where M_w is the molecular weight of water, equal to 0.018 02 kg/mol.

(4) Molecule-Molecule Interaction Term. Due to the nature of these interactions, their contributions solely affect water activity and SO_2 activity coefficient. The order of magnitude of molecular sulfur dioxide in the electrolyte makes it possible to neglect the ternary self-interaction term. The contributions depend on the binary self-coefficient λ_{2-2}, equal to -0.05, and are given by the following expressions:

$$T_{\text{mol-mol}}(1) = -\lambda_{2-2} m^2(2)$$

$$T_{\text{mol-mol}}(2) = 2\lambda_{2-2} m(2) \qquad \text{(A16)}$$

The various expressions established for every contribution lead to the expressions of activity coefficients and water activity:

$$\text{H}_2\text{O} \quad a_{\text{H}_2\text{O}} = \exp[M_w\{T_{\text{mol-mol}}(1) - \sum_{k=2}^{8} m(k)\} + T_{\text{ion-mol}}(1)]$$

$$\text{SO}_2 \quad \gamma(2) = \exp[T_{\text{ion-mol}}(2) + T_{\text{mol-mol}}(2)]$$

$$\text{ions} \quad \gamma(k) = \exp[z(k)^2\text{FAC} + T_{\text{ion-ion}}(k) + T_{\text{ion-mol}}(\text{k})] \qquad \text{(A17)}$$

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Received for review July 13, 1989. Accepted June 25, 1990. The present work has been sponsored by the Commission of the European Communities through the BRITE program (Contract R I 1B-0223 C).

Dielectric Constants and Excess Volumes of 2-Pyrrolidone + Water at Several Temperatures

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The dielectric constants and volumes of mixing of 2-pyrrolidone + water mixtures were measured at 25, 35, 45, and 55 °C over the entire composition range. The excess dielectric constants and the polarizations were calculated. The observed deviations from ideality, decreasing with increasing temperature, are interpreted in terms of hydrogen-bonding interactions.

Introduction

Recently, the petroleum industry has given much attention to the high density high boiling point, and high polarity solvents. This interest has resulted from their high efficiency in the extraction of monocyclic aromatic hydrcarbons (C_6–C_9) from petroleum products. 2-Pyrrolidone (C_4H_7ON) has the solvent properties that may make it an interesting extraction agent. 2-Pyrrolidone has a comparable selectivity (*1*) to *N*-formylmorpholine (*2*), glycol (*3*), and *N*-methylpyrrolidone (*4*) and less than that of sulfone (*5*). Cosolvents are used in the petroleum industry to increase the selectivity and solvent power of aromatic extractants; therefore we have initiated a program to study some thermodynamic properties of the binary mixtures containing aromatic extractants as a common solvent. The present work reports the density ρ (g cm^{-3}), refractive index n_D, dielectric constant ϵ, excess dielectric constant $\Delta\epsilon$, and excess molar volume V^E of 2-pyrrolidone + water mixtures at 25, 35, 45, and 55 °C.

Experimental Section

2-Pyrrolidone (Fluka AG pure grade) was purified as previously described (*6*). The water content, as determined by

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0021-9568/90/1735-0463$02.50/0

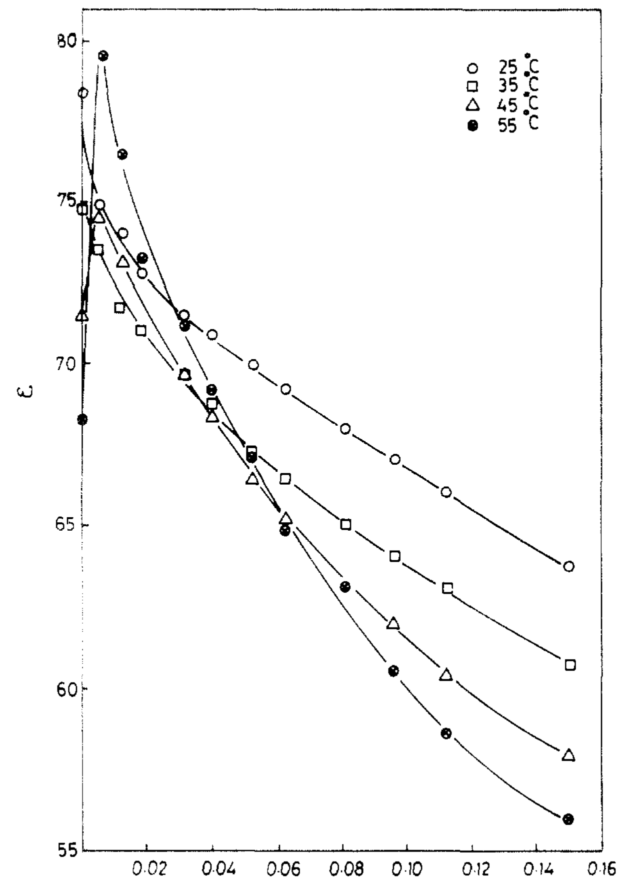


Figure 1. Dielectric constant ε versus x, mole fraction of 2-pyrrolidone.

gas-liquid chromatography, was less than 0.1 ± 0.01%. Binary mixtures of 2-pyrrolidone with degassed, doubly distilled, and deionized water with specific conductivity less than 1×10^{-6} S cm^{-1} were prepared by weighing.

Dielectric constant ε of the pure and binary mixtures of 2-pyrrolidone + water over the whole mole fraction range at 25, 35, 45, and 55 °C were measured at 1 MHz with use of Radelkis precision dielectrometer (type OH-302). The measuring cell was OH-911 type. Details of the apparatus and of the calibration of the cell were described elsewhere (*7*). The cell temperature was kept constant within ±0.01 °C. Reproducibility of dielectric constants data was within ±0.05.

Densities were measured with a vibrating U tube densimeter (an Anton Paar, Model DMA 60/602). Details of the instrument and the calibration were adequately covered in a previous work (*8*). The overall precision of the density measured was estimated to be better than $\pm 2 \times 10^{-5}$ g cm^{-3}.

Refractive index n_D was measured by using sodium light and an Abbé refractometer with a precision of the reading of ±0.0002. In all measurements the temperature was maintained at ±0.05 °C.

Results and Discussions

The experimental results of the dielectric constant of 2-pyrrolidone + water at 25, 35, 45, and 55 °C are presented in Table I. The data are plotted as a function of the mole fraction x of 2-pyrrolidone at all temperatures studied (Figure 1). The excess dielectric constants were calculated from the following equation

$$\Delta\epsilon = \epsilon_{mix} - [x\epsilon_1 + (1 - x)\epsilon_2] \qquad (1)$$

where ϵ_{mix} is the dielectric constant of 2-pyrrolidone + water mixtures, ϵ_1 and ϵ_2 are the dielectric constants of 2-pyrrolidone and water, respectively. Δε obtained are plotted against x, the mole fraction of 2-pyrrolidone, in Figure 2.

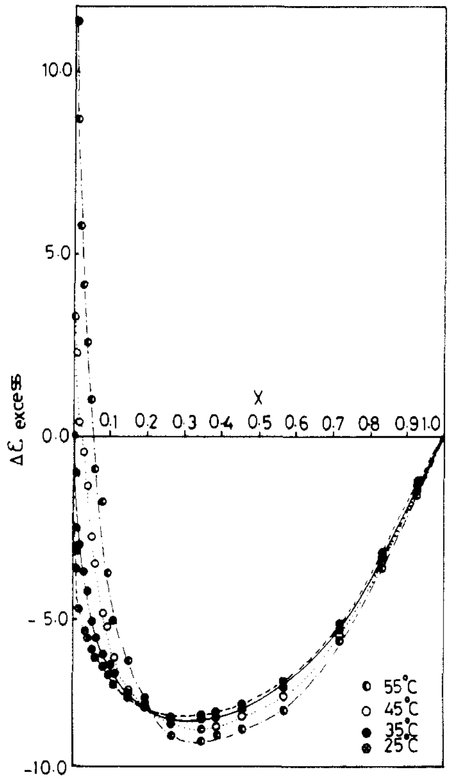


Figure 2. Excess dielectric constants Δε versus x, mole fraction of 2-pyrrolidone.

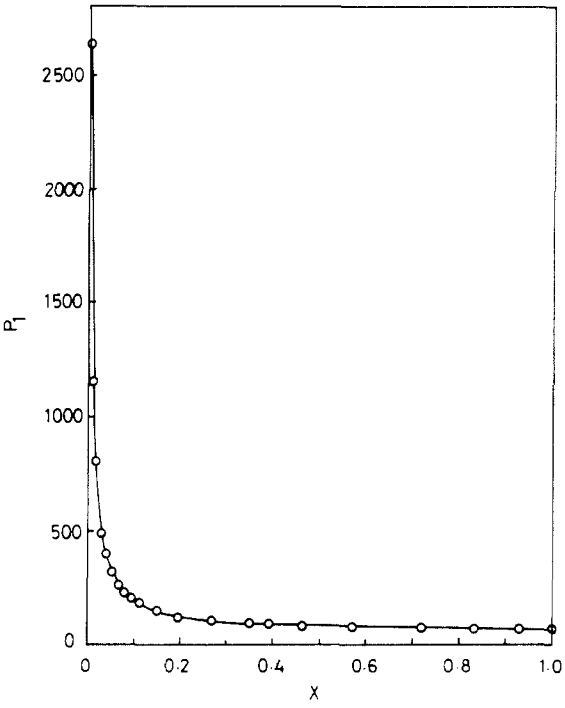


Figure 3. Polarization P_1 versus x, mole fraction of 2-pyrrolidone, at 25 °C.

The polarization P of the 2-pyrrolidone + water mixture was calculated from the following equation (*9*, *10*)

$$P = \frac{\epsilon_{mix} - 1}{\epsilon_{mix} + 2}\left[\frac{xM_1 + (1 - x)M_2}{\rho}\right] \qquad (2)$$

where M_1, M_2, and ρ are the molecular weights of 2-pyrrolidone

Table I. Experimental Densities ρ, Dielectric Constants ϵ, and Excess Molar Volumes V^E of 2-Pyrrolidone + Water ($xC_4H_7ON + (1 - x)H_2O$) at 25, 35, 45, and 55 °C

x	ρ/(g cm^{-3})	ϵ	V^E/(cm^3 mol^{-1})	x	ρ/(g cm^{-3})	ϵ	V^E/(cm^3 mol^{-1})
			T = 25 °C				
0.0000	0.99707	78.36	0.0000	0.1501	1.05645	63.68	−0.3111
0.0053	0.99976	74.95	−0.0047	0.1975	1.06776	61.00	−0.4021
0.0125	1.00340	74.09	−0.0136	0.2689	1.07996	57.22	−0.4964
0.0183	1.00631	72.75	−0.0222	0.3514	1.08918	53.25	−0.5490
0.0316	1.01269	71.45	−0.0437	0.3933	1.09232	51.12	−0.5495
0.0402	1.01668	70.86	−0.0601	0.4626	1.09628	47.85	−0.5309
0.0525	1.02230	69.93	−0.0882	0.5723	1.10051	42.62	−0.4667
0.0624	1.02861	69.18	−0.1219	0.7213	1.10400	37.07	−0.3372
0.0813	1.03367	67.98	−0.1445	0.8369	1.10551	33.16	−0.0821
0.0962	1.03911	67.03	−0.1776	1.0000	1.10701	28.18	0.0000
0.1123	1.04515	65.97	−0.2270				
			T = 35 °C				
0.0000	0.99406	74.85	0.0000	0.1501	1.04982	60.71	−0.2721
0.0053	0.99661	73.55	−0.0039	0.1975	1.06048	58.22	−0.3535
0.0125	1.00002	71.75	−0.0108	0.2689	1.07228	54.39	−0.4451
0.0183	1.00276	71.00	−0.0182	0.3514	1.08107	50.49	−0.4912
0.0316	1.00882	69.63	−0.0378	0.3933	1.08372	48.61	−0.4963
0.0402	1.01258	68.74	−0.0522	0.4626	1.08768	45.58	−0.4608
0.0525	1.01778	67.32	−0.0753	0.5723	1.09182	40.94	−0.3967
0.0674	1.02381	66.38	−0.1073	0.7213	1.09551	35.45	−0.2823
0.0813	1.02846	65.04	−0.1244	0.8369	1.09740	31.99	−0.1750
0.0962	1.03402	64.05	−0.1640	0.9312	1.09850	29.48	−0.0773
0.1123	1.03919	63.03	−0.1972	1.0000	1.09915	27.58	0.0000
			T = 45 °C				
0.0000	0.99024	71.50	0.0000	0.1505	1.04303	57.93	−0.2436
0.0035	0.99262	74.53	−0.0024	0.1975	1.05307	55.46	−0.3157
0.0125	0.99588	73.19	−0.0086	0.2689	1.06431	51.66	−0.3989
0.0183	0.99854	71.05	−0.0162	0.3514	1.07282	47.85	−0.4428
0.0316	1.00419	69.63	−0.0316	0.3933	1.07552	46.09	−0.4474
0.0402	1.00784	68.33	−0.0461	0.4626	1.07941	43.31	−0.4287
0.0525	1.01268	66.42	−0.0651	0.5723	1.08367	38.91	−0.3669
0.0624	1.01841	65.22	−0.0944	0.7213	1.08732	33.93	−0.2598
0.0813	1.02291	63.08	−0.1114	0.8369	1.08924	30.07	−0.1612
0.0962	1.02805	62.03	−0.1450	0.9312	1.09035	28.52	−0.0683
0.1123	1.03296	60.43	−0.1754	1.0000	1.09105	26.98	0.0000

x	ϵ	x	ϵ	x	ϵ	x	ϵ
			T = 55 °C				
0.0000	68.30	0.0525	67.10	0.1975	52.88	0.5723	36.84
0.0053	79.49	0.0624	64.79	0.2689	84.78	0.7213	32.41
0.0125	67.64	0.0813	63.09	0.3514	45.22	0.8369	29.65
0.0183	73.30	0.0962	60.49	0.3933	43.65	0.9312	27.62
0.0316	71.11	0.1123	58.59	0.4626	40.90	1.0000	26.38
0.0402	69.17	0.1501	55.92				

and water and the density of the binary mixtures, respectively. The value of P at any composition of the mixture is related to the contribution of 2-pyrrolidone P_1 and that of water P_2. The contribution of water P_2 to the total polarization P is given by

$$P_2 = \left(\frac{n_D^2 - 1}{n_D^2 + 1}\right)\left(\frac{M_2}{\rho_2}\right) \tag{3}$$

where ρ_2 and n_D are respectively the density and refractive index of the pure water. The contribution of 2-pyrrolidone P_1 can be calculated by (*9*, *10*)

$$P = xP_1 + (1 - x)P_2 \tag{4}$$

The calculated polarization P_1 of 2-pyrrolidone in the 2-pyrrolidone + water mixture at 25 °C is plotted as a function of the mole fraction x of 2-pyrrolidone in Figure 3.

Excess molar volumes V^E of 2-pyrrolidone + water at 25, 35, and 45 °C over the whole mole fraction range were determined from the precise density measurements by using the following equation:

$$V^E\ (\text{cm}^3\ \text{mol}^{-1}) = xM_1(\rho^{-1} - \rho_1^{-1}) + (1 - x)M_2(\rho^{-1} - \rho_2^{-1}) \tag{5}$$

The resulting V^E values are given in Table I and plotted in Figure 4. Each set of V^E results was fitted to the Redlick–Kister equation:

$$V^E\ (\text{cm}^3\ \text{mol}^{-1}) = x(1 - x)\sum_{j=1}^{n} A_j(1 - 2x)^j \tag{6}$$

Table II. Coefficient A_j and Standard Deviations for Least-Squares Representation of V^E (cm^3 mol^{-1}) by Equation 6 for $xC_4H_7NO + (1 - x)H_2O$

	V^E at various T		
	298.15 K	308.15 K	318.15 K
A_1	−2.0107	−1.7493	−1.5941
A_2	−1.2431	−1.2799	−1.1048
A_3	−0.9926	−0.8672	−0.8727
A_4	1.1788	1.3661	1.1792
A_5	2.1415	1.7822	1.8256
s	0.0049	0.0068	0.0079

The coefficients A_j are given in Table II, along with the standard deviations s.

The dependence of the dielectric constants for solutions of 2-pyrrolidone in water on the 2-pyrrolidone concentration and on temperature is shown in Figure 1. At 25 and 35 °C, the initial addition of 2-pyrrolidone to water decreases the dielectric constant. The ϵ versus x curves show maxima at 45 and 55 °C. In the water-rich region of the 2-pyrrolidone + water

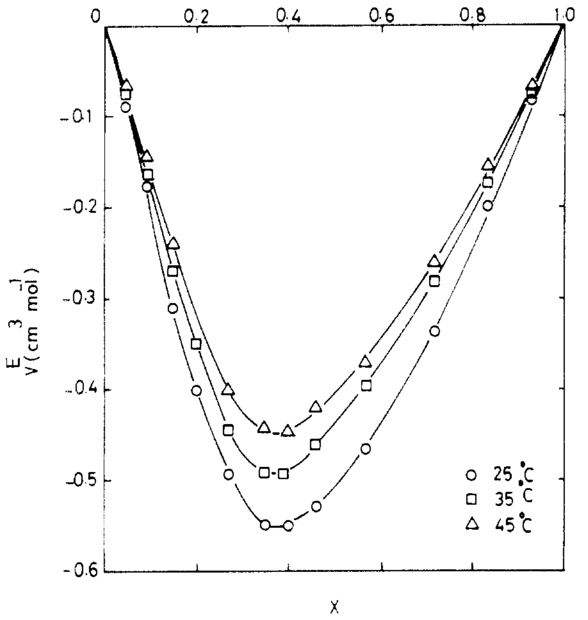
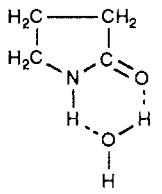


Figure 4. Excess molar volume V^E versus x, mole fraction of 2-pyrrolidone.

mixture ($x \leq 0.005$), the 2-pyrrolidone molecules enhance the formation of the "bulky structure" in water. The corresponding structures become less stable as the temperature increases. This feature is more evident in Figure 2, where the excess dielectric constants are plotted against x. Such arrangement in close packing in the disordered regions and ordering of the water molecules not bound in the ice I tetrahedral structure and the dipole-dipole interactions between water and 2-pyrrolidone molecules enhance the polarization of the 2-pyrrolidone molecules. This reflects the initial sharp rise of the 2-pyrrolidone polarization P_1 to the maximum at $x \leq 0.005$, as illustrated in Figure 3.

The excess molar volumes are negative over the entire mole fraction range, which suggests the strong hydrogen bonding in the 2-pyrrolidone-water mixtures. This is illustrated in Figure 4. In the region of 0.39 mole fraction of 2-pyrrolidone, each isotherm exhibits a minimum that decreases with an increase in temperature and shifts slightly toward a higher 2-pyrrolidone concentration. On this basis, V^E has minimum deviation from linearity, which is related to the composition of 2-pyrrolidone-water at a ratio of 2 mol of water to 1 mol of 2-pyrrolidone. This has been observed in the excess dielectric constants (Figure 2). Such behavior obtained here for 2-pyrrolidone-water mixtures is similar to that obtained previously (*7*) for the γ-butyrolactone and water system.

The results obtained here indicate that there is a stronger hydrogen bonding in 2-pyrrolidone-water mixtures than in water alone, which may be explained in terms of the presences of the polar carbonyl (C=O) and N-H groups. The 2-pyrrolidone molecule hydrogen bonding with water molecules can be presented by forms I and II. Excess dielectric constants and excess volumes results showed a minimum for the composition of 2-pyrrolidone-water mixtures at a ratio of 2 mol of water to 1 mol of 2-pyrrolidone (Figures 2 and 4), which is evidence for the 2-pyrrolidone-water complex in form II. This hypothesis cannot be proved on the basis of the data presented; further investigation would be necessary to established its existence and composition.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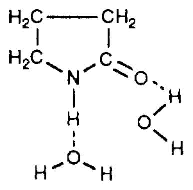
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Registry No. 2-Pyrrolidone, 616-45-5.

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Received for review May 5, 1989. Revised December 5, 1989. Accepted May 10, 1990.