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Partial Molar Volumes At Infinite Dilution For The Binary Liquid Mixtures of N-Methyl-2-Pyrrolidone - A Green Solvent With Methyl Acetate or Ethyl Acetate or Butyl Acetate

D. Bala Karuna Kumar[1*], G. R. Satyanarayana[2], R.Venumadav[3] And Rambabu.C[4]

[1]*Department of Chemistry, Andhra Loyola College, Vijayawada, Andhra Pradesh, India-520 008*
[2]*Department of PG Chemistry, Sir C.R Reddy College, Eluru, Andhra Pradesh, India-534007*
[3]*Department of Botany, SS&N College, Narasaraopet, Guntur, Andhra Pradesh, India*
[4]*Department of Chemistry, Acharya Nagarjuna University, Nagarjuna Nagar, Andhra Pradesh, India*

Abstract: *The densities for pure liquids N-methyl-2-pyrrolidone (NMP – a green solvent), methyl acetate (MA), ethyl acetate (EA), butyl acetate (BA) and their binary mixtures containing NMP as a common component have been measured at atmospheric pressure as a function of composition of NMP in the temperature range 303.15 - 318.15 K with an interval of 5K. From these experimental values partial molar volumes and excess partial molar volumes are computed. The values of excess partial molar volumes are found to be negative. The partial molar volumes at infinite solution are determined to highlight the solute-solvent interactions among the molecules in the studied mixtures. The strength of interaction of MA, EA, BA with NMP was found to decrease with the increase in the alkyl chain length of the ester.*

Key Words*: Fluid mixture; molecular interactions; partial molar volumes; density;*

I. Introduction

The temperature variation of physicochemical and acoustic properties of liquid-liquid mixtures has attracted much attention from both the theoretical and engineering application points of view. The data on some of the properties associated with liquids and liquid mixtures, like viscosity, density and excess volume find extensive application in chemical engineering design, process simulation, solution theory and molecular dynamics. These properties are important from practical and theoretical point of view to understand liquid theory and provide information about molecular interactions [1-4]. N-methyl-2-pyrrolidone (NMP) is a water-miscible organic fluid which is hygroscopic colorless and strongly polar. NMP is used as a solvent to improve surface coating and in the cleaning and degreasing of single-crystal silicon wafers. In the plastics industry, it is used to dissolve many polymers. It is also used in the manufacture of various compounds, including cosmetics, pigments, insecticides, herbicides, pigments, and fungicides.

The present work is focused to explore the solute solvent interactions by the study of partial molar volumes in the binary mixtures of NMP with some alkyl acetates (methyl acetate, ethyl acetate, butyl acetate) over the complete composition range of NMP at temperatures of 303.15, 308.15, 313.15 and 318.15 K and atmospheric pressure at infinite dilution.

II. Experimental Section

The pure solvents, of highest purity commercially available were used in the present investigation. NMP (Merck >99%) was distilled at low pressure and stored over freshly activated 3A molecular sieves. methyl acetate (MA), ethyl acetate (EA) of AR grade procured from S.D fine chemicals (India) and butyl acetate (BA) procured from Loba Chemicals were purified by using fractionating column [5] and the middle fractions were used for the experimental study. The purity of the chemicals was assessed by comparing their measured densities (ρ) and ultrasonic velocities (U) which were in good agreement with literature [6-9] values as can be seen in Table 1.

The mixtures were prepared gravimetrically using an electronic balance (Shimadzu AY120) with an uncertainty of $\pm$ 1x 10^{-7} kg and were stored in air-tight glass bottles. The uncertainty in mole fraction was estimated to be less than 1x 10^{-4}. It was ensured that the components were adequately mixed before being transferred in to the apparatus. The required properties were measured within one day of the mixture preparation.

The densities, ρ, of pure liquids and their mixtures were determined using a 10^{-5} m^3 double-arm pycnometer as described by Nikam et al [10]. The density values from triplicate replication at each temperature were reproducible within (4 x 10^{-2} kg·m^{-3}).

The ultrasonic velocity of pure components was measured by single crystal variable path fixed frequency interferometer provided by Mittal Enterprises, New Delhi (Model-F 05). The measurements of ultrasonic velocity were taken at a fixed frequency of 2 MHz. The calibration of ultrasonic interferometer was done by measuring the velocity in AR grade benzene and carbon tetrachloride. Standard value of '*U*' for benzene and carbon tetrachloride were calculated from the literature value[38] of '*U*' at 298 K and velocity gradient with respect to temperature i.e., the rate of change of velocity with temperature. Our measured values of '*U'* agree closely with the literature values. The measured speeds of sound were found to be accurate up to 0.1 $m \cdot s^{-1}$. Temperature control for the measurement of viscosity, density and ultrasonic sound speed was achieved by using a microprocessor assisted circulating water bath, (supplied by Mac, New Delhi) regulated to ±0.01 K, using a proportional temperature controller.

Table 1
Comparison of experimental values of density, ρ, ultrasonic speed, U, and of pure liquids with the corresponding literature values at 303.15 K

	$10^{-3} \times \rho$ (kg · m^{-3})			U (m · s^{-1})	
Liquid	Expt	Lit.		Expt	Lit.
N-methyl-2-pyrrolidone	1.0238	1.02376 [6]		1552.8	1552 [7]
Methyl Acetate	0.9205	0.92013 [8]		1132.3	1133 [8]
Ethyl Acetate	0.8884	0.88842 [8]		1117.2	1118.5 [9]
		0.8889 [9]			
Butyl Acetate	0.8715	0.8719 [8]		1165.1	1163.6 [8]

III. Theoretical Considerations

Assuming that ultrasonic absorption is negligible, using the measured data, the thermodynamic parameters such as molar volume (V_m) and partial, excess partial molar volumes are calculated using standard expressions [2],

The molar volumes (V_m) of the binary mixtures are calculated using the equation

$$V_m = \left[\frac{x_1 M_1 + x_2 M_2}{\rho} \right] \qquad \text{…….. (1)}$$

where M_1, M_2 are the molecular masses and x_1, x_2 are the mole fractions of liquid 1 and liquid 2 respectively.
The partial molar volumes of components 1 (NMP) and 2 (alkylamine PA or BA or DPA), respectively, inside the binary liquid mixtures are calculated from their molar volumes, using the relations given below [3]

$$\overline{V}_{m,1} = V_m^E + V_1^0 + (1 - x_1)\left(\frac{\partial V_m^E}{\partial x_1} \right)_{T,P} \qquad \text{…….. (2)}$$

$$\overline{V}_{m,2} = V_m^E + V_2^0 - x_1\left(\frac{\partial V_m^E}{\partial x_1} \right)_{T,P} \qquad \text{…….. (3)}$$

where V_1^0 and V_2^0 are the molar volumes of the pure NMP and alkyl amine (PA or BA or DPA) respectively. This method leads to the partial molar volumes as conveyed by the relationships given below**:**

$$\overline{V}_{m,1} = V_1^0 + x_2^2 \sum_{i=0}^{n} A_i (1 - 2x_2)^i - 2x_2^2 (1 - x_2) \sum_{i=1}^{n} iA_i (1 - 2x_2)^{i-1} \qquad \text{…….. (4)}$$

$$\overline{V}_{m,2} = V_2^0 + (1 - x_2)^2 \sum_{i=0}^{n} A_i (1 - 2x_2)^i + 2x_2 (1 - x_2)^2 \sum_{i=1}^{n} iA_i (1 - 2x_2)^{i-1} \qquad \text{… (5)}$$

The excess partial molar volumes are calculated using the partial molar volumes with the help of the following equations

$$\overline{V}_{m,1}^E = \overline{V}_{m,1} - V_1^* \qquad \text{…… (6)}$$

$$\overline{V}_{m,2}^E = \overline{V}_{m,2} - V_2^* \qquad \text{….. (7)}$$

IV. Results And Discussion

The values of partial molar volumes $\overline{V}_{m,1}$ and $\overline{V}_{m,2}$ are placed in Table 2. From Table 2 it is evident that for both the components in the mixture the values of $\overline{V}_{m,1}$ and $\overline{V}_{m,2}$ are smaller than their respective molar volumes in the pure state, i.e, a reduction in volume is found to occur on mixing NMP with alkyl amines under study.

Table 2

Partial molar volumes ($\overline{V}_{m,i}$) for the binary mixtures of NMP and alkyl esters (MA or EA or BA) at temperatures of 303.15, 308.15, 313.15 and 318.15 K

x_1	$10^6 x\overline{V}_{m,1}$ /m^3·mol^{-1}				$10^6 x\overline{V}_{m,2}$ /m^3·mol^{-1}			
	303.15K	308.15K	313.15K	18.15K	303.15K	308.15K	313.15K	318.15K
N-methyl-2-pyrrolidone(1) + methyl acetate(2)								
0.0000	94.935	95.652	96.053	95.663	80.478	81.157	81.532	82.311
0.0845	95.925	96.044	96.051	96.100	80.445	81.144	81.531	82.292
0.1720	96.018	96.104	96.199	96.481	80.435	81.136	81.508	82.236
0.2626	95.916	96.148	96.438	96.823	80.463	81.123	81.440	82.141
0.3565	95.951	96.304	96.720	97.136	80.444	81.051	81.313	82.001
0.4539	96.172	96.560	97.006	97.426	80.290	80.874	81.118	81.803
0.5549	96.463	96.830	97.262	97.687	79.992	80.599	80.857	81.538
0.6598	96.681	97.028	97.466	97.902	79.659	80.297	80.544	81.205
0.7688	96.765	97.123	97.597	98.050	79.459	80.065	80.219	80.839
0.8821	96.787	97.163	97.651	98.115	79.349	79.870	79.973	80.545
1.0000	96.826	97.196	97.655	98.119	78.457	79.187	79.983	80.566
N-methyl-2-pyrrolidone(1) + ethyl acetate(2)								
0.0000	93.472	96.061	96.322	95.977	99.167	99.819	100.617	101.323
0.1022	93.945	96.093	96.269	96.610	99.140	99.816	100.614	101.290
0.2038	94.485	96.256	96.576	97.074	99.041	99.785	100.556	101.207
0.3050	95.004	96.491	96.920	97.397	98.864	99.704	100.439	101.098
0.4057	95.466	96.730	97.185	97.621	98.609	99.572	100.294	100.975
0.5060	95.860	96.925	97.362	97.787	98.279	99.409	100.147	100.837
0.6057	96.188	97.053	97.481	97.918	97.868	99.250	99.998	100.673
0.7050	96.453	97.122	97.569	98.021	97.362	99.122	99.832	100.477
0.8038	96.654	97.155	97.629	98.090	96.744	99.021	99.646	100.268
0.9021	96.781	97.180	97.656	98.118	96.000	98.872	99.500	100.110
1.0000	96.826	97.196	97.655	98.119	95.129	98.495	99.583	100.148
N-methyl-2-pyrrolidone(1) + butyl acetate(2)								
0.0000	96.077	96.286	96.495	96.572	133.287	134.072	134.819	135.780
0.1327	96.107	96.486	96.908	97.331	133.117	133.828	134.498	135.406
0.2560	96.499	96.849	97.291	97.744	132.917	133.591	134.247	135.157
0.3711	96.740	97.072	97.504	97.949	132.749	133.448	134.098	135.020
0.4785	96.816	97.157	97.589	98.042	132.544	133.264	133.867	134.758
0.5792	96.819	97.171	97.616	98.082	132.279	132.978	133.554	134.411
0.6737	96.814	97.169	97.627	98.101	131.989	132.624	133.274	134.152
0.7626	96.820	97.172	97.639	98.111	131.738	132.286	133.095	134.052
0.8463	96.830	97.183	97.650	98.117	131.576	132.041	132.928	133.922
0.9253	96.831	97.193	97.655	98.119	131.523	131.926	132.471	133.245
1.0000	96.826	97.196	97.655	98.119	131.556	131.918	134.819	131.178

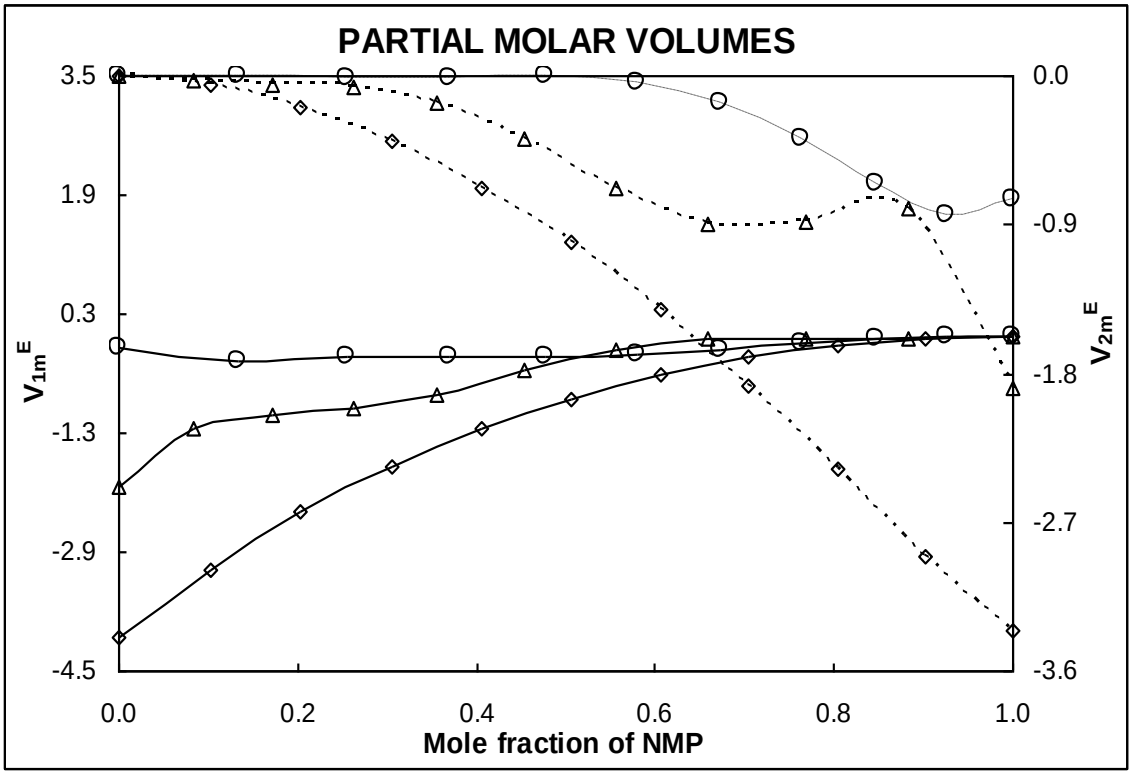
Table 3

Excess partial molar volumes ($\overline{V}^{E}_{m,i}$) for the binary mixtures of NMP and alkyl esters (MA or EA or BA) at temperatures of 303.15, 308.15, 313.15 and 318.15 K

x_1	$10^6 x\overline{V}^{E}_{m,1}$ /m^3·mol^{-1}				$10^6 x\overline{V}^{E}_{m,2}$ /m^3·mol^{-1}			
	303.15K	308.15K	313.15K	18.15K	303.15K	308.15K	313.15K	318.15K
N-methyl-2-pyrrolidone(1) + methyl acetate(2)								
0.0000	-1.891	-1.544	-1.602	-2.456	0.000	0.000	0.000	0.000
0.0845	-0.901	-1.152	-1.604	-2.019	-0.033	-0.013	-0.001	-0.019
0.1720	-0.808	-1.092	-1.456	-1.638	-0.043	-0.021	-0.024	-0.075
0.2626	-0.910	-1.048	-1.217	-1.296	-0.015	-0.034	-0.092	-0.170
0.3565	-0.875	-0.892	-0.935	-0.983	-0.034	-0.106	-0.219	-0.310

0.4539	-0.654	-0.636	-0.649	-0.693	-0.188	-0.283	-0.414	-0.508
0.5549	-0.363	-0.366	-0.393	-0.432	-0.486	-0.558	-0.675	-0.773
0.6598	-0.145	-0.168	-0.189	-0.217	-0.819	-0.860	-0.988	-1.106
0.7688	-0.061	-0.073	-0.058	-0.069	-1.019	-1.092	-1.313	-1.472
0.8821	-0.039	-0.033	-0.004	-0.004	-1.129	-1.287	-1.559	-1.766
1.0000	0.000	0.000	0.000	0.000	-2.021	-1.971	-1.549	-1.745
N-methyl-2-pyrrolidone(1) + ethyl acetate(2)								
0.0000	-3.355	-1.135	-1.333	-2.142	0.000	0.000	0.000	0.000
0.1022	-2.881	-1.103	-1.386	-1.509	-0.027	-0.003	-0.003	-0.033
0.2038	-2.341	-0.940	-1.079	-1.045	-0.126	-0.034	-0.061	-0.116
0.3050	-1.822	-0.705	-0.735	-0.722	-0.303	-0.115	-0.178	-0.225
0.4057	-1.360	-0.466	-0.470	-0.498	-0.558	-0.247	-0.323	-0.348
0.5060	-0.966	-0.271	-0.293	-0.332	-0.888	-0.410	-0.470	-0.486
0.6057	-0.638	-0.143	-0.174	-0.201	-1.299	-0.569	-0.619	-0.650
0.7050	-0.373	-0.074	-0.086	-0.098	-1.805	-0.697	-0.785	-0.846
0.8038	-0.172	-0.041	-0.026	-0.029	-2.423	-0.798	-0.971	-1.055
0.9021	-0.045	-0.016	0.001	-0.001	-3.167	-0.947	-1.117	-1.213
1.0000	0.000	0.000	0.000	0.000	-4.038	-1.324	-1.034	-1.175
N-methyl-2-pyrrolidone(1) + butyl acetate(2)								
0.0000	-0.749	-0.910	-1.160	-1.547	0.000	0.000	0.000	0.000
0.1327	-0.719	-0.710	-0.747	-0.788	-0.014	-0.021	-0.033	-0.051
0.2560	-0.327	-0.347	-0.364	-0.375	-0.109	-0.109	-0.124	-0.147
0.3711	-0.086	-0.124	-0.151	-0.170	-0.217	-0.209	-0.219	-0.239
0.4785	-0.010	-0.039	-0.066	-0.077	-0.270	-0.269	-0.280	-0.306
0.5792	-0.007	-0.025	-0.039	-0.037	-0.273	-0.284	-0.309	-0.351
0.6737	-0.012	-0.027	-0.028	-0.018	-0.264	-0.279	-0.328	-0.382
0.7626	-0.006	-0.024	-0.016	-0.008	-0.282	-0.290	-0.360	-0.408
0.8463	0.004	-0.013	-0.005	-0.002	-0.321	-0.336	-0.406	-0.431
0.9253	0.005	-0.003	0.000	0.000	-0.322	-0.413	-0.442	-0.447
1.0000	0.000	0.000	0.000	0.000	-0.158	-0.484	-0.417	-0.443

The values of excess partial molar volumes are provided in Table 3. From table 3 it is evident that excess partial molar volumes are negative indicating inter molecular interactions in the binary mixtures under study. The computed results for excess partial molar volumes ($\overline{V}^{E}_{m,i}$) of alkyl esters, Ma or EA or BA ($\overline{V}^{E}_{m,2}$) in their binary mixtures with NMP ($\overline{V}^{E}_{m,1}$) at 303.15 K are shown in Fig. 1.



From Fig. 1 it is clear that the calculated results for excess partial molar volumes ($\overline{V}_{m,2}^{E}$) of alkyl acetates, MA (Δ) or EA (□) or BA (o) and in their binary mixtures with NMP ($\overline{V}_{m,1}^{E}$) at 303.15 K are negative. Examination of figure 1 indicates that contraction in partial molar volume takes place either NMP is mixed with the three alkyl acetates (solid line) or vice versa (dotted line) confirming the strong interactions between the unlike molecules which support the dipole-dipole type of interaction between ester and NMP as reported by us previously [2]. The $\overline{V}_{m,i}^{E}$ values at other higher temperatures follow the same trends but show different values, and hence the data is not graphically displayed to minimize the number of plots.

V. Conclusions

Partial molar volumes and excess partial molar volumes are computed for the binary mixtures of N-methyl-2-pyrrolidone (NMP) or methyl acetate (MA), ethyl acetate (EA), butyl acetate (BA) in the temperature range 303.15 - 318.15 K with an interval of 5K. The computed values of $\overline{V}_{m,i}^{E}$ are found to be negative for all the three binary mixtures over the entire range of composition in the temperature range 303.15 to 318.15 K. The negative values of partial molar volumes of the systems in the present investigation indicate the contraction in volume of the other component, by the addition of NMP, suggesting the stronger intermolecular interactions. A comparison of data at different temperatures shows that the temperature coefficient is decreasing for all mixtures with increasing temperature. The interaction of NMP with the alkyl esters under study decreases with the increase in alkyl chain length and follows the order: ***NMP + MA > NMP +EA > NMP + BA***

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