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Excess Volumes For 2-Chloroaniline with Ethanoic Acid, Propanoic Acid and Butanoic Acid at the Temperature 298.15K

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ABSTRACT
Excess molar volume, V^E for mixtures of 2-Chloroaniline ((C_6H_4) Cl (NH_2)) with ethanoic acid (CH_3COOH), propanoic acid ($C_3H_6O_2$) and butanoic acid ($C_4H_8O_2$) at the temperature 298.15K and under atmospheric pressure have been determined by using dilatometric technique. Temperature is controlled using water bath. The results obtained have been discussed in context of donor-acceptor interaction between the constituents in the liquid state. The experimental values of V^E obtained are negative for all the three systems in the liquid state, thus showing creation of intermolecular complex.
Keywords: Excess Volume, 2-Chloroaniline, Dilatometer, Acetic Acid, Cathetometer

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1. INTRODUCTION

Process design and operation requires data on thermodynamic parameters and transport properties. The non-ideal behavior of binary liquid mixtures is the way to achieve conclusion about interactions between the components [1–3]. The lone pair electron present on N atom of ((C_6H_4) Cl (NH_2)) can act as n-donor towards CH_3COOH, $C_3H_6O_2$ and ($C_4H_8O_2$). The latter compounds may form hydrogen bonding via H atom with lone pair electrons of 2-chloroaniline.

2. EXPERIMENTAL

((C_6H_4) Cl (NH_2)) is taken from Qualikems, India. Ethanoic acid (CH_3COOH), propanoic acid ($C_3H_6O_2$) and butanoic acid ($C_4H_8O_2$) are purchased from Reidel, India. Before using the chemicals were fractionally distilled and dried with the help of 0.4 nm molecular sieves for absorbing moisture. Measurement of densities at 303.15K, were undertaken for checking purity of chemicals. The values of densities obtained from pycnometer, agreed well with the literature values (Riddick and Bungar, 1970) [4].

The dilatometer is used for the determination of excess volume at 298.15K. Temperature of water bath is controlled within ±0.01K. The dilatometric assembly used during the current study was effectively alike as given in our earlier communication. It is made up of two pyrex glass made bulbs disconnected through a curved glass tubing for stopper fitting and a capillary which was connected to one of the two bulbs. The components to be merged were put in the two bulbs and disconnected with the help of Hg. The components and Hg were introduced with the help of hypodermic syringe.

The two components were mixed by slanting the bulb and the variation in volume on mixing was established by noting the height of the mercury meniscus in the vertical capillary by using a cathetometer, which could be read to

±0.001cm. Binary mixtures are made by weighing pure components on a digital balance (Bosch, Germany) having reproducibility of ±0.0001g. . Preparation of mixtures was done by weighing mass in air-tight stoppered glass bottles. Mixing of the mixtures was done without evaporation of the constituents.

3. RESULTS AND DISCUSSION

The values of excess molar volume for the mixture of 2-Chloroaniline ((C_6H_4) Cl (NH_2)) with ethanoic acid (CH_3COOH), propanoic acid ($C_3H_6O_2$) and butanoic acid ($C_4H_8O_2$) at the temperature 298.15K and atmospheric pressure are collected in Table1. The values of excess molar volume, V^E /$cm^3.mol^{-1}$ for the different mixtures of 2-Chloroaniline have been graphically shown in opposition to the mole fraction, x_1, of 2-Chloroaniline, in Figure 1.

V^E data for different mixtures were fitted to an appropriate equation as given below:

$$V^E = x_1(1-x_1)\sum_{i=1}^{N} A_i(2x_1-1)^{i-1} \quad \textbf{(1)}$$

The values of the all the coefficients arising from the fits and the consequent standard deviations are summarized in Table 2. Standard deviation is calculated in the same way as given in our earlier paper. (Tripathi, AD et. al., 2021) [5]. The values of excess volume, V^E for the mixtures of 2-Chloroaniline with carboxylic acids increase in the order:

Acetic acid > $C_3H_6O_2$ > $C_4H_8O_2$

The negativity in the values of excess volume shown by all systems in the present case is due to possibility of contraction of volume for binary mixtures is more as compared to expansion factors in the liquid state at the particular temperature. The negativity in the values of excess volume is also an indication of donor-acceptor interaction between components through H- bonding, it may also arise because of interaction of dipolar forces or weaker forces or adjustment of molecules of one component into the interstitials gaps situated in the association of 2nd component.

Table 1: Excess volumes for various mixtures at 298.15K

2-chloroaniline + ethanoic acid		**2-Chloroaniline + Propanoic acid**		**2-Chloroaniline + Butanoic acid**	
X_1	**V^E**	**X_1**	**V^E**	**X_1**	**V^E**
0.0951	-0.0513	0.1123	-0.0521	0.0988	-0.0421
0.2023	-0.0875	0.2114	-0.0784	0.1865	-0.0639
0.2774	-0.1051	0.3016	-0.0987	0.2677	-0.0816
0.3113	-0.1101	0.3554	-0.1037	0.3194	-0.0902
0.3665	-0.1179	0.3882	-0.1089	0.3663	-0.0952
0.4912	-0.1193	0.5005	-0.1098	0.4822	-0.1003
0.6034	-0.1047	0.6337	-0.0956	0.5991	-0.0933
0.6881	-0.0912	0.7057	-0.0821	0.6772	-0.0804
0.7662	-0.0731	0.8005	-0.0615	0.7562	-0.0645
0.8223	-0.0611	0.8115	-0.0543	0.8223	-0.0412
0.9112	-0.0311	0.9112	-0.0267	0.8931	-0.0265
0.9223	-0.0247	0.9343	-0.0198	0.9156	-0.0212

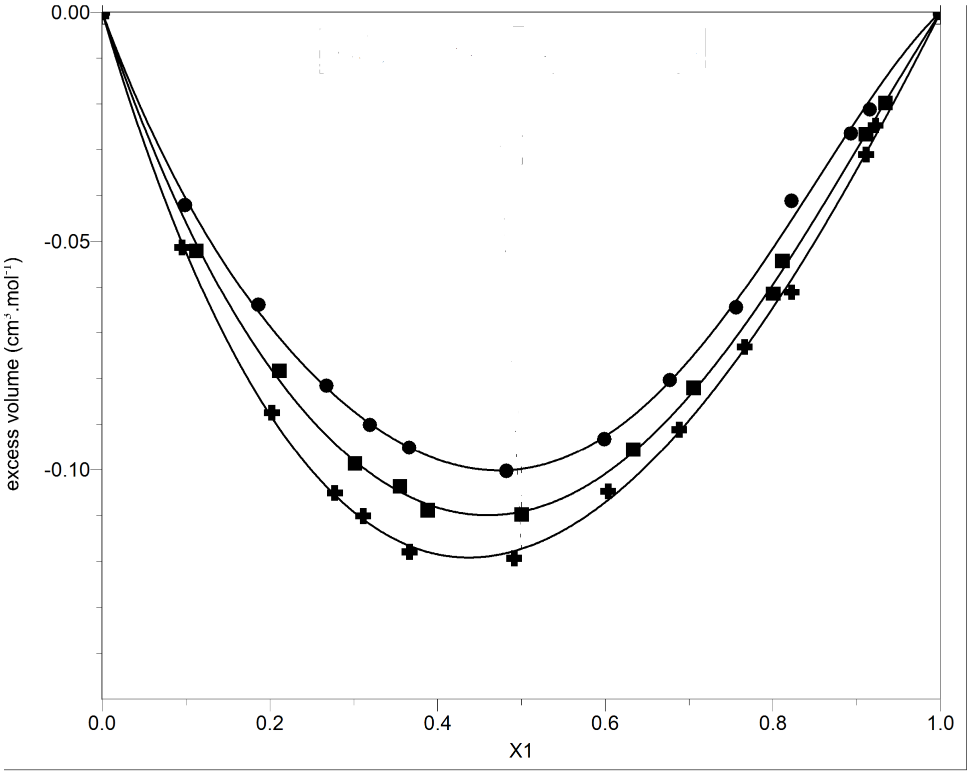

Figure 1: Excess molar enthalpies of binary liquid mixtures of x1 of 2chloroaniline+ ethanoic acid (2) (✚) + propionic acid(■)(2) , + Butanoic acid(●) (2), at 298.15 K

Table 2: Least Squares Coefficients of Eq 1 for the Excess Molar Volumes, and the standard deviations, σ, of 2 chloroaniline(1) + ethanoic acid (2), +propionic acid(2) ,+butanoic acid (2) at the temperature 298.15 K.

System	**A_0**	**A_1**	**A_2**	**A_3**	**σ/ (J mol^{-1})**
2-chloroaniline (1) + ethanoic acid (2)	-0.4691	0.1173	-0.0201	0.0119	0.002
2-chloroaniline (1) + propionic acid (2)	-0.4367	-0.07422	0.02356	0.0567	0.0014
2-chloroaniline (1) + butanoic acid (2	-0.3993	0.04809	0.06694	0.1132	0.002

Figure 1 shows that all the values obtained experimentally for the systems of ((C_6H_4) Cl (NH_2)) with CH_3COOH, $C_3H_6O_2$ and $C_4H_8O_2$ at the temperature 298.15K, are negative throughout total composition range, it represents that there is amendment of 'free volume' in the real mixtures and the occurrence of electron donor–acceptor interactions between ethanoic acid, propanoic acid and butanoic acid with ((C_6H_4) Cl (NH_2)), which performs as an n-donor component toward all acids. Additionally, a weak physical interaction e.g.dipole–dipole interaction also occurs between the carboxylic acid and amino group of ((C_6H_4) Cl (NH_2)) .Thus making V^E values in negative sign. Figure 1 also shows that the V^E values are superior in negativity for the system ((C_6H_4) Cl (NH_2)) + CH_3COOH mixture. This behavior clearly indicates the existence of strong bond creation i.e.H-bonding between carbonyl group of all the mentioned carboxylic acid and H atom of amino group of ((C_6H_4) Cl (NH_2)). It may also be assumed that minor molecules fill into the empty spaces formed by larger molecules of ((C_6H_4) Cl (NH_2)). This is confirmation that negative excess volume proves the occurrence of strong molecular association in the system.

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