



# **VOLUMETRIC AND VISCOMETRIC STUDIES ON N, N-DIMETHYLACETAMIDE AND METHANOL BINARY MIXTURES AT DIFFERENT TEMPERATURES**

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## **ABSTRACT**

Densities and viscosities of binary liquid mixtures of N, N-dimethylacetamide with polar solvent viz. methanol have been measured at 303.15, 308.15, 313.15 and 318.15 K. From the density and viscosity data, the values of various properties viz. excess molar volume ( $V^E$ ), excess viscosity ( $\eta^E$ ) and excess Gibb's free energy of activation of flow ( $\Delta G^E$ ) have been determined. Further, the viscosities of binary mixtures have been correlated to various viscosity models. On the basis of the values of interaction parameters of these viscosity models and also on the basis of the values of various excess properties, the nature of molecular interactions between the components of mixtures have been explained.

**Key words:** Viscometric studies, Mixed solvent, Binary mixture, N, N-dimethylacetamide, Methanol, Viscosity models.

## **INTRODUCTION**

The solution properties of binary mixtures of N, N-dimethylacetamide with alkanols have been the subject of intensive research, owing to their importance as super solvent for chemical reactions and many industrial processes. The viscosity of multi component mixture is required in many engineering calculations involving fluid flow, heat transfer and mass transfer. Alkanols serves as simple example of biologically and industrially important amphiphilic materials. In view of the practical importance of these liquids, accurate and extensive data on physico-chemical properties of these systems are often required for their industrial applications.

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Viscosities and excess molar volumes of binary mixtures of ethanalamine with water at different temperatures have been studied by Kapadi, et al.<sup>1</sup>. Using density and viscosity values, the excess molar volume  $V^E$ , the excess viscosity  $\eta^E$  and Gibbs free energy of activation of viscous flow  $\Delta G^E$  have been calculated. The molecular interactions between the components have been discussed.

After having an exhaustive literature survey<sup>2-12</sup>, it has been observed that molecular interactions among alcohols and important industrial solvent like N, N-dimethylacetamide have not been much explored over the entire composition range and at different temperatures.

The thermodynamic and transport properties of N, N-dimethylacetamide with methanol have been studied, herewith, over the entire composition range, at 303.15, 308.15, 313.15 and 318.15 K. The present study reveals the nature and extent of interactions between the component molecules in their binary mixtures.

In the present paper, densities ( $\rho$ ) and viscosities ( $\eta$ ) of binary mixtures of N, N-dimethylacetamide with methanol covering the entire composition range (expressed by mole fraction  $x$  of N, N-dimethylacetamide) at 305.15, 308.15, 313.15 and 318.15 K are reported. From experimental values of densities and viscosities, excess molar volume ( $V^E$ ), excess viscosity ( $\eta^E$ ) and excess free energy of activation of viscous flow ( $\Delta G^E$ ) of methanol in N, N-dimethylacetamide have been calculated. These functions offer a convenient approach for the study of thermodynamic properties of liquid mixtures. The extreme sensitivity of excess functions is due to the size, shape of the molecule and interaction among themselves and gives important information about intermolecular forces, which are responsible for these interactions.

The several models (equations) have been used from time to time for correlating the viscosity of binary mixtures with those of component liquid systems and have been used to test the reliability of the results.

## EXPERIMENTAL

N, N-Dimethylacetamide and methanol were from S. D. Fine Chemicals (spectroscopic HPLC, A. R. Grade) and were further purified according to standard procedures<sup>13,15</sup>. The purities were checked by comparing their densities and viscosities with literature values (in the accuracy  $\pm 1 \times 10^{-4}$  g cm<sup>3</sup> and  $\pm 3 \times 10^{-3}$  mPaS, respectively) and are given in Table 1.

All the binary mixtures were prepared gravimetrically in stoppard bottles. The densities of pure liquids and their binary mixtures were measured using a single capillary pycnometer (made up of Borosil glass) having bulb capacity of  $8 \times 10^{-3} \text{ m}^3$ . Viscosity of pure liquid and their binary mixture was measured using Ubbelohde type suspended level viscometer calibrated with tripled distilled water. The viscometer containing the test liquid was allowed to stand for about 30 min in thermostatic bath. The thermostatically controlled water bath, whose temperature was maintained constant by circulating water Julabo F 25 MP thermostat (made in Germany) capable of maintaining constant temperature ( $\pm 0.02^\circ\text{C}$ ) was used.

**Table 1: Comparison of experimental density ( $\rho$ ) and viscosity ( $\eta$ ) of pure liquids with literature values at 303.15, 308.15, 313.15 and 318.15 K**

Liquids	Density ( $\rho$ ) g cm <sup>-3</sup>				Viscosity ( $\eta$ ) mPas.			
	303.15 K	308.15 K	313.15 K	318.15 K	303.15 K	308.15 K	313.15 K	318.15 K
Methanol	0.7823	0.7772	0.7721	0.7692	0.5063	0.4740	0.4408	0.3802
	0.7822	0.7772	0.7722	0.7693	0.5064	0.4752	0.4400	0.3812
N, N-Dimethyl acetamide	0.9321	0.9280	0.9240	0.9191	0.8800	0.8030	0.7470	0.7080
	0.9320	0.9280	0.9240	0.9192	0.8802	0.8031	0.7482	0.7085

a : Experimental values; b : Literature values<sup>2</sup>

## RESULTS AND DISCUSSION

The excess function is a measure of deviation from the ideal behavior of the mixture and found to be highly sensitive towards molecular interactions between the component molecules of liquid mixtures. The sign and magnitude of these excess functions from ideality depends on the strength of interaction between unlike molecules.

### Excess molar volume ( $V^E$ )

The excess molar volume ( $V^E$ ) of binary mixture was evaluated from the molar volume of mixture ( $V$ ) and that of pure components ( $V_1$  and  $V_2$ ) using the following equation<sup>16</sup> –

$$V^E = V - (x_1 V_1 + x_2 V_2) \quad \dots (1)$$

The molar volumes  $V$  of the binary liquid mixture were calculated from the measured density ( $\rho$ ) of the mixture using following equation<sup>17</sup>.

$$V = (x_1 M_1) + (x_2 M_2) / \rho \quad \dots (2)$$

Where  $x_1$  and  $x_2$  are the mole fractions of component 1 and 2 of binary liquid mixtures, respectively,  $V_1$  is  $M_1 / \rho_1$  and  $V_2$  is  $M_2 / \rho_2$ .  $\rho_1$  and  $\rho_2$  are densities of component 1 and 2.

The excess viscosity ( $\eta^E$ ) of the given binary liquid mixture was calculated from the observed viscosity of mixture and that of its pure components using following equation<sup>18</sup> –

$$\eta^E = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad \dots (3)$$

Where  $\eta$  is viscosity of binary mixture,  $\eta_1$  and  $\eta_2$  are the viscosities of pure component 1 and 2 respectively and  $x_1$  and  $x_2$  are the mole fraction of the component 1 and 2 respectively.

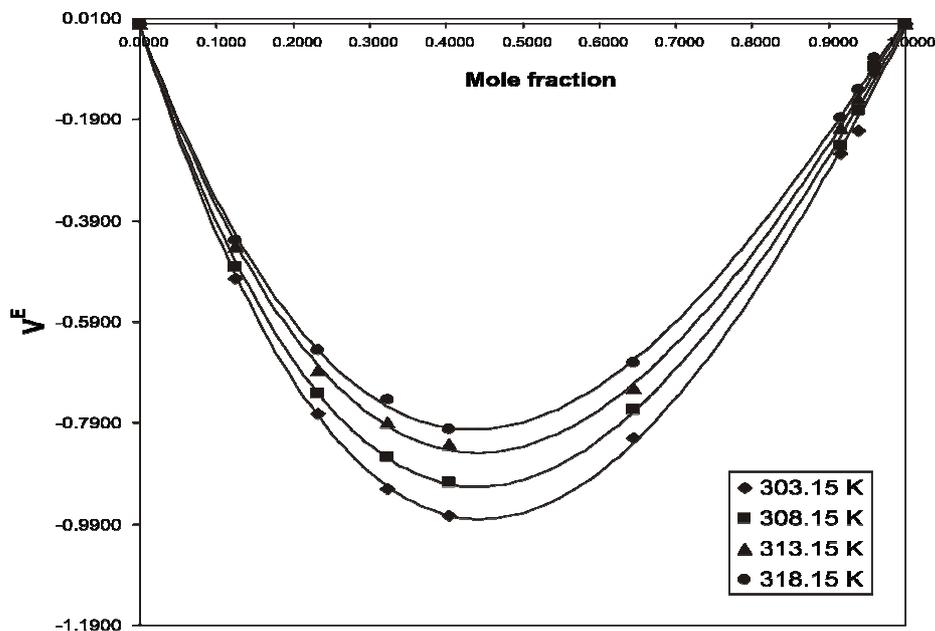
The excess Gibb's free energy of flow ( $\Delta G^E$ ) for the binary liquid mixture was computed from the Eyring equation<sup>19</sup> –

$$\Delta G^E = RT ( \ln \eta V - x_1 \ln \eta_1 V_1 - x_2 \ln \eta_2 V_2 ) \quad \dots (4)$$

Where the symbols have their usual significance.

The values of density ( $\rho$ ), viscosity ( $\eta$ ), molar volume ( $v$ ) and excess thermodynamic properties viz. excess molar volume ( $V^E$ ), excess viscosity ( $\eta^E$ ), excess Gibb's free energy of activation of flow ( $\Delta G^E$ ) at various temperatures 303.15, 308.15, 313.15 and 318.15K as a function of composition of binary mixtures have been presented in Table 2.

The data in Table 2 shows that the values of  $V^E$  of binary mixture of N, N-dimethylacetamide + methanol are negative over entire range of composition and for all experimental temperatures. The Fig. 1 exhibits the variation of  $V^E$  with mole fraction  $x_1$  of methanol at 303.15, 308.15, 313.15 and 318.15 K. Increase in temperature from 303.15 to 318.15 K results in a decrease in the  $V^E$  for N, N-dimethylacetamide + methanol.



**Fig. 1: Variation of excess molar volumes ( $V^E$ ) with mole fraction ( $x_1$ ) for methanol (1) + N, N dimethyl acetamide (2) at 303.15, 308.15, 313.15 and 318.15 K**

The negative values of  $V^E$  are due to the chemical or specific interactions, which can result in decrease in volume and these includes possible depolymerisation of self associated alcohol by the addition of N, N-dimethylacetamide or formation of new bonds (hydrogen bond) between N, N-dimethylacetamide and alcohol and other complex forming interactions, All the values of  $V^E$  are fitted to Redlich-Kister type polynomial<sup>20</sup>.

$$V^E = x_1 x_2 \sum a_i (x_1 - x_2)^i \dots \quad \dots (5)$$

The values of parameters obtained by least square method are included in Table 3.

The standard deviation ( $\sigma$ ) calculated as

$$\sigma (V^E) = [ (\sum V^E_{\text{experimental}} - V^E_{\text{calculated}}) / D - N ]^{1/2} \quad \dots (6)$$

Where D is number of experimental data points and N is number of parameters.

The values of standard deviation at different temperatures for methyl alcohol are of the order  $10^{-3}$ .

**Table 2: Densities, viscosities, excess properties and interaction parameters ( $d_{12}$ ,  $T_{12}$ ,  $H_{12}$ ) of binary liquid mixtures of methanol and N-N dimethyl acetamide at 303.15, 308.15, 313.15 and 318.15 K**

**303.15 K**

$x_1$	$\rho$ ( $\text{g cm}^{-3}$ )	$\eta$ (m Pas.)	$\eta^E$ (m Pas.)	$v^E$ ( $\text{cm}^3$ $\text{mol}^{-1}$ )	$\Delta G^E$ (J $\text{mol}^{-1}$ )	$d_{12}$	$T_{12}$	$H_{12}$
0.000	0.932	0.880	0.000	0.000	0.000	0.000	0.000	0.000
0.125	0.929	0.872	0.039	-0.505	212.960	0.546	0.008	0.869
0.232	0.924	0.856	0.063	-0.771	362.240	0.567	0.022	0.870
0.324	0.918	0.832	0.074	-0.919	449.880	0.565	0.035	0.861
0.405	0.911	0.797	0.068	-0.974	472.690	0.517	0.043	0.834
0.644	0.880	0.697	0.058	-0.819	484.520	0.538	0.045	0.819
0.915	0.816	0.567	0.029	-0.258	236.850	0.850	0.007	0.878
0.939	0.809	0.544	0.015	-0.200	147.600	0.662	0.004	0.822
0.961	0.800	0.529	0.009	-0.098	94.970	0.611	0.002	0.806
1.000	0.782	0.506	0.000	0.000	0.000	0.000	0.000	0.000

**308.15 K**

$x_1$	$\rho$ ( $\text{g cm}^{-3}$ )	$\eta$ (m Pas.)	$\eta^E$ (m Pas.)	$v^E$ ( $\text{cm}^3$ $\text{mol}^{-1}$ )	$\Delta G^E$ (J $\text{mol}^{-1}$ )	$d_{12}$	$T_{12}$	$H_{12}$
0.000	0.928	0.803	0.000	0.000	0.000	0.000	0.000	0.000
0.125	0.924	0.795	0.033	-0.481	206.590	0.512	0.007	0.790
0.232	0.919	0.784	0.057	-0.731	360.540	0.552	0.021	0.799
0.324	0.912	0.763	0.067	-0.858	447.970	0.549	0.032	0.791
0.405	0.905	0.733	0.064	-0.907	474.910	0.509	0.040	0.770



**318.15 K**

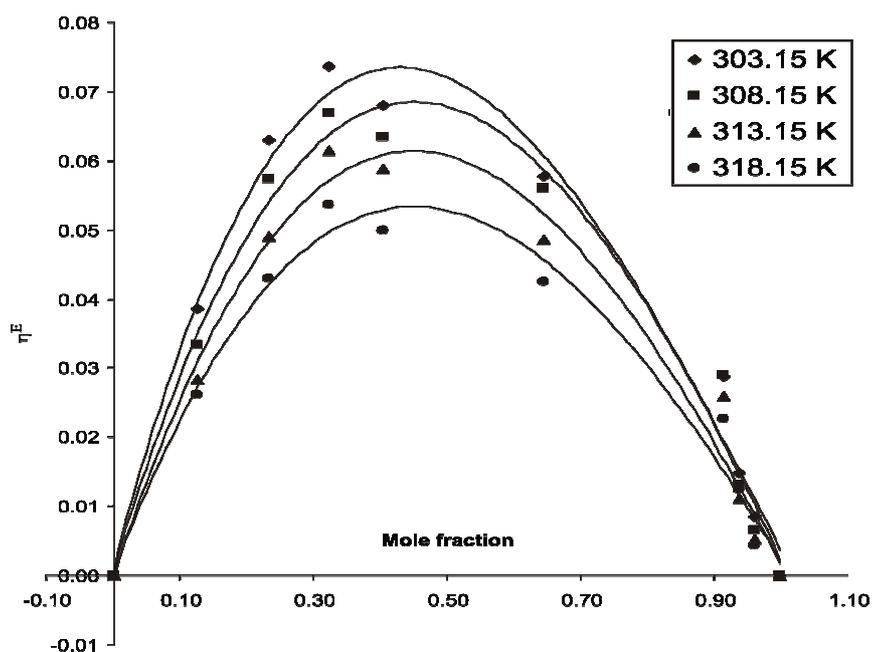
$x_1$	$\rho$ (g cm <sup>-3</sup> )	$\eta$ (m Pas.)	$\eta^E$ (m Pas.)	$v^E$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\Delta G^E$ (J mol <sup>-1</sup> )	$d_{12}$	$T_{12}$	$H_{12}$
0.000	0.919	0.708	0.000	0.000	0.000	0.000	0.000	0.000
0.125	0.915	0.693	0.026	-0.428	216.130	0.516	0.006	0.663
0.232	0.909	0.675	0.043	-0.645	370.180	0.542	0.016	0.665
0.324	0.902	0.655	0.054	-0.744	477.140	0.567	0.026	0.666
0.405	0.894	0.625	0.050	-0.803	507.110	0.529	0.032	0.648
0.644	0.862	0.539	0.043	-0.671	526.150	0.562	0.035	0.637
0.915	0.799	0.431	0.023	-0.186	266.540	0.924	0.006	0.690
0.939	0.791	0.413	0.012	-0.131	173.580	0.766	0.003	0.652
0.961	0.783	0.398	0.004	-0.068	92.710	0.531	0.001	0.603
1.000	0.769	0.380	0.000	0.000	0.000	0.000	0.000	0.000

**Table 3: Redlich-Kister coefficient of excess molar volume and standard deviation for methanol (1) + N, N-dimethyl acetamide (2) at 303.15, 308.15, 313.15 and 318.15 K**

Temperature (K)	$A_0$	$A_1$	$A_2$	$\sigma$
303.15	-5.2231	1.3512	0.2868	$2.89 \times 10^{-3}$
308.15	-5.1723	1.2912	0.2789	$1.11 \times 10^{-3}$
313.15	-4.9783	1.2852	0.2579	$6.59 \times 10^{-3}$
318.15	-4.7230	1.2732	0.2472	$1.23 \times 10^{-3}$

**Table 4: Redlich-Kister coefficient of excess molar viscosity and standard deviation for methanol (1) + N, N-dimethyl acetamide (2) at 303.15, 308.15, 313.15 and 318.15 K**

Temperature (K)	$A_0$	$A_1$	$A_2$	$\sigma$
303.15	0.7132	0.1889	-0.0142	$2.97 \times 10^{-3}$
308.15	0.6982	0.1779	-0.0572	$1.62 \times 10^{-3}$
313.15	0.6851	0.1623	-0.0912	$1.53 \times 10^{-3}$
318.15	0.6231	0.1567	-0.0483	$1.72 \times 10^{-3}$



**Fig. 2: Variation of excess viscosities ( $\eta^E$ ) with mole fraction ( $x_1$ ) for methanol (1) + N, N dimethyl acetamide (2) at 303.15, 308.15, 313.15 and 318.15 K.**

### Excess viscosity ( $\eta^E$ )

A perusal of Table 2 shows that the values of  $\eta^E$  of binary mixtures of N, N-dimethylacetamide + methanol are positive over entire range of composition and at all experimental temperatures.

The negative values of  $\eta^E$  suggest that dispersion type<sup>21</sup> of forces are predominant

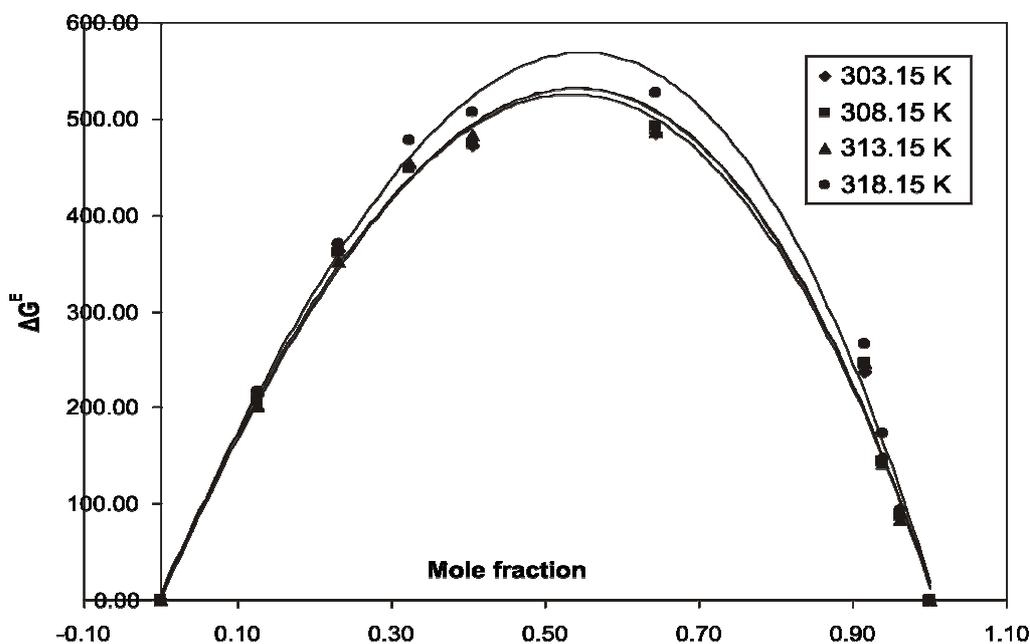
in these mixtures while positive values may be attributed to the presence of strong interactions<sup>22</sup>.

The plot of  $\eta^E$  versus  $x_1$  (mole fraction of alcohol) for the binary mixtures have been presented in the Fig. 2

### Excess Gibb's free energy activation of flow ( $\Delta G^E$ )

The values of  $\Delta G^E$  for binary mixtures N, N-dimethylacetamide and alcohol have been presented in Table 2. It is seen that the values of  $\Delta G^E$  are positive over entire range of composition for methanol.

The values of  $\Delta G^E$  for above binary mixtures have been plotted against  $x_1$  and, the plots have been represented in Fig. 3.



**Fig. 3:** Variation of excess Gibb's free energy of activation of flow ( $\Delta G^E$ ) with mole fraction ( $x_1$ ) for methanol (1) + N, N dimethyl acetamide (2) at 303.15, 308.15, 313.15 and 318.15 K.

The plots are parabolic in shape. The negative values of  $\Delta G^E$  may be attributed to the dominance of dispersion forces while positive one to the size effect of the mixing components<sup>23</sup>. According to Mayer<sup>24</sup>  $\Delta G^E$  may be considered as a reliable measure to

detect the presence of interaction between the molecule. Positive values of  $\Delta G^E$  can be seen in binary mixture where specific interactions (hydrogen bonding) between the molecules are dominant where as negative  $\Delta G^E$  indicates characteristic behavior of mixture in, which dispersion forces are dominant<sup>25</sup>.

### Viscosity models and interaction parameters

The several models (equations) have been put forth for correlating the viscosity of binary liquid mixtures with those of component liquid with a view to interpret the molecular interaction in the liquid mixture in terms of interaction parameter of the viscosity model.

- (i) Grunberg and Nissan<sup>26</sup> have suggested the following logarithmic relation between viscosity of the binary liquid mixture and pure components.

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d_{12} \quad \dots (7)$$

Where  $d_{12}$  is constant proportional to interaction energy it is approximate measure of strength of the molecular interaction between the mixing components.

- (ii) Tumara and Kurata<sup>27</sup> developed the following equation for the viscosity of binary mixture.

$$\eta = x_1 \Phi_1 \eta_1 + x_2 \Phi_2 \eta_2 + 2(x_1 x_2 \Phi_1 \Phi_2)^{0.5} T_{12} \quad \dots (8)$$

Where  $T_{12}$  is interaction parameter and depend on temperature and composition of mixture.  $\Phi_1, \Phi_2$  are the volume fraction;  $x_1, x_2$  are mole fraction  $\eta_1, \eta_2$  are viscosities of pure components 1 and 2, respectively.

- (iii) Hind and Ubbelohde<sup>28</sup> suggested the following equation for the viscosity of binary mixtures.

$$\eta = x_1^2 \eta_1 + x_2^2 \eta_2 + 2 x_1 x_2 H_{12} \quad \dots (9)$$

Where  $x_1$  and  $x_2$  are the mole fraction,  $\eta_1$  and  $\eta_2$  are the viscosities of liquid component 1 and 2, respectively.  $\eta$  is viscosity of binary mixture and  $H_{12}$  is Hind interaction parameter.

According to Fort and Moore<sup>18</sup> the value of  $d_{12}$  (vide equation-(7)) provides better measure of strength of interaction. The variation with composition is large where strong specific interaction might be expected, which vary with composition.

The negative values of  $d_{12}$  indicate the domination of dispersion forces<sup>18</sup>. On the

other hand, the positive values of  $d_{12}$  may be attributed to presence of strong interactions. A perusal of the values of  $d_{12}$  shows that these are positive for all binary mixture showing strong specific interactions.

The values of  $T_{12}$  and  $H_{12}^{2-5}$  (vide equation – 8 and – 9) for given mixture did not show very different variation expect where there is a strong interaction between the components.

A perusal of values of  $T_{12}$  and  $H_{12}$  shows that they are positive for all the binary mixtures, showing strong specific interactions.

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