Excess Molar Volumes and Apparent Molar Volumes of Some Amide + Water Systems at 303.15 and 308.15 K

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Excess molar volumes V_m^E for the binary mixtures of *N*-methylformamide, *N*,*N*-dimethylformamide, 2-pyrrolidinone, *N*-methyl-2-pyrrolidinone, and *N*,*N*-dimethylacetamide with water have been measured using a continuous-dilution dilatometer at 303.15 and 308.15 K as a function of composition. In all mixtures, the excess molar volumes are negative over the entire composition range. The results were used to estimate the apparent molar volumes of the components. The values of these two properties have been discussed in terms of intermolecular interactions between the mixing components of the binary mixture.

Introduction

The present work concerns the study of the composition dependence of excess molar volumes in amide + water mixtures in order to seek evidence of the existence of metastable amide aggregates and to explore the effects of their interaction with water upon self-aggregation.

In this paper, excess molar volumes, V_m^E, measured using a continuous-dilution dilatometer, are reported for the systems containing water + *N*-methylformamide (NMF), + *N*,*N*-dimethylformamide (DMF), + 2-pyrrolidinone (2P), + *N*-methyl-2-pyrrolidinone (NM2P), and + *N*,*N*-dimethylacetamide (DMA) at 303.15 and 308.15 K over the entire mole fraction range.

Apparent molar volumes have been calculated from densities obtained from the V_m^E results. To the best of our knowledge, no previous measurements on these systems at higher temperature, except 2-pyrrolidinone and *N*-methyl-2-pyrrolidinone, have been reported. An attempt has been made to interpret the results in terms of the existence of ordered patterns of molecular aggregation, and changes in these aggregates as a function of temperature.

Experimental Section

The water used was deionized by means of ion-exchange resins and then glass distilled. Its conductivity was always less than $1.0 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. *N*-Methylformamide (Fluka purum grade), *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, and *N*-methyl-2-pyrrolidinone (S.D. Fine Chemicals, spectroanalyzed reagents), and 2-pyrrolidinone (E. Merck, Gold Label, FRG) were used after purification (*1*), and their purities were checked by density, ϱ, and refractive index, n_D, determinations at 303.15 and 308.15 K; they agreed reasonably with the available literature values (*1*−*3*). All samples were stored and protected against atmospheric moisture and CO_2. The manufacturer's estimates of the purity were, in each case, greater than mass fraction 0.990. The water content was measured for *N*-methylformamide, *N*,*N*-dimethylformamide, 2-pyrrolidinone, *N*-methyl-2-pyrrolidinone, and *N*,*N*-dimethylacetamide by the Karl-Fischer method, and was always found to be less than mass fraction 0.0003.

Densities, ϱ, for the pure substances were measured by use of a bicapillary pycnometer of about 15 cm^3 capacity.

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Table 1. Densities ϱ for the Pure Liquids

component	*T*/K	ϱ/(kg·m^{-3}) measd	lit.
water	303.15		995.647 (*4*)
	308.15		994.032 (*4*)
N-methylformamide	303.15	995.1	
	308.15	991.0	990.5 (*2*)
N,*N*-dimethylformamide	303.15	939.7	941.2 (*1*)
	308.15	935.6	936.1 (*1*), 935.5 (*2*)
2-pyrrolidinone	303.15	1104.8	
	308.15	1099.9	1098.96 (*3*)
N-methyl-2-pyrrolidinone	303.15	1023.7	
	308.15	1019.3	1019.10 (*3*)
N,*N*-dimethylacetamide	303.15	931.9	932.3 (*1*)
	308.15	927.8	

The pycnometer was calibrated with doubly-distilled and degassed water and benzene at 303.15 and 308.15 K. The sensitivity of the pycnometer corresponded to a precision in density of 1×10^{-2} kg·m^{-3}. The reproducibility of the density estimated at both temperatures was found to be on the order of 3×10^{-1} kg·m^{-3}. Densities, ϱ, for the liquids are given in Table 1, at two temperatures.

Liquid components were introduced in the bulb of the dilatometer from a glass syringe by mass, taking into account the effect of buoyancy. The pure liquids were degassed under vacuum just prior to loading them into the dilatometer so as to avoid air bubbles. The accuracy of the mole fraction was $\pm 1 \times 10^{-4}$. The excess molar volumes, which are accurate to ± 0.003 cm^3·mol^{-1}, were measured with a continuous-dilution dilatometer similar to that described by Dickinson, Hunt, and McLure (*5*) over the entire mole fraction range at 303.15 and 308.15 K.

The dilatometer was clamped vertically into the water bath. The temperature of the water bath was controlled to within ±0.01 K. Readings of the reference marks and those of liquid levels filling the dilatometer in each capillary were measured with a cathetometer which could read correct to ±0.001 cm. The measurements over the full mole fraction range were completed in two runs, i.e., one for the aqueous-rich regions starting from pure water and the other for the organic-rich regions starting from pure amides up to half of the mole fraction range. For testing the dilatometer, measurements were made on H_2O (1) + CH_2OHCH_2OH (2) at 303.15 and 308.15 K. The values of

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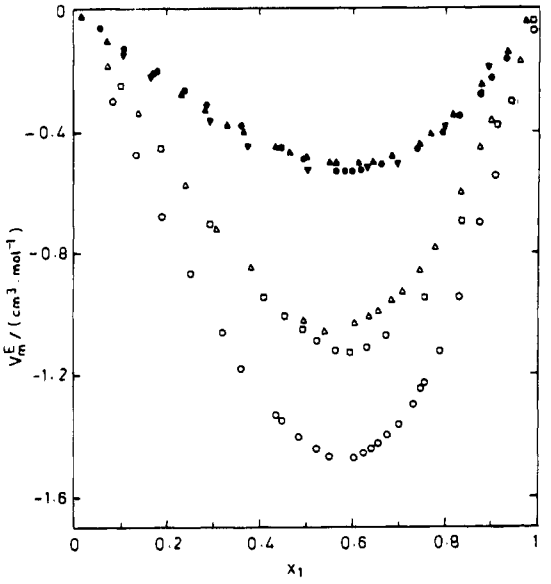

Figure 1. Excess molar volume V_m^E versus mole fraction of water (1) at 303.15 K for mixtures of water + (●) NMF, (▲) 2P, (▼) 2P, ref 12, (△) DMF, (□) NM2P, and (○) DMA.

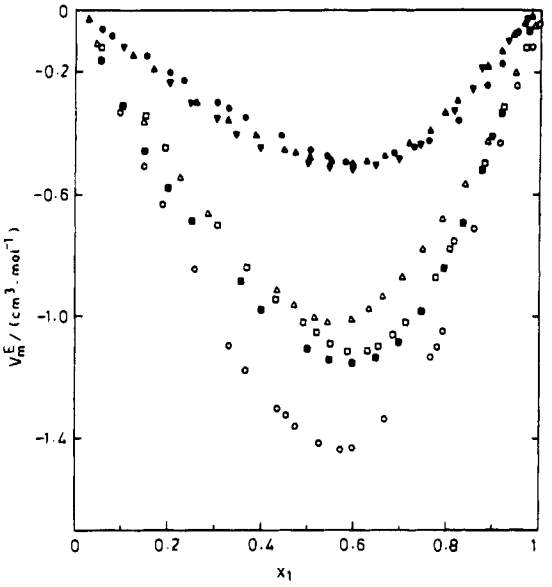

Figure 2. Excess molar volumes V_m^E versus mole fraction of water (1) at 308.15 K for mixtures of water + (●) NMF, (▲) 2P, (▼) 2P, ref 8, (△) DMF, (□) NM2P, (■) NM2P, ref 8, and (○) DMA.

V_m^E at 303.15 K are correlated by

$$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2[-1.2840 + 0.5815(x_2 - x_1) - 0.2166(x_2 - x_1)^2 - 0.2228(x_2 - x_1)^3 + 0.4477(x_2 - x_1)^4] \quad (1)$$

with a standard deviation of $S(V_m^E) = \pm 0.001$ cm^3·mol^{-1}; V_m^E at $x_1 = 0.5$ is -0.326 cm^3·mol^{-1} compared with -0.324 cm^3·mol^{-1} reported by Douhéret et al. (*6*). The values of V_m^E at 308.15 K are estimated by

$$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2[-1.2668 + 0.6507(x_2 - x_1) + 0.2254(x_2 - x_1)^2 - 0.5952(x_2 - x_1)^3 - 0.2569(x_2 - x_1)^4] \quad (2)$$

with a standard deviation of $S(V_m^E) = \pm 0.003$ cm^3·mol^{-1}; V_m^E at $x_1 = 0.5$ is -0.314 cm^3·mol^{-1} compared with -0.311 cm^3·mol^{-1} reported by Douhéret et al. (*6*).

Results and Discussion

The experimental excess molar volumes V_m^E of the binary mixtures as a function of composition at 303.15 and 308.15 K are given in Table 2 and are shown graphically in Figures 1 and 2. The results for all the mixtures were fitted to the expression

$$V_m^E/(\text{cm}^3\cdot\text{mol}^{-1}) = x_1x_2\sum_{i=0}^{n} a_i(x_2 - x_1)^i \quad (3)$$

where x_1 and x_2 are the mole fractions of water and amide, respectively. The values of the parameters a_i obtained by the least squares procedure with all points weighted equally are summarized in Table 3 along with standard deviations $S(V_m^E)$. The values of $S(V_m^E)$ were obtained by the equation

$$S(V_m^E) = [\sum(V_{\text{exptl}}^E - V_{\text{calcd}}^E)^2/(n - p)]^{1/2} \quad (4)$$

where n is the total number of data points and p is number of parameters considered.

The V_m^E values for water + 2-pyrrolidinone reported by Ruostesuo et al. (*7*) at 303.15 K and Uosaki et al. (*3*) at 308.15 K from density values obtained using both the pycnometer and Paar vibrating-tube densimeter are in agreement with the V_m^E values at 303.15 and 308.15 K obtained in this laboratory over the whole mole fraction range. The V_m^E values for water + *N*-methyl-2-pyrrolidinone reported by Uosaki et al. (*3*) at 308.15 K are uniformly more negative than ours at mole fraction $x_1 < 0.7$, but agree with those of Awwad et al. (*8*) over the whole composition range.

Table 2 and Figures 1 and 2 show that the V_m^E values at 303.15 and 308.15 K are negative for all the mixtures over the entire composition range. This suggests that, in the aqueous mixtures, the different magnitudes of V_m^E values reflect the difference in strength of the hydrogen bonding between the polar groups of the amides and water. The hydrogen bond strength is in the order *N*,*N*-dimethylacetamide > *N*-methyl-2-pyrrolidinone > *N*,*N*-dimethylformamide > *N*-methylformamide > 2-pyrrolidinone. The steric hindrance of the two methyl groups of *N*,*N*-dimethylformamide (*9*) makes *N*,*N*-dimethylformamide weaker than *N*,*N*-dimethylacetamide in hydrogen-bonding ability. For the *N*-methyl-2-pyrrolidinone and 2-pyrrolidinone, the pyrrolidinone ring affords better packing in the liquid state as is evidenced by its larger density compared with the *N*,*N*-dialkylamides. On the other hand, the positive contribution to the V_m^E of *N*-alkylamides by breaking the self-association causes less negative V_m^E values compared with those of the other mixtures.

A further comparison of Figures 1 and 2 shows an interesting difference in behavior with respect to the variation in V_m^E with temperature at fixed composition. The minimum value of V_m^E becomes less negative; at the same time, it is shifted toward the amide-rich region with a rise in temperature and decreases in the sequence 2-pyrrolidinone < *N*-methylformamide < *N*,*N*-dimethylformamide < *N*-methyl-2-pyrrolidinone < *N*,*N*-dimethylacetamide. In the different mixtures it is reasonable to assume that there is a tendency toward the formation of molecular aggregation in which there is minimal contact between the OH group of a water molecule and the carbonyl oxygen in the amide.

The apparent molar volume $V_{2,\phi}$ property of solute component 2 defined in terms of mole fraction concentra-

Table 2. Experimental Excess Molar Volumes V_m^E and Thermodynamic Parameters for Water + Amide

x_2	V_m^E/ (cm^3·mol^{-1})	V_m^E/x_2/ (cm^3·mol^{-1})	$V_{2,\phi}$/ (cm^3·mol^{-1})	$V_{1,\phi}$/ (cm^3·mol^{-1})	x_2	V_m^E/ (cm^3·mol^{-1})	V_m^E/x_2/ (cm^3·mol^{-1})	$V_{2,\phi}$/ (cm^3·mol^{-1})	$V_{1,\phi}$/ (cm^3·mol^{-1})
Water (1) + *N*-Methylformamide (2)									
T = 303.15 K									
0.0734	−0.168	−2.289	57.07	17.91	0.4333	−0.521	−1.202	58.16	17.17
0.0999	−0.226	−2.262	57.10	17.84	0.5012	−0.493	−0.984	58.38	17.11
0.1263	−0.281	−2.225	57.13	17.77	0.5537	−0.451	−0.815	58.54	17.08
0.1671	−0.354	−2.118	57.24	17.67	0.6380	−0.383	−0.600	58.76	17.04
0.2034	−0.409	−2.011	57.35	17.58	0.7113	−0.317	−0.446	58.91	17.00
0.2594	−0.468	−1.804	57.55	17.46	0.7591	−0.267	−0.352	59.01	16.99
0.3366	−0.511	−1.518	57.84	17.32	0.8195	−0.206	−0.252	59.11	16.96
0.3845	−0.521	−1.355	58.00	17.25	0.8890	−0.127	−0.143	59.22	16.95
0.4038	−0.528	−1.308	58.05	17.21	0.9438	−0.065	−0.069	59.29	16.94
0.4111	−0.529	−1.287	58.07	17.20					
T = 308.15 K									
0.0813	−0.174	−2.140	57.46	17.93	0.4911	−0.450	−0.916	58.69	17.24
0.1152	−0.241	−2.092	57.51	17.85	0.5554	−0.409	−0.736	58.87	17.20
0.1754	−0.354	−2.018	57.59	17.69	0.6332	−0.346	−0.546	58.06	17.18
0.2342	−0.419	−1.789	57.82	17.58	0.6744	−0.310	−0.460	59.14	17.17
0.2693	−0.442	−1.641	57.96	17.52	0.6842	−0.303	−0.443	59.16	17.16
0.3113	−0.460	−1.478	58.13	17.46	0.7669	−0.225	−0.295	59.31	17.15
0.3749	−0.485	−1.295	58.31	17.35	0.7930	−0.203	−0.256	59.35	17.14
0.4041	−0.488	−1.208	58.40	17.30	0.8497	−0.149	−0.175	59.43	17.13
0.4145	−0.489	−1.180	58.42	17.30	0.9209	−0.080	−0.087	59.52	17.11
0.4566	−0.476	−1.042	58.56	17.29	0.9424	−0.060	−0.064	59.54	17.08
Water (1) + *N*,*N*-Dimethylformamide (2)									
T = 303.15 K									
0.0448	−0.170	−3.795	73.99	17.92	0.3655	−1.015	−2.777	75.01	16.49
0.1004	−0.369	−3.675	74.11	17.68	0.3944	−1.045	−2.650	75.14	16.37
0.1238	−0.454	−3.667	74.12	17.58	0.4534	−1.060	−2.338	75.45	16.15
0.1643	−0.601	−3.658	74.13	17.38	0.5068	−1.025	−2.022	75.76	16.02
0.2236	−0.782	−3.497	74.29	17.09	0.6233	−0.849	−1.362	76.42	15.84
0.2548	−0.862	−3.383	74.40	16.94	0.6958	−0.724	−1.041	76.74	15.71
0.2916	−0.933	−3.200	74.59	16.78	0.7624	−0.578	−0.758	77.03	15.66
0.3144	−0.956	−3.041	74.75	16.70	0.8625	−0.344	−0.399	77.38	15.59
0.3441	−0.995	−2.892	74.89	16.58	0.9277	−0.186	−0.200	77.58	15.52
T = 308.15 K									
0.0102	−0.041	−4.020	74.11	18.08	0.4026	−1.013	−2.516	75.61	16.43
0.0501	−0.200	−3.992	74.13	17.91	0.4538	−1.020	−2.248	75.88	16.26
0.1117	−0.424	−3.796	74.33	17.65	0.4866	−1.005	−2.065	76.06	16.17
0.1600	−0.565	−3.531	74.60	17.45	0.5246	−0.965	−1.839	76.29	16.09
0.2067	−0.682	−3.299	74.83	17.26	0.5646	−0.919	−1.628	76.50	16.01
0.2467	−0.783	−3.174	74.95	17.08	0.7118	−0.663	−0.931	77.19	15.82
0.2965	−0.876	−2.954	75.17	16.88	0.7718	−0.542	−0.702	77.42	15.75
0.3334	−0.935	−2.804	75.32	16.72	0.8507	−0.356	−0.420	77.71	15.73
0.3655	−0.978	−2.676	75.45	16.58	0.9527	−0.115	−0.121	78.01	15.69
Water (1) + 2-Pyrrolidinone (2)									
T = 303.15 K									
0.0245	−0.048	−1.959	75.07	18.04	0.4985	−0.486	−0.975	76.06	17.13
0.0699	−0.140	−2.003	75.03	17.94	0.5368	−0.460	−0.876	76.16	17.08
0.1226	−0.250	−2.039	74.99	17.81	0.5658	−0.452	−0.799	76.23	17.05
0.1832	−0.350	−1.910	75.12	17.67	0.6353	−0.403	−0.634	76.40	16.99
0.2302	−0.412	−1.790	75.24	17.56	0.6671	−0.377	−0.565	76.47	16.96
0.2503	−0.442	−1.766	75.27	17.50	0.7147	−0.330	−0.462	76.57	16.94
0.3170	−0.483	−1.524	75.51	17.39	0.7680	−0.277	−0.361	76.67	16.90
0.3546	−0.505	−1.424	75.61	17.31	0.8282	−0.213	−0.257	76.78	16.85
0.3857	−0.514	−1.333	75.70	17.26	0.9241	−0.106	−0.115	76.92	16.70
0.4344	−0.509	−1.172	75.86	17.19	0.9830	−0.024	−0.024	77.01	16.68
0.4477	−0.502	−1.121	75.91	17.19					
T = 308.15 K									
0.0180	−0.017	−0.944	76.43	18.11	0.4037	−0.493	−1.221	76.15	17.30
0.0312	−0.040	−1.282	76.09	18.08	0.4488	−0.488	−1.087	76.29	17.24
0.0551	−0.076	−1.379	76.00	18.04	0.4914	−0.478	−0.973	76.40	17.18
0.0849	−0.131	−1.543	75.83	17.98	0.5261	−0.461	−0.876	76.50	17.15
0.1138	−0.183	−1.608	75.77	17.92	0.5477	−0.451	−0.823	76.55	17.13
0.1752	−0.293	−1.672	75.70	17.77	0.6100	−0.398	−0.652	76.72	17.10
0.2019	−0.325	−1.610	75.77	17.72	0.6741	−0.351	−0.521	76.86	17.05
0.2359	−0.385	−1.632	75.75	17.62	0.7375	−0.295	−0.400	76.98	17.00
0.2790	−0.431	−1.545	75.83	17.53	0.8332	−0.194	−0.233	77.14	16.96
0.3324	−0.471	−1.417	75.96	17.42	0.8742	−0.149	−0.170	77.21	16.94
0.3701	−0.485	−1.310	76.07	17.35	0.9714	−0.031	−0.025	77.34	16.92

Table 2 (Continued)

x_2	V_m^E/ (cm^3·mol^{-1})	V_m^E/x_2/ (cm^3·mol^{-1})	$V_{2,\phi}$/ (cm^3·mol^{-1})	$V_{1,\phi}$/ (cm^3·mol^{-1})	x_2	V_m^E/ (cm^3·mol^{-1})	V_m^E/x_2/ (cm^3·mol^{-1})	$V_{2,\phi}$/ (cm^3·mol^{-1})	$V_{1,\phi}$/ (cm^3·mol^{-1})
Water (1) + *N*,*N*-Dimethylacetamide (2)									
				T = 303.15 K					
0.0122	−0.070	−5.738	87.75	18.02	0.3752	−1.455	−3.878	89.61	15.78
0.0527	−0.301	−5.712	87.78	17.78	0.3956	−1.466	−3.706	89.78	15.67
0.0962	−0.546	−5.676	87.81	17.49	0.4514	−1.468	−3.252	90.24	15.42
0.1239	−0.700	−5.650	87.84	17.30	0.4775	−1.445	−3.026	90.46	15.33
0.1683	−0.949	−5.639	87.85	16.95	0.5158	−1.401	−2.716	90.77	15.20
0.2132	−1.121	−5.258	88.23	16.67	0.5515	−1.351	−2.450	91.04	15.08
0.2497	−1.223	−4.898	88.59	16.46	0.5617	−1.337	−2.380	91.11	15.04
0.2555	−1.239	−4.849	88.64	16.43	0.6392	−1.182	−1.849	91.64	14.82
0.2727	−1.299	−4.763	88.73	16.31	0.6818	−1.058	−1.552	91.94	14.77
0.3052	−1.361	−4.459	89.03	16.14	0.7458	−0.871	−1.168	92.32	14.67
0.3257	−1.399	−4.295	89.19	16.02	0.8082	−0.682	−0.844	92.64	14.54
0.3515	−1.429	−4.065	89.42	15.89	0.8658	−0.479	−0.553	92.94	14.52
0.3678	−1.447	−3.934	89.55	15.81	0.9169	−0.301	−0.328	93.16	14.47
				T = 308.15 K					
0.0088	−0.048	−5.455	88.45	18.08	0.4744	−1.415	−2.983	90.92	15.43
0.0220	−0.118	−5.364	88.54	18.00	0.5239	−1.362	−2.600	91.30	15.26
0.0473	−0.245	−5.180	88.72	17.87	0.5467	−1.325	−2.424	91.48	15.20
0.0836	−0.429	−5.132	88.77	17.66	0.5624	−1.303	−2.317	91.58	15.15
0.1392	−0.711	−5.101	88.80	17.30	0.6331	−1.179	−1.862	92.04	14.91
0.2121	−1.061	−5.002	88.90	16.78	0.6648	−1.098	−1.652	92.25	14.85
0.2200	−1.100	−5.000	88.90	16.71	0.7426	−0.845	−1.138	92.76	14.84
0.2307	−1.124	−4.872	89.03	16.66	0.8087	−0.632	−0.782	93.12	14.82
0.3317	−1.339	−4.037	89.86	16.12	0.8473	−0.509	−0.601	93.30	14.79
0.3773	−1.429	−3.787	90.11	15.83	0.9023	−0.330	−0.366	93.54	14.75
0.4249	−1.438	−3.384	90.52	15.62					
Water (1) + *N*-Methyl-2-pyrrolidinone (2)									
				T = 303.15 K					
0.0109	−0.048	−4.404	92.44	18.05	0.4796	−1.082	−2.256	94.58	16.01
0.0893	−0.381	−4.267	92.57	17.68	0.5068	−1.052	−2.076	94.76	15.96
0.1654	−0.699	−4.226	92.61	17.26	0.5451	−1.012	−1.857	94.98	15.87
0.2433	−0.950	−3.905	92.93	16.84	0.5910	−0.948	−1.604	95.23	15.78
0.2781	−1.077	−3.872	92.97	16.60	0.7055	−0.702	−0.995	95.84	15.71
0.3670	−1.122	−3.057	93.78	16.32	0.8134	−0.453	−0.557	96.28	15.67
0.4074	−1.131	−2.776	94.06	16.19	0.8972	−0.252	−0.281	96.56	15.64
0.4353	−1.107	−2.543	94.30	16.13					
				T = 308.15 K					
0.0278	−0.118	−4.245	93.01	18.00	0.4130	−1.112	−2.692	94.56	16.23
0.0737	−0.309	−4.193	93.06	17.79	0.4479	−1.087	−2.427	94.83	16.15
0.1193	−0.492	−4.124	93.13	17.56	0.4781	−1.054	−2.205	95.05	16.10
0.1849	−0.758	−4.100	93.16	17.19	0.5078	−1.020	−2.009	95.25	16.05
0.1915	−0.779	−4.068	93.19	17.16	0.5690	−0.946	−1.663	95.59	15.93
0.2226	−0.876	−3.935	93.32	17.00	0.6272	−0.835	−1.331	95.93	15.88
0.2864	−1.022	−3.568	93.62	16.69	0.6914	−0.702	−1.015	96.24	15.85
0.3141	−1.059	−3.372	93.89	16.58	0.8063	−0.446	−0.553	96.70	15.82
0.3461	−1.095	−3.164	94.09	16.45	0.8489	−0.349	−0.411	96.85	15.81
0.3641	−1.109	−3.046	94.21	16.38	0.9492	−0.118	−0.124	97.13	15.80

Table 3. Values of the Parameters a_i and Standard Deviation $S(V_m^E)$ for Least Squares Representations of Excess Molar Volume V_m^E by Eq 3

amide	T/K	a_0	a_1	a_2	a_3	a_4	a_5	$S(V_m^E)$/ (cm^3·mol^{-1})
N-methylformamide	303.15	−1.9629	1.1228	−0.0858	0.5486	0.2781		0.004
	308.15	−1.7978	1.1539	0.0465	−0.5680			0.006
N,*N*-dimethylformamide	303.15	−4.0929	1.5575	0.9538	−1.1500			0.009
	308.15	−3.9679	1.4219	1.4976	−1.6371	−1.0902	1.3937	0.007
2-pyrrolidinone	303.15	−1.9448	0.9033	−0.1552	−0.6449	0.4318		0.004
	308.15	−1.8910	0.8693	0.1612	−0.9487	0.6373		0.004
N-methyl-2-pyrrolidinone	303.15	−4.2545	2.3577	−0.4677	−1.6007	2.0786		0.019
	308.15	−4.1562	2.4152	0.1221	−1.7203	1.1205		0.007
N,*N*-dimethylacetamide	303.15	−5.6929	2.0851	0.1933	−0.0686	0.8708	−1.3643	0.008
	308.15	−5.5774	1.9480	0.5629	0.0829	1.0817	−1.5916	0.015

tion units and $|V_m^E/x_2|$ is calculated from the relation

$$V_{2,\phi} = V_m^E/x_2 + PM_2/\varrho_2^\circ \qquad (5)$$

where x_2, PM_2, and ϱ_2° are the mole fraction, molar mass, and density of solute component 2.

The values of apparent molar volumes calculated using eq 5 are plotted in Figures 3 and 4. The apparent molar volumes of amide and water increase with an increase in temperature. It would appear that an increase in temperature affects the molecular organization in these systems so as to increase the amount of free water through

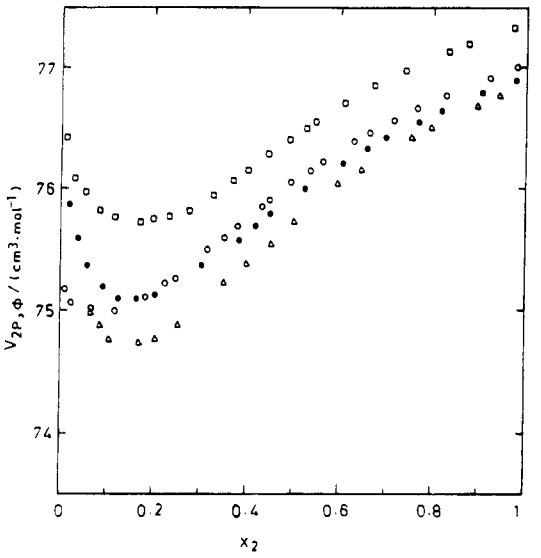

Figure 3. Variation in apparent molar volume of 2P in mixtures of water + 2P: (●) 298.15 K, ref 16, (△) 298.15 K, ref 8; (○) 303.15 K; (□) 308.15 K.

breakdown of the less dense hydrogen-bonded structures and/or breakdown of self-associated amide aggregates and hence contribute to a denser packing of the molecules. Figure 3 shows the variation of apparent molar volumes of 2-pyrrolidinone with composition. The volumes show a similar trend at 298.15 K with that reported by Uosaki et al. (*3*), but that by Davis et al. (*10*) deviates at $x_{2P} < 0.25$. The sharp skew at low 2-pyrrolidinone concentration in the Davis data may be due to the difference in the purity of solvents or, less probably, an experimental error.

Figure 4 shows the spline-smoothed curve of the excess molar volume divided by the mole fraction x_2 of the nonaqueous component: V_m^E/x_2. The composition dependence of $V_{2,\phi}$ is typical of mixtures of water + amphiphilic molecules (*11*–*13*) and appears most clearly in Figure 4 by plots of V_m^E/x_2 against x_2. This is consistent with the view that the excess volumes of aqueous mixtures reflect the structural changes of water introduced by the nonaqueous molecules (*12*). The water-rich region, in this instance, appears to terminate at that value of x_2 at which all the water molecules are involved in solvation, with a tendency toward the formation of molecular aggregates, which depends strongly on the mole fraction.

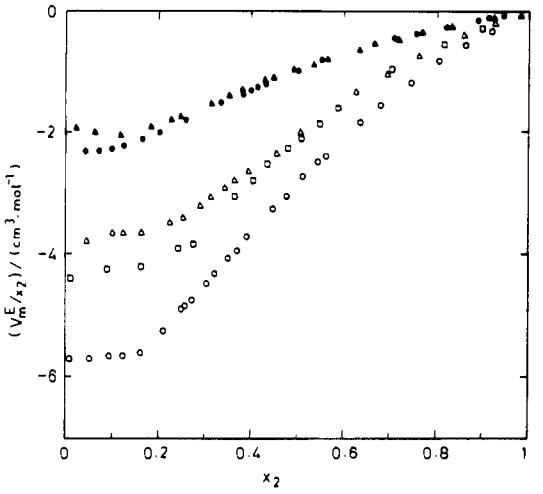

Figure 4. Spline-smoothed curve of V_m^E/x_2 for the mixtures of water + amide at 303.15 K: (●) NMF; (▲) 2P; (△) DMF; (□) NM2P; (○) DMA.

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