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Densities, Viscosities, Speeds of Sound, and Relative Permittivities for Water + Cyclic Amides (2-Pyrrolidinone, 1-Methyl-2-pyrrolidinone, and 1-Vinyl-2-pyrrolidinone) at Different Temperatures

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Experimental densities, ρ, viscosities, η, speeds of sound, v, and relative permittivities, ϵ_r, for three binary mixtures of water + 2-pyrrolidinone, + 1-methyl-2-pyrrolidinone, and + 1-vinyl-2-pyrrolidinone were measured over the entire composition range and at different temperatures. The variations of ρ, η, and v with water mole fractions were typical of systems which show large nonidealities. The excess molar volumes, V_m^E, excess isentropic compressibilities, κ_s^E, and deviations in dynamic viscosities, $\delta\eta$, and relative permittivities, $\delta\epsilon_r$, were calculated, and their compositional variation was mathematically represented by a Redlich−Kister type equation. The partial molar volumes of water at infinite dilution, $\bar{V}_1^\infty$, were calculated from the smoothed V_m^E values of three binary mixtures at different temperatures. The variation of the Kirkwood correlation factor, g_K, was examined across the entire composition range. The analysis of these functions revealed that both hydrophobic and hydrophilic hydrations are responsible for the complex nature of the thermophysical behavior in these mixtures.

Introduction

Cyclic amides in general are high density, high boiling point, and high polarity solvents. They are completely miscible over the entire composition range with water. 2-Pyrrolidinone and its methyl and vinyl derivatives, that is, 1-methyl-2-pyrrolidinone and 1-vinyl-2-pyrrolidinone, have been used as cosolvents in the petroleum industry to increase the selectivity and solvent power for extracting aromatic hydrocarbons. These cyclic amides further have excellent thermal and chemical stability and are used as absorbents of sour gases from crude natural gas. In these applications, the combination of the amides with small amounts of water is usually preferred so that the mixed selective solvent system functions effectively. Hence the knowledge of the thermophysical properties of systems of water + cyclic amides over the entire composition range and at different temperatures is highly useful in establishing efficient and economical conditions for processes such as extractive distillation. A perusal of the literature revealed that among various thermophysical properties only few studies have reported on the measurements of excess molar enthalpies[1−4] for the binary systems of water + 1-methyl-2-pyrrolidone in the temperature range (0 to 143) °C, excess molar volumes[2,5−11] at (25 to 55) °C, dynamic viscosities[8,12] at 25 °C, speeds of sound[6] at 25 °C, and relative perimttivities[5,13−15] at (25 to 55) °C for water + 2-pyrrolidinone or 1-methyl-2-pyrrolidinone binary systems.

With an aim (i) to collect various thermophysical properties on mixtures of cyclic amides + water at different temperatures and over the entire composition range and (ii) to understand the role of substituents such as methyl and vinyl groups on the overall bulk interactions in pyrrolidinone aqueous systems, we report the experimental densities, dynamic viscosities, and speeds of sound in the temperature range (298.15 to 328.15) K and relative permittivities at T = (298.15 and 328.15) K for the three binary mixtures of water + 2-pyrrolidinone, + 1-methyl-2-pyrrolidinone, and + 1-vinyl-2-pyrrolidinone. The typical characteristic profiles showing the compositional variations of each property and the analysis of deviation and excess functions derived therefrom were used to adjudge the interactions in such systems.

Experimental Section

Materials. 2-Pyrrolidinone with a stated purity of 99% (on a mole basis) was purchased from Sisco-Chem, India. 1-Methyl-2-pyrrolidinone and 1-vinyl-2-pyrrolidinone were of Fluka make (with more than 99 and 97% purities, respectively). The three chemicals were fractionally distilled under reduced pressure (0.001 to 0.002 MPa) through a 1 m column packed with glass helices. The initial and final fractions were rejected, while the middle fractions [boiling at (128, 78.5, and 93) °C for 2-pyrrolidinone, 1-methyl-2-pyrrolidinone, and 1-vinyl-2-pyrrolidinone, respectively, under 0.001 MPa pressure] constituting about 60% of the initial volume were collected for mixture preparation. Water was four times distilled in a glass still. Degassing of the water was effected by boiling before the solution preparation.

Methods. The binary solutions were prepared by mass in hermetically sealed glass vials. The solutions of each composition were prepared fresh, and all the properties were measured on the same day. The mass measurements, accurate to ±0.01 mg, were made on a single-pan analytical balance (Dhona 100 DS, India). The estimated uncertainty in the mole fraction was ±0.0001.

Densities, ρ, of the pure liquids and their mixtures were measured with a high-precision vibrating tube digital

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Table 1. Densities, ρ, Viscosities, η, Speeds of Sound, v, Relative Permittivities, ϵ_r, and Refractive Indexes, n_D, at T = (298.15 to 338.15) K for the Pure Components

		ρ/(g·cm^{-3})		η/(mPa·s)		v/ (m·s^{-1})		ϵ_r		n_D	
	T/K	expt	lit.	expt	lit.	expt	lit.	expt	lit.	expt	lit.
water	298.15	0.99704 5	0.997047[16]	0.890	0.89025[16]	1498.0	1497.4[18]	78.439	78.435[18]	1.3323	1.3325[16]
	308.15	0.99403 2	0.994031[16]	0.719	0.71903[16]	1519.0	1519.7[18]				
	318.15	0.99021 0	0.990216[16]	0.596	0.59716[16]	1535.1	1535.6[18]				
	328.15	0.98569 2	0.985695[16]	0.503	0.50415[16]	1545.0	1546.1[18]	68.345	68.345[18]		
	338.15	0.98055 0	0.980552[16]	0.438	0.43407[16]	1551.0	1551.9[18]				
2-pyrrolidinone	298.15	1.10701 9	1.10701[5]	13.363	13.3[16]	1633.2		28.173	28.18[5]	1.4860	1.486[16]
	308.15	1.09914 8	1.09915[5]	8.844		1603.1					
	318.15	1.09105 7	1.09105[5]	6.259		1563.2					
	328.15	1.08286 7		4.677		1549.7		26.604	26.607[13]		
	338.15	1.07067 9		3.451		1520.1					
1-methyl-2-pyrrolidinone	298.15	1.02831 1	1.02832[8]	1.663	1.666[16]	1545.1	1544.5[6]	32.170	32.16[16]	1.4675	1.4675[16]
	308.15	1.01932 9		1.365		1518.4					
	318.15	1.01010 8		1.210		1477.8					
	328.15	1.00117 8		1.117		1448.7		27.933			
	338.15	0.99223 4		0.986		1407.3					
1-vinyl-2-pyrrolidinone	298.15	1.04204 0		4.322		1530.1		21.242		1.5100	
	308.15	1.03319 2		2.942		1499.4					
	318.15	1.02438 5		2.590		1467.6					
	328.15	1.01557 9		2.259		1430.2		18.924			
	338.15	1.00676 9		1.836		1403.3					

density meter (Anton Paar, DMA 5000). The instrument has a built-in thermostat for maintaining the desired temperatures in the range of (0 to 90) °C. The repeatability of the temperature has been found to be (±0.002 and ±0.003) °C for a given session and two different sessions, respectively. The uncertainty in the temperature during the measurements, however, is ±0.01 °C because Pt 100 measuring sensors were used. The instrument was calibrated with air and four times distilled and freshly degassed water at T = (293.15, 313.15, and 333.15) K during every session. The repeatability in the densities for the distilled water, freshly distilled pure liquids, and prepared binary mixtures has been found to be better than 3×10^{-6} g·cm^{-3}. We have estimated the uncertainty in our measured densities of the amides by comparing our data at different temperatures with the literature values, as listed in Table 1. This comparison gave a mean absolute deviation of 1.0×10^{-5} g·cm^{-3}. Hence the densities reported in the present work have an uncertainty of 1.0×10^{-5} g·cm^{-3}. The viscosity, η, of pure liquids and liquid mixtures was determined using modified suspended-level Ubbelohde capillary viscometers. Two different viscometers (one for the mixtures of water + 2-pyrrolidinone and another for the other two mixtures) were used to cover the medium and low viscosities in these systems. Each of the viscometers was calibrated at each of the measuring temperatures with four times distilled water, using the densities and dynamic viscosities from Table 1 and triple distilled pure cyclohexane (measured ρ_{25} = (0.77389 1, ρ_{35} = 0.76446 1, ρ_{45} = 0.75473 0, ρ_{55} = 0.74514 9, and ρ_{65} = 0.73529 5) g·cm^{-3}; η_{25} = (0.886, η_{35} = 0.755, η_{45} = 0.651, η_{55} = 0.566, and η_{65} = 0.496) mPa·s (the η values for the cyclohexane are the interpolated values from the viscosity−temperature correlating equation[16])) to estimate the viscometer constants, A and B, by solving the simultaneous equations of the type

$$\eta = \rho(At - B/t) \tag{1}$$

The viscometers were suspended in a thermostated water bath maintained to ±0.01 K. Four sets of readings for the flow times were taken using a Racer stop watch that can register time to ±0.1 s, and the arithmetic mean was taken for the calculation of the viscosity. The uncertainty in the measured viscosities (as estimated from the comparison of our values at T = 298.15 K with the literature data at the same temperature) has been found to be ±0.033 mPa·s. The speeds of sound, v, were measured using an ultrasonic interferometer (Mittal Enterprises, New Delhi, India) operating at a fixed frequency of 2 MHz. The measured speeds of sound have a precision of ±0.8 m·s^{-1} and an uncertainty better than ±1.0 m·s^{-1}. The relative permittivities of the individual pure components and binary mixtures at 3 MHz were calculated from the capacitance measurements with a universal dielectrometer, type OH-301 of Radelkis, Hungary. The procedure used in the calibration of dielectric cells was the same as described in detail elsewhere.[17] The measured relative permittivities have an uncertainty of ±0.006. The refractive indexes, n_D, for the sodium D line were measured with an Abbé type research refractometer. The temperatures during the v, ϵ_r, and n_D measurements were maintained within ±0.01 °C using an INSREF (India) circulator (model 020A).

Results and Discussion

Densities (ρ), Dynamic Viscosities (η), Speeds of Sound (v), and Relative Permittivities (ϵ_r). The experimental data of ρ, η, v, and ϵ_r at different temperatures are listed in Tables 2−5. The variation of ρ with water mole fraction was found to be typical; for water + pyrrolidinone and + 1-vinyl-2-pyrrolidinone systems, the values decreased gradually with an inflection around $x_1 \approx 0.75-0.825$ beyond which the decrease was found to be sharp. In the water + 1-methyl-2-pyrrolidinone mixture, a maximum was noted in the water-rich regions. The compositional variations of η and v also showed a nonlinear but complex behavior. The representative η versus x_1 and v versus x_1 profiles at T = (298.15 and 338.15) K in the water-rich compositions for the three binary mixtures are displayed in Figures 1 and 2. The η values varied in a parabolic manner for the water + 2-pyrrolidinone system; however, definable maxima at each temperature were observed in the water + 1-methyl-2-pyrrolidinone system. Interestingly, the profiles for water + 1-vinyl-2-pyrrolidinone showed an initial broad minimum followed by maxima in the water-rich region. We made an attempt to calculate the number of water molecules per amide molecule from the relative mole proportions of water and amide at which the dynamic viscosities showed either a maximum or an

Table 2. Densities, ρ ($g\cdot cm^{-3}$), for Water (1) + Cyclic Amides (2) at T = (298.15 to 338.15) K

	T/K				
x_1	298.15	308.15	318.15	328.15	338.15
	Water (1) + 2-Pyrrolidinone (2)				
0.0549	1.10652 6	1.09869 5	1.09054 2	1.08232 7	1.07015 9
0.1506	1.10577 3	1.09766 1	1.08950 9	1.08119 6	1.06904 6
0.2552	1.10443 1	1.09597 8	1.08786 8	1.07948 3	1.06739 8
0.3500	1.10241 4	1.09380 9	1.08568 7	1.07726 6	1.06529 3
0.4496	1.09952 8	1.09093 7	1.08274 6	1.07429 3	1.06247 6
0.5000	1.09770 7	1.08917 4	1.08094 4	1.07247 6	1.06075 6
0.5566	1.09519 8	1.08676 3	1.07850 8	1.07003 4	1.05845 2
0.6422	1.08977 8	1.08157 1	1.07338 2	1.06497 0	1.05370 6
0.7532	1.07706 8	1.06946 0	1.06172 4	1.05371 5	1.04327 9
0.8516	1.05603 2	1.04957 1	1.04281 0	1.03573 8	1.02674 6
0.8714	1.05024 0	1.04411 4	1.03763 4	1.03083 6	1.02224 1
0.8856	1.04571 4	1.03985 3	1.03359 4	1.02701 0	1.01872 5
0.9000	1.04079 5	1.03522 4	1.02920 6	1.02285 3	1.01490 2
0.9249	1.03147 7	1.02646 0	1.02090 2	1.01497 9	1.00765 3
0.9369	1.02661 2	1.02188 4	1.01656 7	1.01086 4	1.00385 9
0.9526	1.01987 5	1.01554 6	1.01056 5	1.00515 6	0.99859 2
0.9651	1.01421 2	1.01021 6	1.00551 9	1.00034 8	0.99414 7
0.9748	1.00963 7	1.00590 7	1.00144 1	0.99645 5	0.99054 3
0.9906	1.00187 0	0.9957 5	0.9952 0	0.98983 3	0.98434 3
	Water (1) + 1-Methyl-2-pyrrolidinone (2)				
0.0522	1.02954 6	1.02048 8	1.01119 4	1.00219 3	0.99318 2
0.1684	1.03290 4	1.02358 3	1.01409 3	1.00489 9	0.99570 6
0.2465	1.03515 1	1.02509 9	1.01608 4	1.00676 6	0.99745 5
0.3481	1.03813 2	1.02858 3	1.01881 1	1.00933 5	0.99987 0
0.4534	1.04164 9	1.03202 0	1.02207 6	1.01242 0	1.00278 1
0.5018	1.04341 1	1.03373 6	1.02371 5	1.01397 5	1.00425 4
0.5493	1.04511 4	1.03539 4	1.02531 0	1.01549 9	1.00570 5
0.6504	1.04771 1	1.03797 5	1.02789 6	1.01804 9	1.00820 3
0.7520	1.04606 2	1.03673 3	1.02711 7	1.01763 1	1.00808 6
0.8536	1.03521 1	1.02731 6	1.01908 5	1.01076 9	1.00225 1
0.8742	1.03143 5	1.02401 6	1.01622 2	1.00828 2	1.00009 6
0.8849	1.02924 1	1.02209 8	1.01455 5	1.00683 1	0.99883 6
0.8996	1.02596 7	1.01923 4	1.01206 3	1.00465 9	0.99694 8
0.9257	1.01942 8	1.01351 7	1.00708 3	1.00031 6	0.99317 1
0.9368	1.01638 3	1.01085 6	1.00476 7	0.99829 6	0.99141 6
0.9557	1.01088 4	1.00605 6	1.00059 1	0.99466 0	0.98826 1
0.9641	1.00833 2	1.00383 1	0.99866 0	0.99298 2	0.98680 8
0.9754	1.00482 2	1.00077 5	0.99601 3	0.99068 7	0.98482 7
0.9900	1.00020 8	0.99676 9	0.99255 7	0.98770 5	0.98226 6
	Water (1) + 1-Vinyl-2-pyrrolidinone (2)				
0.0557	1.04230 4	1.03343 4	1.02460 0	1.01576 9	1.00693 5
0.1591	1.04332 6	1.03435 6	1.02541 4	1.01648 5	1.00756 3
0.2543	1.04419 0	1.03514 1	1.02610 7	1.01709 6	1.00809 9
0.3503	1.04482 8	1.03573 2	1.02663 3	1.01756 0	1.00850 7
0.4525	1.04546 1	1.03632 6	1.02716 4	1.01803 2	1.00892 1
0.5028	1.04581 7	1.03666 1	1.02746 4	1.01829 8	1.00915 5
0.5539	1.04618 9	1.03701 4	1.02778 1	1.01858 1	1.00940 3
0.6546	1.04656 4	1.03740 7	1.02814 5	1.01891 1	1.00969 5
0.7505	1.04506 2	1.03616 3	1.02708 4	1.01799 7	1.00890 0
0.8519	1.03772 0	1.02980 1	1.02155 6	1.01318 1	1.00469 0
0.8751	1.03449 9	1.02699 0	1.01910 4	1.01104 0	1.00281 5
0.8852	1.03284 2	1.02554 1	1.01784 0	1.00993 6	1.00185 0
0.9001	1.03007 8	1.02312 1	1.01572 7	1.00808 8	1.00022 9
0.9251	1.02444 9	1.01818 5	1.01141 1	1.00431 0	0.99691 7
0.9357	1.02163 2	1.01571 1	1.00924 5	1.00241 3	0.99525 2
0.9554	1.01559 6	1.01040 2	1.00459 3	0.99833 3	0.99167 1
0.9649	1.01226 5	1.00746 9	1.00202 0	0.99607 5	0.98968 7
0.9749	1.00842 7	1.00408 5	0.99905 0	0.99346 7	0.98739 3
0.9903	1.00176 7	0.99820 6	0.99388 3	0.98892 4	0.98339 6

Table 3. Dynamic Viscosities, η (mPa·s), for Water (1) + Cyclic Amides (2) at T = (298.15 to 338.15) K

	T/K				
x_1	298.15	308.15	318.15	328.15	338.15
	Water (1) + 2-Pyrrolidinone (2)				
0.0549	13.020	8.614	6.104	4.562	3.370
0.1506	12.295	8.126	5.778	4.323	3.198
0.2552	11.766	7.761	5.543	4.147	3.076
0.3500	11.319	7.452	5.344	4.000	2.973
0.4496	10.630	6.988	5.034	3.772	2.810
0.5000	10.127	6.657	4.807	3.605	2.690
0.5566	9.408	6.188	4.480	3.364	2.516
0.6422	8.014	5.289	3.845	2.895	2.177
0.7532	5.772	3.853	2.823	2.143	1.630
0.8516	3.645	2.489	1.852	1.427	1.110
0.8714	3.231	2.224	1.663	1.288	1.009
0.8856	2.940	2.038	1.530	1.191	0.938
0.9000	2.651	1.852	1.398	1.095	0.867
0.9249	2.171	1.544	1.179	0.932	0.749
0.9369	1.948	1.401	1.078	0.858	0.695
0.9526	1.667	1.220	0.950	0.764	0.627
0.9651	1.451	1.082	0.851	0.690	0.574
0.9748	1.290	0.977	0.778	0.637	0.535
0.9906	1.036	0.812	0.662	0.551	0.473
	Water (1) + 1-Methyl-2-pyrrolidinone (2)				
0.0522	1.721	1.405	1.232	1.124	0.987
0.1684	1.985	1.588	1.350	1.194	1.026
0.2465	2.147	1.702	1.429	1.234	1.048
0.3481	2.535	1.979	1.613	1.357	1.129
0.4534	3.346	2.567	2.030	1.647	1.332
0.5018	3.838	2.925	2.287	1.827	1.460
0.5493	4.338	3.289	2.547	2.011	1.591
0.6504	5.159	3.885	2.973	2.308	1.799
0.7520	5.071	3.814	2.905	2.241	1.740
0.8536	3.650	2.760	2.117	1.645	1.292
0.8742	3.224	2.446	1.882	1.470	1.161
0.8849	2.992	2.273	1.754	1.374	1.089
0.8996	2.668	2.034	1.576	1.240	0.990
0.9257	2.093	1.609	1.261	1.004	0.813
0.9368	1.857	1.435	1.130	0.907	0.740
0.9557	1.487	1.160	0.928	0.753	0.627
0.9641	1.338	1.051	0.845	0.092	0.580
0.9754	1.160	0.920	0.747	0.618	0.524
0.9900	0.978	0.785	0.045	0.541	0.467
	Water (1) + 1-Vinyl-2-pyrrolidinone (2)				
0.0557	4.243	2.907	2.552	2.221	1.807
0.1591	4.052	2.809	2.454	2.128	1.736
0.2543	3.875	2.718	2.362	2.042	1.668
0.3503	3.750	2.667	2.305	1.983	1.624
0.4525	3.717	2.694	2.310	1.975	1.621
0.5028	3.742	2.742	2.340	1.993	1.639
0.5539	3.792	2.807	2.385	2.025	1.667
0.6546	3.910	2.954	2.488	2.096	1.730
0.7505	3.904	3.001	2.509	2.103	1.739
0.8519	3.466	2.703	2.249	1.876	1.557
0.8751	3.255	2.545	2.115	1.763	1.466
0.8852	3.145	2.463	2.046	1.705	1.420
0.9001	2.962	2.324	1.929	1.609	1.340
0.9251	2.591	2.040	1.692	1.411	1.180
0.9357	2.408	1.900	1.576	1.314	1.100
0.9554	2.021	1.600	1.326	1.108	0.931
0.9649	1.082	1.437	1.191	0.995	0.840
0.9749	1.573	1.252	1.037	0.868	0.736
0.9903	1.169	0.932	0.776	0.652	0.560

inflection. It was found that the bulk heterocomplexes have one, two, and three water molecules per 2-pyrrolidinone, 1-methyl-2-pyrrolidinone, and 1-vinyl-2-pyrrolidinone molecules, respectively. The υ versus x_1 profiles were typically nonlinear and were characterized by broad maxima in the water-rich regions. The complex variation as described above indicates that the water + cyclic amide systems show large nonidealities due to strong specific heterointeractions. To gain further insight into the nature of these interactions, we discuss below the features in the excess and deviation functions for these binary mixtures at different temperatures.

Excess Molar Volumes (V_m^E). The $V_{\mathrm{m}}^{\mathrm{E}}$ values were calculated using the equation

$$V_{\mathrm{m}}^{\mathrm{E}}/(\mathrm{cm^3\cdot mol^{-1}}) = \frac{x_1 M_1 + x_2 M_2}{\rho_{12}} - \left\{\frac{x_1 M_1}{\rho_1} + \frac{x_2 M_2}{\rho_2}\right\} \quad (2)$$

The $V_{\mathrm{m}}^{\mathrm{E}}$ values were smoothed through a Redlich–Kister equation of the type

Table 4. Speed of Sound, v (m·s^{-1}), for Water (1) + Cyclic Amides (2) at T = (298.15 to 338.15) K

x_1	T/K 298.15	308.15	318.15	328.15	338.15
	Water (1) + 2-Pyrrolidinone (2)				
0.0549	1637.8	1609.2	1570.0	1556.0	1526.1
0.1506	1641.1	1618.7	1576.7	1562.4	1532.8
0.2552	1662.0	1635.9	1589.9	1574.8	1545.0
0.3500	1691.1	1657.3	1608.9	1592.4	1562.0
0.4496	1711.7	1679.0	1630.3	1612.3	1581.5
0.5000	1717.9	1688.1	1640.2	1621.7	1590.8
0.5566	1723.5	1696.7	1650.3	1631.3	1600.7
0.6422	1728.3	1706.4	1663.9	1644.8	1615.2
0.7532	1730.9	1711.6	1678.2	1659.9	1632.8
0.8516	1715.4	1695.1	1675.0	1660.2	1638.6
0.8714	1704.6	1686.1	1669.5	1656.2	1636.4
0.8856	1694.1	1677.9	1664.0	1652.0	1633.7
0.9000	1681.0	1667.7	1656.8	1646.3	1629.8
0.9249	1650.9	1645.0	1639.6	1632.4	1619.7
0.9369	1632.7	1631.3	1628.8	1623.5	1613.0
0.9526	1605.5	1610.1	1611.8	1609.4	1602.2
0.9651	1580.7	1590.4	1595.5	1595.8	1591.6
0.9748	1559.8	1573.1	1581.1	1583.8	1582.0
0.9906	1522.6	1540.9	1553.7	1560.8	1563.7
	Water (1) + 1-Methyl-2-pyrrolidinone (2)				
0.522	1548.8	1521.3	1480.9	1451.9	1410.7
0.1684	1561.0	1533.3	1493.0	1463.8	1422.8
0.2465	1579.5	1549.9	1508.9	1478.8	1437.4
0.3481	1616.8	1578.3	1535.9	1504.2	1461.9
0.4534	1653.8	1610.1	1566.5	1533.2	1490.2
0.5018	1667.7	1624.8	1580.9	1547.1	1504.0
0.5493	1682.0	1639.5	1595.4	1561.1	1518.0
0.6504	1711.3	1672.0	1628.2	1593.5	1551.0
0.7520	1738.2	1702.6	1661.2	1627.4	1587.1
0.8536	1748.1	1707.3	1674.5	1646.4	1613.3
0.8742	1738.4	1700.3	1670.7	1645.0	1614.4
0.8849	1730.9	1694.9	1667.3	1643.2	1614.4
0.8996	1716.8	1685.4	1660.9	1639.2	1613.0
0.9257	1681.1	1661.1	1643.6	1627.2	1602.6
0.9368	1661.0	1647.4	1633.5	1619.9	1602.1
0.9557	1621.2	1618.8	1611.9	1603.9	1591.8
0.9641	1600.8	1603.6	1600.4	1595.2	1585.9
0.9754	1571.3	1580.6	1582.7	1581.7	1576.7
0.9900	1529.1	1546.1	1556.1	1561.2	1562.4
	Water (1) + 1-Vinyl-2-pyrrolidinone (2)				
0.0557	1533.7	1502.5	1470.5	1433.0	1406.0
0.1591	1548.1	1514.3	1480.4	1441.7	1413.8
0.2543	1563.3	1526.7	1490.9	1451.2	1422.3
0.3503	1580.9	1541.2	1503.3	1462.3	1432.4
0.4525	1598.7	1556.2	1516.6	1474.7	1444.1
0.5028	1609.9	1565.6	1524.9	1482.4	1451.3
0.5539	1618.5	1573.3	1532.1	1489.6	1458.3
0.6546	1635.8	1589.3	1547.7	1505.7	1474.6
0.7505	1649.2	1603.4	1563.3	1523.4	1493.7
0.8519	1648.2	1609.5	1576.0	1542.9	1517.9
0.8751	1646.7	1610.5	1579.4	1548.6	1525.2
0.8852	1644.4	1609.8	1580.1	1550.7	1528.2
0.9001	1640.0	1608.2	1580.9	1553.7	1532.8
0.9251	1623.7	1599.1	1577.9	1556.2	1539.1
0.9357	1613.8	1593.2	1575.3	1556.5	1541.5
0.9554	1589.5	1578.2	1567.9	1556.6	1545.5
0.9649	1574.7	1568.8	1562.9	1554.4	1547.0
0.9749	1556.5	1557.1	1556.6	1552.6	1548.4
0.9903	1523.1	1535.4	1544.4	1548.5	1550.2

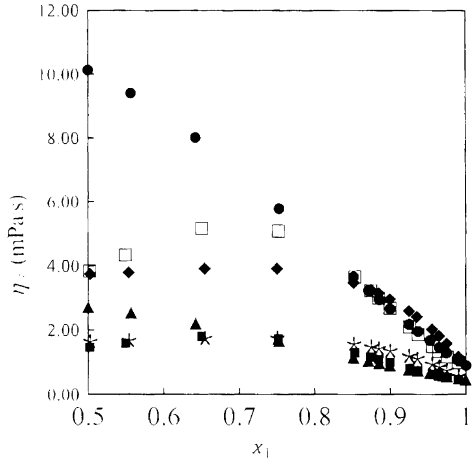

Figure 1. Variation of dynamic viscosities, η, with water mole fraction for the binary mixtures of water + 2-pyrrolidinone at T = ((●) 298.15 and (▲) 338.15) K, of water + 1-methyl-2-pyrrolidinone at T = ((□) 298.15 and (■) 338.15) K, and of water + 1-vinyl-2-pyrrolidinone at T = ((◆) 298.15 and (*) 338.15) K.

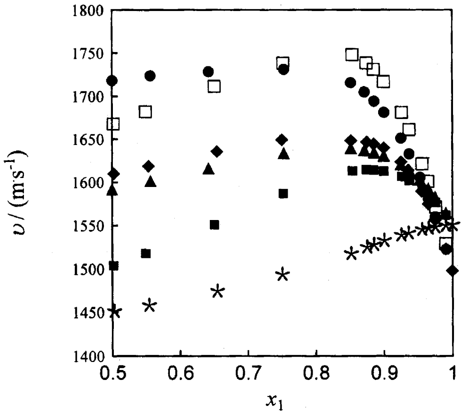

Figure 2. Variation of speeds of sounds, v, with water mole fraction for the binary mixtures of water + 2-pyrrolidinone, water + 1-methyl-2-pyrrolidinone, and water + 1-vinyl-2-pyrrolidinone. The symbols are the same as those in Figure 1.

$$Y^{E} = x_1(1 - x_1)\sum_{i=0}^{i=n} a_i(2x_1 - 1)^i \tag{3}$$

where $Y^E = V_m^E$ and a_i are the smoothing coefficients. a_i were estimated by multiple regression analysis based on a least-squares method. The summary of a_i along with the standard deviation, σ, between calculated and fitted values is given in Table 6. The graphical variation of smoothed V_m^E as a function of water mole fraction for water + 2-pyrrolidinone and + 1-methyl-2-pyrrolidinone mixtures at T = (298.15 to 338.15) K is shown in parts a and b of Figure 3. The literature values for the same mixtures are also shown in the figure for comparison. Our smoothed V_m^E values for water + 2-pyrrolidinone at T = (298.15 and 308.15) K are in excellent agreement with the literature values of Al-Azzwal et al.,[5] while our data for the same mixture and temperature were found to be less negative (in the x_1 region of 0.2 to 0.6) than those reported by Uosaki et al.[10] Surprisingly, the literature V_m^E values[8] for the same mixture at T = 298.15 K were found to be far more negative in the x_1 range of 0.1 to 0.4 and less negative beyond $x_1 > 0.4$ not only from our data but also from the other literature values.[5,10] These discrepancies are mainly attributable to the source and purity of pure amides. Similarly, our V_m^E values for water + 1-methyl-2-pyrrolidinone at T = 298.15 K (in the whole range of mole fraction) and T = 308.15 K ($x_1 > 0.6$) are in excellent agreement with the literature data for the same mixtures at the same temperature.[10] Again, literature values from Garcia et al.[8] for this mixture were found to show similar deviations from our data as described above for the water + 2-pyrrolidinone mixture. We did not find any literature V_m^E values for the water + 1-vinyl-2-pyrrolidinone system. In the three mixtures of water + cyclic amides, the rise in the temperature resulted in less negative V_m^E especially in the middle to water-rich mole fraction regions. A similar temperature

Table 5. Relative Permittivities, ϵ_r, for Water (1) + Cyclic Amides (2) at T = (298.15 and 328.15) K

	ϵ_r			ϵ_r			ϵ_r	
x_1	T = 298.15 K	T = 328.15 K	x_1	T = 298.15 K	T = 328.15 K	x_1	T = 298.15 K	T = 328.15 K
Water (1) + 2-Pyrrolidinone (2)			Water (1) + 1-Methyl-2-pyrrolidinone (2)			Water (1) + 1-Vinyl-2-pyrrolidinone (2)		
0.0459	28.973	27.246	0.0522	33.019	28.617	0.0557	22.291	19.761
0.1506	32.132	29.717	0.1684	35.117	30.321	0.1591	24.461	21.488
0.2552	35.671	32.500	0.2465	36.991	31.837	0.2543	27.294	23.726
0.3500	39.103	35.214	0.3481	39.876	34.173	0.3503	30.776	26.471
0.4496	43.320	38.553	0.4534	43.201	36.895	0.4525	34.744	29.649
0.5000	45.734	40.477	0.5018	44.854	38.266	0.5028	36.750	31.282
0.5566	48.613	42.780	0.5493	46.611	39.723	0.5539	38.875	33.025
0.6422	53.063	46.379	0.6504	51.030	43.432	0.6546	43.615	36.991
0.7532	58.429	50.876	0.7520	56.890	48.397	0.7505	49.479	41.967
0.8516	63.088	55.002	0.8536	64.428	54.952	0.8519	57.978	49.347
0.8714	64.212	56.012	0.8742	66.147	56.489	0.8751	60.355	51.465
0.8856	65.105	56.810	0.8849	67.064	57.321	0.8852	61.455	52.445
0.9000	66.112	57.706	0.8996	68.353	58.501	0.9001	63.145	53.977
0.9249	68.159	59.513	0.9257	70.722	60.710	0.9251	66.231	56.800
0.9369	69.328	60.532	0.9368	71.764	61.705	0.9357	67.645	58.104
0.9526	71.074	62.048	0.9557	73.608	63.491	0.9554	70.483	60.763
0.9651	72.677	63.431	0.9641	74.463	64.326	0.9649	71.976	62.168
0.9748	74.070	64.630	0.9754	75.645	65.507	0.9749	73.650	63.753
0.9906	76.671	66.846	0.9900	77.262	67.139	0.9903	76.467	66.452

Table 6. Coefficients of Equation 4 for the Mathematical Representation of Deviation and Excess Functions for Water (1) + Cyclic Amides (2) at Different Temperatures

	T/K	a_0	a_1	a_2	a_3	a_4	σ
Water (1) + 2-Pyrrolidinone (2)							
$V_m^E/(cm^3 \cdot mol^{-1})$	298.15	−2.010	−1.241	−0.987	1.168	2.134	0.001
	308.15	−1.748	−1.284	−0.864	1.374	1.769	0.001
	318.15	−1.596	−1.105	−0.859	1.183	1.804	0.001
	328.15	−1.435	−0.986	−0.778	1.044	1.642	0.001
	338.15	−1.291	−0.893	−0.703	0.954	1.466	0.001
$\delta\eta/(mPa \cdot s)$	298.15	12.001	2.482	−13.317	−3.783	5.341	0.001
	308.15	7.501	1.550	−8.330	−2.363	3.343	0.001
	318.15	5.516	1.138	−6.120	−1.733	2.450	0.001
	328.15	4.056	0.835	−4.495	−1.269	1.793	0.001
	338.15	2.980	0.621	−3.296	−0.949	1.311	0.001
$\kappa_s^E/(TPa)^{-1}$	298.15	−247.2	−223.4	−57.3	−479.2	−520.5	0.4
$\delta\epsilon_r$	298.15	31.977	37.162	22.590	−28.002	−47.660	0.001
	328.15	23.987	27.865	16.897	−20.993	−35.683	0.001
Water (1) + 1-Methyl-2-pyrrolidinone (2)							
$V_m^E/(cm^3 \cdot mol^{-1})$	298.15	−4.379	−2.771	−1.452	2.621	3.320	0.001
	308.15	−4.088	−2.603	−1.124	2.484	2.854	0.001
	318.15	−3.785	−2.417	−1.047	2.319	2.645	0.001
	328.15	−3.503	−2.236	−0.992	2.142	2.476	0.001
	338.15	−3.248	−2.062	−0.859	1.972	2.213	0.001
$\delta\eta/(mPa \cdot s)$	298.15	10.165	22.603	14.766	−19.656	−21.582	0.001
	308.15	7.476	16.618	10.826	−14.451	−15.826	0.001
	318.15	5.494	12.225	7.988	−10.641	−11.669	0.001
	328.15	4.043	8.978	5.847	−7.798	−8.557	0.001
	338.15	2.969	6.615	4.349	−5.761	−6.353	0.001
$\kappa_s^E/(TPa)^{-1}$	298.15	−298.6	−310.6	−140.3	−641.4	−613.6	0.6
$\delta\epsilon_r$	298.15	21.237	21.407	15.278	36.989	30.604	0.001
	328.15	15.931	16.044	11.413	27.758	23.012	0.001
Water (1) + 1-Vinyl-2-pyrrolidinone (2)							
$V_m^E/(cm^3 \cdot mol^{-1})$	298.15	−2.453	−1.778	−2.004	−0.016	1.812	0.001
	308.15	−2.204	−1.609	−1.864	−0.001	1.713	0.001
	318.15	−1.963	−1.432	−1.651	0.006	1.500	0.001
	328.15	−1.755	−1.265	−1.411	−0.023	1.273	0.001
	338.15	−1.560	−1.136	−1.310	−0.002	1.197	0.001
$\delta\eta/(mPa \cdot s)$	298.15	4.541	8.340	9.138	3.715	0.629	0.001
	308.15	3.627	6.684	7.401	2.955	0.371	0.001
	318.15	2.977	5.482	6.039	2.422	0.342	0.001
	328.15	2.442	4.492	4.933	1.992	0.307	0.001
	338.15	2.000	3.685	4.087	1.629	0.194	0.001
$\delta\epsilon_r$	298.15	28.448	24.162	2.527	33.082	37.532	0.001
	328.15	20.769	17.636	1.818	24.155	27.438	0.001

dependence of V_m^E for the water + 2-pyrrolidinone mixture was also reported by Pirila-Honkanen and Ruostesuo.[9] Among the three amides, at a given composition V_m^E values followed the order 1-methyl-2-pyrrolidinone > 2-vinyl-2-pyrrolidinone > 2-pyrrolidinone. The equimolar V_m^E values became 2.2 and 2.5 times more negative at T = (298.15 and 338.15) K, respectively, from water + 2-pyrrolidinone to water + 1-methyl-2-pyrrolidinone mixtures. So the presence of a $-CH_3$ group on the nitrogen of 1-methyl-2-pyrrolidinone contributes more negatively to V_m^E. However, the negative contribution of the vinyl $-CH{=}CH_2$ group is less than that of the $-CH_3$ group.

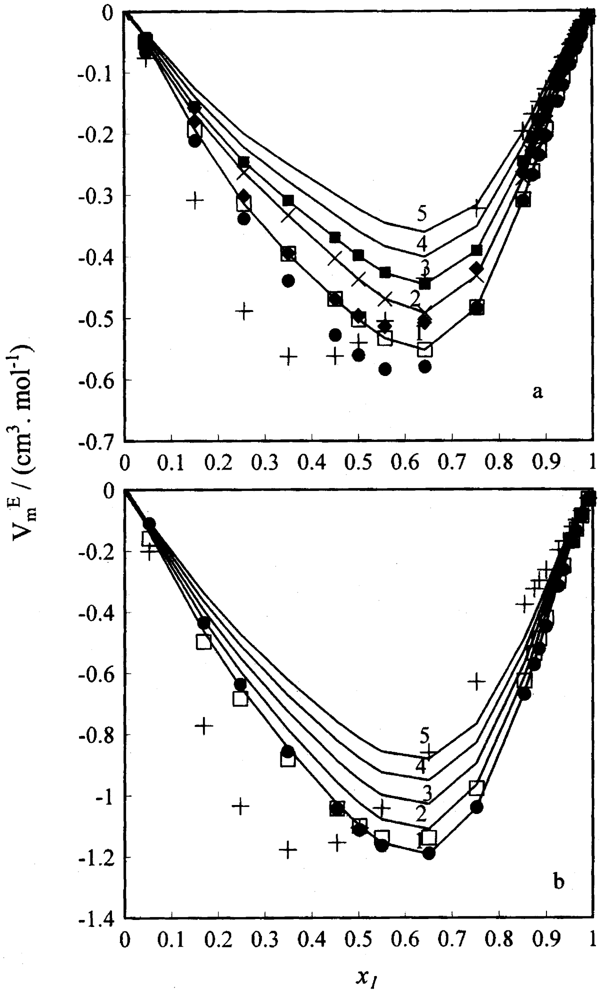

Figure 3. Variation of excess molar volumes, V_m^E, with water mole fraction for representative binary mixtures: (a) Water + 2-pyrrolidinone at different temperatures. Curves represent smoothed values using eq 3 and coefficients from Table 6; curves 1, 2, 3, 4, and 5 are at T = (298.15, 308.15, 318.15, 328.15, and 338.15) K. Literature values at T = 298.15 K ((+) ref 8, (●) ref 10, (□) ref 5) and T = 308.15 K ((◆) ref 10, (×) ref 5). (b) Water + 1-methyl-2-pyrrolidinone. Curves are the same as for water + 2-pyrrolidinone. Literature values at T = 298.15 K ((+) ref 8, (●) ref 10) and at T = 308.15 K ((□) ref 10).

Viscosity Deviations ($\delta\eta$). The $\delta\eta$ values were calculated using the equation

$$\delta\eta = \eta_{12} - (x_1\eta_1 + x_2\eta_2) \quad (4)$$

Thus-calculated $\delta\eta$ values were smoothed by eq 3, and the values of the smoothing coefficients, a_i, and σ are listed in Table 6. The $\delta\eta$ values in general were large and positive in the three mixtures at the five measured temperatures. Pronounced and steep maxima of $\delta\eta$ were observed in the three mixtures. A representative profile of $\delta\eta$ versus x_1 for the water + 2-pyrrolidinone mixture at different temperatures is depicted in Figure 4. The $\delta\eta$ values have been found to be maximally positive in water + 1-methyl-2-pyrrolidinone followed by water + 2-pyrrolidinone and + 1-vinyl-2-pyrrolidinone systems. Our calculated $(\delta\eta)_{0.5}$ values of (3.000 and 2.541) mPa·s for water + 2-pyrrolidinone and + 1-methyl-2-pyrrolidinone mixtures at 298.15 K are in excellent agreement with the reported values of (3.00[8] and 2.55[8]) mPa·s for the same systems at the same temperature.

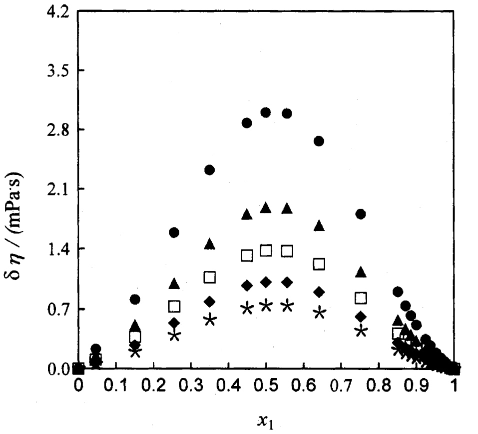

Figure 4. Variation of deviations in dynamic viscosities, $\delta\eta$, with water mole fraction for the binary mixture of water + 2-pyrrolidinone at T = ((●) 298.15, (▲) 308.15, (□) 318.15, (◆) 328.15, and (*) 338.15) K.

Excess Isentropic Compressibilities (κ_s^E). κ_s^E values were calculated by

$$\kappa_s^E/(\mathrm{TPa}^{-1}) = \kappa_s - \kappa_s^{id} \quad (5)$$

where κ_s is the isentropic compressibility and was calculated using the Laplace relation, that is, $\kappa_s = 1/(v^2\rho)$, and κ_s^{id} was calculated from the relations

$$\kappa_s^{id} = \sum_{i=1}^{2}\phi_i[\kappa_{s.i} + TV_i(\alpha_i^2)/C_{p.i}] - \{T(\sum_{i=1}^{2}x_iV_i)(\sum_{i=1}^{2}\phi_i\alpha_i)^2/\sum_{i=1}^{2}x_iC_{p.i}\} \quad (6)$$

where ϕ_i is the ideal state volume fraction and is defined by the relation

$$\phi_i = x_iV_i/(\sum_{i=1}^{2}x_iV_i) \quad (7)$$

V_i is the molar volume, α_i is the isobaric thermal expansion coefficient (calculated from the measured densities of the pure components at different temperatures in the range of T = (288.15 to 353.15) K, and $C_{p.i}$ is the molar heat capacity of pure water (1) or amide (2). We could find in the literature the molar heat capacities, $C_{p.i}$ (in J·K^{-1}·mol^{-1}), for 2-pyrrolidinone (169.5[18]) and for 1-methyl-2-pyrrolidinone (307.8[18]) at T = 298.15 K and hence calculate κ_s^{id}, that is, ideal state isentropic compressibility, and κ_s^E values for water + 2-pyrrolidinone and + 1-methyl-2-pyrrolidinone at T = 298.15 K only. The coefficients a_i and σ values for the mathematical representation of κ_s^E values by eq 3 are given in Table 6. The graphical variation of κ_s^E values with the water mole fraction is shown in Figure 5. It can be seen that the κ_s^E values are negative and the profiles are found to be highly skewed toward the water-rich region. As far as the κ_s^E values corresponding to the minima region are concerned, the system water + 1-methyl-2-pyrrolidinone has been characterized by more negative values than the water + 2-pyrrolidinone mixture.

Relative Permittivities (ϵ_r) and Deviations in Relative Permittivities ($\delta\epsilon_r$). The experimental ϵ_r values for the three binary mixtures at T = (298.15 and 328.15) K

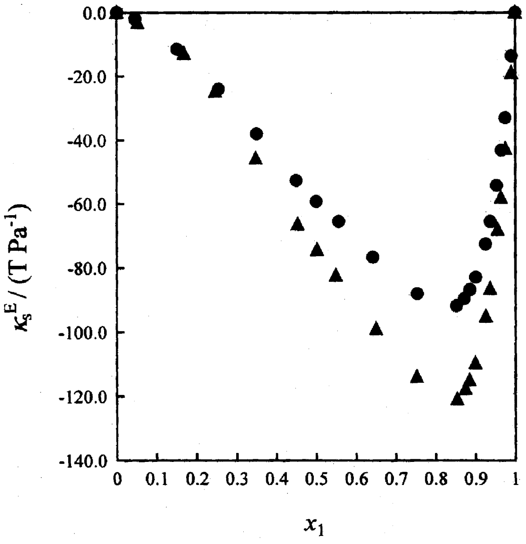

Figure 5. Variation of excess isentropic compressibilities, κ_s^E, with water mole fraction for the binary mixtures of water + (●) 2-pyrrolidinone and + (▲) 1-methyl-2-pyrrolidinone at T = 298.15 K.

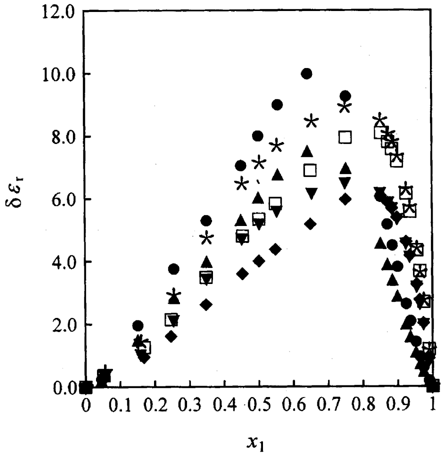

Figure 6. Variation of the deviation in relative permittivities, $\delta\epsilon_r$, with water mole fraction for the binary mixtures of water + 2-pyrrolidinone at ((●) 298.15 and (▲) 328.15) K, water + 1-methyl-2-pyrrolidinone at ((□) 298.15 and (◆) 3281.5) K, and water + 1-vinyl-2-pyrrolidinone at ((*) 298.15 and (▼) 328.15) K.

are listed in Table 5. The $\delta\epsilon_r$ was calculated using the relation

$$\delta\epsilon_r = \epsilon_{r.12} - (\phi_1\epsilon_{r.1} + \phi_2\epsilon_{r.2}) \tag{8}$$

The $\delta\epsilon_r$ values were also fitted to eq 3, and the summary of fits in terms of coefficients, a_i, and σ values is given in Table 6. The variation of $\delta\epsilon_r$ with the water mole fraction for the three mixtures at T = (298.15 and 328.15) K is graphically depicted in Figure 6. The $\delta\epsilon_r$ values for the mixtures in general have been found to be large and positive with maxima skewed toward the water-rich region. The $\delta\epsilon_r$ values for each of the amides in the water-rich region are close to each other. But the values of $(\delta\epsilon_r)_{0.5}$ among the three amides at both temperatures showed the order 2-pyrrolidinone > 1-vinyl-2-pyrrolidinone > 1-methyl-2-pyrrolidinone. Ruostesuo and Pirila-Honkanen[15] have reported relative permittivities at 2 MHz for the water + 2-pyrrolidinone mixture at T = (303.15 and 323.15) K. The authors calculated the deviations in relative permittivities based on a mole fraction average of pure component values to the ideal state. Al-Azzwal et al.[5] have also calculated the deviations in relative permittivities for the same mixture using a similar approach. The authors noticed that the $\delta\epsilon_r$ values were large and negative over most of the mole fraction range. Similarly, Dachwitz and Stockhausen[14] made a dielectric relaxation study of water + 2-pyrrolidinone and + 1-methyl-2-pyrrolidinone at T = 293.15 K by measuring the complex permittivity of the binary mixtures in the frequency range of 20 MHz to 36 GHz. Since the experimental conditions and treatment of the dielectric functions in these literature reports are different than in the present study, we could not make any direct comparison with the literature data.

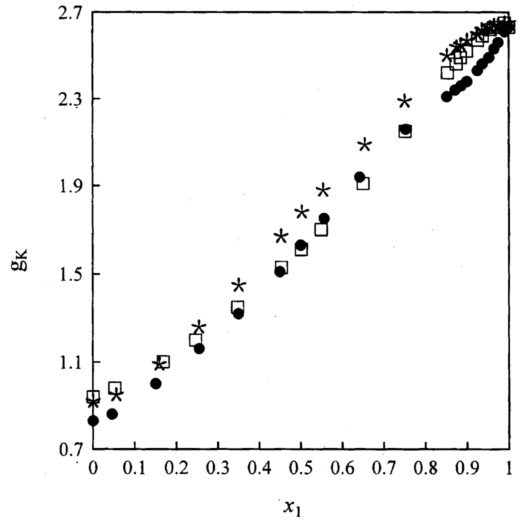

Figure 7. Variation of the Kirkwood correlation factor, g_K, with water mole fraction for the binary mixtures of water + (●) 2-pyrrolidinone, + (□) 1-methyl-2-pyrrolidinone, and + (*) 1-vinyl-2-pyrrolidinone at T = 298.15 K.

To ascertain information on the nature of structural order in terms of alignment of dipoles or correlation among dipoles, the values of the Kirkwood correlation factor, g_K, were calculated using the relation

$$g_K = \left\{\frac{(\epsilon_{r.12} - \epsilon_\alpha)(2\epsilon_{r.12} + \epsilon_\alpha)}{\epsilon_{r.12}(\epsilon_\alpha + 2)^2}\right\}\left\{\frac{9kT}{4\pi N(x_1\mu_1 + x_2\mu_2)^2}\right\}V_{m.12} \tag{9}$$

where k and μ_i are the Boltzmann constant and the dipole moments of the pure components. The μ_i values were determined by the standard procedure.[21] The same at T = 298.15 K are (1.332, 1.486, 1.468, and 1.510) D for water, 2-pyrrolidinone, 1-methyl-2-pyrrolidinone, and 1-vinyl-2-pyrrolidinone, respectively. ϵ_α was equated to $1.1n_D^2$, where n_D is the refractive index of the binary mixtures. The variation of g_K over the entire water mole fraction at T = 298.15 K for the three mixtures has been examined. Such a variation of g_K versus x_1 profiles is shown in Figure 7. The pure cyclic amides have g_K values close to 1.0. They gradually and monotonically increase with an increase in water mole fraction up to $x_1 \approx 0.8-0.90$. However, in the water extreme rich region $x_1 \approx 0.90$, the variation in g_K is very much less in water + 1-methyl-2-pyrrolidinone and + 1-vinyl-2-pyrrolidinone mixtures. Thus, in the binary mixtures of water + cyclic amides, heteroassociates are formed with a high dipolar orientation. Dachwitz and Stockhausen[14] also gave evidence from the dielectric relaxation studies on such mixtures that the formation of heteroassociates takes place preferentially at the expense of self-association of water molecules.

Partial Molar Volumes and Transfer Functions. Partial molar volumes at infinite dilution, $\bar{V}_1^\infty$, for water in

Table 7. Partial Molar Volumes at Infinite Dilution, $\bar{V}_1^\infty$, and Standard Function of Transfer for Volumes, $\bar{V}_{1.tr}^\infty$, of Water in Water + Cyclic Amide Mixtures at Different Temperatures[a]

	$\bar{V}_1^\infty$/ ($cm^3 \cdot mol^{-1}$)			$\bar{V}_{1.tr}^\infty$/ ($cm^3 \cdot mol^{-1}$)		
T/K	water (1) + Pyr (2)	water (1) + Mpyr (2)	water (1) + Vpyr (2)	Pyr → Mpyr	Pyr → Vpyr	Mpyr → Vpyr
298.15	17.28	15.71	17.22	−1.57	−0.06	1.51
308.15	17.37	15.88	17.38	−1.49	0.01	1.50
318.15	17.46	16.10	17.50	−1.36	0.04	1.40
328.15	17.65	16.36	17.68	−1.29	0.03	1.32
338.15	17.78	16.57	17.84	−1.21	0.06	1.27

[a] Pyr, 2-pyrrolidinone; Mpyr, 1-methyl-2-pyrrolidinone; Vpyr, 1-vinyl-2-pyrrolidinone.

water + amide systems were calculated from the smoothed V_m^E values using the coefficients from Table 6 and relations as reported in the literature.[19] The $\bar{V}_1^\infty$ values along with the transfer functions, $\bar{V}_{1.tr}^\infty$ (i.e., the difference in $\bar{V}_1^\infty$ for two given binary systems of water + different amides), are listed in Table 7. It can be seen that the function for the water becomes (i) large and negative from the 2-pyrrolidinone environment to 1-methyl-2-pyrrolidinone, (ii) small but positive from 2-pyrrolidinone to 1-vinyl-2-pyrrolidinone, and (iii) large and positive from 1-methyl-2-pyrrolidinone to 1-vinyl-2-pyrrolidinone. The three cyclic amides have two main sites for the hydration. The pyrrolidinone oxygen atom provides a site for hydrophilic hydration, and the $-CH_3$ and $-CH{=}CH_2$ groups can induce hydrophobic hydration. Molecular dynamics calculations of 1-methyl-2-pyrrolidinone in liquid water[20] revealed that on average, only 2.5 water molecules were found to occupy the first solvation shell around the oxygen with typically 1.5 hydrogen bonds to this site. In contrast, the first solvation shell of the methyl group contained 15.5 water molecules with cooperative hydrogen bonding among water molecules around the methyl moiety. What was more unusual was that there was strong evidence of cooperative solvation between these two sites. The water involved tended to hydrogen bond both to the pyrrolidinone oxygen atom and around the methyl group at the same time. Thus both hydrophilic and hydrophobic hydrations are responsible for the complex variations in the thermophysical properties in mixtures of water + cyclic amides.

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