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Effect of various substituents on benzene ring and their impact on volumetric, acoustic and transport properties of binary liquid mixtures with dimethylacetamide

V. Syamala [a], L. Venkatramana [b], C. Narasimha Rao [c], K. Sivakumar [d], P. Venkateswarlu [c], R.L. Gardas [e,*]

[a] Department of Chemistry, Bapatla Engineering College, Bapatla 522101, India
[b] Department of Chemistry, P.V.K.N. Govt. College, Chittoor 517501, India
[c] Department of Chemistry, Sri Venkateswara University, Tirupati 517502, India
[d] Department of Chemistry, SV Arts UG & PG College (TTD'S), Tirupati 517502, India
[e] Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India

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ABSTRACT

Excess volume (V^E), excess isentropic compressibility (κ_S^E) and deviation in viscosity ($\Delta\eta$) were studied for eight binary systems of dimethylacetamide (DMA) with 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,2,4-trichlorobenzene, *o*-chlorotoluene, *m*-chlorotoluene, *p*-chlorotoluene, *o*-nitrotoluene and *m*-nitrotoluene in the entire composition range at 303.15 K and atmospheric pressure. Excess volume data for the studied mixtures were measured directly using a single composition loading type dilatometer and compared with predictive expressions proposed by Redlich–Kister and Hwang. Moreover, the V^E data in the present investigation were analyzed by using Prigogine–Flory–Patterson (PFP) theory. The speed of sound data was measured with a single crystal interferometer at a frequency of 3 MHz and data were analyzed in terms of free length theory (FLT) and collision factor theory (CFT). Experimental viscosity data were measured by a suspended Ubbelohode-type viscometer, which in turn used to calculate deviation in viscosity and interaction parameters for various models such as Gruenberg–Nissan, Tamura and Kurata and Hind et al. The experimental data were discussed on the basis of intermolecular interactions between unlike molecules.

1. Introduction

The study of behavior of industrially important chemicals and their mixtures has considerable importance in recent years. Selection of systems for thermodynamic investigation should be based not only on the molecular structure of the industrial components but also on their industrial and ecological importance. A vast knowledge of thermodynamic properties of binary liquid mixtures is essential in many industrial applications such as design calculation, heat transfer, mass transfer, fluid flow etc. [1]. Systematic study on phase equilibrium behavior, excess thermodynamic and transport properties of liquid mixtures are providing ample information for the design and separation processes. Moreover, mixed solvents, rather than single pure liquids are of great practical importance in most chemical, industrial and biological processes, since they provide a wide range of mixtures with requisite properties.

Further, the knowledge of the structure and molecular interactions of liquid mixtures is very important for the fundamental and chemical engineering aspects. The study of molecular interaction in the liquid mixtures is of considerable in the elucidation of the structural properties of the molecules. The inter-molecular interactions influence the structural arrangement along with the shape of the molecules. The sign and magnitude of these properties guide us to understand possible interactions between the component molecules [2].

Thermodynamic and transport properties of the liquid mixtures generally deviate from ideal behavior. An extensive survey of literature revealed that, V^E data for the binary systems of the dimethylacetamide (DMA) with 1-alkanols [3], water [4], substituted benzenes [5], chloroalkanes [6], and esters [7] have been reported. Further, isentropic compressibility data for the binary mixtures of DMA with ketones [8] and substituted benzenes [4]

* Corresponding author. Tel.: +91 44 2257 4248; fax: +91 44 2257 4202.
E-mail addresses: gardas@iitm.ac.in, http://www.iitm.ac.in/info/fac/gardas (R.L. Gardas).

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were also reported. Further non-ideal thermodynamic behavior of liquid mixture may be discussed in terms of differences in molecular size and shape, dispersion forces, polarity, polarizability, molecular association, etc. The liquid components selected as binary mixtures, are well-known organic liquids and also had a wide range of applications at various fields of chemistry besides being used in industries and routine analytical work.

Since *N*,*N*-dimethylacetamide is a highly polar aprotic solvent, it has large dipole moment and dielectric constant [9] (μ = 3.72 and € = 37.78 at 293.15 K) and is practically unassociated [10,11] liquid. DMA is popularly known as super solvent in various fields such as chemical, biological processes and chemical intermediates [12]. 1,2-Dichlorobenzene is used as an intermediate for dyes and certain agricultural chemicals. 1,3-Dichlorobenzene is a good solvent and chemical intermediate. 1,2,4-Trichlorobenzene functions as dye carrier in the textile industry. The role of chlorotoluenes is an intermediate in the pesticide, pharmaceutical and dye manufacturing industries. Further, nitrotoluenes are employed in the synthesis of intermediates for dye industry. Since the above said liquids find many applications in various fields of science and technology has motivated us to study their thermophysical properties. Moreover, the present study provides useful information when introduction of second/third chloro group in chlorobenzene molecule and similarly substituting a chloro and nitro group in toluene molecule that may influence both the nature and extent of molecular interactions that are prevailing in the liquid mixtures. To the best of our knowledge, no volumetric, sound speed and transport data were reported so far in the literature for the above said systems.

We report here new experimental data of V^E,κ_S^E and $\Delta\eta$ of eight binary systems containing DMA with dichloro/trichlorobenzenes, chlorotoluenes and nitrotoluenes at 303.15 K. The measured excess volume data of all the mixtures were compared interms of Prigogine–Flory–Patterson (PFP) theory. In addition to this, the experimental sound speed and viscosity data were compared with various theoretical models.

2. Experimental

2.1. Materials

All the solvents were used analytical grade and obtained from S.D. Fine Chemicals Ltd., India and Merck. All liquids purified as described in the literature [13,14] and degassed with a vacuum pump under an inert atmosphere. The measured data of pure solvents were compared with those reported literature [13,15] and presented in Table 1 along with their supplier, CAS number and purity.

2.2. Apparatus and procedure

All the binary liquid mixtures were prepared by weighing appropriate amount of pure liquids with an analytical balance (Afoset, ER-120A, India) with a precision of ±0.1 mg. The uncertainty in the mole fraction was found to be ±0.0001. Excess volumes of binary liquid mixtures were measured directly using a single composition loading type dilatometer as described earlier [16]. The uncertainties in measured V^E were found to be ±0.003 $cm^3\ mol^{-1}$.

The sound speed data of pure liquids and their mixtures were measured with a single crystal interferometer (Mittal Enterprise, New Delhi, M-82) at a frequency of 3 MHz with an uncertainty of ±1.0 $m\ s^{-1}$. The densities of pure liquids were measured using a single-capillary pycnometer (made of Borosil glass) which was described earlier [17]. The uncertainty in density measurements was found to be ±0.00001 $g\ cm^{-3}$. A suspended Ubbelohode-type viscometer was employed to measure viscosities of pure liquids and liquid mixtures [18]. The viscometer was kept in a transparent water bath with a thermal stability of ±0.01 K for about 20 min to obtain thermal equilibrium. The uncertainty of the flow time measurement was ±0.1 s. The estimated uncertainty in viscosity was about ±0.005 mPa s. The temperature of the all the samples were maintained at 303.15 ± 0.01 K in an electronically controlled thermostatic water bath.

3. Results and discussion

The excess volumes (V^E) of studied eight binary systems of dimethylacetamide (DMA) with di/trichlorobenzenes, chlorotoluenes and nitrotoluenes are listed in Table 2 and also graphically represented in Figs. 1–3 along with binary mixtures of DMA with chlorobenzene [5] and toluene [19]. Further, V^E data were also correlated in terms of Redlich–Kister [20] and Hwang [21] equations and these are also given in Table 2. The method of computation of V^E data using Hwang equation was described earlier [22,23].

The sign and magnitude of V^E generally depends on the following contractive and expansive effects.

The factors responsible for contraction in volume are:

(a) specific interaction between unlike molecules
(b) dipole–dipole (or) dipole-induced dipole interactions
(c) interstitial accommodation of molecules of one component in the voids of the other

The factors that cause expansion of volume are:

(a) dissociation of component molecules
(b) formation of weak bonds between unlike molecules due to Van der Waal forces.

Table 1
Name of the component, suppliers, CAS number and purity. Densities (ρ) and viscosities (η) of pure component data at T = 303.15 K and p = 0.1 MPa.

Component	Supplier	CAS number	Purity (received from supplier)	Purity (after purification)	Density (ρ)/g cm^{-3}		Viscosity (η)/mPa s	
					Exp.	Lit. [16,18]	Exp.	Lit. [16,18]
N,*N*-dimethylacetamide	Merck	127-19-5	0.990	0.995	0.94135	0.94114	0.865	0.867
1,2-Dichlorobenzene	Merck	95-50-1	0.990	0.995	1.29920	1.29922	1.301	1.302
1,3-Dichlorobenzene	Merck	541-73-1	0.990	0.995	1.27716	1.27718	1.023	1.025
1,2,4-Trichlorobenzene	S.D. Fine	120-82-1	0.990	0.995	1.44212	1.44215	1.611	1.613
o-Chlorotoluene	Merck	95-49-8	0.990	0.995	1.07282	1.07279	0.884	0.887
m-Chlorotoluene	Merck	108-41-8	0.990	0.995	1.07215[a]	1.07220[a]	0.782	0.780
p-Chlorotoluene	Merck	106-43-4	0.990	0.995	1.06514[b]	1.06510[b]	0.902	0.900
o-Nitrotoluene	S.D. Fine	88-72-2	0.990	0.995	1.15324	1.15321	1.908	1.911
m-Nitrotoluene	S.D. Fine	99-08-1	0.990	0.995	1.14767	1.14766	1.775	1.777

The standard uncertainties are $u(T)$ = 0.01 K, $u(p)$ = 0.1 kPa, $u(\rho)$ = 0.00001 g cm^{-3}, and $u(\eta)$ = 0.005 mPa s.
[a] at 293.15 K.
[b] at 298.15 K.