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Steric parameters and excess properties of hydroxamic acids

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ABSTRACT

Steric parameters of *N*-phenylbenzo-, *N*-phenyl-4-methyl-3-nitrobenzo-, and *N*-phenyl-4-nitrobenzo-, hydroxamic acids were measured in *N*,*N*-dimethylformamide (DMF) as a function of their concentrations at T = (298.15, 303.15, 308.15, and 313.15) K. The apparent molar volume (V_ϕ), limiting apparent molar volume (V_ϕ^0) at infinite dilution and the slope (S_V^*) are calculated from the experimental values of density (ρ) by applying the Masson's equation. The apparent molar expansibility at infinite dilution (ϕ_E^0), molar volume (V) and the excess molar volume (V^E) are also computed. The refractive indices (n) have been used to calculate the steric parameters, *viz.* molar refraction (R_M), polarizability (α) and excess molar refraction (R) of these molecules. The results show the strong solute–solvent interactions present in the system and thus, help to explore the molecular structure.

1. Introduction

There are several correlations between steric parameters and thermophysical properties that indicate the importance of this parameter [1]. Properties such as densities, refractive indices and their variation with temperature and composition of the solution are useful to design engineering processes and in chemical and biological industries [2–5]. The steric and excess properties measurements are expected to shed some light on both solute–solvent and solvent–solvent interactions. The parameters, apparent molar volumes and limiting apparent molar volumes of dilute solutions can be used for the development of molecular models for describing the thermodynamic behaviour of solutions. The V_ϕ^0 depends upon molecular size, shape, interactions, and structural effects among the solvent [6]. Excess properties of solutions, such as deviation in molar refraction called excess molar refraction, R_M^E and V^E are useful for the design of separation techniques and to test theories of solutions [7].

N,*N*-Dimethylformamide (DMF) is a versatile solvent with large dipole moment and a relatively high dielectric constant [8]. The hydroxamic acid functionality, –C(=O)·N·OH, is a key structural constituent of many biomolecules, some of which, are naturally occurring [9] and others, such as peroxidase, matrix metalloproteinase and urease inhibitors [10,11] are of synthetic origin. Hydroxamic acid derivatives have received increasing attention due to their biological activity especially as enzyme inhibitors [12] and metal chelators [13]. Hydroxamic acids are versatile reagents in analytical chemistry [14,15] and are widely used in medicine as analgetics, anti-inflamatories [16], antibiotics [17], anticancer agents [18], antifungal and hypotentive agents [19]. Extensive work has been carried out to study the volumetric and steric parameters of various binary and liquid mixtures in both aqueous and aquo-organic phase. Recently, Sahin and Ayranci [20] have studied the volumetric properties at different temperatures using various solvents. Anouti *et al.* [21] have investigated volumetric properties and refractive index of binary mixture. Ivona *et al.* [22] studied the densities and refractive indices of ternary mixture at different temperatures.

Over the past decade, our research group has made some remarkable efforts to study the steric and excess properties of binary and pure systems of different derivatives of hydroxamic acids. The data are lacking in the literature on the densities and optical properties of PBHA, PMNHA, and PNHA in pure DMF at different temperatures. Therefore, in the present paper, we report ρ, n of solution over entire range of concentration and at temperatures, T = (298.15, 303.15, 308.15, and 313.15) K. These data are further used to calculate V_ϕ, V_ϕ^0, ϕ_E^0, V^E, n^E and R_M, in order to understand molecular behaviour and the nature of solute–solvent interactions [23–25].

2. Experimental

2.1. Materials

Three hydroxamic acids namely *N*-phenylbenzohydroxamic acid (PBHA), *N*-phenyl-4-methyl-3-nitrobenzohydroxamic acid (PMNHA) and *N*-phenyl-4-nitrobenzohydroxamic acid (PNHA)

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Thermophysical and excess properties of hydroxamic acids in DMSO

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ABSTRACT

In this work, densities (ρ) and refractive indices (n) of *N*-o-tolyl-2-nitrobenzo- and *N*-o-tolyl-4-nitrobenzo-, hydroxamic acids have been determined for dimethyl sulfoxide (DMSO) as a function of their concentrations at T = (298.15, 303.15, 308.15, 313.15, and 318.15) K. These measurements were carried out to evaluate some important parameters, *viz*, molar volume (V), apparent molar volume (V_ϕ), limiting apparent molar volume (V_ϕ^0), slope (S_V^*), molar refraction (R_M) and polarizability (α). The related parameters determined are limiting apparent molar expansivity (ϕ_E^0), thermal expansion coefficient (α_2) and the Hepler constant ($\partial^2 V_\phi^0/\partial T^2$). Excess properties such as excess molar volume (V^E), deviations from the additivity rule of refractive index (n^E), excess molar refraction (R_M^E) have also been evaluated. The excess properties were fitted to the Redlich–Kister equations to estimate their coefficients and standard deviations were determined. The variations of these excess parameters with composition were discussed from the viewpoint of intermolecular interactions in these solutions. The excess properties are found to be either positive or negative depending on the molecular interactions and the nature of solutions. Further, these parameters have been interpreted in terms of solute–solute, solute–solvent interaction and structure making ability of solute in DMSO.

1. Introduction

Studies on different thermophysical (volumetric properties, refractive index) and thermodynamic properties of solution within wide ranges of concentration and temperatures are valuable sources of information that may be used to examine the relationship between the internal structure of the system, nature of intermolecular interactions and the physical properties of the solute, solvent studied [1–11]. Thermodynamic properties obtained through experimentation are the fundamental basis for the development of empirical, semi-empirical or theoretical model used to represented and predict the behaviour of fluids [12]. The volumetric properties of solutions have proven to be a very useful tool in elucidating the structural interactions (*i.e.*, solute–solvent, solute–solute, and solvent–solvent) occurring in solution, because they provide an indirect insight into the conformational feature of the components in solution. The design and operation of the industrial processes that involve nonelectrolyte solutions require knowledge of rigorous models or experimental data to represent the non-ideality of the solutions. Accurate predictions of densities and refractive indices of solutions are of great importance in design engineering processes in chemical and biological industries [13–15]. The density, refractive index and thermodynamic parameters have been extensively employed to study molecular packing, different kinds of association and nature as well as extent of molecular interactions existing in solutions. Further, these properties are also used to test the applicability of differential data and also provide information about the nature and extent of molecular interactions in solution. The parameters, apparent molar volumes and limiting apparent molar volumes of dilute solutions are useful for the development of molecular models for describing the thermodynamic behaviour of solutions. The V_ϕ^0 depends upon molecular size, shape, interactions and structural interactions occurring in solution [16]. Excess properties of solutions, such as excess molar volume, V^E, refractive index deviation, n^E, and excess molar refraction, R_M^E are applicable for the design of separation techniques and to test theories of solutions [17].

Dimethyl sulfoxide (DMSO) is an important solvent in chemistry owing to their miscibility with almost all common polar and nonpolar solvents, resulting from their wide applications in industrial and medical field. It is a versatile dipolar aprotic (having a dielectric constant ε = 46.50) self-associated solvent due to S=O group with large dipole moment (μ = 3.96D at T = 298.15 K) [18]. The hydroxamic acid functionality, –C(=O).N.OH, is a key structural constituent of many biomolecules, some of which are naturally occurring [19] and others such as peroxidase, matrix metalloproteinase and urease inhibitors [20,21] are of synthetic origin. Hydroxamic acid derivatives have received increasing attention due to their biological activity especially as enzyme inhibitors [22] and metal chelators [23]. Hydroxamic acids are versatile reagents in analytical chemistry [24,25] and are widely used in medicine as analgetics, anti-inflamatories [26], antibiotics [27], anticancer agent [28], antifungal and hypotentive [29] agent.

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