THERMODYNAMIC AND TRANSPORT PROPERTIES OF BINARY LIQUID MIXTURES OF N-METHYLACETAMIDE WITH ALKYL (METHYL, ETHYL, n-PROPYL AND n-BUTYL) ACETATES AT 308.15 K

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ABSTRACT

The values of density (ρ) and viscosity (η) have been measured for the binary liquid mixtures of methyl acetate (MA), ethyl acetate (EA), n-propyl acetate (PA) and n-butyl acetate (BA) with N-methylacetamide (NMA) over the whole composition range at T = (308.15) K and atmospheric pressure. From these data, excess molar volume (V^E) and deviation in viscosity ($\Delta\eta$) are calculated. The results are fitted to a Redlich–Kister type polynomial equation to derive binary coefficients and standard deviations.
Keywords: *N-methylacetamide; alkyl esters; excess molar volume; deviation in viscosity.*

INTRODUCTION

In recent years, there has been considerable advancement in the experimental investigation of excess thermodynamic properties of liquid mixtures. These properties have been adequately employed in understanding the nature of molecular interactions in binary liquid mixtures. In the chemical industry knowledge of the thermodynamic properties of non-electrolyte solutions is essential in the design involving chemical separation, heat transfer, mass transfer and fluid flow. Furthermore, thermodynamic properties of binary mixtures containing components capable of undergoing specific interactions exhibit significant deviations from ideality arising not only from differences in molecular size and shape but also due to structural changes.

The present study is a continuation of our earlier research [1-6] on thermodynamic properties of binary liquid mixtures. The liquids were chosen in the present investigation on the basis of their industrial importance. N-methylacetamide is chosen as a solvent because of its solvent properties, have been the subject of considerable interest due to the versatility as a solvent and its close relationship peptides and proteins. Mixtures of N-methylacetamide with other solvents are also of particular interest. Esters, on the other hand, find applications such as plasticizers in polymer-processing industries in order to impart favorable thermoplastic behavior and also in the flavor and fragrance industries.

Several researchers elucidated in the literature for the density, viscosity and ultrasonic studies of binary mixtures of esters with N-methylacetamide[7-8], N,N-dimethylacetamide[9] and with N,N-dimethylformamide[10-11]. However, no effort appears to have been made to collect the molecular interactions between N-methylacetamide in terms of V^E and $\Delta\eta$. In order to characterize the type and magnitude of the molecular interactions between NMA and esters (methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate), we present here the V^E and $\Delta\eta$ of NMA with esters at 308.15 K and at atmospheric pressure. These results have been fitted to Redlich-Kister polynomial equation[12] using multiparametric non-linear regression analysis to derive the binary coefficients and to estimate the standard deviation (σ).

EXPERIMENTAL

Materials:

All the esters methyl acetate (99.5 %), ethyl acetate (99.8 %), n-propyl acetate (99.5 %) and n-butyl acetate (≥99 %) were made of Sigma-Aldrich, USA are stored over molecular sieves (0.3 nm Merck, India). The high purity grade N-methylacetamide (99.9 %) is also furnished by Sigma-Aldrich chemicals, USA and was used without further purification. Densities and viscosities of pure substances and their comparison with literature values are listed Table 1.

Apparatus and procedure:

Binary mixtures were prepared by mass in air tight bottles. The mass measurements were performed on a Dhona 100 DS, India, single pan analytical balance with a resolution of ± $0.01 \cdot 10^{-6}$ kg. The required properties of the mixture were measured on the same day. The possible error in mole fraction was estimated to be less than ± $1 \cdot 10^{-4}$.

Density of pure liquids and their mixtures were determined by using a $1 \cdot 10^{-5}$ m^3 double arm pycnometer[3]. The density values from triplicate replication at the temperature of 308.15 K were reproducible within ± $2 \cdot 10^{-2}$ $kg \cdot m^{-3}$. The uncertainty in density values was found to be ± 0.04 $kg \cdot m^{-3}$. An Ubbelohde viscometer[13] having a capacity of about $1.5 \cdot 10^{-5}$ m^3 and the capillary having a length of about $9 \cdot 10^{-2}$ m with $5 \cdot 10^{-4}$ m internal diameter has been used to measure the flow times of pure liquids and liquid mixtures. The detailed experimental procedure and the calibration of viscometer were discussed in our earlier paper[3]. Viscosity values (η) of pure liquids and mixtures were calculated using the relation:

$$\eta = (at - b / t)\, \rho \qquad (1)$$

where 'a' and 'b' are the characteristic constants of the viscometer, ρ is the density and 't' represents the flow time. The flow time of pure liquids and liquid mixtures were repeated for five times. The uncertainty of viscosity and deviation in viscosity values are ± $0.5 \cdot 10^{-5}$ $kg \cdot m^{-1} \cdot s^{-1}$ and ± $0.3 \cdot 10^{-6}$ $kg \cdot m^{-1} \cdot s^{-1}$ respectively.

In all the property measurements the temperature was controlled within ± 0.01 K using a constant temperature bath (INSREF model IRI – 016 C, India) by circulating water from the thermostat.

RESULTS AND DISCUSSION

Experimental values of densities (ρ) and viscosities (η) for the binary mixtures of N-methylacetamide with methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate at 308.15 K are listed as a function of mole fraction in Table 2.

The density values have been used to calculate excess molar volumes (V^E) using the following equation;

$$V^E/(m^3 \cdot mol^{-1}) = (x_1 M_1 + x_2 M_2) / \rho_m - (x_1 M_1 / \rho_1 + x_2 M_2 / \rho_2) \qquad (2)$$

where ρ_m is the density of the mixture; x_1, M_1, ρ_1 and x_2, M_2 and ρ_2 are the mole fraction, molecular weight and density of pure components respectively. The deviation in viscosity is calculated using the relation

$$\Delta\eta/(kg \cdot m^{-1} \cdot s^{-1}) = \eta_m - (x_1 \eta_1 + x_2 \eta_2) \qquad (3)$$

where η_m, is the viscosity of the liquid mixture; x_1, η_1 and x_2, η_2 are the mole fraction and viscosities of the pure components 1 and 2 respectively.

The excess or deviation properties Y^E were fitted by the method of non linear least squares to a Redlich-Kister type polynomial

$$Y^E = x_1 x_2 \Sigma A_i (x_1 - x_2)^i \qquad (4)$$

In each case, the optimum number of coefficients A_i was determined from an examination of the variation of standard deviation (σ) as calculated by

$$\sigma (Y^E) = [\Sigma (Y^E_{obs} - Y^E_{cal}) / (n - m)]^{1/2} \quad (5)$$

where 'n' represents the number of experimental points and 'm' is the number of coefficients. It is found that for the solution of the fifth degree polynomial, the agreement between the experimental values and the calculated ones is satisfactory. The derived parameters (A_i) and the estimated standard deviation (σ) for V^E and $\Delta\eta$ are given in Table 3.

Excess molar volumes of N-methylacetamide + esters at 308.15 K are displayed in figure 1. The values of V^E are negative for all the mixtures of N-methylacetamide +methyl acetate, +ethyl acetate, +propyl acetate and +butyl acetate over the whole mole fraction range and show a increasing tendency with increasing chain length of the ester molecules. The negative values of V^E vary in the algebraic order:

MA > EA > PA > BA

The maximum interactions are exhibited by all the esters around the mole fraction $x_1 = 0.5$. The negative excess molar volumes increase with increase in the chain length of the ester which implies that butyl acetate has maximum interaction, while methyl acetate has minimum interaction.

Esters (methyl acetate, ethyl acetate, n-propyl acetate and n-butyl acetate) are weak hydrogen accept acceptors and they are not donors due to the lack of an acidic proton. In these mixtures the observed negative values of V^E are attributed to the combined effect of specific interactions and free volume is outweighed the dispersion interactions. The graphical evidence supports the above said forces are operating between the unlike molecules of NMA and esters.

N-methylacetamide is strongly associated liquid, when it is mixed with esters it looses its aggregates contributing to the expansion of volume, hence declustering of NMA molecules. From the isothermal curves at 308.15 K shown in the figure 1, it is clear that in case of esters with NMA the volume reduction factors are preponderant.

The variation of $\Delta\eta$ with the mole fraction of N-methylacetamide (x_1) at 308.15 K is presented in figure 2, for the binary systems of (NMA + MA, + EA, + PA and + BA). Viscosity deviation is negative over the entire composition range for all the mixtures and decreases in absolute value. The dispersion and dipolar forces between NMA and esters may also give rise to negative $\Delta\eta$ values. The negative $\Delta\eta$ values at equimolar concentration on N-methylacetamide and esters vary as per the sequence:

BA > PA > MA > EA

Viscosity of these binary mixtures decrease with decrease in chain length excepting MA which is due to accommodation of MA molecules in the declustered NMA molecules because of their small size.

A correlation between the sign of $\Delta\eta$ and V^E has been observed for a number of binary solvent systems. $\Delta\eta$ being negative, whereas V^E is positive or vice versa. The observed data of V^E and $\Delta\eta$ do not obey the general rule. The trend of $\Delta\eta$ is same that of V^E excepting BA.

CONCLUSIONS

Densities, viscosities, and speed of sound for binary mixtures consisting of N-methylacetamide with methyl acetate, ethyl acetate, propyl acetate and butyl acetate have been measured at 308.15 K. The corresponding excess molar volumes, viscosity deviations and excess isentropic compressibility have been calculated and correlated using the Redlich-Kister polynomial equation. The derived values have been discussed.

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Table-1: Physical properties of the pure components at 308.15 K.

Component	$10^{-3}\cdot\rho$ (kg·m^{-3})		$10^{3}\cdot\eta$ (kg·m^{-1}·s^{-1})	
	Exptl.	Lit.	Exptl.	Lit
N-methylacetamide	0.94591	0.94604[14]	3.312	3.313[15]
Methyl acetate	0.91242	0.91522[16]	0.291	
Ethyl acetate	0.88260	0.88250[16]	0.361	0.385[17]
n-Propyl acetate	0.87305	0.8718[18]	0.460	
n-Butyl acetate	0.86711	0.8655[18]	0.569	0.594[16]

Table-2: The values of density *(ρ)*, viscosity (*η)*, excess molar volume (VE), and deviation in viscosity (*Δη*) of the binary mixtures of N-methyl -acetamide (1) + aliphatic ester (2) at T = (308.15) K

x_1	$10^{-3}\cdot\rho$ ($kg \cdot m^{-3}$)	$10^{-3}\cdot\eta$ ($kg \cdot m^{-1} \cdot s^{-1}$)	$10^{6} \cdot V^{E}$ ($m^{3} \cdot mol^{-1}$)	$10^{3} \cdot \Delta\eta$ ($kg \cdot m^{-1} \cdot s^{-1}$)
		N-methylacetamide (1) + methyl acetate (2)		
0.0000	0.9124	0.2914	0.0000	0.0000
0.0237	0.9142	0.3020	-0.0908	-0.0610
0.1524	0.9195	0.3800	-0.1944	-0.3718
0.2806	0.9244	0.5414	-0.2527	-0.5977
0.4083	0.9288	0.7841	-0.2698	-0.7408
0.5122	0.9323	1.0400	-0.2672	-0.7988
0.6165	0.9356	1.3899	-0.2470	-0.7640
0.7419	0.9394	1.9250	-0.2052	-0.6077
0.8605	0.9427	2.5201	-0.1381	-0.3708
0.9809	0.9457	3.1900	-0.0385	-0.0647
1.0000	0.9459	3.3124	0.0000	0.0000
		N-methylacetamide (1) + ethyl acetate (2)		
0.0000	0.8826	0.3612	0.0000	0.0000
0.0683	0.8875	0.4062	-0.1663	-0.1566
0.2257	0.8969	0.5635	-0.2796	-0.4638
0.3530	0.9046	0.6996	-0.3255	-0.7034
0.4615	0.9114	0.8907	-0.3489	-0.8325
0.5616	0.9179	1.1052	-0.3594	-0.9134
0.6537	0.9239	1.3653	-0.3426	-0.9251
0.7466	0.9300	1.7060	-0.3030	-0.8586
0.7892	0.9328	1.9080	-0.2761	-0.7823
0.9579	0.9439	2.9430	-0.1161	-0.2452
1.0000	0.9459	3.3124	0.0000	0.0000

N-methylacetamide (1) + n-propyl acetate (2)				
0.0000	0.8731	0.4595	0.0000	0.0000
0.0368	0.8761	0.4811	-0.1657	-0.0834
0.1965	0.8873	0.6210	-0.5066	-0.3992
0.3600	0.8991	0.8626	-0.7212	-0.6240
0.4843	0.9083	1.1100	-0.7925	-0.7310
0.5997	0.9172	1.4235	-0.8041	-0.7469
0.6863	0.9235	1.7000	-0.7188	-0.7173
0.7615	0.9286	2.0212	-0.5728	-0.6108
0.8301	0.9333	2.3820	-0.4171	-0.4457
0.9865	0.9453	3.2112	-0.0723	-0.0627
1.0000	0.9459	3.3124	0.0000	0.0000
N-methylacetamide (1) + n-butyl acetate (2)				
0.0000	0.8671	0.5687	0.0000	0.0000
0.0375	0.8705	0.6038	-0.2511	-0.0678
0.2288	0.8862	0.9300	-1.0345	-0.2665
0.3883	0.8999	1.2700	-1.4521	-0.3641
0.5321	0.9120	1.6100	-1.5570	-0.4186
0.6317	0.9205	1.8650	-1.5148	-0.4369
0.7260	0.9276	2.1401	-1.2869	-0.4205
0.8245	0.9350	2.4480	-0.9644	-0.3829
0.8647	0.9380	2.5900	-0.8071	-0.3512
0.9105	0.9409	2.8040	-0.5664	-0.2628
1.0000	0.9459	3.3124	0.0000	0.0000

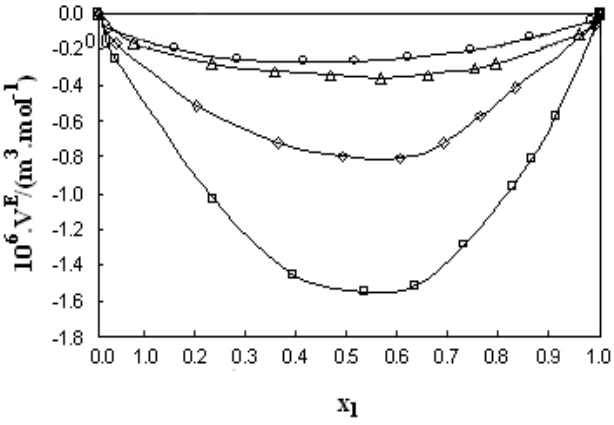

Fig.-1: Plots of excess molar volumes $V^E/(m^3 \cdot mol^{-1})$ against mole fraction (x_1) of NMA for {(x_1)NMA +(x_2) MA (○), +(x_2) EA (Δ), +(x_2) PA (◊) and +(x_2) BA (□)} at T = 308.15 K.

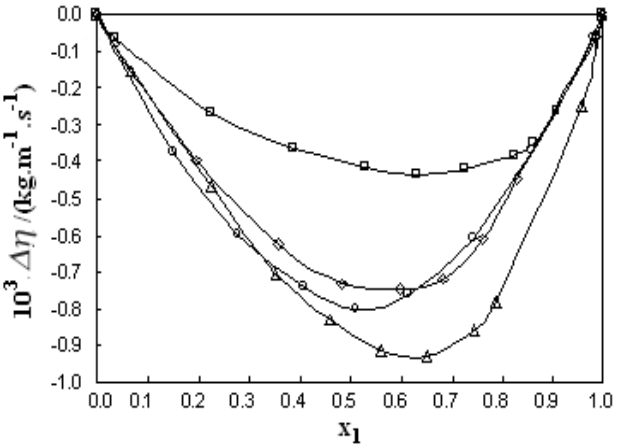

Figure 2. Plots of excess viscosity $\Delta\eta$/(kg·m^{-1}·s^{-1}) against mole fraction (x_1) of NMA for {(x_1) NMA +(x_2) MA (○), +(x_2) EA (Δ), +(x_2) PA (◊) and +(x_2) BA (□)} at T = 308.15 K.

Table –3: Binary coefficients (A_i) and Standard deviations (σ) for the binary mixtures at T/K=308.15

Binary system	Function	A_0	A_1	A_2	A_3	A_4	σ
N-methylacetamide (1) +	$V^E \cdot 10^6/(m^3 \cdot mol^{-1})$	-1.14455	-0.19794	1.17981	1.29531	-3.48382	0.14719
Methyl acetate (2)	$\Delta\eta \cdot 10^3/(kg \cdot m^{-1} \cdot s^{-1})$	-3.18107	-0.10534	0.69928	-0.31553	-0.59341	0.07953
Ethyl acetate (2)	$V^E \cdot 10^6/(m^3 \cdot mol^{-1})$	-1.44137	-0.11077	0.05729	0.17912	-2.15630	0.02819
	$\Delta\eta \cdot 10^3/(kg \cdot m^{-1} \cdot s^{-1})$	-3.51008	-1.70095	-0.28469	-0.32472	-0.74287	0.04046
Propyl acetate (2)	$V^E \cdot 10^6/(m^3 \cdot mol^{-1})$	-3.36478	-0.01046	2.43625	-0.05975	-4.74109	0.21453
	$\Delta\eta \cdot 10^3/(kg \cdot m^{-1} \cdot s^{-1})$	-3.03425	-0.52035	1.05437	-0.64482	-1.69644	0.19592
Butyl acetate (2)	$V^E \cdot 10^6/(m^3 \cdot mol^{-1})$	-6.26959	-0.86394	0.70341	0.76270	-2.02153	0.08570
	$\Delta\eta \cdot 10^3/(kg \cdot m^{-1} \cdot s^{-1})$	-1.62513	-0.64591	-0.91020	-0.44283	-0.57363	0.05793

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