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Thermodynamic and spectroscopic properties of 2-pyrrolidinones.
Part 5. Dielectric properties of 2-pyrrolidinone + benzyl alcohol, + 1,4-dioxane, and + hexamethylphosphortriamide at 303.15 and 323.15 K

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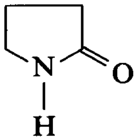
Abstract

The dielectric permittivities, densities and refractive indices were measured for the systems of 2-pyrrolidinone + benzyl alcohol, + 1,4-dioxane, and + hexamethylphosphortriamide at 303.15 and 323.15 K. Excess dielectric permittivities and excess molar polarisations were calculated. These quantities are all negative for 2-pyrrolidinone + 1,4-dioxane mixtures. The curves are S-shaped for 2-pyrrolidinone + benzyl alcohol and for 2-pyrrolidinone + hexamethylphosphortriamide mixtures, with the positive values in the benzyl alcohol-rich mole fraction for the former and the 2-pyrrolidinone-rich mole fraction for the latter. The results are discussed in terms of the strength of the dipolar and hydrogen-bonding interactions between the molecules.

INTRODUCTION

2-Pyrrolidinone (I) is a particularly interesting compound because of its acidic NH group and basic carbonyl group, which may function as competitive groups in hydrogen-bonding interactions. The properties of carboxamides are of general interest because the amide group is a structural part of peptides and proteins.



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We have studied previously the thermodynamic and dielectric properties of binary systems with an amide as one component and a different basic or acidic compound as the other [1–5]. The present work continues our studies on the behaviour and properties of 2-pyrrolidinone in various mixtures. Dielectric studies were carried out on 2-pyrrolidinone systems with benzyl alcohol, 1,4-dioxane and hexamethylphosphortriamide, which were investigated earlier for their excess molar volumes [1].

The molecular interaction and association properties of compounds depend on their environment and structure. Thus the relatively strong self-association of 2-pyrrolidinone, which IR spectroscopic studies confirm [6–8], is disturbed in basic or acidic solvents. The dielectric method offers a means of studying the dipolar interaction properties of 2-pyrrolidinone in various binary mixtures.

EXPERIMENTAL

2-Pyrrolidinone (purum, Fluka AG, Buchs, Switzerland) was purified by distillation above CaO and was preserved over 4A molecular sieves [9], as was benzyl alcohol (puriss. p.a. Fluka AG). 1,4-Dioxane (pro analys, Merck, Darmstadt, F.R.G.) was refluxed for 12 h with an HCl–water mixture under nitrogen atmosphere. It was then refluxed twice with sodium, distilled above sodium and preserved over 4A molecular sieves [10]. Hexamethylphosphortriamide (für die Spektroskopie, Merck AG) was purified by distillation and preserved over 4A molecular sieves.

The densities of the mixtures and pure compounds were measured as described earlier [1]. Refractive indices were measured with an Abbe refractometer and the dielectric permittivities were measured as described earlier [2].

Excess dielectric permittivities (ϵ^E) were calculated using the equation

$$\epsilon^E = \epsilon_{obs} - \epsilon_{calc} = \epsilon_{obs} - (x_1\epsilon_1 + x_2\epsilon_2) \tag{1}$$

where ϵ_1 and ϵ_2 are the dielectric permittivities of the pure compounds and x_1 and x_2 are the mole fractions of the components in the mixture.

Molar polarisations [11–15] were calculated by the Kirkwood–Fröhlich equation

$$P = \frac{(\epsilon - n_D^2)(2\epsilon + n_D^2)}{9\epsilon} V \tag{2}$$

where ϵ is the dielectric permittivity, n_D the refractive index and V the molar volume of the mixture. Excess molar polarisations were calculated using the equation

$$P^E = P_{obs} - P_{calc} = P_{obs} - (x_1P_1 + x_2P_2) \tag{3}$$

The values of ϵ^E and P^E were fitted to the equation

$$y^E = x_1(1 - x_1) \sum_{k=0}^{n} A_k(1 - 2x_1)^k \tag{4}$$

where $k = 0, 1, \ldots, n$ and x_1 = mole fraction of 2-pyrrolidinone. The parameters A_k were evaluated by the method of least squares.

The standard deviation $\sigma(y^E)$ was defined by the equation

$$\sigma(y^E) = \left[\sum \left(y^E_{obs} - y^E_{calc}\right)^2/(N - M)\right]^{1/2} \tag{5}$$

where N is the number of experimental points and M is the number of parameters.

RESULTS AND DISCUSSION

The values of densities, dielectric permittivities and refractive indices of the pure compounds and of the 2-pyrrolidinone–benzyl alcohol, –1,4-dioxane and –hexamethylphosphortriamide mixtures at 303.15 and 323.15 K are given in Table 1. The parameters of eqn. (4) and the standard deviations for excess dielectric permittivities and excess molar polarisations are given in Tables 2 and 3, respectively. Figures 1 and 2 present the excess dielectric permittivities and excess molar polarisations of the systems at both temperatures.

In earlier work, the excess molar volumes for the above systems [1] and for 2-pyrrolidinone–acetone, – dimethyl sulphoxide, –dichloromethane, –2-propanol and –water [3] were measured. All values were negative at 303.15 and 323.15 K. At 303.15 K, the V^E values decrease in the order of the second component, as follows: dimethyl sulphoxide > 1,4-dioxane > benzyl alcohol > dichloromethane > 2-propanol > water > hexamethylphosphortriamide > acetone.

The excess dielectric permittivities and excess molar polarisations are negative for 2-pyrrolidinone–1,4-dioxane systems (Figs. 1 and 2). For the 2-pyrrolidinone–benzyl alcohol system they are negative except at low amide mole fraction, and for the 2-pyrrolidinone–hexamethylphosphortriamide system they are positive in the 2-pyrrolidinone-rich mole fraction and negative in the hexamethylphosphortriamide-rich mole fraction.

2-Pyrrolidinone and benzyl alcohol are both self-associating and in mixtures of the two the association between the like molecules is disturbed, with the effect of making the values of ϵ^E more positive. At the same time, benzyl alcohol has an OH proton which can act as a proton donor towards the carbonyl oxygen of 2-pyrrolidone. This weak hydrogen-bonding interaction can be expected to have a negative influence on the ϵ^E values by changing the charge distribution within the interacting molecules. This is supported by the decrease in the size of the deviation as the temperature increases, and the amount of hydrogen bonding between the unlike molecules decreases.

1,4-Dioxane is a weakly basic solvent, which has two oxygen atoms to act as proton acceptors. In the 2-pyrrolidinone–1,4-dioxane system, as in the 2-pyrrolidinone–benzyl alcohol system, the deviation from ideal behaviour

TABLE 1

Densities, dielectric permittivities and refractive indices of 2-pyrrolidinone–solvent mixtures at 303.15 and 323.15

Solvent	X_{amide}	$T = 303.15$ K			$T = 323.15$ K		
		d (g cm^{-3})	ϵ	n_D	d (g cm^{-3})	ϵ	n_D
Benzyl alcohol	0.0000	1.0378	12.34	1.5371	1.0226	10.75	1.5286
	0.0496	1.0410	13.16	1.5355	1.0252	11.73	1.5270
	0.1264	1.0457	14.20	1.5324	1.0301	12.91	1.5243
	0.1753	1.0490	14.75	1.5313	1.0333	13.59	1.5231
	0.2840	1.0558	15.84	1.5270	1.0400	14.85	1.5188
	0.3611	1.0607	16.82	1.5237	1.0449	15.86	1.5157
	0.4929	1.0693	18.01	1.5172	1.0534	17.26	1.5088
	0.5911	1.0753	19.20	1.5122	1.0594	18.48	1.5041
	0.7404	1.0850	21.74	1.5032	1.0689	20.85	1.4956
	0.8757	1.0942	24.54	1.4938	1.0780	23.31	1.4871
	0.9216	1.0978	25.51	1.4909	1.0816	24.19	1.4847
	1.0000	1.1034	27.41	1.4839	1.0875	25.88	1.4769
1,4-Dioxane	0.0000	1.0224	2.200	1.4183	1.0002	2.166	1.4090
	0.0579	1.0275	3.180	1.4222	1.0057	3.093	1.4131
	0.1266	1.0332	4.189	1.4267	1.0121	4.061	1.4177
	0.1900	1.0383	5.167	1.4310	1.0177	4.989	1.4221
	0.2952	1.0467	6.980	1.4379	1.0270	6.696	1.4294
	0.3881	1.0544	8.869	1.4440	1.0353	8.438	1.4359
	0.4877	1.0624	11.29	1.4507	1.0439	10.71	1.4432
	0.5567	1.0679	13.07	1.4552	1.0499	12.50	1.4480
	0.6533	1.0758	15.74	1.4623	1.0583	15.10	1.4545
	0.7399	1.0828	18.38	1.4676	1.0658	17.67	1.4605
	0.8122	1.0884	20.69	1.4658	1.0717	19.87	1.4654
	0.8977	1.0953	23.64	1.4783	1.0789	22.58	1.4712
	0.9299	1.0978	24.78	1.4804	1.0816	23.96	1.4732
Hexamethylphosphortriamide	0.0000	1.0157	28.49	1.4558	0.9988	25.47	1.4472
	0.1223	1.0222	28.23	1.4579	1.0054	25.33	1.4498
	0.1920	1.0265	28.01	1.4593	1.0099	25.27	1.4517
	0.3282	1.0350	28.08	1.4617	1.0186	25.43	1.4549
	0.4160	1.0413	28.04	1.4644	1.0249	25.53	1.4570
	0.5256	1.0500	28.30	1.4677	1.0337	25.91	1.4601
	0.6206	1.0584	28.30	1.4702	1.0422	26.04	1.4624
	0.7212	1.0682	28.32	1.4733	1.0520	26.22	1.4656
	0.8290	1.0774	28.12	1.4772	1.0613	26.28	1.4691
	0.9255	1.0907	27.79	1.4810	1.0745	26.24	1.4727

decreases with increasing temperature, suggesting decreasing hydrogen-bonding interaction with temperature. Large negative excess dielectric permittivities have also been reported for the ethanol–1,4-dioxane system, with the maximum deviation appearing at the mole fraction of 1,4-dioxane of

TABLE 2

Parameters of eqn. (4) (cm^3 mol^{-1}) and standard deviations of ϵ^E for 2-pyrrolidinone–solvent mixtures at 303.15 and 323.15 K

Solvent	T (K)	A_0	A_1	A_2	A_3	A_4	A_5	$\sigma(\epsilon^E)$
Benzyl alcohol	303.15	−6.830	8.948	2.740	−14.095	1.021	14.828	0.064
	323.15	−3.871	7.066	3.762	−8.390	−0.849	10.438	0.042
1,4-Dioxane	303.15	−12.921	−0.349	−0.357	2.486	4.938	–	0.065
	323.15	−11.922	−2.645	1.106	10.475	6.481	−12.311	0.085
Hexamethyl-phosphortri-amide	303.15	1.025	−4.754	0.287	1.897	–	–	0.055
	323.15	0.534	−4.031	−1.333	0.037	4.661	–	0.041

TABLE 3

Parameters of eqn. (4) (cm^3 mol^{-1}) and standard deviations of P^E for 2-pyrrolidinone–solvent mixtures at 303.15 and 323.15 K

Solvent	T (K)	A_0	A_1	A_2	A_3	A_4	A_5	$\sigma(P^E)$
Benzyl alcohol	303.15	−50.144	161.719	75.445	−278.865	19.905	308.149	1.316
	323.15	11.735	136.426	95.267	−171.455	−11.303	228.808	0.896
1,4-Dioxane	303.15	−161.237	−2.174	1.060	62.720	95.839	41.056	0.387
	323.15	−147.075	−40.598	26.177	191.414	145.653	−187.161	1.523
Hexamethyl-phosphortri-amide	303.15	−12.419	−103.818	−24.648	–	–	–	1.849
	323.15	7.071	−108.987	−71.759	6.327	127.123	–	1.153

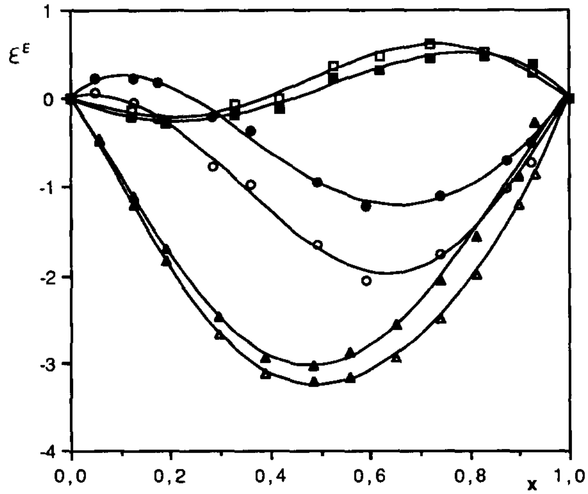

Fig. 1. Excess dielectric permittivities of 2-pyrrolidinone–benzyl alcohol (○) –1,4-dioxane (△) and –hexamethylphosphortriamide (□) at 303.15 (open symbols) and 323.15 K (filled symbols).

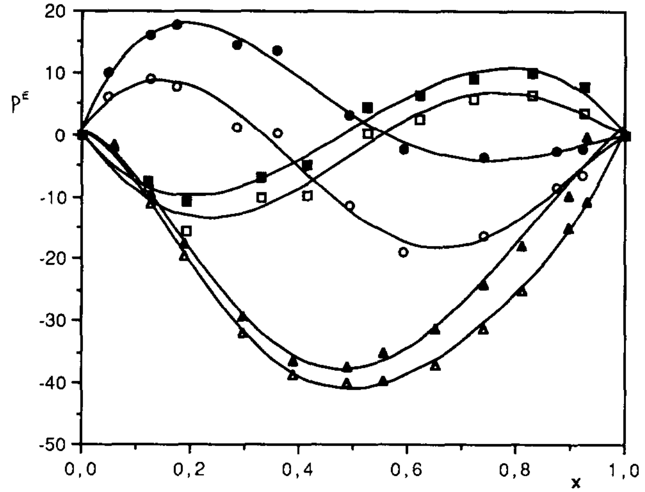

Fig. 2. Excess molar polarizations of 2-pyrrolidinone–benzyl alcohol (○), –1,4-dioxane (△) and –hexamethylphosphortriamide (□) at 303.15 (open symbols) and 323.15 K (filled symbols).

$x = 0.45$. This might be due to the formation of complexes of ethanol and 1,4-dioxane in molar ratios of both 1 : 1 and 2 : 1 [16].

Hexamethylphosphortriamide is a dipolar, aprotic solvent and the oxygen atom of the PO group is a very efficient proton acceptor, e.g. towards the OH protons of alcohols [17]. The 2-pyrrolidinone–hexamethylphosphortriamide system has the most positive ϵ^E values of all the 2-pyrrolidinone–solvent systems studied. As the most basic solvent, hexamethylphosphortriamide disturbs most the self-association of 2-pyrrolidinone, causing a large positive contribution to the values of ϵ^E. Usually, a parallel alignment of dipoles is required to effect an increase in excess dielectric permittivities.

Like the 2-pyrrolidinone molecule, *N*-methylbenzenesulphonamide has an NH proton. We have earlier obtained positive ϵ^E and P^E values for *N*-methylbenzenesulphonamide–hexamethylphosphortriamide mixtures [4]. Self-association of NH-proton-containing sulphonamides is stronger than that of 2-pyrrolidinone according to near-infrared spectroscopic and dielectric studies [6–8,18,19]. Accordingly the positive deviation of ϵ^E from ideal behaviour is greater for *N*-methylbenzenesulphonamide–hexamethylphosphortriamide than for 2-pyrrolidinone–hexamethylphosphortriamide systems [4]. Both 2-pyrrolidinone and *N*-methylbenzenesulphonamide form cyclic self-associated species and the destruction of these structures by hexamethylphosphortriamide increases the charge distribution of the molecules in both the present and earlier presented systems, as the positive P^E values show.

1,4-Dioxane–*N*-methylbenzenesulphonamide and 1,4-dioxane–2-pyrrolidinone systems behave in a similar way, both exhibiting clearly negative ϵ^E

and P^E values. The electron-donor property and the dielectric permittivity of 1,4-dioxane are very much smaller than the same values for hexamethylphosphortriamide, as the donor numbers (DN) [20] and ϵ values show: 14.8 and 2.200 for 1,4-dioxane, and 38.8 and 28.49 for hexamethylphosphortriamide. Clearly, therefore, dipole–dipole interactions between the unlike molecules in 1,4-dioxane–NH-proton-containing amide mixtures are not important relative to the corresponding hexamethylphosphortriamide mixtures.

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