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Study of Volumetric Properties of N,N-Dimethyl Acetamide and 1-Alkanols Binary Mixtures at 298.15 K

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In this study, the densities, excess molar volumes and partial molar volumes of four binary systems containing N,N-dimethyl acetamide (DMAc) with 1-alkanols (1-butanol up to 1-heptanol) are measured at 298.15 K. The results showed both constructive and expansive excess volumetric behavior for studying binary mixtures. Deviation values of heavy alcohol have more positive and less negative excess properties. The excess molar volumes of binary systems consisting of DMAc and 1-alkanols are fitted by the fifth degree of Redlich-Kister equation, and resulting coefficients have been calculated.

Keywords: Binary mixture, N,N-Dimethylacetamide, 1-Alkanol

INTRODUCTION

The study of deviation from ideal properties is a common method to investigate the nature and properties of materials [1]. This method also provides thermodynamically essential and helpful information to explain the behavior of materials. Todays, with industrial development and needs to optimize, reduce costs and increase productivity, predicting the materials thermodynamic behavior that are used in industry is more important than ever before. Excess functions are analyzed due to their importance in inferring the dominant interaction liquid. Alkanols serves as a simple example of biologically and industrially important amphiphilic materials. In terms of practical importance of these liquids, accurate and extensive data on their physical-chemical properties are often required for industrial applications [2].

Our exhaustive literature survey [3-17] has revealed that molecular interactions among alcohols and important industrial solvent like N,N-dimethylacetamide have not been much explored over the entire composition range and temperature.

In present study, volumetric properties of DMAc with 1-alkanols have been studied over the entire composition range, at 298.15 K. The results reveal the nature and extent of interactions between the molecular components in their binary 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 responsible for these interactions [2]. We also report densities (ρ), excess molar volumes (V_m^E) and partial molar volumes ($\overline{V}$) of binary mixtures formed by DMAc with 1-butanol, 1-pentanol, 1-hexanol and 1-heptanol covering the entire composition range (expressed by mole fraction x_1 of DMAc) at 298.15 K. From experimental values of densities, excess molar volumes and partial molar volumes of above-mentioned binary mixtures are calculated. These functions offer a convenient approach to study the thermodynamic properties of the liquid mixtures.

EXPERIMENTAL

1-Butanol, 1-pentanol, 1-hexanol, 1-heptanol and DMAc are purchased from Merck with a molar percentage purity of higher than 99. Materials were used without further

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purification. The purity of substances was checked by comparing their density with literature data [18-21] in Table 1.

Density was measured by Anton-Paar Stabinger (SVM) Model 3000 density-viscosity meter automatically. This device has this ability to measure dynamic viscosity and density in two separate cells simultaneously. Both cells filled up with 2.5 ml of the sample. Temperature accuracy of 0.02 Kelvin in the temperature range of 288.15-378.15 K is reported by the manufacturer. Density accuracy of 0.0005 g cm^{-3} in the density range of 0.65-1.5 g cm^{-3} is reported by the manufacturer too. Measuring density is based on fluctuations in a U-tube. This method is based on the natural frequency of the U-tube when the liquid and gas are various. The oscillator is excited by an electromagnetic force on a regular basis. The oscillating frequency of the vibrating tube is placed just under the influence of fluid. Measuring the viscosity of the system is based on the speed and torque. The torque of the induced current is measured with a resolution of 50 pN m. The cell for the measurement is very small and contains one tube rotating at constant speed. In the measurement, the rotor with the magnet is floating on the sample. The rotor floats freely with no need of bearing. The absence of bearing means that there is no friction.

RESULTS AND DISCUSSION

Atmospheric densities of binary mixtures including DMAc with 1-Alkanols have been measured over various mole fractions and temperature 298 K. The corresponding results are reported in Tables 2. The density of these mixtures has been reported in the literature. Some reports about density and viscosity are found in the mixtures DMAc with 1-butanol and 1-pentanol [4-6].

The density values have been used to calculate excess molar volumes based on the following equation:

$$V_m^E = x_1 M_1 \left(\frac{1}{\rho} - \frac{1}{\rho_1}\right) + x_2 M_2 \left(\frac{1}{\rho} - \frac{1}{\rho_2}\right) \tag{1}$$

where M_1 and M_2 are the molar masses, ρ_1 and ρ_2 are the densities of components 1 and 2, respectively, and ρ is the density of the mixture. Also, the excess molar volumes are shown in Tables 2 (±0.003 cm^3 mol^{-1}). The excess molar volumes for mixtures of DMAc and 1-alkanols are shown in Fig. 1 in temperature 298.15 K.

The dependency of excess molar volume (V_E) on composition is also expressed using a Redlich-Kister equation [22]:

$$Y^E = x_1 (1 - x_1) \sum_{i=0}^{n} A_i (1 - 2x_1)^i \tag{2}$$

where Y^E is either V^E, n is the number of estimated parameters and A_i data are the coefficients of the Redlich-Kister polynomial. These coefficients are obtained using a least square technique from Mathematica®. For whole data,

Table 1. Experimental Densities of Pure 1-Alkanols Compared with Literature Values

Compound	ρ (g cm^{-3})	
	Exp.	Lit.
1-Butanol	0.8055	-
1-Pentanol	0.8108	0.81079[18]
		0.8116[19]
		0.81096[20]
1-Hexanol	0.8151	0.81526[18]
		0.81499[21]
1-Heptanol	0.8187	0.8187[18]
		0.818732[21]

Table 2. Density, Excess Molar Volumes and Partial Molar Volumes for the Binary Mixture of N,N-Dimethylacetamide (1) + 1-Butanol, 1-Pentanol, 1-Hexanol and 1-Heptanol (2) in Temperature 298.15K

x_1	$\rho(g.cm^3)$	$V_m^E(cm^3.mol^{-1})$	$\overline{V_1}(cm^3.mol^{-1})$	$\overline{V_2}(cm^3.mol^{-1})$
		DMAc+1-butanol		
0.000	0.8055	0.000	-	-
0.081	0.8172	-0.113	155.221	91.995
0.159	0.8280	-0.171	155.285	91.983
0.238	0.8385	-0.178	155.334	91.966
0.349	0.8528	-0.136	155.917	91.917
0.436	0.8637	-0.077	155.458	91.885
0.559	0.8789	0.024	155.505	91.829
0.649	0.8901	0.077	155.513	91.812
0.741	0.9016	0.110	155.529	91.764
0.850	0.9159	0.109	155.546	91.682
0.939	0.9279	0.058	155.561	91.535
1.000	0.9364	0.000	-	-
		DMAc+1-pentanol		
0.000	0.8108	0.000	-	-
0.081	0.8203	-0.0849	155.783	108.672
0.160	0.8293	-0.1226	155.766	108.677
0.239	0.8383	-0.1139	155.745	108.689
0.349	0.8507	-0.0436	155.705	108.705
0.439	0.8609	0.0325	155.659	108.734
0.560	0.8751	0.1412	155.627	108.764
0.650	0.8860	0.2121	155.602	108.801
0.739	0.8975	0.2407	155.587	108.833
0.849	0.9129	0.2011	155.569	108.904
0.938	0.9265	0.1066	155.562	108.962
1.000	0.9364	0.000	-	-
		DMAc+1-hexanol		
0.000	0.8151	0.000	-	-
0.082	0.8231	-0.058	155.894	125.343
0.157	0.8303	-0.054	155.903	125.366
0.244	0.8385	0.001	155.907	125.389

Table 2. Continued

0.351	0.8489	0.117	155.866	125.404
0.439	0.8580	0.218	155.799	125.418
0.558	0.8713	0.331	155.676	125.473
0.650	0.8823	0.370	155.615	125.543
0.740	0.8942	0.366	155.577	125.619
0.849	0.9104	0.279	155.565	125.684
0.940	0.9253	0.139	15.562	125.759
1.000	0.9364	0.000	-	-
		DMAc+1-heptanol		
0.000	0.8187	0.000	-	-
0.081	0.8254	-0.034	156.192	139. 996
0.159	0.8318	0.001	156.086	140.614
0.238	0.8383	0.079	156.004	140.673
0.349	0.8493	0.219	155.898	140.751
0.436	0.8584	0.347	155.821	140.789
0.559	0.8687	0.474	155.744	140.855
0.649	0.8793	0.517	155.649	140.925
0.741	0.8911	0.497	155.599	141.071
0.850	0.9080	0.378	155.587	141.165
0.939	0.9241	0.188	155.563	141.431
1.000	0.9364	0.000	-	-

Table 3. Standard Deviation and Coefficients of Redlich Kister Equation for the Density of Binary Mixture of N,N-Dimethylacetamide (1) + 1-Alkanols (2) in Temperature 298.15 K

System	A_0	A_1	A_2	A_3	A_4	A_5	σ
DMAc+1-Butanol	-0.101	-1.584	-0.303	0.130	0.103	0.025	0.0028
DMAc+1-Pentanol	0.360	-1.877	-0.041	0.029	-0.029	0.205	0.0043
DMAc+1-Hexanol	1.125	-1.888	-0.618	0.171	0.220	-0.363	0.0018
DMAc+1-Heptanol	1.672	-2.189	-0.569	0.223	0.210	-0.298	0.0019

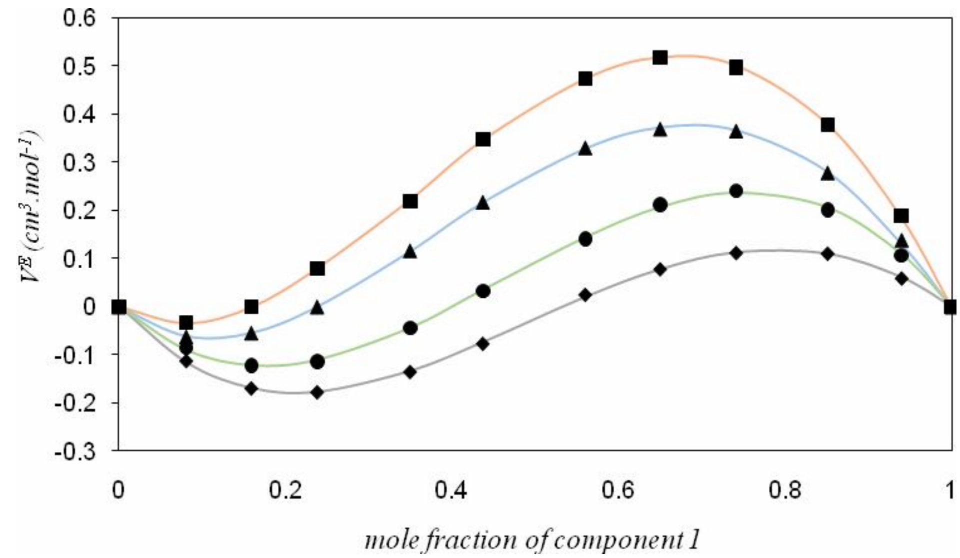

Fig. 1. Experimental and calculated excess molar volume for the binary mixture of N,N-dimethyl acetamide (1) + 1-alkanols (2) at 298.15 K. (♦) experimental of 1-butanol, (●) experimental of 1-pentanol, (▲) experimental of 1-hexanol, (■) experimental of 1-heptanol, (–) calculated by Redlich-Kister.

five A_i coefficients are needed. the coefficient values are shown in Table 3 for all the mixtures.

The partial molar volumes $\overline{V_1}$ and $\overline{V_2}$ in these mixtures were evaluated over the entire composition range by way of Eqs. (3) and (4): [24,25]

$$\overline{V_1} = V^E + V_1^* + (1-x_1)(\partial V^E/\partial x_1)_{p,T} \tag{3}$$

$$\overline{V_2} = V^E + V_2^* + (1-x_2)(\partial V^E/\partial x_2)_{p,T} \tag{4}$$

where V_1^* and V_2^* represent the molar volume of the pure components.

The deviations in Eqs. (3) and (4) were obtained by differentiation of V^E from Eq. (3). It leads to Eqs. (5) and (6) for the partial molar volumes of the DMAc (1) (V_1) and 1-alkanols (2) (V_2):

$$\overline{V_1} = V_1^* + (1-x_1)^2\sum_{j=1}^{n} a_j(2x_1-1)^{j-1} + (1-x_1)^2 \times x_1\sum_{j=1}^{n} 2(j-1)a_j(2x_1-1)^{j-2} \tag{5}$$

$$\overline{V_2} = V_2^* + (1-x_2)^2\sum_{j=1}^{n} a_j(1-2x_2)^{j-1} + x_2(1-x_2)^2 \times \sum_{j=1}^{n}(-2)(j-1)a_j(1-2x_2)^{j-2} \tag{6}$$

The partial molar volumes of all binary systems are reported in Table 2.

The standard deviation is calculated by:

$$\sigma = \left[\frac{\left(Y_{\exp}^E - Y_{cal}^E\right)^2}{N-n}\right]^{1/2} \tag{7}$$

And the standard deviation values are shown in Table 3. In Eq. (7), σ is the standard deviation, N is the number of experimental data, and n is the degree of the adjusting polynomial. $Y_{\exp}^E$ and Y_{cal}^E are the values of the experimentally measured property and the corresponding value calculated from Eq. (2), respectively.

Among the studied systems, V_m^E values of DMAc with 1-alkanols are initially negative and then positive. This behavior can be ascribed to the chain length of alcohols and the balance between the various effects in these mixtures [23].

CONCLUSIONS

This work aimed to measure the atmospheric densities of binary mixtures including DMAc with 1-Alkanols over various mole fractions and temperature 298K; furthermore, the excess volumetric and partial volumetric behavior of those mixtures was studied. Excess molar volumes and partial molar volumes were calculated from experimental data. Excess molar volumes, V_m^E is negative and then positive for mixtures of DMAc with 1-alkanols.

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