J. Chem. Eng. Data **1995,** *40,* 674–678

Excess Molar Volumes for *N*,*N*-Dimethylacetamide + Water at 25 °C

Michael I. Davis* and M. Elena Hernandez

Department of Chemistry, University of Texas at El Paso, El Paso, Texas 79968-0513

Densities have been measured for the system *N*,*N*-dimethylacetamide (DMA) + water at 25 °C. The values have been converted to excess molar volumes. The values for water-rich mixtures were found to agree well with the more sparse results given in earlier publications. For equimolar and amide-rich mixtures the additional measurements reported here complement the previous results. The present measurements seem to confirm an earlier observation that the value of the apparent molar volume of DMA, at infinite dilution in water, is significantly lower than would be predicted on the basis of a simple group additivity scheme. The results of some molecular modeling computations of various small amides seem to support the suggestion that DMA is a particularly crowded molecule.

Introduction

Several years ago, we reported values for the excess molar volumes of a number of low molecular weight amide + water systems (Davis, 1987). In that paper, attention was drawn to an apparent anomaly in the value of the partial molar volume of *N*,*N*-dimethylacetamide (DMA) at infinite dilution in water, when placed in the context of a simple group additivity scheme. There existed, at that time, two sets of DMA + water density measurements of relatively recent origin (Boje and Hvidt, 1971; de Visser et al., 1978) which, at first consideration, had made the obtention of another set seem to be redundant. The level of mutual consistency between those two data sets is quite good at low amide mole fractions but somewhat less so as the amide content increases. Our decision to make additional measurements for the DMA + water system was largely prompted by our wish to check upon the aforesaid anomaly and to make sure that it was not an experimental artifact. The earlier values were relatively sparse, particularly beyond the water-rich range of compositions, and we felt that a more substantial set of measurements might prove to be useful for any future detailed analyses.

Experimental Section

The sample of *N*,*N*-dimethylacetamide used was Aldrich Gold Seal Grade. A conscious effort was made to protect the sample, which was used directly from the original containers, from atmospheric moisture. Mixtures with deionized–distilled water were prepared by weight; their mole fraction compositions were judged to be reliable to within 1×10^{-4}.

Densities were measured using a SODEV 03-D densimeter (Picker et al., 1974) which employs the vibrating tube principle. The temperature of the densimeter was maintained at (25.00 ± 0.02) °C by means of a SODEV CT-L programmable circulating thermostat. Each measurement of the period of the vibrating tube for the organic component or one of its aqueous mixtures was bracketed by two measurements for water. Kell's value of 997.048 kg m^{-3} was adopted for the density of water (Kell, 1975), which served as a calibrant for the apparatus. The calibration constant for the instrument was determined on the basis of accepted density values of water and methanol at 25 °C. The derived density measurements were judged to be reproducible to within 2×10^{-2} kg m^{-3}.

Table 1. Excess Molar Volumes of *N*,*N*′-Dimethylacetamide (1) + Water (2) at 298.15 K

x_1	V^E/ (cm^3·mol^{-1})	x_1	V^E/ (cm^3·mol^{-1})	x_1	V^E/ (cm^3·mol^{-1})
0	0.000	0.0419	−0.215	0.2699	−1.417
0.002 5	−0.009	0.0429	−0.221	0.2990	−1.489
0.004	−0.015	0.0449	−0.233	0.3272	−1.539
0.005 62	−0.021	0.0455	−0.238	0.3369	−1.551
0.006 89	−0.026	0.0457	−0.238	0.3534	−1.569
0.008 39	−0.033	0.0516	−0.276	0.3534	−1.568
0.008 59	−0.034	0.0536	−0.288	0.3671	−1.595
0.009 23	−0.036	0.0554	−0.300	0.3879	−1.589
0.011 15	−0.044	0.0588	−0.322	0.3879	−1.589
0.012 07	−0.049	0.0616	−0.340	0.3999	−1.603
0.012 43	−0.051	0.0623	−0.343	0.4298	−1.591
0.014 79	−0.062	0.0675	−0.379	0.4768	−1.560
0.015 06	−0.063	0.0698	−0.393	0.4982	−1.541
0.015 71	−0.067	0.0765	−0.436	0.5191	−1.511
0.016 54	−0.071	0.0791	−0.455	0.5388	−1.491
0.016 58	−0.071	0.0871	−0.507	0.5589	−1.440
0.017 28	−0.074	0.0897	−0.525	0.5609	−1.438
0.020 16	−0.090	0.0936	−0.547	0.5972	−1.369
0.021 98	−0.099	0.0958	−0.565	0.6448	−1.262
0.022 27	−0.101	0.1062	−0.631	0.6830	−1.132
0.023 19	−0.106	0.1179	−0.706	0.7287	−1.003
0.023 89	−0.110	0.1217	−0.731	0.7749	−0.839
0.026 86	−0.126	0.1394	−0.839	0.8224	−0.674
0.028 92	−0.138	0.1673	−0.998	0.8521	−0.560
0.031 37	−0.152	0.1722	−1.024	0.8672	−0.499
0.031 72	−0.153	0.1832	−1.081	0.8764	−0.473
0.031 86	−0.154	0.1998	−1.159	0.9225	−0.302
0.032 89	−0.160	0.2110	−1.210	0.9661	−0.135
0.034 89	−0.172	0.2405	−1.323	1.0000	0.000

Results

Our value for the density of *N*,*N*-dimethylacetamide, at 298.15 K, is 936.15 kg m^{-3}. That compares favorably with the literature values of 936.33 and 936.18 kg m^{-3} of Boje and Hvidt (1971) and de Visser et al. (1978), respectively. The density values of the mixtures were converted to molar, and thereafter to excess molar, volumes by standard procedures. The excess molar volume values are given in Table 1. The three sets of excess molar volumes are shown in Figure 1. There is quite good agreement at low amide mole fractions, but there are some fairly substantial disparities in the values for the amide-rich mixtures.

Figure 2 provides a comparison of our values for the excess molar volumes of the *N*,*N*-dimethylacetamide + water system with those reported for three other amide + water systems. The values used for formamide + water were derived from a combination of the results given by

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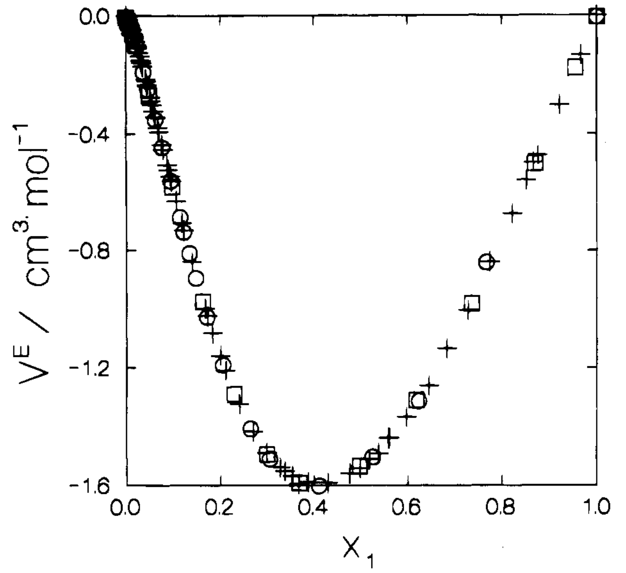

Figure 1. Excess molar volumes of *N,N*-dimethylacetamide + water at 25 °C. Units: cm^3 mol^{-1}. Symbols: (+) this work, (○) Boje and Hvidt (1971), (□) de Visser et al. (1978).

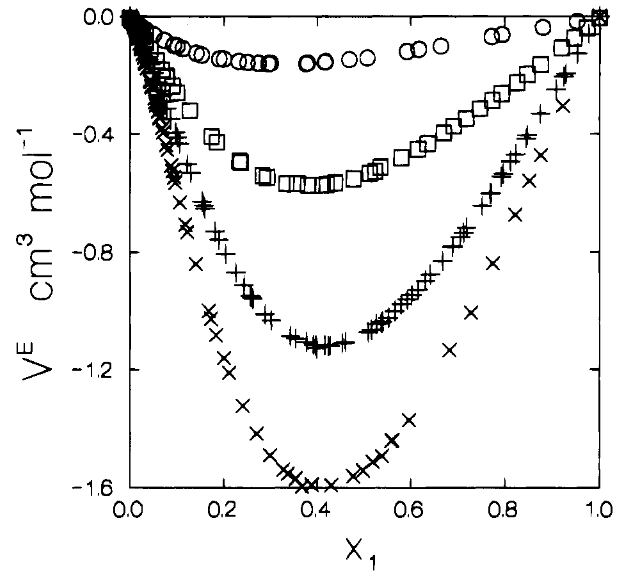

Figure 2. Excess molar volumes of some amide + water systems at 25 °C. Units: cm^3 mol^{-1}. Symbols: (×) *N,N*-dimethylacetamide + water, (+) *N,N*-dimethylformamide + water, (□) *N*-methylformamide + water, (○) formamide + water.

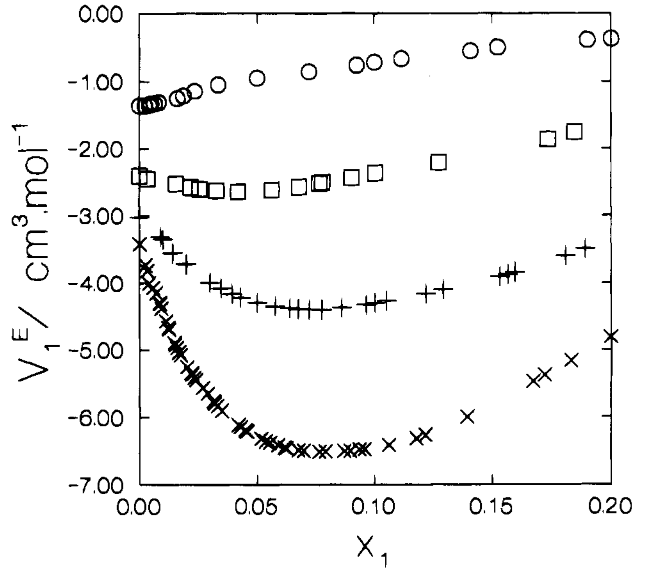

Figure 3. Partial excess molar volumes of amides in some water-rich amide + water systems at 25 °C. Units and symbols as for Figure 2.

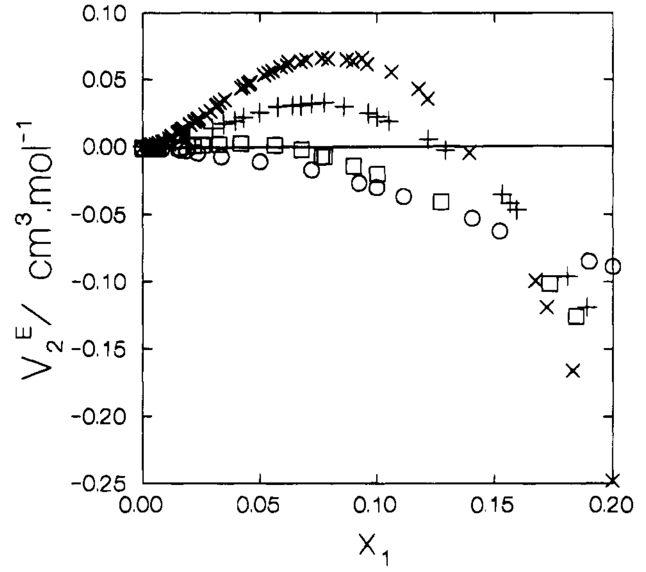

Figure 4. Partial excess molar volumes of water in some water-rich amide + water systems at 25 °C. Units and symbols as for Figure 2.

Boje and Hvidt (1971) and de Visser et al. (1978). The values for *N*-methylformamide + water and *N,N*-dimethyformamide + water were both taken from Davis (1987). The excess molar volumes are seen to become progressively, and fairly uniformly, more negative with the addition of each methyl group.

There are several ways in which one can present volumetric data for binary liquid systems that provide the more important features of their composition dependence. The partial excess molar properties have frequently proved to be particularly helpful in that respect.

The partial excess molar volumes were calculated from

$$V_2^E = V^E - X_1(dV^E/dX_1) \tag{1a}$$

$$V_1^E = V^E + (1 - X_1)(dV^E/dX_1) \tag{1b}$$

where V_2^E and V_1^E are the partial excess molar volumes of water and an amide, respectively. The derivatives of the excess molar volumes with respect to amide mole fraction, dV^E/dX_1, were determined using a modified cubic splines procedure that has been briefly described by Davis (1993). For partial molar properties to be reliable, the estimation of the derivatives needs to be accurate. We believe that our procedure is quite adequate.

Figure 3 shows the partial excess molar volumes of each of the four amides in their aqueous mixtures. The stepwise substitution of methyl groups, for hydrogens, at either the carbonyl carbon or the amine nitrogen leads to a progressive deepening of the minima at the water-rich end. This may be classified as some sort of a "hydrophobic" effect. A slightly different perspective of the same situation is obtained from looking at the water-rich partial excess molar volumes of water (Figure 4). That the values should become more positive as the number of methyl groups increases has been attributed to an "iceberg" or structure-making effect being promoted in the aggregative character

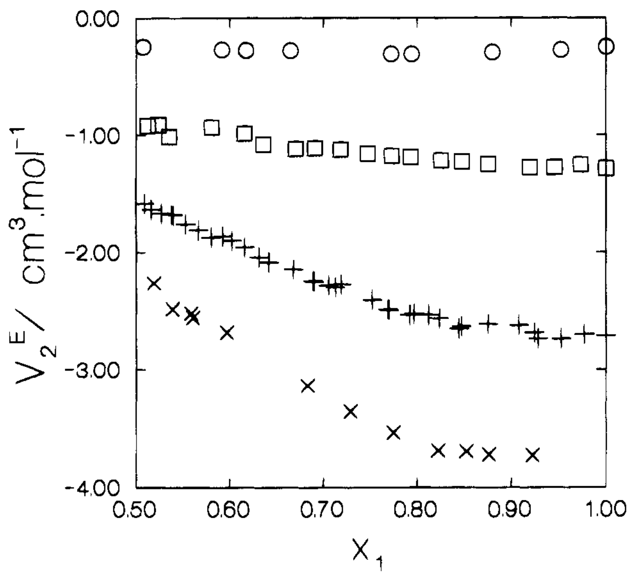

Figure 5. Partial excess molar volumes of water in some amide-rich amide + water systems at 25 °C. Units and symbols as for Figure 2.

of the water molecules that are in direct contact with the methyl groups (Davis, 1992).

Figure 5 shows the excess partial molar volumes of water in the amide-rich mixtures. Here, there is seen to be a fairly steady decrease in the values as the number of methyl groups is increased. The presence of the water may well be responsible for enhancing the tendency of the amide molecules to aggregate in some type of a relatively compact metastable reverse micellar scheme.

Discussion

The anomaly that we mentioned in the Introduction concerned the sequence of apparent molar volumes of the amides at infinite dilution in water. We reproduce here, in Table 2, an updated version of the table that was given by Davis (1987). There are some very minor differences from the values that were originally given, which reflect improvements in our analytic procedures. The value for DMA + water seems, as before, to be inconsistent with the others. The present value for DMA + water differs only marginally from that obtained previously from the combined data of Boje and Hvidt (1971) and de Visser et al. (1978) and thus serves to confirm the original observation that these infinite dilution apparent molar volumes fail to conform to a simple group additivity scheme.

In Table 2 we also show the molar volumes of the pure liquid amides at 25 °C. Since acetamide is a solid at that temperature, it had to be excluded. *N*-Methylacetamide is also a solid at 25 °C, but it was possible to obtain a reasonable value for the molar volume of the supercooled liquid by extrapolation of the densities of its aqueous mixtures (Boje and Hvidt, 1971). It is seen that the DMA value again deviates markedly from what otherwise appears to be a fairly well defined group additivity scheme. That suggests that the departure from group additivity has nothing to do with DMA's behavior in water but is an inherent molecular feature.

In Table 2, the excess apparent (and partial) molar volumes of the amides at infinite dilution are shown, with acetamide again omitted. These values appear to come somewhat closer to conforming to a simple group additivity scheme than do either the apparent or pure molar volumes. That is to say that there are no particularly well defined trends other than a general modest decrease with an increasing number of methyl groups. What the three sets of values collectively suggest is that *N*,*N*-dimethylacetamide is an inherently crowded molecule.

It is possible to estimate the molecular volumes of isolated molecules using various types of molecular mechanics and semiempirical quantum mechanical computational schemes for structural optimization. Values of the combined volumes of 1 mol of gaseous amide molecules, as calculated using the Allinger molecular mechanics approach, as embodied in the MMX force field of PCMODEL for Windows (PCMODEL 1993), are presented in Table 2. The similarity in the trends exhibited by these values and those of the molar volumes of the pure liquids is quite remarkable. Both *N*-methylformamide and *N*-methylacetamide have two possible conformations. In both cases the average of the two computed molecular volumes, which do not differ by much, has been presented. Values that were calculated using the AM1 semiempirical program for

Table 2. Comparisons of Various Experimental and Calculated Properties of Small Amides[a]

	$^{\infty}V_1$/ (cm^3·mol^{-1})	V_1^*/ (cm^3·mol^{-1})	$^{\infty}V_1^E$ (cm^3·mol^{-1})	$V_{1(\mathrm{mm})}$ (cm^3·mol^{-1})	$V_{1(\mathrm{se})}$ (cm^3·mol^{-1})	Δ_fH(mm)/ (kJ·mol^{-1})	Δ_fH(se)/ (kJ·mol^{-1})
F	38.51	39.88	−1.37	35	40.7	−182 (−194)	−185
NMF	56.76	59.13	−2.37	58	58.6	−190	−172
DMF	74.46	77.45	−2.99	81	76.2	−180(−192)	−149
A	55.66			55	57.6	−238(−238)	−210
NMA	73.78	76.43	−2.65	78	75.3	−242	−195
DMA	89.48	93.06	−3.58	97	92.7	−224(−228)	−169
2Py	76.30	76.92	−0.62	81	82.0	−205	−185
NM2P	94.48	96.47	−1.99	105	99.7	−206	−168
NMF−F	18.25	19.25	−1.00	23	17.9	−12	13
DMF−NMF	17.70	18.32	−0.62	23	17.6	10	23
NMA−A	18.12			23	17.7	−4	15
DMA−NMA	15.70	16.63	−0.93	19	17.4	18	26
NM2P−2Py	18.18	19.95	−1.37	24	17.7	−1	17
A−F	17.14			20	16.9	−56(−44)	−25
NMA−NMF	17.08	17.30	−0.28	20	16.7	−52	−23
DMA−DMF	15.01	15.61	−0.59	16	16.5	−44(−36)	−20

[a] $V_1^{|M\psi}$ = apparent molar volumes of the amides at infinite dilution in water. V_1^* = molar volumes of pure liquid amides. $V_1^{E|M\psi}$ = excess apparent molar volumes at infinite dilution in water. V_1(mm) = molecular mechanics estimates of amide volumes. V_1(se) = semiempirical (AM1) estimates of amide volumes. Δ_fH(mm) = molecular mechanics estimates of enthalpies of formation of gas phase amides. The experimental values in parentheses were taken from Pedley (1994). Δ_fH(se) = semiempirical (AM1) estimates of enthalpies of formation of gas phase amides. Sources of data: formamide (F), Boje and Hvidt (1971) and de Visser et al. (1978); acetamide (A), Tasker et al. (1983); *N*-methylformamide (NMF), Davis (1987); *N*-methylacetamide (NMA), Boje and Hvidt (1971); *N*,*N*-dimethylformamide (DMF), Davis (1987); *N*,*N*-dimethylacetamide (DMA), this work; 2-pyrrolidone (2Py) and *N*-methyl-2-pyrrolidone (NM2P), Davis (1987).

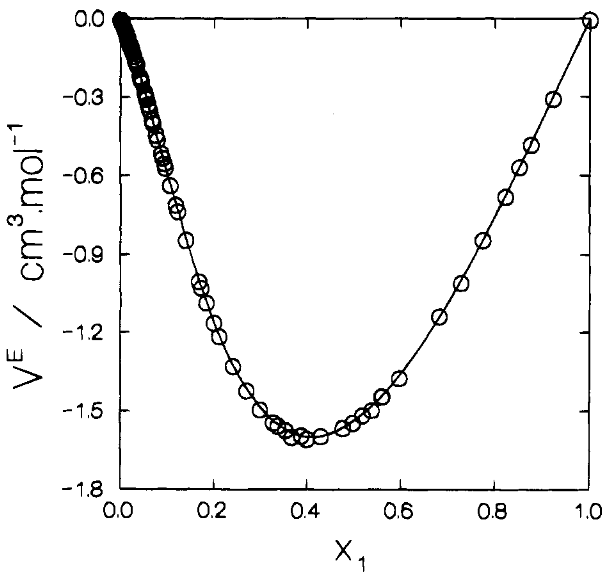

Figure 6. Excess molar volumes of *N,N*-dimethylacetamide + water at 25 °C. Units: cm^3 mol^{-1}. Symbols: (O) experimental values from this work, (- - -) calculated curve.

geometric optimization, which is included in HyperChem, (HyperChem 1994), with the structure–activity algorithms of ChemPlus are shown in Table 2 The AM1 results show a modest indication of the DMA molecular volumes being on the small side, relative to the other amides. The differences between these and the molecular mechanics values appear to be more a function of differing ways of defining gas-phase molecular volumes than they are of the different methods for optimizing the molecular geometries.

Using the same molecular modeling programs, it is possible to obtain estimates of the gas-phase molar enthalpies of formation at 298.15 K, $\Delta_f H_g°$. We were interested to see if there were any particularly interesting trends among the values for the same set of amides. The PCModel MMX results are set out in table 2 Since 2-pyrrolidinone (2PY) and *N*-methyl-2-pyrrolidinone (NM2P) both contain five-membered rings, they might well have been excluded from consideration here. The results of the semiempirical AM1 calculations are also given in that table. The appearance, from both sets of calculations, is that there is some small measure of inherent relative instability in the dimethylacetamide molecule. It should be noted that we also carried out the MNDO and PM3 semiempirical calculations, using HyperChem. The pattern of the MNDO calculations parallels that of the PCModel MMX. The PM3 calculations, however, do no single out DMA as being destabilized relative to the others. The PCModel calculations, in addition, estimate DMA to have a significant intramolecular van der Waals repulsive contribution, which would be consistent with molecular crowding.

Conclusions

Excess molar volumes have been determined from density measurements for the *N,N*-dimethylacetamide + water system at 25 °C. More experimental values than previously published are given, and while of a somewhat higher level of internal consistency, they do not exhibit any major deviations from the water-rich mixture results given of Boje and Hvidt (1971) and de Visser et al. (1978). Our prime motivation for the investigation was to check the previous best existing value for the apparent molar volume of the amide at infinite dilution in water, which had been observed (Davis, 1987) to conflict with a simple group additivity scheme that was fairly closely adhered to by a number of other small amides. We found that our experimental results confirmed that DMA anomaly. We suggest, and have offered some supportive evidence from molecular modeling, that the anomaly can be attributed to "crowding" in the individual DMA molecules.

Appendix: Curve Fitting

Figure 6 shows the data of Table 1 together with a fitted curve that was obtained using the four-segment composition model. The rationale for that model has been described in some detail by Davis (1993). The total composition range is partitioned into four segments. Across each segment, the excess molar properties are assumed to have a distinctive dependence upon mole fractional composition. Both the excess molar volume V^E and its mole fraction derivative dV^E/dX_1 are constrained to be single valued at each of the three segment junctions.

Four-Segment Model Equations

water–rich segment: $0 \le x_1 \le x_I$

$$V^E = a_w(x_1 - x_1^3) + b_w(x_1^2 - x_1^3) + c_w x_1^3$$

pseudolamellar segment: $x_{II} \le x_1 \le x_{III}$

$$V^E = q_w(1 - x_1) + q_A x_1 + b_L x_1(1 - x_1)$$

transitional segment: $x_I \le x_1 \le x_{II}$

$$V^E\ b_T(f_T^2 - 2f_T^3 + f_T^4) + V^E(x_I)(4f_T^3 - 3f_T^4) + V^E(x_{II})(1 - 4f_T^3 + 3f_T^4) + (dV^E/dx_1)(x_I)(x_{II} - x_I)(f_T^3 - f_T^4) - (dV^E/dx_1)(x_{II})(x_{II} - x_I)(f_T - 3f_T^3 + 2f_T^4)$$

where

$$f_T = (x_{II} - x_1)/(x_{II} - x_I)$$

$$V^E(x_I) = a_w(x_I - x_I^3) + b_w(x_I^2 - x_I^3) + c_w x_I^3$$

$$V^E(x_{II}) = q_w(1 - x_{II}) + q_A x_{II} + b_L x_{II}(1 - x_{II})$$

$$(dV^E/dx_1)(x_I) = a_w(1 - 3x_I^2) + b_w(2x_I - 3x_I^2) + 3c_w x_I^2$$

$$(dV^E/dx_1)(x_{II}) = q_A - q_w + b_L(1 - 2x_{II})$$

organic–rich segment: $x_{III} \le x_1 \le 1$

$$V^E = a_A(1 - x_1)(1 - f_A)^2 + 3V^E(x_{III})(3f_A^2 - 2f_A^3) + (dV^E/dx_1)(x_{III})(1 - x_1)(f_A - f_A^2)$$

where

$$f_A = (1 - x_1)/(1 - x_{III})$$

$$V^E(x_{III}) = q_w(1 - x_{III}) + q_A x_{III} + b_L x_{III}(1 - x_{III})$$

$$(dV^E/dx_1)(x_{III}) = q_A - q_w + b_L(1 - 2x_{III})$$

The optimum values for the eight parameters of the foregoing equations, derived from a least squares optimization, with the three segment junction values of the DMA mole fraction being $x_{I} = 0.06$, $x_{II} = 0.25$, and $x_{III} = 0.425$ are

$$a_w = -3.58 \quad b_w = -47.5 \quad c_w = 207 \quad b_T = 0.6$$

$$q_w = 0.02 \quad q_A = 1.80 \quad b_L = -9.7 \quad a_A = -3.80$$

The standard deviation was 3.0×10^{-3} cm^3 mol^{-1}.

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Received for review December 1, 1994. Accepted February 20, 1995.® We wish to acknowledge financial support from the National Institutes of Health in the form of an institutional Minority Biomedical Research Support Grant (RR 08012).

JE940254Y

® Abstract published in *Advance ACS Abstracts,* April 1, 1995.