}		
	288.15 K	298.15 K	303.15 K
0.00	1.2642	1.2583	1.2563
3.04	1.2613	1.2554	1.2531
6.51	1.2580	1.2522	1.2494
9.11	1.2557	1.2501	1.2469
11.54	1.2583	1.2478	1.2450
14.08	1.2511	1.2456	1.2421
16.94	1.2485	1.2430	1.2392
19.97	1.2459	1.2404	1.2368
22.48	1.2438	1.2381	1.2343
25.12	1.2412	1.2354	1.2318
28.01	1.2384	1.2326	1.2293
30.52	1.2362	1.2301	1.2268
33.04	1.2385	1.2275	1.2242
35.99	1.2306	1.2245	1.2211
39.50	1.2271	1.2208	1.2170
44.03	1.2219	1.2156	1.2125
49.25	1.2166	1.2099	1.2065
51.02	1.2147	1.2079	1.2041
53.88	1.2118	1.2043	1.2007
56.50	1.2082	1.2011	1.1974
59.47	1.2046	1.1975	1.1943
60.99	1.2030	1.1955	1.1916
64.61	1.1991	1.1910	1.1872
67.10	1.1950	1.1875	1.1835
70.03	1.1906	1.1832	1.1740
74.91	1.1833	1.1759	1.1715
81.08	1.1735	1.1663	1.1621
84.61	1.1669	1.1599	1.1550
87.99	1.1607	1.1534	1.1492
92.54	1.1528	1.1451	1.1489
94.29	1.1495	1.1422	1.1316
98.02	1.1423	1.1339	1.1293
100.00	1.1394	1.1295	1.1256

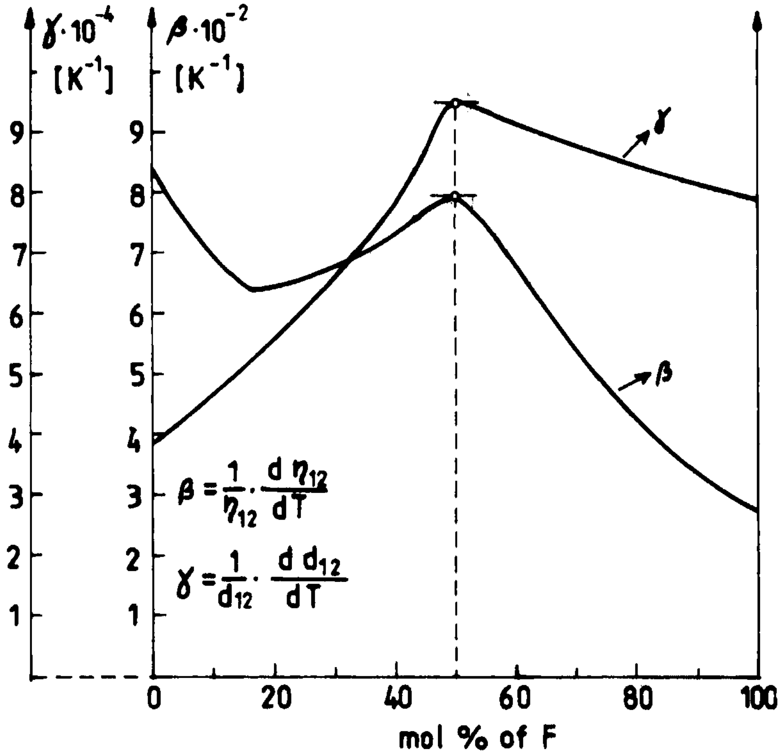
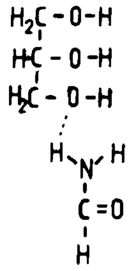


FIGURE 4 Changes in the temperature coefficient of density and viscosity drawn as a function of composition for the liquid formamide-glycerol mixtures, at 298.15 K.

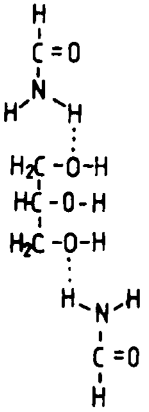
This composition range should be treated as the most dense and maximally packed.

The analysis of changes of temperature coefficient of density $[(1/d_{12})\cdot(dd_{12}/dT)]$ and viscosity $[(1/\eta_{12})\cdot(d\eta_{12}/dT)]$, which attain their maxima within the composition range corresponding to ca. 50 mol.% of F, indicates the greater susceptibility of complexes of the type F·PT-1, 2, 3 for temperature changes.

Therefore, due to all aforementioned literature data [2, 4–6], concerning the structure of liquid F and PT-1, 2, 3 and the present studies, the structure of the mentioned above "complexes" of the



complex : F·PT-1,2,3



complex: 2F·PT-1,2,3

FIGURE 5

F·PT-1,2,3 and 2F·PT-1,2,3 types can be suggested as given on Figure 5.

The "complexes" of these types which are internally H-bonded form subsequently flickering internal structures of types: (F·PT-1,2,3)$_n$ and (2F·PT-1,2,3)$_m$. At the present moment it seems impossible to suggest a model of such internal structure and this will require further studies.

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