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Excess Molar Volume Parameters of Amido-aromatic Ketone Binary Solvent Systems at 308.15 K

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Densities have been measured for the systems, N,N-dimethyl acetamide + phenones (acetophenone, propiophenone, *p*-methyl acetophenone and *p*-chloroacetophenone) at 308.15 K. These values have been converted to excess molar volumes. The excess molar volumes are negative for all the mixtures over the entire composition range. The molecular interactions existing between the components are discussed.

Key Words: Excess molar volume parameters, Amido-aromatic ketone, Binary solvent systems.

INTRODUCTION

Several workers[1–7], have reported studies on N,N-dimethyl acetamide with polar organic solvents including water. They have measured different properties like density, viscosity, ultrasonic velocity, refractive index, etc. They have interpreted their excess parameters in terms of molecular interactions between the components. We are here reporting the intermolecular behaviour of amido-aromatic ketone binary liquid mixtures. In continuation of our earlier work[8, 9] on solvent mixtures, we have undertaken the study of the density of the binary liquid mixtures of N,N-dimethyl acetamide with aromatic ketones at 308.15 K. The values of excess thermodynamic quantity, *viz.*, excess molar volume (V^E) have been calculated.

The main interest of this investigation is to correlate the experimental data with the nature of interacting components of the mixtures and to stress the factors affecting the interactions. N,N-dimethylacetamide has been chosen because it is a highly polar non-aqueous aprotic solvent with high dielectric constant and dipole moment ($\varepsilon = 37.8$, $\mu = 3.71$) having three methyl groups in it enhancing the polarity on the oxygen atom of carbonyl functionality.

EXPERIMENTAL

High-purity grade N,N-dimethyl acetamide (DMA) purchased from S.D. Fine Chemicals, Ltd (AR) was dried over anhydrous potassium carbonate and fractionally distilled[2]. The middle fraction of the distillate was retained and stored over 0.3 nm molecular sieves to reduce the water content, if any, and to avoid the absorption of atmospheric moisture and carbon dioxide gas. All the four phenones[10, 11] [acetophenone (Aph), propiophenone (Pph), *p*-methyl acetophenone (Me-Aph), *p*-chloro acetophenone (Cl-Aph)] purchased from SISCO company were dried over anhydrous potassium carbonate for three days. After three days they were filtered and distilled. The middle fractions of the distillates were retained and stored over 0.4 nm molecular sieves. Experimental values of densities for the pure liquids are compared with the literature values at 298.15 K in Table-1.

TABLE-1
COMPARISON OF EXPERIMENTAL DENSITIES OF PURE LIQUIDS WITH LITERATURE VALUES AT 298.15 K

Component	ρ/g cm^{-3}	
	This work	lit.
Acetophenone	1.0231	1.0225[a]
Propiophenone	1.0092	1.0087[b]
p-Methyl acetophenone	0.9963*	—
p-Chloroacetophenone	1.1889	1.1880[b]
N,N-Dimethyl acetamide	0.9384	0.9375[c]

Value at 308.15 K. References: a = 16, b = 17, c = 5.

Binary mixtures were prepared by mixing appropriate volumes of the liquid components in specially designed air-tight teflon coated caps of glass bottles and the mass measurements were performed on Dhona single pan analytical balance, Dhona 100 DS (India) with an accuracy of ±0.01 mg. The required parameters were measured on the same day immediately after preparing each composition. The uncertainty in the mole fraction was ±0.0001.

Measurements

A double-arm pycnometer with a bulb of 10 cm^3 and a capillary of an internal diameter of about 1 mm was used to measure the densities (ρ) of pure liquids and binary liquid mixtures. The pycnometer was calibrated by using conductivity water (conductivity less than 1×10^{-6}) with 0.9970 and 0.9940 g cm^{-3} as its densities at 298.15 and 308.15 K respectively. The pycnometer filled with air bubble free liquids was kept in a thermostat [INSREF model IRI-017C] with a thermal stability of ±0.01 K, for 25–30 min to attain thermal equilibrium. The accuracy in the density values was $\pm 1 \times 10^{-3}$ g cm^3.

RESULTS AND DISCUSSION

Solvent Parameters and Excess Parameters of the Mixtures

The densities of DMA with acetophenone, propiophenone, *p*-methyl acetophenone and *p*-chloro acetophenone and their corresponding excess molar volumes as a function of mole fraction of phenone are presented in Table-2 at 308.15 K.

TABLE-2
EXPERIMENTAL DENSITIES (ρ) AND EXCESS MOLAR VOLUMES (V^E) AT 308.15 K

x_1	ρ (g·cm^{-3})	V^E (cm^3 mol^{-1})	x_1	ρ (g·cm^{-3})	V^E (cm^3 mol^{-1})	x_1	ρ (g·cm^{-3})	V^E (cm^3 mol^{-1})
Acetophenone (1) + DMA (2)								
0.0000	0.9497	0.0000	0.3143	0.9815	–0.2579	0.7227	1.0071	–0.1212
0.0686	0.9581	–0.1018	0.3938	0.9881	–0.2476	0.8517	1.0133	–0.0509
0.1380	0.9656	–0.1732	0.4912	0.9941	–0.2365	1.0000	1.0200	0.0000
0.2189	0.9736	–0.2437	0.6042	1.0006	–0.1695	—	—	—
Propiophenone (1) + DMA (2)								
0.0000	0.9497	0.0000	0.2778	0.9732	–0.2912	0.6929	0.9905	–0.0192
0.0600	0.9572	–0.2003	0.3654	0.9773	–0.2106	0.8315	0.9950	0.0382
0.1269	0.9637	–0.3185	0.4649	0.9817	–0.1397	1.0000	1.0006	0.0000
0.1862	0.9680	–0.3356	0.5709	0.9860	–0.0814	—	—	—
p-Methyl acetophenone (1) + DMA (2)								
0.0000	0.9497	0.0000	0.2836	0.9723	–0.3410	0.6890	0.9889	–0.2508
0.0617	0.9563	–0.1519	0.3629	0.9765	–0.3520	0.8305	0.9930	–0.1920
0.1321	0.9624	–0.2517	0.4632	0.9810	–0.3458	1.0000	0.9963	0.0000
0.2004	0.9676	–0.3355	0.5582	0.9846	–0.3114	—	—	—
p-Chloroacetophenone (1) + DMA (2)								
0.0000	0.9497	0.0000	0.2825	1.0487	– 0.5363	0.7003	1.1390	–0.4298
0.0644	0.9765	–0.2110	0.3696	1.0718	–0.5889	0.8405	1.1604	–0.2520
0.1311	1.0010	–0.3300	0.4664	1.0945	–0.5934	1.0000	1.1813	0.0000
0.2036	1.0252	–0.4530	0.5774	1.1172	–0.5393	—	—	—

The excess molar volumes (V^E) have been evaluated from density using the equations

$$V^E = V - (V_1X_1 + V_2X_2) \qquad (1)$$

$$V = (X_1M_1 + X_2M_2)/\rho$$

where V and ρ are the molar volume and density of the mixture; X_1, V_1, M_1, X_2, V_2 and M_2 are the mole fraction, molar volume and molecular weight of pure components 1 and 2 respectively.

Excess molar volumes of DMA (2) + phenone (1) displayed in Fig. 1 at 308.15 K show parabolic curves with their vertices in the fourth quadrant indicating the negative deviation over the entire range of phenone composition. On a qualitative basis the negative excess volumes have been analysed in terms of structure making interactions. This is attributed to the specific interactions between unlike molecules of the components in the mixture. Though the experimental results support the chemical forces acting between dissimilar molecules as indicated by the isotherms in Fig. 1, the physical forces are also present in the systems under investigation.

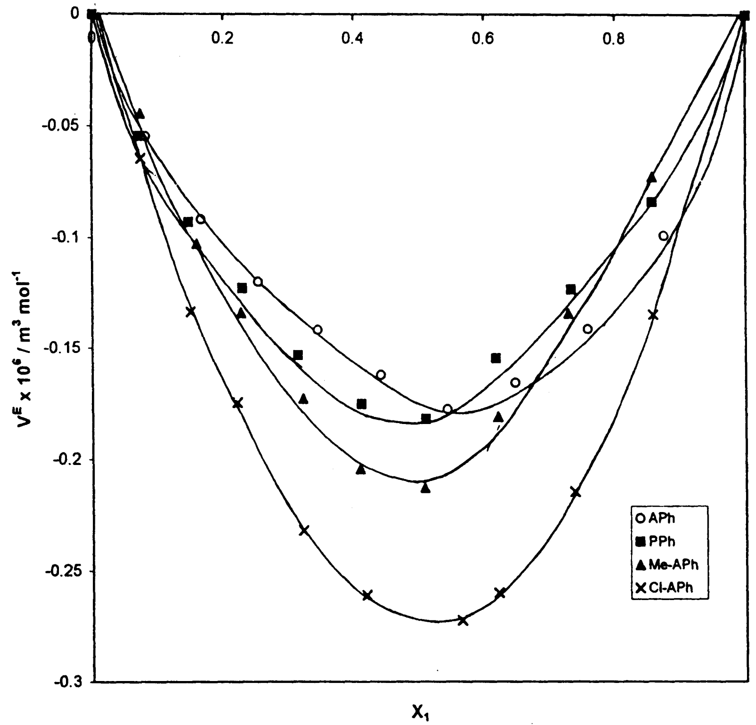

Fig. 1. Variation of V^E of the binary liquid mixtures of N,N-dimethylacetamide (2) with acetophenone (1); propiophenone (1); *p*-methylacetophenone (1) and *p*-chloroacetophenone (1) at 308.15 K

All phenones are dipolar associated liquids and DMA is also an associated liquid due to its polar nature stabilized by three methyl groups in it. Because of the mutual structure disrupting interactions of the solvent and cosolvent, the volumes of the mixtures naturally increase. But, after the breakage of the associated fetters, the individual moieties of two components participate in different chemical interactions leading to a decrease in volume. The graphs are evincive for the preponderance of chemical forces (specific interactions). The chemical forces are due to the formation of new structures between the ketone carbonyl group and the amido carbonyl group (dipole-dipole) packing effects in the form of $n \rightarrow \pi$ complex formation between the 2*p* level vacant molecular orbital of oxygen atom of DMA and π-electrons present in the phenyl ring of aromatic ketones[12, 13]. In addition to this there is an interaction of electron donor-acceptor type between chlorine atom of *p*-chloroacetophenone and oxygen atom of carbonyl group of DMA[14, 15].

Based on the negative magnitudes of V^E parameter the molecular interaction order among the phenones at mole fraction $x = 0.5$ decreases in the following order:

$$\text{Cl-Aph} > \text{Me-Aph} > \text{Pph} \geq \text{Aph}$$

The above order is quite legitimized; *p*-chloroacetophenone is more interactive because the free electron loan pair on chlorine atom increases the polarity on the oxygen atom of carbonyl group entering into conjugation with phenyl ring of ketone. The hyperconjugation present in *p*-methyl acetophenone involves the bonded electrons leading to a lesser interaction than *p*-chloro acetophenone, but a greater interaction than acetophenone. The propiophenone is having a little more +I inductive effect than acetophenone, which should give a slight edge over the acetophenone. But the "crowdedness" of DMA due to its three methyl groups is levelling the +I inductive effect.

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