

# Densities and Viscosities of Binary Mixtures of *N,N*-Dimethylacetamide with Aliphatic Alcohols

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Densities and viscosities of binary liquid mixtures of *N,N*-dimethylacetamide (DMA) with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol have been determined at 303.15 K. The excess volume, the excess viscosity, and the excess Gibbs energy of activation of flow have been calculated from the experimental data and are presented as functions of composition. Intermolecular interactions in the mixtures are considered in the discussion of the results.

## Introduction

The properties of carboxamides have been the subject of considerable interest because of the versatility of these compounds as solvents and their close relationship to peptides and proteins. Densities and viscosities of aqueous mixtures of several carboxamides have been determined to gain insight into the interactions in these systems (1-5). Surprisingly there have been practically no systematic studies on the density and viscosity behavior of mixtures of these amides with cosolvents other than water. To our knowledge, as far as alcohols are concerned, only the excess volumes for mixtures of *N,N*-dimethylacetamide (DMA) at 298.15 K have been determined (6). In earlier studies we have concentrated upon the properties of binary mixtures of *N*-methylmethanesulfonamide and *N,N*-dimethylmethanesulfonamide with aliphatic alcohols (7, 8). Now we extend our studies to the corresponding carboxamides. We report the densities and viscosities of binary mixtures of *N,N*-dimethylacetamide with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol at 303.15 K.

## Experimental Section

**Materials.** Methanol, 2-propanol, 1-butanol, 2-methyl-2-propanol (pro analysi products of E. Merck AG, FRG), and 1-propanol (a purissimum product of Fluka AG, Switzerland) were purified by distillation. Ethanol (an absolute alcohol, grade Aa product of Alko, the State Alcohol Monopoly, Finland) was dried over molecular sieves type 4A (9). *N,N*-Dimethylacetamide (a purissimum product of Fluka AG) was shaken with BaO, refluxed with BaO, and distilled under reduced pressure (9). The reagents were stored over molecular sieves.

**Measurements.** Densities were measured with a digital density meter DMA 40 (Anton Paar K. G., Austria). The reproducibility in the density measurements was at worst  $\pm 0.0001$  g cm<sup>-3</sup>. Dynamic viscosities were determined with Cannon-Ubbelohde viscometers (Cannon Instrument Co., USA) equipped with an optoelectronic device for measuring the efflux time. The dimensions of the viscometers are such that the kinetic energy correction is not needed (10). Viscosities are expressed in units of centipoise equal to 10<sup>-3</sup> N s m<sup>-2</sup>. The reproducibility in the viscosity measurements was at least  $\pm 0.005$  cP. The measured densities and viscosities of the pure components together with values from the literature are shown in Table I.

## Results and Discussion

The experimental results of measurements of densities and viscosities of the binary mixtures are collected in Table II. The excess volume  $V^E$ , the excess viscosity  $\eta^E$ , and the excess Gibbs energy of activation of flow  $\Delta G^{*E}$  were calculated from the experimental data with the following equations:

$$V = [(1-x)M_1 + xM_2]/\rho \quad (1)$$

$$V^E = V - [(1-x)V_1^* + xV_2^*] \quad (2)$$

$$\eta^E = \eta - [(1-x)\eta_1^* + x\eta_2^*] \quad (3)$$

$$\Delta G^{*E} = RT\{\ln \eta V - [(1-x) \ln \eta_1^* V_1^* + x \ln \eta_2^* V_2^*]\} \quad (4)$$

where  $\rho$ ,  $\eta$ , and  $V$  are the density, viscosity, and molar volume of the mixture,  $M_1$  and  $M_2$  are the molar masses,  $\eta_1^*$  and  $\eta_2^*$  are the viscosities,  $V_1^*$  and  $V_2^*$  are the molar volumes of the alcohol and DMA, respectively, and  $x$  is the mole fraction of DMA.

The results for  $V^E$ ,  $\eta^E$ , and  $\Delta G^{*E}$  are plotted in Figures 1-3. They were fitted with the equation

$$Y^E = x(1-x) \sum_{i=0}^3 A_i(1-2x)^i \quad (5)$$

where  $Y^E$  is  $V^E/(\text{cm}^3 \text{ mol}^{-1})$  or  $\eta^E/\text{cP}$  or  $\Delta G^{*E}/(\text{J mol}^{-1})$ . Coefficients  $A_i$  of these fitting equations together with the standard deviations  $\sigma(Y^E)$  are summarized in Table III.

Since the excess quantities represent the differences between the properties of the mixtures and those of the pure

Table I. Densities ( $\rho$ ) and Viscosities ( $\eta$ ) of the Pure Components at 303.15 K

compd	$\rho/(\text{g cm}^{-3})$		$\eta/\text{cP}$	
	exptl	lit.	exptl	lit.
methanol	0.781 82	0.781 78 (11), 0.781 65 (12)	0.513	0.510 (14)
ethanol	0.780 72	0.780 96 (11), 0.780 64 (12)	0.994	0.991 (14)
1-propanol	0.795 60	0.795 78 (11), 0.795 61 (12)	1.728	1.72 (14)
2-propanol	0.776 56	0.776 64 (11), 0.776 75 (12)	1.779	1.77 (14)
1-butanol	0.801 97	0.802 04 (11), 0.801 91 (12)	2.271	2.28 (14)
2-methyl-2-propanol	0.775 49	0.775 46 (11)	3.378	3.383 (15) <sup>a</sup>
<i>N,N</i> -dimethylacetamide	0.931 69	0.931 64 (13) <sup>a</sup>	0.871	

<sup>a</sup> Interpolated value.

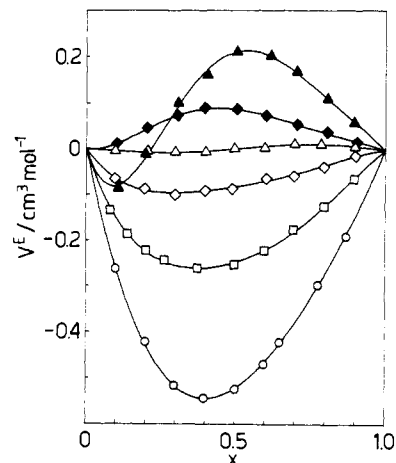
**Table II.** Densities ( $\rho$ ) and Viscosities ( $\eta$ ) of the Binary Mixtures at 303.15 K<sup>a</sup>

$x$	$\rho/(\text{g cm}^{-3})$	$\eta/\text{cP}$	$x$	$\rho/(\text{g cm}^{-3})$	$\eta/\text{cP}$
DMA + Methanol					
0.0976	0.816 09	0.572	0.5962	0.903 26	0.780
0.1993	0.843 02	0.626	0.6480	0.907 98	0.795
0.2967	0.863 18	0.673	0.7762	0.918 22	0.829
0.3971	0.879 55	0.712	0.8699	0.924 51	0.846
0.4998	0.892 96	0.750			
DMA + Ethanol					
0.0809	0.800 90	0.944	0.4935	0.875 26	0.861
0.1399	0.814 02	0.915	0.5953	0.888 92	0.862
0.2001	0.826 36	0.894	0.6938	0.900 71	0.863
0.2626	0.838 16	0.878	0.7965	0.912 05	0.865
0.3738	0.857 19	0.865	0.8971	0.922 16	0.867
DMA + 1-Propanol					
0.0966	0.812 20	1.470	0.6025	0.885 03	1.000
0.1975	0.828 29	1.293	0.6970	0.896 90	0.963
0.2992	0.843 70	1.193	0.7955	0.908 66	0.930
0.3986	0.857 86	1.103	0.9012	0.920 73	0.898
0.4894	0.870 33	1.048			
DMA + 2-Propanol					
0.1016	0.795 10	1.428	0.6012	0.875 95	0.945
0.2027	0.812 56	1.222	0.7055	0.891 28	0.939
0.3046	0.829 51	1.100	0.8055	0.905 43	0.900
0.3968	0.844 34	1.028	0.9060	0.919 24	0.884
0.5032	0.861 06	0.994			
DMA + 1-Butanol					
0.0968	0.814 72	1.862	0.5990	0.880 01	1.097
0.1997	0.828 22	1.585	0.6978	0.892 67	1.029
0.2976	0.840 97	1.430	0.7867	0.904 16	0.975
0.4000	0.854 29	1.281	0.9006	0.918 89	0.917
0.4956	0.866 63	1.181			
DMA + 2-Methyl-2-propanol					
0.1094	0.792 97	2.544	0.6154	0.868 94	1.128
0.2069	0.807 30	2.032	0.7028	0.882 97	1.046
0.3062	0.821 73	1.651	0.8064	0.899 86	0.973
0.4037	0.836 31	1.422	0.8954	0.914 45	0.924
0.5026	0.851 24	1.255			

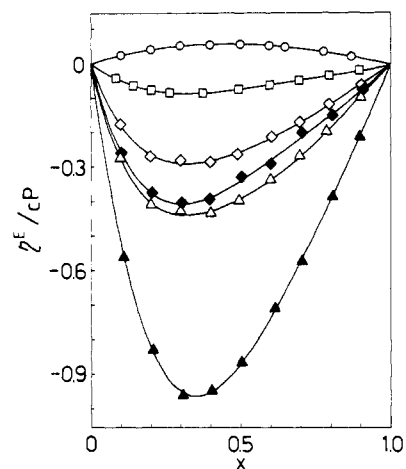
<sup>a</sup>  $x$  is the mole fraction of DMA.

components, a look at the properties of the pure components is appropriate. Alcohols are self-associated through hydrogen bonding. DMA has a considerable proton-accepting ability (16–18): for example, at 298 K the equilibrium constant of the DMA–phenol complex is nearly 10 times that of the acetone–phenol complex, both of which have a  $\text{C}=\text{O}\cdots\text{H}-\text{O}$  hydrogen bond (19). Lacking a proton donor group in its molecule, DMA does not, however, self-associate through hydrogen bonding. At the same time, the presence of self-association by dipolar interactions has been demonstrated, though there is some dispute about the significance of the association (20–23). At 303.15 K the molar volume of DMA is  $93.51 \text{ cm}^3 \text{ mol}^{-1}$  and the molar volumes of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-methyl-2-propanol are 40.98, 50.01, 75.53, 77.39, 92.42, and  $95.58 \text{ cm}^3 \text{ mol}^{-1}$ , respectively.

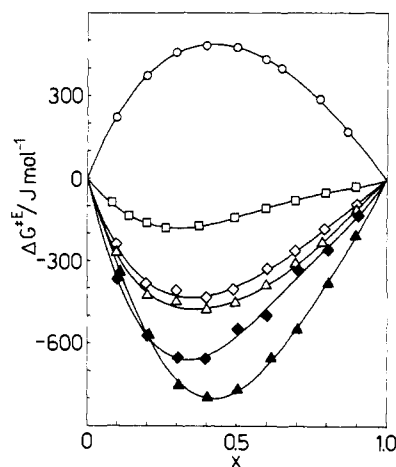
Mixing of DMA with an alcohol tends, for one thing, to occasion breakup of the associates present in the pure liquids, which should lead to an expansion in volume. The excess volume is slightly positive for DMA–1-butanol mixtures in the amide-rich region, but for the other mixtures of primary alcohols negative contributions are predominant. The values of  $V^E$  decrease in the sequence: 1-butanol > 1-propanol > ethanol > methanol (Figure 1). In view of the proton-accepting ability of DMA it seems justifiable to attribute at least part of the negative contributions to formation of hydrogen bonds between DMA and alcohol molecules. Just this contribution would be expected to be most significant for the lower alcohols (24). Another probable source of the negative contributions is the differences in the sizes and shapes of the component molecules allowing



**Figure 1.** Excess volumes  $V^E$  of the mixtures of DMA with aliphatic alcohols against the mole fraction,  $x$ , of DMA: (O) methanol; (□) ethanol; (◇) 1-propanol; (◆) 2-propanol; (△) 1-butanol; (▲) 2-methyl-2-propanol.



**Figure 2.** Excess viscosities  $\eta^E$  of the mixtures of DMA with aliphatic alcohols against the mole fraction,  $x$ , of DMA. The symbols are the same as in Figure 1.



**Figure 3.** Excess Gibbs energies of activation of flow  $\Delta G^{*E}$  of the mixtures of DMA with aliphatic alcohols against the mole fraction,  $x$ , of DMA. The symbols are the same as in Figure 1.

them to fit into each other's structure (2, 25).

The viscosities of the mixtures vary smoothly, without distinct extremes, from the value of the pure alcohol to that of DMA as the mole fraction of the amide increases. Deviations from

Table III. Coefficients  $A_i$  of Eq 5 and the Standard Deviations  $\sigma(Y^E)$  at 303.15 K

function	$A_0$	$A_1$	$A_2$	$A_3$	$\sigma(Y^E)$
DMA + Methanol					
$V^E/(\text{cm}^3 \text{ mol}^{-1})$	-2.0883	-0.8348	-0.2816	0.0664	0.004
$\eta^E/\text{cP}$	0.2325	0.0432	0.0113	0.0069	0.001
$\Delta G^{\ddagger E}/(\text{J mol}^{-1})$	1914	559.0	207.6	112.8	3
DMA + Ethanol					
$V^E/(\text{cm}^3 \text{ mol}^{-1})$	-0.9852	-0.4017	-0.2718	-0.3504	0.004
$\eta^E/\text{cP}$	-0.2877	-0.2472	-0.1196	0.0433	0.001
$\Delta G^{\ddagger E}/(\text{J mol}^{-1})$	-552.9	-653.3	-274.6	183.0	2
DMA + 1-Propanol					
$V^E/(\text{cm}^3 \text{ mol}^{-1})$	-0.3248	-0.2205	-0.1739	-0.2170	0.003
$\eta^E/\text{cP}$	-1.0117	-0.6674	-0.4640	-0.2899	0.005
$\Delta G^{\ddagger E}/(\text{J mol}^{-1})$	-1561	-951.6	-450.1	-228.2	9
DMA + 2-Propanol					
$V^E/(\text{cm}^3 \text{ mol}^{-1})$	0.3527	0.1502	-0.2634	-0.3252	0.002
$\eta^E/\text{cP}$	-1.3488	-1.1070	-0.7643	-0.1938	0.007
$\Delta G^{\ddagger E}/(\text{J mol}^{-1})$	-2289	-1804	-754.0	402.6	17
DMA + 1-Butanol					
$V^E/(\text{cm}^3 \text{ mol}^{-1})$	0.0064	-0.1298	0.0215	0.0831	0.006
$\eta^E/\text{cP}$	-1.5532	-0.9071	-0.7696	-0.6261	0.006
$\Delta G^{\ddagger E}/(\text{J mol}^{-1})$	-1765	-836.7	-563.0	-507.6	10
DMA + 2-Methyl-2-propanol					
$V^E/(\text{cm}^3 \text{ mol}^{-1})$	0.8448	-0.3186	-1.4995	-1.0249	0.006
$\eta^E/\text{cP}$	-3.4707	-2.2427	-0.8806	0.0493	0.005
$\Delta G^{\ddagger E}/(\text{J mol}^{-1})$	-3091	-1235	377.3	823.7	9

linear dependence on composition, as expressed by the excess viscosity, are positive for methanol-containing mixtures, turn negative for ethanol-containing mixtures, and decrease further as the length of the alkyl chain of the primary alcohol increases (Figure 2). The excess Gibbs energies of activation of flow decrease in a similar order, and they, too, are positive only in the case of methanol (Figure 3). The viscosity behavior of the mixtures thus supports the view that the predominance of interactions between unlike molecules over the dissociation effects is more pronounced in DMA-methanol mixtures than in the other mixtures studied. Namely, mixtures where a strong specific interaction between unlike molecules is predominant are characterized by distinct maxima in the viscosity vs. composition curves, by positive excess viscosities, and by positive values of  $\Delta G^{\ddagger E}$  (2, 26-29).

The lack of predominant unlike interactions appears still more clearly in the mixtures of DMA with the secondary alcohol, 2-propanol, and with the tertiary alcohol, 2-methyl-2-propanol. Except at low concentrations of 2-methyl-2-propanol the excess volumes are positive and greater than for the mixtures of the corresponding primary alcohol. Further, the values of  $\eta^E$  and  $\Delta G^{\ddagger E}$  are, especially for the mixtures of 2-methyl-2-propanol, more negative than for the mixtures of the primary alcohols.

From the foregoing it is evident that the volume and viscosity behavior of the DMA-alcohol mixtures is affected by different contributions, whose relative significance appears to vary with the length and branching of the alkyl chain of the alcohol.

### Glossary

$V_i^*$	molar volume of pure component $i$ , $\text{cm}^3 \text{ mol}^{-1}$
$V$	molar volume of the mixture, $\text{cm}^3 \text{ mol}^{-1}$
$V^E$	excess molar volume of the mixture, $\text{cm}^3 \text{ mol}^{-1}$
$\Delta G^{\ddagger E}$	molar excess Gibbs energy of activation of flow of the mixture, $\text{J mol}^{-1}$
$M_i$	molar mass of component $i$
$x$	mole fraction of DMA
$R$	gas constant, $\text{J K}^{-1} \text{ mol}^{-1}$
$T$	temperature, K
$A_i$	coefficient of eq 5

### Greek Letters

$\rho$	density of the mixture
$\eta_i^*$	viscosity of pure component $i$ , cP
$\eta$	viscosity of the mixture, cP
$\eta^E$	excess viscosity of the mixture, cP
$\sigma$	standard deviation

### Subscripts

1	component 1, alcohol
2	component 2, DMA

**Registry No.** Methanol, 67-56-1; ethanol, 64-17-5; 1-propanol, 71-23-8; 2-propanol, 67-63-0; 1-butanol, 71-36-3; 2-methyl-2-propanol, 75-65-0; *N,N*-dimethylacetamide, 127-19-5.

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## Heat Capacities of Titanium Disulfide from 5.87 to 300.7 K

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The heat capacity of  $\text{TiS}_2$  was determined from 5.87 to 300.7 K by adiabatic calorimetry. The values at 298.15 K for  $C_p^\circ$ ,  $S^\circ(T) - S^\circ(0)$ ,  $-[G^\circ(T) - H(0)]/T$ , and  $H^\circ(T) - H^\circ(0)$  are 67.34, 78.21, 36.69 J mol<sup>-1</sup> K<sup>-1</sup>, and 12.38 kJ mol<sup>-1</sup>, respectively.

### Introduction

One of the goals of the U.S. Bureau of Mines is to provide thermodynamic data on minerals and related inorganic compounds. As part of this effort, the heat capacity of  $\text{TiS}_2$  was measured from 5.87 to 300.72 K by adiabatic calorimetry, thereby extending the range of existing measurements to below 53 K. The heat capacity of  $\text{TiS}_2$  has been measured previously by Todd and Coughlin (1) from 53 to 297 K by isoperibol calorimetry, and by Mraw and Naas (2) from 100 to 700 K using a differential scanning calorimeter.

### Experimental Section

**Sample Preparation.** The sample of titanium disulfide was provided by A. H. Thompson of Exxon Research and Engi-

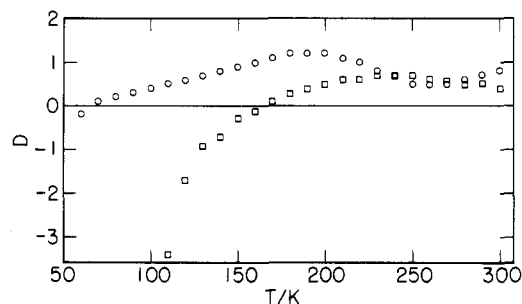


Figure 1. Heat capacity deviation:  $D = 100\{[C_p(\text{ref 1 or 2})/C_p(\text{this work})] - 1\}$ ; open circles, Todd and Coughlin (1); open squares, Mraw and Naas (2).

neering Co. Details of the preparation and analysis of the  $\text{TiS}_2$  sample have been reported previously (3). Optical emission spectrographic analysis detected the following impurities, in parts per million by mass of metal: Al, 100; Ca, 40; Cr, 30; Cu, 400; Fe, 50; Mg, 8. X-ray powder diffraction analysis showed only  $\text{TiS}_2$ . Ignition in air at 1475 K showed the sample to have the theoretically correct amounts of titanium and sulfur to within  $\pm 0.05$  mass %.

Table I. Experimental Heat Capacities of  $\text{TiS}_2$

T/K	$C_p^\circ$ /(J mol <sup>-1</sup> K <sup>-1</sup> )	T/K	$C_p^\circ$ /(J mol <sup>-1</sup> K <sup>-1</sup> )	T/K	$C_p^\circ$ /(J mol <sup>-1</sup> K <sup>-1</sup> )	T/K	$C_p^\circ$ /(J mol <sup>-1</sup> K <sup>-1</sup> )
Series I				Series II			
48.48	11.333	188.65	56.678	19.04	1.436	34.49	6.133
47.71	11.039	196.80	57.924	20.77	1.841	37.43	7.178
52.47	12.998	204.81	59.031	22.30	2.248	40.64	8.347
57.10	14.934	212.69	60.069	23.59	2.630	44.15	9.657
62.23	17.153	220.48	60.989	25.10	3.043	47.98	11.152
67.85	19.638	228.17	61.809	27.07	3.644	52.15	12.869
74.04	22.365	235.79	62.592	29.34	4.366	56.72	14.773
80.86	25.378	243.33	63.306	31.79	5.195	61.74	16.940
88.38	28.624	250.79	63.974	Series III			
96.68	32.059	235.03	62.484	250.24	63.929	279.93	66.212
105.81	35.623	242.54	63.221	257.74	64.530	287.25	66.673
115.42	39.082	249.98	63.972	265.18	65.096	294.53	67.112
125.15	42.283	257.36	64.569	272.57	65.724		
134.99	45.201	264.69	65.167	Series IV			
144.70	47.805	271.96	65.708	5.87	0.034	10.96	0.248
154.03	50.056	279.21	66.121	6.90	0.055	12.05	0.335
163.05	52.038	286.41	66.602	7.52	0.075	13.25	0.454
171.79	53.775	293.57	67.108	8.26	0.102	14.55	0.616
180.32	55.332	300.72	67.507	9.07	0.139	15.99	0.837
				9.97	0.185	17.57	1.134