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DETERMINATION AND ANALYSIS OF THE EXCESS MOLAR VOLUMES OF SOME AMIDE–WATER SYSTEMS

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ABSTRACT

Densities have been measured and excess molar volumes calculated for the systems water + *N*-methylformamide, + *N,N*-dimethylformamide, + 2-pyrrolidinone and + *N*-methyl-2-pyrrolidinone. These and some excess molar volume data, for related systems, which were extracted from the literature have been analysed using the segmented-composition model. Some tentative suggestions are offered to explain the results of those analyses in terms of prevalent patterns of molecular aggregation.

INTRODUCTION

Numerous studies have been made of the composition dependence of the physical properties of amide–water systems. A major motivation for such studies is the belief that an enhanced understanding of the structural and energetic consequences of the interactions between amide and water molecules will ultimately lead to a better appreciation of the manner in which water exercises thermodynamic and kinetic control over the chemical activities of polypeptides in aqueous media.

A substantial number of these studies have been carried out on relatively dilute aqueous solutions of the amides. Typically, the data are reduced to the form of apparent molar properties of the organic solute and analysed as polynomial functions of its molality. Such analyses typically yield two types of parameters; the apparent molar properties of the solute at infinite dilution $\Phi_Q^{\ominus}$ and pair interaction constants q_2. For enthalpies and Gibbs free energies of solution, the constants q_2, for a wide range of solutes, appear to conform quite well to the group-pair additivity principle that is set forth in the Savage–Wood rules [1].

Fewer studies have been made of the composition dependence of physical properties of amide–water systems across the entire range of mole fractions. Some of them are either too sparse or too erratic to warrant detailed analysis. It is essential to study mixtures in which there is an appreciable

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mole fraction of the organic component if one wishes to seek evidence of the existence of metastable amide aggregates and to explore the effects, upon the character of aqueous self aggregation, of their interactions with water.

Of the various approaches that have been suggested for the analysis and interpretation of the composition dependence of the physical properties of binary hydro-organic systems, across the entire composition range, that which is favored in this laboratory is the segmented composition model [2,3].

The excess molar volumes of binary aqueous systems frequently exhibit a marked sensitivity to changes in composition. Modern techniques of densimetry [4] and dilatometry [5] can provide estimates of their values with an accuracy of the order of 1 $mm^3\ mol^{-1}$. Consequently, this property is particularly suitable for providing evidence of changing patterns of molecular aggregation.

In this article, excess molar volumes, obtained by vibrating-tube densimetry, are reported for the systems water +*N*-methylformamide (NMF), +*N*,*N*-dimethylformamide (DMF), +2-pyrrolidinone (2P) and +*N*-methyl-2-pyrrolidinone (NM2P). Four-segment model analyses have been carried out on these excess molar volumes and on literature data sets for three related systems.

An attempt has been made to furnish a rationale for the values of the model parameters in terms of the existence of metastable patterns of molecular aggregation.

EXPERIMENTAL DETAILS

Materials

Mixtures were prepared using distilled and deionized water which was stored in tight polyethylene containers. No evidence could be found of any difference in density from the water taken directly from the containers and samples subjected to a degassing process.

The NMF samples were of Aldrich 99% grade. The DMF samples were Fisher Spectrophotometric grade for which there is a claimed water content of 0.034%. The 2-pyrrolidinone samples were of Aldrich Gold Label 99+% grade. The NM2P samples were of Aldrich HPLC grade.

All amide samples were used directly from the manufacturers' bottles, which were kept tightly sealed to minimize absorption of atmospheric water. There was no evidence of any significant density changes of neat samples over the several-day period required to collect a complete set of aqueous mixture densities.

Density values obtained at 25 ° C for the amide samples are given in Table 1, together with values taken from the literature. No 25 ° C literature value for 2-pyrrolidinone could be found. With the possible exception of the NMF

TABLE 1

Densities (g cm^{-3}) of some amides at 25 °C

Amide	This work	Literature	Ref.
NMF	0.99889	0.99824	6
DMF	0.94383	0.94376	7
		0.94388	7
2P	1.10643		
NM2P	1.02759	1.0283	8
		1.0286	9

sample, it is believed that the effects of possible contaminants present upon the excess molar volumes lie within the range of experimental error.

Measurements

Densities were determined using a Sodev Model 03-D high precision flow densimeter, which employs the vibrating-tube principle [4]. The densities are derived from the periods of oscillation of a hollow reed that is filled with the sample liquid, by means of the equation

$$\tau^2(\text{sample}) = \tau^2(\text{water}) + K(\rho(\text{sample}) - \rho(\text{water})) \qquad (1)$$

where the density of water at 25 °C is assumed to be 0.997047 g cm^{-3} [10] and K is a calibration constant.

In view of the newness of the apparatus, the calibration constant was determined several times during the course of these investigations, revealing a modest increase with time [11]. The calibration constant was estimated from the measured periods of oscillation and the literature values of the densities of water, HPLC grade *n*-heptane, HPLC grade methanol and spectrophotometric grade tetrachloromethane. The periods of oscillation were found, in each instance, to be linearly dependant upon the literature densities to within 2×10^{-5} g cm^{-3}.

The temperature of the densimeter was controlled at 25.00 ± 0.02 °C by means of a Sodev Model CT-L programmable circulating thermostat. In view of the fact that the τ values for water were found to exhibit a modest downward drift during the course of a day of continuous operation, each sample measurement was bracketed by a pair of water measurements.

The compositions of the mixtures were determined by weight, their mole fractions being generally reliable to 1×10^{-4}. The sensitivity of the densimeter corresponds to a precision of 1×10^{-6} g cm^{-3}. The reproducibility of the density estimates was found to be of the order of 2×10^{-5} g cm^{-3}. Individual measurements are subject to errors arising from imperfect mixing of the samples and absorption of atmospheric gases.

TABLE 2

Excess molar volumes (cm^3) of four amide–water mixtures at 25 °C

X_A	$\Delta\bar{V}$	X_A	$\Delta\bar{V}$	X_A	$\Delta\bar{V}$
N-Methylformamide – water					
0.0000	0.0000	0.1734	−0.4020	0.6157	−0.4454
0.0034	−0.0081	0.1846	−0.4209	0.6362	−0.4271
0.0076	−0.0184	0.2327	−0.4866	0.6702	−0.3888
0.0110	−0.0263	0.2365	−0.4915	0.6707	−0.3903
0.0154	−0.0377	0.2827	−0.5345	0.6911	−0.3669
0.0216	−0.0532	0.2922	−0.5415	0.7183	−0.3408
0.0254	−0.0630	0.3335	−0.5617	0.7476	−0.3063
0.0326	−0.0818	0.3565	−0.5627	0.7735	−0.2779
0.0418	−0.1058	0.3800	−0.5675	0.7935	−0.2551
0.0563	−0.1435	0.4109	−0.5678	0.8255	−0.2172
0.0678	−0.1733	0.4196	−0.5653	0.8479	−0.1897
0.0765	−0.1961	0.4377	−0.5601	0.8759	−0.1568
0.0778	−0.1980	0.4774	−0.5459	0.9079	−0.1192
0.0902	−0.2289	0.5124	−0.5269	0.9198	−0.1003
0.1003	−0.2516	0.5238	−0.5210	0.9461	−0.0672
0.1274	−0.3128	0.5354	−0.5068	0.9731	−0.0340
0.1631	−0.3778	0.5806	−0.4748	1.0000	0.0000
N,N-Dimethylformamide – water					
0.0000	0.0000	0.2032	−0.8065	0.6316	−0.8961
0.0027	−0.0083	0.2255	−0.8685	0.6416	−0.8756
0.0057	−0.0170	0.2422	−0.9110	0.6421	−0.8761
0.0088	−0.0280	0.2560	−0.9469	0.6681	−0.8297
0.0099	−0.0314	0.2586	−0.9507	0.6889	−0.7830
0.0139	−0.0454	0.2618	−0.9573	0.6900	−0.7810
0.0196	−0.0663	0.2880	−1.0091	0.7056	−0.7491
0.0199	−0.0675	0.3013	−1.0296	0.7128	−0.7345
0.0275	−0.0978	0.3171	−1.0423	0.7192	−0.7174
0.0298	−0.1058	0.3419	−1.0842	0.7466	−0.6493
0.0345	−0.1242	0.3531	−1.0925	0.7521	−0.6452
0.0393	−0.1453	0.3771	−1.1049	0.7690	−0.6040
0.0429	−0.1601	0.3917	−1.1144	0.7700	−0.6012
0.0498	−0.1894	0.3967	−1.1147	0.7925	−0.5460
0.0503	−0.1914	0.3987	−1.1150	0.7969	−0.5352
0.0576	−0.2224	0.4160	−1.1161	0.8124	−0.4936
0.0639	−0.2509	0.4233	−1.1179	0.8236	−0.4699
0.0674	−0.2668	0.4274	−1.1189	0.8447	−0.4151
0.0675	−0.2675	0.4536	−1.1088	0.8474	−0.4042
0.0721	−0.2870	0.4602	−1.1054	0.8716	−0.3491
0.0775	−0.3104	0.4663	−1.1023	0.8758	−0.3301
0.0860	−0.3481	0.5090	−1.0707	0.9029	−0.2658
0.0965	−0.3946	0.5161	−1.0621	0.9085	−0.2467
0.1002	−0.4108	0.5271	−1.0425	0.9248	−0.2033
0.1052	−0.4324	0.5376	−1.0377	0.9286	−0.1941
0.1219	−0.5021	0.5396	−1.0341	0.9530	−0.1258
0.1293	−0.5327	0.5527	−1.0219	0.9580	−0.1150

TABLE 2 (continued)

X_A	$\Delta\bar{V}$	X_A	$\Delta\bar{V}$	X_A	$\Delta\bar{V}$
0.1533	−0.6291	0.5666	−0.9984	0.9771	−0.0589
0.1567	−0.6423	0.5803	−0.9756	0.9772	−0.0614
0.1596	−0.6524	0.5927	−0.9598	1.0000	0.0000
0.1809	−0.7302	0.6026	−0.9438		
0.1891	−0.7575	0.6160	−0.9270		
2-Pyrrolidinone – water					
0.0000	0.0000	0.0801	−0.1320	0.4202	−0.5106
0.0029	−0.0016	0.0953	−0.1630	0.4553	−0.5059
0.0035	−0.0024	0.0957	−0.1659	0.4772	−0.4985
0.0068	−0.0051	0.1179	−0.2076	0.5245	−0.4833
0.0070	−0.0045	0.1257	−0.2280	0.5548	−0.4623
0.0097	−0.0075	0.1517	−0.2789	0.5965	−0.4333
0.0098	−0.0073	0.1538	−0.2787	0.6072	−0.4238
0.0158	−0.0162	0.1691	−0.3080	0.6302	−0.4077
0.0159	−0.0144	0.1754	−0.3180	0.6600	−0.3841
0.0211	−0.0220	0.2065	−0.3703	0.7011	−0.3436
0.0213	−0.0224	0.2317	−0.4043	0.7395	−0.3069
0.0257	−0.0287	0.2495	−0.4249	0.7705	−0.2736
0.0262	−0.0286	0.2538	−0.4242	0.7988	−0.2404
0.0313	−0.0377	0.2708	−0.4460	0.8215	−0.2141
0.0325	−0.0396	0.3062	−0.4775	0.8685	−0.1569
0.0335	−0.0411	0.3092	−0.4748	0.9079	−0.1103
0.0410	−0.0542	0.3326	−0.4938	0.9495	−0.0575
0.0518	−0.0747	0.3498	−0.4993	0.9816	−0.0157
0.0620	−0.0926	0.3857	−0.5149	1.0000	0.0000
0.0624	−0.0957	0.3888	−0.5133		
0.0720	−0.1154	0.4195	−0.5131		
N-Methyl-2-pyrrolidinone – water					
0.0000	0.0000	0.1591	−0.7390	0.5318	−1.0823
0.0018	−0.0037	0.1613	−0.7450	0.5586	−1.0473
0.0047	−0.0105	0.1905	−0.8688	0.5754	−1.0109
0.0089	−0.0215	0.2211	−0.9695	0.6073	−0.9536
0.0146	−0.0388	0.2511	−1.0522	0.6520	−0.8703
0.0233	−0.0708	0.2635	−1.0770	0.6636	−0.8451
0.0351	−0.1207	0.2764	−1.0982	0.6986	−0.7672
0.0482	−0.1829	0.2998	−1.1444	0.7310	−0.6918
0.0583	−0.2338	0.3286	−1.1775	0.7745	−0.5854
0.0684	−0.2850	0.3356	−1.1800	0.8049	−0.5052
0.0773	−0.3302	0.3925	−1.2011	0.8327	−0.4392
0.0897	−0.3973	0.3992	−1.1974	0.8624	−0.3637
0.1092	−0.4987	0.4162	−1.1923	0.8882	−0.2965
0.1158	−0.5326	0.4358	−1.1863	0.9397	−0.1696
0.1422	−0.6536	0.4630	−1.1644	0.9753	−0.0721
0.1516	−0.7038	0.4910	−1.1369	1.0000	0.0000
0.1542	−0.7192	0.5085	−1.1133		

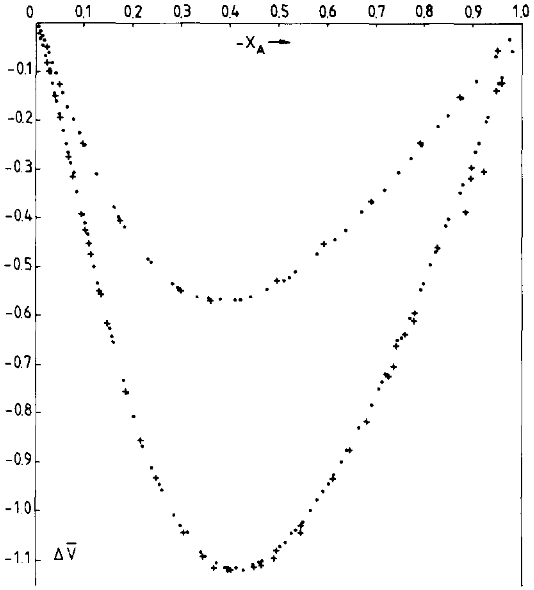

Fig. 1. Excess molar volumes at 25° C. Upper curve, NMF–water mixtures: ●, this work; +, ref. 6. Lower curve, DMF–water mixtures: ●, this work; +, ref. 7.

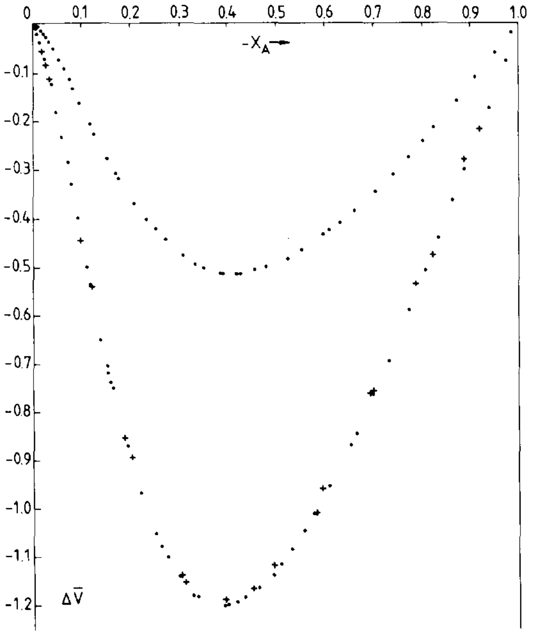

Fig. 2. Excess molar volumes at 25° C. Upper curve, 2P–water mixtures. Lower curve, NM2P–water mixtures: ●, this work; +, refs. 8 and 9.

The data are presented in the form of excess molar volumes in Table 2 and in Figs. 1 and 2. The most obvious feature of the two figures is their similarity. All four curves have minima close to $X_A = 0.4$. In each figure the extremum of the secondary amide is roughly half that of the tertiary. One notes, however, that the extrema for NMA–water and DMA–water are roughly -1.1 and -1.6 cm^3 mol^{-1}, respectively [12].

Only modest differences appear to exist between the excess molar volumes found in this work and those taken from the literature.

DATA ANALYSES

The model

The derivation and evolution of the four-segment model, for binary hydro-organic mixtures, have been described at some length in earlier papers [2,3]. The model equations stem from the premise that it is reasonable to analyse the excess molar properties of such systems as if their total composition ranges consist of four distinct segments. Within each segment, the excess molar properties are assumed to possess relatively simple functional dependence upon mole fractional composition, reflecting uniform variation of the patterns of molecular aggregation. At each of the three segment junctions, the functional dependence is permitted to change, allowing for the existence of new trends in the nature of the aggregates.

The model has been found to be an effective curve-fitting tool for various types of excess property data of a number of different binary hydro-organic systems [3,13–15]. The parameters of the model equations are of a form that offers a possible basis for exploring hypotheses concerning the structural and dynamic characteristics of the patterns of molecular aggregation.

In earlier publications, results have been presented of analyses of excess molar properties of water + acetonitrile, + tetrahydrofuran [3] and + each of the five alkanols with which it is totally miscible [16]. For each of those systems it was found to be appropriate to set the two segment-junction compositions X_{II} and X_{III} at 1/3 and 2/3, respectively. That decision was largely based upon the observation that the functions $d\Delta\overline{Q}/dX_A$ (where $\Delta\overline{Q}$ is an excess molar property and X_A is the mole fraction of the organic component) appear to vary in a very nearly linear manner with X_A over the central third of the total mole fraction range. The term "microheterogeneous" has been applied to that central segment in view of the conclusion, drawn by Naberukhin and Rogov [17], that its mixtures frequently exhibit composition dependent characteristics that resemble those of truly heterogeneous systems. For the systems studied earlier, it was found to be appropriate to assign individual values for the segment junction X_I.

For the amide–water systems, analyses were carried out to determine optimum values for the three segment-junction compositions. There was a substantial degree of consistency among the optimum sets of the seven systems. It was thought to be appropriate, in this instance, to assign a common set of all three segment-junction compositions of $X_{\rm I} = 0.075$, $X_{\rm II} = 0.250$ and $X_{\rm III} = 0.433$.

The equations of the four-segment model were derived from the assumptions that (1) $\Delta \overline{Q}$ is a quadratic function of $X_{\rm A}$ in the microheterogeneous segment and cubic in the other three segments, (2) $\Delta \overline{Q}$ is single valued at each of the three segment junctions and (3) $\mathrm{d}\Delta \overline{Q}/\mathrm{d}X_{\rm A}$ is single valued at each segment junction. These constraints lead to a set of equations involving seven parameters (see Appendix). If the third constraint is relaxed, the number of independent model parameters is increased to ten. It has been ascertained that, for some exceptionally high quality data sets, there is a significant improvement in the quality of fit on switching from the seven- to the ten-parameter model [18].

TABLE 3

Four-segment model parameters for the excess molar volumes of mixtures of water with *N*-methyl-formamide (NMF), *N,N*-dimethyl-formamide (DMF), 2-pyrrolidinone (2P), *N*-methyl-2-pyrrolidinone (NM2P), formamide (F), *N*-methyl-acetamide (NMA) and *N,N*-dimethyl-acetamide (DMA). Parameter units are cm^3, standard deviations (σ) are expressed in mm^3, and $X_{\rm I} = 0.075$, $X_{\rm II} = 0.250$, $X_{\rm III} = 0.433$

Parameter	NMF	DMF	2P	NM2P	F	NMA	DMA
Seven-parameter version							
B	−3.539	−7.065	−3.431	−7.986	−0.757	−7.116	−9.656
$\Delta \bar{V}_{\rm W}^{\circ}$	−0.046	0.084	0.064	0.007	−0.070	0.014	0.008
$\Delta \bar{V}_{\rm A}^{\circ}$	0.769	1.321	0.681	1.792	0.186	1.467	1.783
$\Delta \bar{V}_{\rm S}^{\circ}$	0.004	0.041	0.040	0.075	0.000	0.058	0.068
$D_{\rm S}$	0.148	0.189	0.098	0.455	0.018	0.316	0.543
$D_{\rm W}$	0.019	−0.011	−0.013	−0.004	−0.008	−0.009	0.004
$D_{\rm A}$	−0.532	−0.764	−0.420	−1.296	−0.120	−0.726	−0.994
σ	1.995	2.580	1.911	3.452	0.565	1.079	5.732
Ten-parameter version							
B	−3.034	−6.544	−3.695	−7.924	−0.744	−7.417	−10.859
$\Delta \bar{V}_{\rm W}^{\circ}$	−0.104	0.031	0.096	−0.002	−0.073	0.042	0.129
$\Delta \bar{V}_{\rm A}^{\circ}$	0.554	1.087	0.790	1.792	0.183	1.609	2.338
$\Delta \bar{V}_{\rm S}^{\circ}$	0.016	0.041	0.030	0.091	0.004	0.078	0.101
$D_{\rm S}$	0.138	0.254	0.132	0.459	0.002	0.222	0.331
$D_{\rm W}$	0.002	0.000	0.006	0.007	−0.013	−0.011	−0.001
$D_{\rm A}$	−0.337	−0.564	−0.523	−1.260	−0.113	−0.830	−1.442
$\Delta B_{\rm S}$	0.059	0.015	−0.046	0.013	0.011	0.012	−0.012
$\Delta B_{\rm W}$	0.001	−0.009	−0.006	−0.026	0.000	−0.022	−0.037
$\Delta B_{\rm A}$	0.068	0.094	−0.029	0.016	−0.003	−0.071	−0.247
σ	1.929	2.442	1.868	3.540	0.557	0.641	5.580

Results

The results of both seven- and ten-parameter analyses of the four data sets generated in this laboratory are set out in Table 3. Analyses were also performed upon excess volumes of the water + formamide system [12,19], the water + *N*-methylacetamide system [12] and the water + *N*,*N*-dimethylacetamide system [12,19]. These results are also given in Table 3.

DISCUSSION

The excess molar volumes appear to exhibit a pleasing level of internal consistency. There are systematic differences between the excess molar volumes for the NMF–water system obtained in this laboratory and those reported by de Visser et al. [6] from density values obtained using a Paar vibrating-tube densimeter. Those differences are consistent with a modest aqueous impurity in the sample employed in this work or, less probably, a low density organic impurity in the de Visser sample. The effect of those differences upon the magnitudes of the four-segment model parameters is quite small.

The de Visser data for the DMF–water system are a composite of measurements employing both Paar and Sodev vibrating-tube densimeters [7]. The Sodev data, of that work, contain an unusually high degree of scatter at high amide mole fractions. The Paar data are very similar to those generated in this laboratory.

Of the two pyknometric data sets for the NM2P–water system, that of Assarsson and Eirich [9] is the more consistent with the results from this laboratory in terms of the excess molar volumes.

The three secondary amides NMF, NMA and 2-pyrrolidinone all have relatively high melting points and boiling points, which are attributable to the existence of strong intermolecular hydrogen bonding.

The *N*,*N*-dialkylamides have no significant intermolecular hydrogen bonding capability, but they are sufficiently polar that their pure liquids are presumed to be highly structured.

In their aqueous mixtures, it seems to be reasonable to assume that there is extensive hydrogen bonding between the polar groups of the amides and water.

The microheterogeneous segment

The model equation for the microheterogeneous segment, in both the seven- and ten-parameter versions, contains the three parameters $\Delta\overline{V}_W^\circ$, $\Delta\overline{V}_A^\circ$ and B. The form of the model equation is such as to identify $\Delta\overline{V}_W^\circ$ and $\Delta\overline{V}_A^\circ$ as excess molar properties of hypothetical standard states of water and the amide, respectively.

The $\Delta\overline{V}_W^\circ$ values are relatively small, with no clear cut trends from one system to another. There is certainly no evidence of the substantial negative values that characterize the THF–water [3] and higher alkanol–water systems [16]. That does not preclude the possibility of the existence, within this segment, of important metastable aqueous aggregates in amide–water mixtures. In the MeOH–water system, $\Delta\overline{V}_W^\circ$ is virtually zero while $\Delta\overline{H}_W^\circ$ is large and negative.

Of considerable interest are the large positive values of the parameters of the type $\Delta\overline{V}_A^\circ$. It is suggested that the magnitudes of these values are consistent with substantial variations in the nature of the patterns of amide self aggregation in switching from the pure liquids to mixtures which contain a significant amount of water. That the pure amides have relatively high densities and boiling points is assumed to arise from significant intermolecular contact between polar groups. In the aqueous mixtures, the polar groups of the amides must be, to a considerable extent, engaged in contact with water molecules. Consequently, contact between pairs of amide molecules becomes more a matter of that between the apolar alkyl groups, and the amide aggregates appear to be that much more voluminous.

One notes that $\Delta\overline{V}_A^\circ$ is relatively small for the formamide–water system but increases significantly with the addition of methyl or methylene groups to the amide.

There are two additional points which seem to be worth raising, in this context. Firstly, the variation among the $\Delta\overline{V}_A^\circ$ values from one system to another reflect not only differences between the natures of the aqueous mixtures but also between those of the pure liquids. Some idea of how one might separate those two components might be gained from the studies of the volumetric characteristics of mixtures of amides with a non-polar liquid such as tetrachloromethane. Further, while the four-segment model analyses are capable of identifying features of the composition dependence of the physical properties of these systems which indicate the existence of interesting molecular-scale phenomena, they do not provide the kind of insight that a statistically based interpretive model might.

B is a simple Margoules type of mixing parameter. It has been suggested [20] that, within this microheterogeneous segment, there is a tendency towards the formation of a metastable laminar pattern of molecular aggregation in which there is minimal contact between hydrophobic groups and water. Such a pattern might be regarded as a crude facsimile of lamellar phase lyotropic liquid crystalline aggregation or bilayer membrane formation. Since $\Delta\overline{V}_W^\circ$ and $\Delta\overline{V}_A^\circ$ are being treated as excess properties of the aqueous and organic aggregates, respectively, B is associated with the interfaces between the two types of laminar aggregates.

With the exception of the formamide–water system, the B values are substantial. Their variation among the different amide–water systems parallels that among the $\Delta\overline{V}_A$ values. It is apparent that the B values are dominant in that they determine the sign and approximate magnitude of the extrema of the total excess molar volumes.

It is interesting that the segment junction compositions that define the limits of this segment, and which appear to be the same for all systems, are significantly different from those found for the alkanol–water systems. Conceivably, this indicates a different mode of molecular aggregation. Alternatively, the mode of aggregation may be the same but, because the amide group is larger than the hydroxyl group of the alkanols, it engages a larger number of water molecules per organic molecule.

The secondary segment

When the mole fraction of the organic component falls below X_{II}, there is a fairly distinct change in the dependence of $\Delta\bar{V}$ upon X_{A}. It is argued that there is too much water present for all of it to be accommodated in the aggregative scheme of the microheterogeneous segment. An additional suggestion, that would seem to have some merit, is that increasing the mole fraction of water might result in a tendency for the metastable polar organic aggregates to adopt some kind of crude, labile micellular form, with the excess water occupying interstitial sites.

The model equations for this segment introduce two new parameters, $\Delta\bar{V}_{\mathrm{S}}^{\circ}$ and D_{S}, in the seven-parameter version and a third ΔB_{S} in the ten. $\Delta\bar{V}_{\mathrm{S}}^{\circ}$ appears in the form of an excess molar property of a new hypothetical standard state of water. ΔB_{S} would vanish if $\mathrm{d}\Delta\bar{V}/\mathrm{d}X_{\mathrm{A}}$ were single valued at X_{II}. D_{S} would vanish if $\mathrm{d}^2\Delta\bar{V}/\mathrm{d}X_{\mathrm{A}}$ were single valued.

It is felt that one should be content to use these parameter values as collective indicators of the relative magnitudes of effects arising from variations in the patterns of molecular aggregation and avoid trying to provide detailed rationales of their individual values.

It is noted that, for the seven-parameter model, the $\Delta\bar{V}_{\mathrm{S}}^{\circ}$ values are very small while the D_{S} values are significant, positive and tend to follow the same trends as exist among the $\Delta\bar{V}_{\mathrm{A}}^{\circ}$ values. For the ten-parameter model, the $\Delta\bar{V}_{\mathrm{S}}^{\circ}$ values, with the exception of that for the formamide–water system, are positive and non-trivial. The combinations of D_{S} and ΔB_{S} values roughly parallel the $\Delta\bar{V}_{\mathrm{A}}^{\circ}$ values.

The water-rich segment

A further change in the model equations is introduced when the organic mole fraction falls below X_{I}. While for the alkanol–water systems it was found to be appropriate to assign different values of X_{I} to different systems, a common value of 0.075 was assigned for all of the amide–water systems. No immediate explanation is offered for this difference in the characteristics of the two families of systems.

It is envisaged that, as the water content rises, there is an increasing tendency for the metastable organic aggregates to disperse. On the basis of analyses of the molar volumes of 1-propanol–water and employing her structural equilibrium model, Hvidt [21] has suggested that measurable effects of hydrophobic aqueous aggregation are limited to $X_A < 0.1$.

The effects of the structural dependence of the excess molar volumes upon composition in this segment are represented by D_W in the seven-parameter model equations and by D_W and ΔB_W in the ten. It was noted, in connection with the volumetric studies in the alkanol–water systems [16], that one might associate large positive D_W values with significant effects arising from hydrophobically induced aqueous aggregation. It is noted that, for the amide–water systems both the D_W and the ΔB_W values are relatively small.

There is an alternative approach to analysing the composition dependence of molar properties of binary aqueous systems in the water-rich region

$$\bar{V} = (1 - X_A)\bar{V}_W^\circ + \Phi_V^\ominus X_A + bX_A^2 + cX_A^3 \qquad (2)$$

where $\Phi_V^\ominus$ is the apparent molar volume of the amide in infinitely dilute aqueous solution.

This is similar to the McMillan–Mayer approach where mole fractions are replaced by the molalities of the organic solutes

$$(\bar{V} - (1 - X_A)\bar{V}_W^\circ)/X_A = \Phi_V^\ominus + v_2 m_A + v_3 m_A^2 \qquad (3)$$

Strictly speaking, the parameters of eqn. (3) should be treated in the manner of virial coefficients and estimated from the successive derivatives of the molar volume with respect to composition [22]. In this instance, the more pragmatic procedure of least-squares fitting over a modest concentration range has been adopted. Values of the parameters $\Phi_V^\ominus$, b and c are set out in Table 4.

The question may be posed as to whether it is possible to correlate the apparent molar (or apparent excess molar) volumes of the various amides in infinitely dilute aqueous solution in some kind of group additivity scheme. With the exception of dimethyl acetamide, the apparent molar volumes appear to fit together very nicely, as shown in Table 4. Since the value given for $\Phi_V^\ominus$ for DMA is reasonably accurate, it might be appropriate to suggest that its non-compliance with the group additivity scheme is indicative of some type of steric effect.

The b values of Table 4 play the same role as do the v_2 values of eqn. (3) and should be roughly equal to $55.5v_2$.

Wood and coworkers [23] have posed the question of whether or not parameters of the type v_2, for a variety of solutes, might be correlated in the context of the group pair additivity scheme of the Savage–Wood rules [1]. They concluded that the data that were available to them at that time were not adequate to resolve the question. There appear to be some fairly

TABLE 4

Parameters of eqns. (2) and (4) for amide–water systems

Amide	$\Phi^{\ominus}_{\mathrm{VA}}$	b	c	$\Phi^{\ominus}_{\mathrm{VW}}$	β	γ
F	38.52	3.8	37	17.84	−0.3	0.4
NMF	56.79	−6.6	54	16.80	−0.1	1.3
DMF	74.55	−31.8	317	15.35	0.1	1.7
2P	76.40	−30.3	278	17.01	−1.7	4.8
NM2P	94.47	−47.7	149	15.10	3.6	−8.4
A	55.66	−9.3	n.a.	n.a.	n.a.	n.a.
NMA	73.87	−45.4	530	n.a.	n.a.	n.a.
DMA	89.63	−62.0	581	14.15	−1.5	3.3

Increments in $\Phi^{\ominus}_{VA}$ from replacing an N-bonded hydrogen by a methyl group (cm^3 mol^{-1})

	First	Second
F	18.27	17.77
A	18.21	15.76
2P		18.07

Increments in $\Phi^{\ominus}_{VA}$ from replacing a C-bonded hydrogen by a methyl group (cm^3 mol^{-1})

F	17.14
NMF	17.08
DMF	15.07

Values cited for acetamide (A) were taken from ref. 23; n.a. denotes not available.

systematic variations in the b values of Table 4 with increasing numbers of methyl groups. It would seem that some kind of additivity scheme exists, but there is too little information to establish its nature.

It is worth noting that the apparent success of the Savage–Wood rules, in other contexts, implies that the second virial coefficients can be predicted on the basis of random orientations of neighbouring solute pairs. In that sense, it seems to be probable that their values are measures of the effects of overlapping aqueous cospheres, rather than of direct solute–solute interactions.

The organic-rich segment

When the mole fraction of the amide excedes X_{III}, it is the organic component which is present in too great an amount for all to be accommodated in the aggregative scheme of the microheterogeneous segment.

It is assumed that the tendency for water molecules to self aggregate persists up to quite high organic mole fractions and that, as the mole fraction of the amide rises, there is an increasing tendency for the aqueous clusters to form the cores of metastable reverse micelle-like structures.

The structural changes that take place, as the organic mole fraction increases from X_{III} to 1, are represented by the single parameter D_{A} in the seven-parameter model and by D_{A} and ΔB_{A} is the ten. From Table 3, it is seen that these parameters are large and negative, with their magnitudes following the same trends as the $\Delta\bar{V}_A$ values.

The somewhat complex nature of the model equations for this segment tends to disguise the fact, which is quite evident from the plots in Figs. 1 and 2, that there is an almost linear dependence of $\Delta\bar{V}$ upon X_A, for organic-rich mixtures. The appearance of the plots prompted an analysis based upon the equation

$$\bar{V} - X_A\bar{V}_A^\circ = \Phi_{VW}^{\ominus} X_W + \beta X_W^3 + \gamma X_W^3 \tag{4}$$

The results of those analyses are set out in Table 4. Since the curve fitting involved such a wide range of mole fractions, the results must be presumed to be insensitive to such structural changes as may occur at very low water concentrations. The $\Phi_{VW}^{\ominus}$ values appear to diminish with increasing methyl content. The β and γ values are generally small and, within the range of their variation, too imprecise to be useful for establishing trends.

SUMMARY

Densities have been measured and excess molar volumes evaluated for the four systems, water + NMF, + DMF, + 2-pyrrolidinone and + *N*-methyl-2-pyrrolidinone. These excess molar volumes were analysed using the four-segment model, together with data sets, taken from the literature, for water + formamide, + NMA and + DMA.

The quality of fit of the four-segment model equations for the various data sets is generally quite good. It was interesting to find that the range of the microheterogeneous segments in the amide–water systems appears to be roughly $1/4 < X_A < 1/2$, in contrast to the $1/3 < X_A < 2/3$ found for the alkanol–water systems [16].

The quality of fit was not found to improve significantly when going from a seven- to a ten-parameter version of the four-segment model. It is questionable whether the increase in the size of the parameter set added to the general level of understanding of the nature of the patterns of molecular aggregation which exist within amide–water mixtures.

It is felt that the four-segment model parameters for the excess molar volumes of binary hydro-organic systems are useful indicators of the existence of important trends in the composition dependence of the patterns of molecular aggregation but that they do not identify what those trends may be.

It would certainly be helpful to have access to reliable information about the composition dependence of other physical properties of these systems. There would appear to be a need for some more statistically based theory for interpreting such data.

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APPENDIX

Seven-parameter version

Microheterogeneous segment: $X_{\mathrm{II}} < X_{\mathrm{A}} < X_{\mathrm{III}}$

$$\Delta\bar{V}(\text{micro}) = BX_{\mathrm{A}}(1 - X_{\mathrm{A}}) + \Delta\bar{V}_{\mathrm{W}}^{\circ}(1 - X_{\mathrm{A}}) + \Delta\bar{V}_{\mathrm{A}}^{\circ} X_{\mathrm{A}}$$

Secondary segment: $X_{\mathrm{I}} < X_{\mathrm{A}} < X_{\mathrm{II}}$

$$\Delta\bar{V}(\text{sec}) = \Delta\bar{V}(\text{micro}) + (\Delta\bar{V}_{\mathrm{S}}^{\circ} - \Delta\bar{V}_{\mathrm{W}}^{\circ})((X_{\mathrm{II}} - X_{\mathrm{A}})/X_{\mathrm{II}})^3 + D_{\mathrm{S}} X_{\mathrm{A}}(X_{\mathrm{II}} - X_{\mathrm{A}})^2/X_{\mathrm{II}}^3$$

Water-rich segment: $0 < X_{\mathrm{A}} < X_{\mathrm{I}}$

$$\Delta\bar{V}(\text{wat}) = \Delta\bar{V}(\text{sec}) - \Delta\bar{V}_{\mathrm{S}}^{\circ}((X_{\mathrm{I}} - X_{\mathrm{A}})/X_{\mathrm{I}})^3 + D_{\mathrm{W}} X_{\mathrm{A}}(X_{\mathrm{I}} - X_{\mathrm{A}})^2/X_{\mathrm{I}}^3$$

Organic-rich segment: $X_{\mathrm{III}} < X_{\mathrm{A}} < 1$

$$\Delta\bar{V}(\text{org}) = \Delta\bar{V}(\text{micro}) - \Delta\bar{V}_{\mathrm{A}}^{\circ}((X_{\mathrm{A}} - X_{\mathrm{III}})/(1 - X_{\mathrm{III}}))^3 + D_{\mathrm{A}}(1 - X_{\mathrm{A}}) \times (X_{\mathrm{A}} - X_{\mathrm{III}})^2/(1 - X_{\mathrm{III}})^3$$

Ten-parameter version

Microheterogeneous segment

$$\Delta\bar{V}(\text{micro}) = BX_{\mathrm{A}}(1 - X_{\mathrm{A}}) + \Delta\bar{V}_{\mathrm{W}}^{\circ}(1 - X_{\mathrm{A}}) + \Delta\bar{V}_{\mathrm{A}}^{\circ} X_{\mathrm{A}}$$

Secondary segment

$$\Delta\bar{V}(\text{sec}) = \Delta\bar{V}(\text{micro}) + (\Delta\bar{V}_{\mathrm{S}}^{\circ} - \Delta\bar{V}_{\mathrm{W}}^{\circ})((X_{\mathrm{II}} - X_{\mathrm{A}})/X_{\mathrm{II}})^3 + D_{\mathrm{S}} X_{\mathrm{A}}(X_{\mathrm{II}} - X_{\mathrm{A}})^2/X_{\mathrm{II}}^3 + \Delta B_{\mathrm{S}} X_{\mathrm{A}}(X_{\mathrm{II}} - X_{\mathrm{A}})/X_{\mathrm{II}}^2$$

Water-rich segment

$$\Delta\bar{V}(\text{wat}) = \Delta\bar{V}(\text{sec}) - \Delta\bar{V}_{\mathrm{S}}^{\circ} X_{\mathrm{A}}((X_{\mathrm{I}} - X_{\mathrm{A}})/X_{\mathrm{I}})^3 + D_{\mathrm{W}} X_{\mathrm{A}}(X_{\mathrm{I}} - X_{\mathrm{A}})^2/X_{\mathrm{I}}^3 + \Delta B_{\mathrm{W}} X_{\mathrm{A}}(X_{\mathrm{I}} - X_{\mathrm{A}})/X_{\mathrm{I}}^2$$

Organic-rich segment

$$\Delta\bar{V}(\text{org}) = \Delta\bar{V}(\text{micro}) - \Delta\bar{V}_{\mathrm{A}}^{\circ}((X_{\mathrm{A}} - X_{\mathrm{III}})/(1 - X_{\mathrm{III}}))^3 + D_{\mathrm{A}}(1 - X_{\mathrm{A}}) \times (X_{\mathrm{A}} - X_{\mathrm{III}})^2/(1 - X_{\mathrm{III}})^3 + \Delta B_{\mathrm{A}}(1 - X_{\mathrm{A}})(X_{\mathrm{A}} - X_{\mathrm{III}}) /(1 - X_{\mathrm{III}})^2$$

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