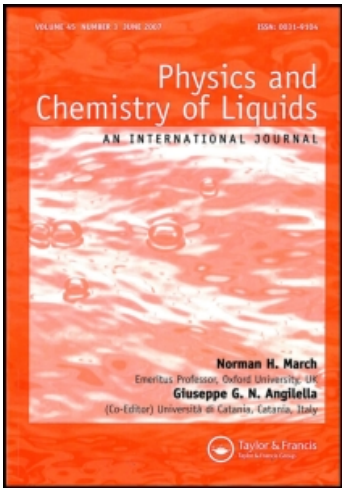


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# Excess Molar Volume of 1-propanol Aniline, *N*-methylaniline, *N,N*-dimethylaniline

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# EXCESS MOLAR VOLUME OF 1-PROPANOL + ANILINE, + *N*-METHYLANILINE, + *N*,*N*-DIMETHYLANILINE

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Densities of the systems, 1-Propanol(P) + aniline(A), 1-Propanol(P) + *N*-Methylaniline (NMA) and 1-Propanol(P) + *N*,*N*-Dimethylaniline(DMA) have been measured from 21°C to 50°C at an interval of 5°C. The excess molar volumes, $V^E$, of the systems, P + A and P + NMA have been found to be negative for the whole range of composition. $V^E$ of the system P + DMA has also been found to be negative, except in DMA-rich region where small positive excess volume is observed. The negative excess volume has been explained primarily in terms of strong specific interaction and size difference of unlike molecules. The magnitude of the negative excess volumes of these systems is of the order, P + A > P + NMA > P + DMA, which has been strongly influenced by steric effect due to $CH_3$ group attached to N-atom of NMA and DMA. In the highly rich region of DMA in P + DMA system the small positive excess volume is accounted for by the steric effect and breaking up of H-bond of 1-Propanol.

*Keywords*: Density; Excess molar volume; 1-Propanol; Aniline; *N*-Methylaniline and *N*,*N*-Dimethylaniline

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## 1. INTRODUCTION

This is a part of our on-going project of studying molecular interaction of binary liquid systems from density and viscosity measurement. As far as we are aware, no work along the line of our research is available involving binary systems of anilines and alkanols, although there are some volumetric studies on systems comprising of alkanols and aliphatic amines [1, 2]. Another piece of work that has some relevance with our research is a study on excess enthalpies of binary solvent mixtures of 1-Butanol and 2-methyl-2-propanol with aniline, *N*-Methylaniline and *N*,*N*-Dimethylaniline by Pikkarainen [3]. In the present investigation we have chosen aniline, *N*-Methylaniline and *N*,*N*-Dimethylaniline, each forming binary system with 1-Propanol over the full composition range. The systems, so chosen, provide us an opportunity of studying the effect of replacement of aminic hydrogen of aniline by methyl group successively on the volumetric properties of these systems.



## 2. EXPERIMENTAL

1-Propanol used for experiment was procured from Aldrich, the quoted purity was 99%. It was allowed to stand over molecular sieves (4A) for 2–3 weeks prior to its use. Aniline, *N*-Methylaniline and *N*,*N*-Dimethylaniline were procured from B.D.H. The quoted purities were 98–99%. Anilines were purified by distillation using a simple distillation set and only colourless middle fractions were collected and used to prepare the mixtures. The mixtures of different compositions were made by carefully weighing the pure liquids. The densities of the pure liquids and mixtures were determined by using a bicapillary pyknometer. The pyknometer was calibrated with redistilled water. An analytical balance with an accuracy of $\pm 0.1$ mg was used for weighing. The temperature was controlled by thermostatic water bath fluctuating to $\pm 0.05$°C.

The excess molar volume, $V^E$, was calculated by the following equation,

$$V^E = \left[\frac{X_1M_1 + X_2M_2}{\rho_{mix}}\right] - [X_1V_1 + X_2V_2] \qquad (1)$$

where $\rho_{mix}$ is the density of the mixture, $M_1$, $M_2$, $V_1$, $V_2$, $X_1$ and $X_2$ are molar masses, volumes and mole fraction of the pure components 1 and 2, respectively. Each set of results covering the whole range of composition at a particular temperature was fitted to Redlich–Kister equation of the type,

$$V^E = X_1X_2 \sum_{j=0}^{n} a_j(2X_1 - 1)^j \qquad (2)$$

where $a_j$ are the coefficients of the polynomial equation. Using $n = 3$, at each temperature four different $a_j$ values and standard deviation, $\sigma$, were obtained through the least squares method.



## 3. RESULTS AND DISCUSSION

The densities of 1-Propanol, aniline, *N*-Methylaniline and *N*,*N*-Dimethylaniline at different temperatures are shown in Table I, together with the literature values. The experimental values are found to correspond well with the literature values. The density of the anilines varies in the order, aniline > *N*-Methylaniline > *N*,*N*-Dimethylaniline. Aniline having two aminic hydrogen is self-associated most extensively through H-bonding. *N*-Methylaniline having one aminic hydrogen is obviously less extensively associated through H-bonding; the association being further hampered by steric hindrance by methyl group attached to N-atom. *N*,*N*-Dimethylaniline has no such aminic hydrogen and is not capable of undergoing self-association through H-bond. However, this compound is associated by rather weak forces, such as, dipole–dipole and dipole–induced dipole interactions.

The excess molar volumes, $V^E$, of the systems, P+A, P+NMA and P+DMA calculated by using Eq. (1) are shown in Table II. The smoothed curves for excess volumes are drawn in accordance with the polynomial Eq. (2) and are shown in Figures 1–3. The coefficients of this equation and the standard deviations, $\sigma$, are listed in Table III.

TABLE I Densities, $\rho$, of pure liquids at different temperatures

| | $\rho/g\ cm^{-3}$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | *Temperature* | | | | | | |
| *Compounds* | 21°C | 25°C | 30°C | 35°C | 40°C | 45°C | 50°C |
| 1-Propanol | 0.8035 | 0.8002<br>0.799353[c] | 0.7962<br>0.79560[a] | 0.7922<br>0.791411[c]<br>0.7918[d] | 0.7879 | 0.7842 | 0.7797 |
| Aniline | 1.0214 | 1.0171<br>1.0174[b] | 1.0128<br>1.0133[b] | 1.0087<br>1.0089[b] | 1.0044<br>1.0046[b] | 1.0004<br>1.0002[b] | 0.9619 |
| *N*-Methylaniline | 0.9865 | 0.9822<br>0.9817[b] | 0.9781<br>0.9777[b] | 0.9739<br>0.9736[b] | 0.9699<br>0.9696[b] | 0.9663<br>0.9658[b] | 0.9619 |
| *N*,*N*-Dimethylaniline | – | 0.9520<br>0.9520[b] | 0.9480<br>0.9480[b] | 0.9437<br>0.9439[b] | 0.9398<br>0.9398[b] | 0.9354<br>0.9357[b] | |

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TABLE II Experimental densities ($\rho$/gcm$^{-3}$) and excess molar volumes $V^E$(cm$^3$mol$^{-1}$) of 1-Propanol + anilines for different molar ratios at different temperatures

| $T$/°C | 21 | | 25 | | 30 | | 35 | | 40 | | 45 | | 50 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $X_2$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ |
| 1-Propanol ($X_1$) + aniline ($X_2$) | | | | | | | | | | | | | | |
| 0.0000 | 0.8035 | – | 0.8002 | – | 0.7962 | – | 0.7922 | – | 0.7881 | – | | | | |
| 0.1006 | 0.8340 | −0.3992 | 0.8306 | −0.4040 | 0.8262 | −0.3758 | 0.8220 | −0.3643 | 0.8177 | −0.3531 | | | | |
| 0.1991 | 0.8602 | −0.5467 | 0.8564 | −0.5265 | 0.8522 | −0.5224 | 0.8476 | −0.4779 | 0.8432 | −0.4618 | | | | |
| 0.2994 | 0.8846 | −0.5827 | 0.8808 | −0.5728 | 0.8762 | −0.5546 | 0.8718 | −0.5128 | 0.8671 | −0.4719 | | | | |
| 0.3992 | 0.9074 | −0.5727 | 0.9036 | −0.5543 | 0.8989 | −0.5300 | 0.8948 | −0.5355 | 0.8899 | −0.4786 | | | | |
| 0.5007 | 0.9290 | −0.5045 | 0.9254 | −0.5305 | 0.9209 | −0.5089 | 0.9166 | −0.4969 | 0.9120 | −0.4692 | | | | |
| 0.6011 | 0.9404 | −0.4691 | 0.9462 | −0.4576 | 0.9418 | −0.4430 | 0.9376 | −0.4198 | 0.9334 | −0.3996 | | | | |
| 0.7001 | 0.9693 | −0.4091 | 0.9651 | −0.3946 | 0.9610 | −0.3732 | 0.9567 | −0.3506 | 0.9520 | −0.3292 | | | | |
| 0.8002 | 0.9880 | −0.3243 | 0.9837 | −0.3115 | 0.9792 | −0.2784 | 0.9750 | −0.2511 | 0.9705 | −0.2390 | | | | |
| 0.8983 | 1.0048 | −0.1709 | 1.0006 | −0.1735 | 0.9964 | −0.1598 | 0.9921 | −0.1316 | 0.9875 | −0.1172 | | | | |
| 1.0000 | 1.0214 | – | 1.0171 | – | 1.0128 | – | 1.0087 | – | 1.0044 | – | | | | |
| 1-Propanol ($X_1$) + $N$-Methylaniline ($X_2$) | | | | | | | | | | | | | | |
| 0.0000 | – | – | – | – | 0.7964 | – | 0.7921 | – | 0.7879 | – | 0.7842 | – | 0.7797 | – |
| 0.1008 | | | | | 0.8247 | −0.2709 | 0.8203 | −0.2687 | 0.8158 | −0.2480 | 0.8114 | −0.1849 | 0.8070 | −0.2012 |
| 0.1995 | | | | | 0.8483 | −0.3448 | 0.8438 | −0.3369 | 0.8394 | −0.3221 | 0.8352 | −0.2812 | 0.8309 | −0.2755 |
| 0.2999 | | | | | 0.8699 | −0.3672 | 0.8655 | −0.3521 | 0.8610 | −0.3342 | 0.8568 | −0.3028 | 0.8524 | −0.2799 |
| 0.4015 | | | | | 0.8893 | −0.3124 | 0.8851 | −0.3392 | 0.8809 | −0.2981 | 0.8767 | −0.2948 | 0.8725 | −0.2485 |
| 0.5015 | | | | | 0.9071 | −0.2736 | 0.9028 | −0.2920 | 0.8985 | −0.2614 | 0.8942 | −0.2202 | 0.8899 | −0.2056 |
| 0.6016 | | | | | 0.9242 | −0.2441 | 0.9196 | −0.2889 | 0.9153 | −0.2285 | 0.9112 | −0.2451 | 0.9066 | −0.1732 |
| 0.7016 | | | | | 0.9393 | −0.2271 | 0.9348 | −0.2272 | 0.9306 | −0.1945 | 0.9265 | −0.1730 | 0.9225 | −0.1385 |
| 0.8003 | | | | | 0.9531 | −0.1509 | 0.9486 | −0.1511 | 0.9442 | −0.1485 | 0.9403 | −0.0889 | 0.9356 | −0.0989 |
| 0.9016 | | | | | 0.9667 | −0.1129 | 0.9622 | −0.1135 | 0.9579 | −0.0923 | 0.9543 | −0.0878 | 0.9496 | −0.0490 |
| 1.0000 | | | | | 0.9784 | – | 0.9739 | – | 0.9699 | – | 0.9663 | – | 0.9619 | – |

TABLE II (Continued)

| $T/°C$ | 21 | | 25 | | 30 | | 35 | | 40 | | 45 | | 50 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $X_2$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ | $\rho$ | $V^E$ |
| 1-Propanol ($X_1$)+*N*,*N*-Dimethylaniline ($X_2$) | | | | | | | | | | | | | | |
| 0.0000 | – | – | – | – | 0.7964 | – | 0.7921 | – | 0.7879 | – | 0.7842 | – | 0.7797 | – |
| 0.1011 | | | | | 0.8221 | −0.1415 | 0.8176 | −0.1249 | 0.8133 | −0.1138 | 0.8095 | −0.1248 | 0.8048 | −0.0889 |
| 0.1989 | | | | | 0.8430 | −0.1751 | 0.8385 | −0.1592 | 0.8340 | −0.1242 | 0.8301 | −0.1340 | 0.8257 | −0.1112 |
| 0.2994 | | | | | 0.8615 | −0.1525 | 0.8570 | −0.1361 | 0.8523 | −0.1190 | 0.8483 | −0.1275 | 0.8435 | −0.0945 |
| 0.4015 | | | | | 0.8784 | −0.1497 | 0.8740 | −0.1438 | 0.8694 | −0.0874 | 0.8653 | −0.1120 | 0.8608 | −0.0721 |
| 0.4992 | | | | | 0.8928 | −0.1353 | 0.8883 | −0.1172 | 0.8838 | −0.0664 | 0.8798 | −0.0884 | 0.8752 | −0.0480 |
| 0.5980 | | | | | 0.9059 | −0.1145 | 0.9013 | −0.0831 | 0.8969 | −0.0384 | 0.8927 | −0.0800 | 0.8883 | −0.0278 |
| 0.7024 | | | | | 0.9182 | −0.0651 | 0.9136 | −0.0314 | 0.9092 | −0.0197 | 0.9050 | −0.0310 | 0.9009 | +0.0024 |
| 0.7980 | | | | | 0.9284 | −0.0139 | 0.9239 | +0.0095 | 0.9194 | +0.0066 | 0.9151 | +0.0083 | 0.9117 | +0.0151 |
| 0.9026 | | | | | 0.9385 | +0.0166 | 0.9345 | +0.0148 | 0.9305 | +0.0226 | 0.9265 | +0.0300 | 0.9223 | +0.0231 |
| 1.0000 | | | | | 0.9480 | – | 0.9437 | – | 0.9398 | – | 0.9354 | – | 0.9315 | – |

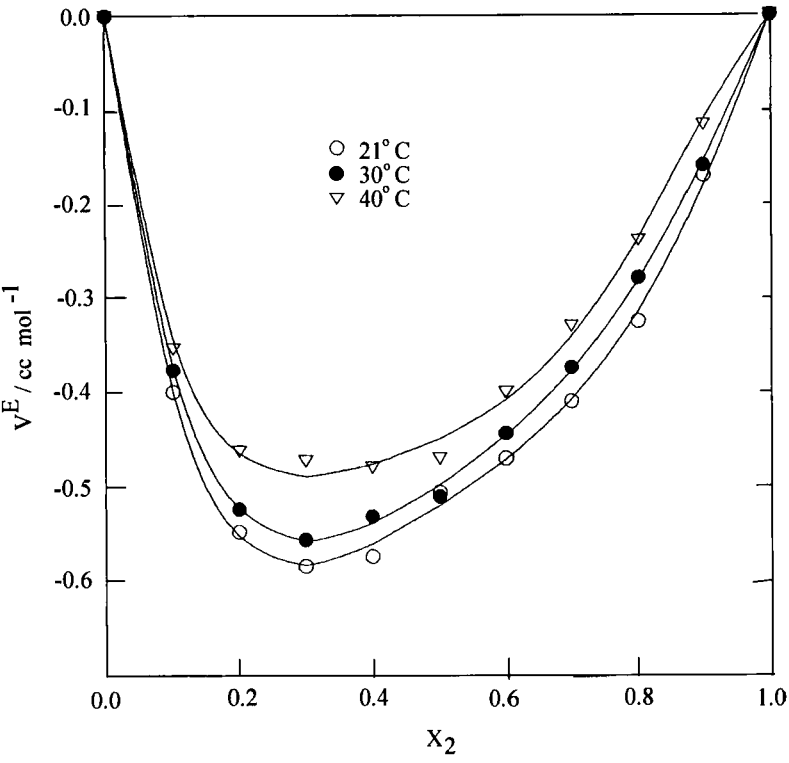


FIGURE 1 Excess molar volume against mole fraction of aniline.

Examination of the figures shows the following characteristics:

(a) The excess molar volumes of the systems, P+A, P+NMA, show negative values for the whole range of composition. However, the magnitude of the negative values is greater for the former than for the latter.
(b) The excess volumes for the system, P+DMA, are negative up to a significant range of concentration of DMA, beyond which the values become positive, although their magnitude is small.
(c) For all the systems, $dV^E/dT$ is positive over the whole composition range.

The following factors contribute to the contraction of volume on mixing:

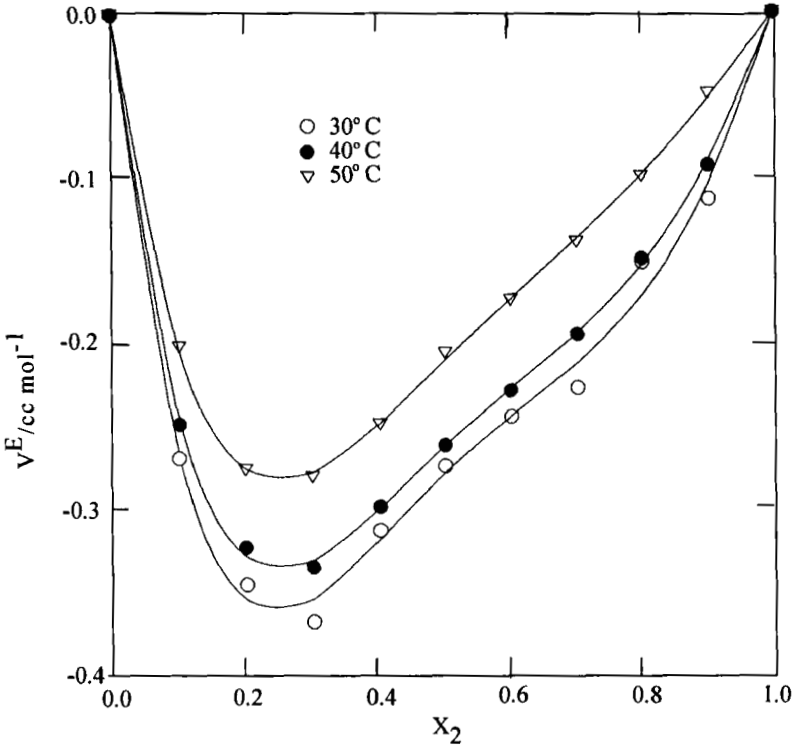


FIGURE 2 Excess molar volume against mole fraction of *N*-Methylaniline.

(i) Strong specific interaction.
(ii) Favourable geometric fitting.
(iii) Accommodation of one species into the interstitial or the void space of the other species.
(iv) Size difference between unlike molecules.

The expansion of volume, on the other hand, is caused by the following factors:

(i) Weak interaction between the component molecules.
(ii) Unfavourable geometric fitting.
(iii) Steric effect which hinders the molecules from approaching each other.
(iv) Break down of association of one or both components in solution system.

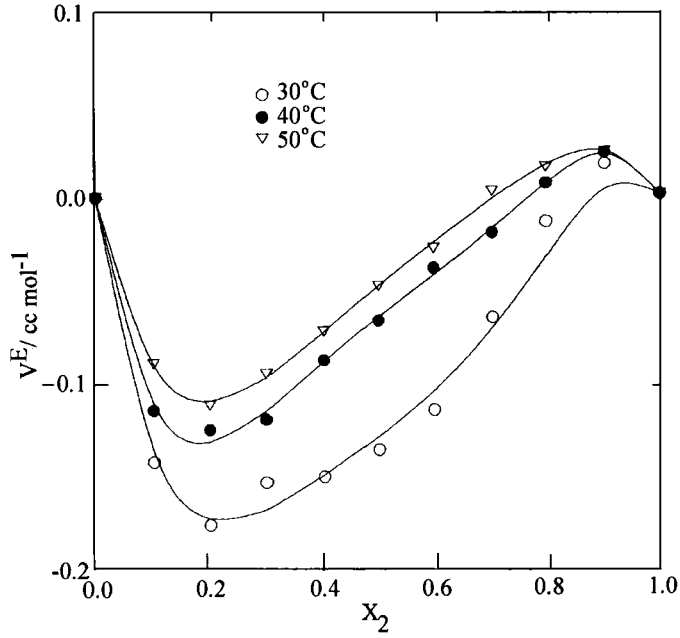


FIGURE 3 Excess molar volume against mole fraction of *N,N*-Dimethylaniline.



TABLE III Coefficients $a_i$ of Redlich–Kister equation (Eq. (2)) and standard deviation, $\sigma$, of the systems

| *System* | *Temperature* | $a_0$ | $a_1$ | $a_2$ | $a_3$ | $\sigma$ ($cm^3mol^{-1}$) |
|---|---|---|---|---|---|---|
| 1-Propanol + Aniline | 21 | −2.0757 | 0.8772 | −1.7503 | 1.0018 | 0.01108 |
| | 25 | −2.0621 | 0.8556 | −1.6280 | 1.0356 | 0.01272 |
| | 30 | −1.9890 | 0.9148 | −1.4518 | 0.9531 | 0.00701 |
| | 35 | −1.9398 | 0.8662 | −1.0447 | 1.0574 | 0.01612 |
| | 40 | −1.7950 | 0.6345 | −1.1047 | 1.5306 | 0.01439 |
| 1-Propanol + *N*-Methylaniline | 30 | −1.1140 | 0.7486 | −1.4653 | 0.5683 | 0.00327 |
| | 35 | −1.2109 | 0.6136 | −1.1544 | 0.7957 | 0.01821 |
| | 40 | −1.0488 | 0.7281 | −1.2562 | 0.5179 | 0.00415 |
| | 45 | −1.0166 | 0.7896 | −0.6327 | 0.0647 | 0.02767 |
| | 50 | −0.8428 | 0.7673 | −0.8954 | 0.4303 | 0.00305 |
| 1-Propanol + *N,N*-Dimethylaniline | 30 | −0.5124 | 0.4398 | −0.3470 | 0.8006 | 0.01548 |
| | 35 | −0.4429 | 0.5766 | −0.1063 | 0.6720 | 0.01224 |
| | 40 | −0.2576 | 0.4623 | −0.3593 | 0.7018 | 0.00445 |
| | 45 | −0.3697 | 0.3585 | −0.1428 | 1.1071 | 0.00704 |
| | 50 | −0.1910 | 0.4883 | −0.2710 | 0.4609 | 0.00272 |

Two types of specific interaction, O—H···N and N—H···O, are envisaged for these systems. The first type of interaction is possible for all the anilines; the second type is possible with A and NMA, but not with DMA. The replacement of aminic hydrogen by methyl group increases the electron density on N-atom. The basicity of the anilines thus varies in the order, DMA > NMA > A. The specific interaction of the type, O—H···N, should also follow the same order, and therefore the magnitude of the negative excess volume is expected to be of the order, P+DMA > P+NMA > P+A, if other effects are not considered for the moment. The second type of interaction, N—H···O, obviously weaker than the first type, should be greater for aniline than for NMA, and is thought to contribute very little to $V^E$.

It is difficult at this stage to say anything about the structural fitting of anilines with 1-Propanol, but we can only guess about the economy of volume due to probable incorporation of smaller species into the void space of larger ones in terms of size difference. The molar volumes of the components at 30°C are, P (75.36 $cm^3$), A (91.82 $cm^3$), NMA (109.36 $cm^3$) and DMA (127.64 $cm^3$), and evidently the size difference between the unlike molecules is of the order, P+DMA > P+NMA > P+A. From this consideration alone, the contribution towards volume contraction should also be of the same order.

Considering the factors that are regarded to be very important for causing volume contraction, such as, O—H···N interaction and size difference, and in the light of the above discussion, one would expect that the magnitude of the negative excess volume should be in the order, P+DMA > P+NMA > P+A, but practically the reverse order is observed as can be seen in Figure 4. The steric effect is regarded to be responsible for the reversal of this order. The methyl group attached to N-atom of NMA and DMA, though apparently increases the basicity of these anilines, hinders these molecules to come closer to 1-Propanol molecule, and thereby reduces the strength of O—H···N interaction drastically. The excess molar volumes of the binary systems, composed of varieties of anilines with *o*-chlorophenol, 2-(2-butoxyethoxy) ethanol, propionic acid, 1-Butanol, 2-Butanol and *t*-Butanol, conclusively support the strong influence of steric effect favouring volume expansion [4–9].

It is to be noted that while the systems, P+A and P+NMA, exhibit negative excess volume in the whole range of composition (Figs. 1

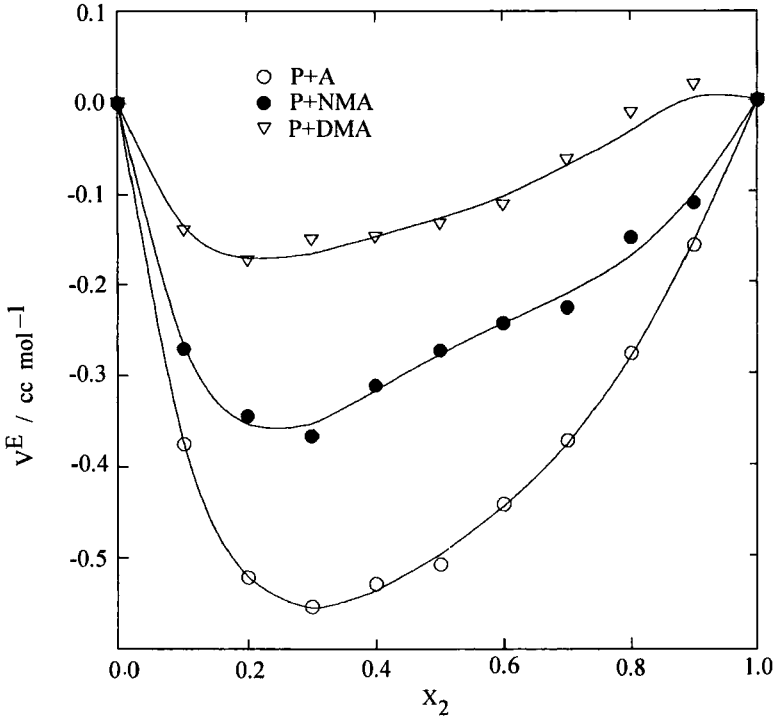


FIGURE 4 Excess molar volume against mole fraction of anilines at 30°C.



and 2), the system, P+DMA, shows small positive excess volume only in the very rich region of DMA (Fig. 3). Such positive excess volume is also observed for the systems, 1-Butanol+DMA [7], 2-Butanol+DMA [8] and *t*-Butanol+DMA [9] in DMA-rich region. In the highly concentrated solution of DMA, 1-Propanol is assumed to be broken up by the rupture of H-bond by dispersion force resulting in an expansion of volume. This effect and the steric effect together more than compensate the factors contributing to the contraction of volume, and hence the positive excess volume in DMA-rich region.

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