

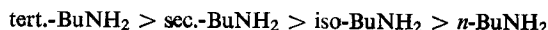
Volume change on mixing : binary mixtures of methanol with isomeric butylamines *

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Abstract. The volume change on mixing (V^E) of binary systems of methanol (1) + *n*-butylamine, isobutylamine, sec. butylamine and tert. butylamine (2) were determined at 25° C by density method. All the four systems showed a large negative volume change on mixing and the maxima were observed nearly at 0.5 mole fraction. This was attributed to the possibility of 1 : 1 type of complex formation between amine and methanol. The V^E was found to depend on the structure of butylamine and the magnitude of V^E increased as



This particular trend is attributed to increase in the number of amine-alcohol species formed on the mixing and the geometric fitting of methanol in the liquid structure of the butylamine.

Keywords. Binary mixtures; volume; mixing; methanol-butylamine isomers.

1. Introduction

As a part of the programme to study the nature of the interactions between methanol and the different isomeric butylamines and to study the effect of branching of alkyl chain of butylamine on the alcohol-amine interaction, the volume change on mixing of the binary mixtures of methanol with normal, iso, secondary and tertiary butylamines was determined at 25° C. The results are reported in the present paper.

2. Experimental

The details of the chemicals and their purifications have been given in the earlier communication (Pradhan and Mathur 1978). The volume change on mixing was calculated from the density measurements of the synthetically prepared binary mixtures of methanol and butylamine. The densities were determined by using

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a Lipkins type two arm pyknometer, properly annealed and previously calibrated. The temperature of the thermostat was maintained constant $\pm 0.01^\circ \text{C}$. The uncertainty involved in the measurements of the volume and the mass of the liquid were 10^{-4} cc and 10^{-4} g respectively. The maximum combined error introduced by these uncertainties is $8 \times 10^{-6} \text{ g/cc}$. The density of the synthetic mixture was determined at least thrice and the standard deviation was found to be less than 10^{-5} g/cc .

The overall working of the experimental set-up was standardised by studying the volume change on mixing of the carbontetrachloride-cyclohexane system at 25°C . The present results are compared with those reported in literature (Scatchard *et al* 1939). The present results are in good agreement with those of Scatchard *et al* (figure 1).

3. Results and discussion

The results on the volume change on mixing of the binary systems of methanol with normal, iso, secondary and tertiary butylamines are given in table 1. The excess volume (V^E) has been fitted by the method of least squares into an equation of the type

$$V^E \text{ ml/mole} = \sum_{n=1}^4 A_n x^n$$

where A is a constant and x is the mole fraction of methanol. The constants of the above equation were calculated by Honeywell-400 computer and are given in table 2 along with the standard deviation.

For ready comparison the plots of V^E as a function of the mole fraction of methanol (x_1) for the four systems are given in figure 2. All the four systems show a large negative volume change on mixing throughout the concentration range. It was also observed that the heats of mixing of these systems were highly negative (Pradhan 1978). It is therefore reasonable to conclude that the negative volume change on mixing for these systems is due to the hydrogen bonded complex formation between the methanol and amine molecules. Huyskens *et al* (1960,

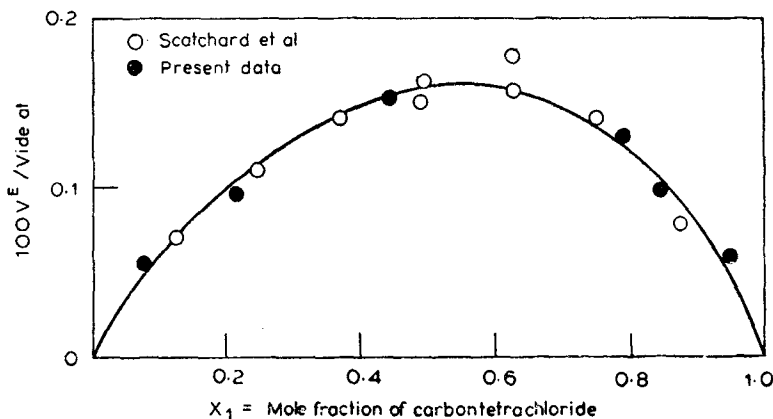


Figure 1. $100 V^E/V_{ideal}$ versus x_1 plot for CCl_4 (1)-cyclohexane (2) system at 25°C .

Table 1. Volume change on mixing of methanol-isomeric butylamine systems at 25° C.

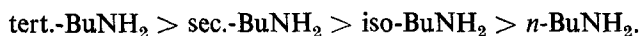
| x_1 Mole fraction of methanol | d_{12} g/cc density of mixture | ν^E ml/mole |
|---------------------------------------|--|--------------------|
| <i>n</i> -butylamine | | |
| 0.0000 | 0.73220 | .. |
| 0.0945 | 0.73843 | - 0.500 |
| 0.1961 | 0.74541 | - 0.925 |
| 0.3307 | 0.75452 | - 1.362 |
| 0.4910 | 0.76591 | - 1.635 |
| 0.6519 | 0.77642 | - 1.550 |
| 0.7742 | 0.78216 | - 1.164 |
| 0.9012 | 0.78675 | - 0.577 |
| 1.0000 | 0.78905 | .. |
| <i>iso</i> -butylamine | | |
| 0.0000 | 0.72425 | .. |
| 0.0989 | 0.73095 | - 0.050 |
| 0.1984 | 0.73855 | - 1.020 |
| 0.3005 | 0.74626 | - 1.380 |
| 0.4009 | 0.75412 | - 1.632 |
| 0.5005 | 0.76157 | - 1.785 |
| 0.5968 | 0.76867 | - 1.763 |
| 0.7012 | 0.77539 | - 1.547 |
| 0.7917 | 0.78238 | - 1.170 |
| 0.8975 | 0.78773 | - 0.638 |
| 1.0000 | 0.79198 | .. |
| <i>sec</i> -butylamine | | |
| 0.0000 | 0.71732 | .. |
| 0.1000 | 0.72568 | - 0.698 |
| 0.2007 | 0.73436 | - 1.274 |
| 0.2995 | 0.74316 | - 1.729 |
| 0.3995 | 0.75234 | - 2.040 |
| 0.4980 | 0.76123 | - 2.191 |
| 0.6001 | 0.76988 | - 2.150 |
| 0.6990 | 0.77591 | - 1.920 |
| 0.7946 | 0.78109 | - 1.456 |
| 0.9043 | 0.78530 | - 0.752 |
| 1.0000 | 0.78993 | .. |
| <i>tert</i> -butylamine | | |
| 0.0000 | 0.68671 | .. |
| 0.1005 | 0.69723 | - 0.916 |
| 0.1964 | 0.70819 | - 1.701 |
| 0.3071 | 0.72042 | - 2.145 |
| 0.3945 | 0.73096 | - 2.663 |
| 0.5009 | 0.74368 | - 2.872 |
| 0.5953 | 0.75440 | - 2.806 |
| 0.6919 | 0.76429 | - 2.478 |
| 0.7925 | 0.77303 | - 1.866 |
| 0.8956 | 0.78062 | - 1.051 |
| 1.0000 | 0.78744 | .. |

Table 2. Least square constants for the volume change on mixing of methanol-isomeric butylamine systems at 25° C

| System | A_1 | A_2 | A_3 | A_4 | Standard deviation |
|----------------------|----------|----------|---------|----------|----------------------|
| <i>n</i> -butylamine | -5.4595 | 2.7168 | 4.02403 | -1.2633 | 7.4×10^{-3} |
| iso-butylamine | -5.17186 | -0.97285 | 10.6007 | -4.4481 | 6.2×10^{-3} |
| sec.-butylamine | -7.2676 | 3.21171 | 6.25085 | -2.1758 | 5.5×10^{-3} |
| tert.-butylamine | -9.6780 | 5.4931 | 6.16391 | -1.94535 | 2.1×10^{-2} |

1963) showed that the complex formation between the *n*-butanol and *n*-butylamine is of 1 : 1 type. Considering the fact that the V^E versus x_1 curves of the present systems are symmetrical and the maxima are observed nearly at 0.5 mole fraction, it may be concluded that the complex formation in the present system is essentially 1 : 1 type.

The structure of butylamine has a considerable effect on the volume change on mixing. The magnitude of volume change on mixing increases in the following order



In the present systems one of the factors governing the volume change on mixing is the number of alcohol-amine complex molecules formed on mixing the two liquids. The number of associated species of broken and the complex species

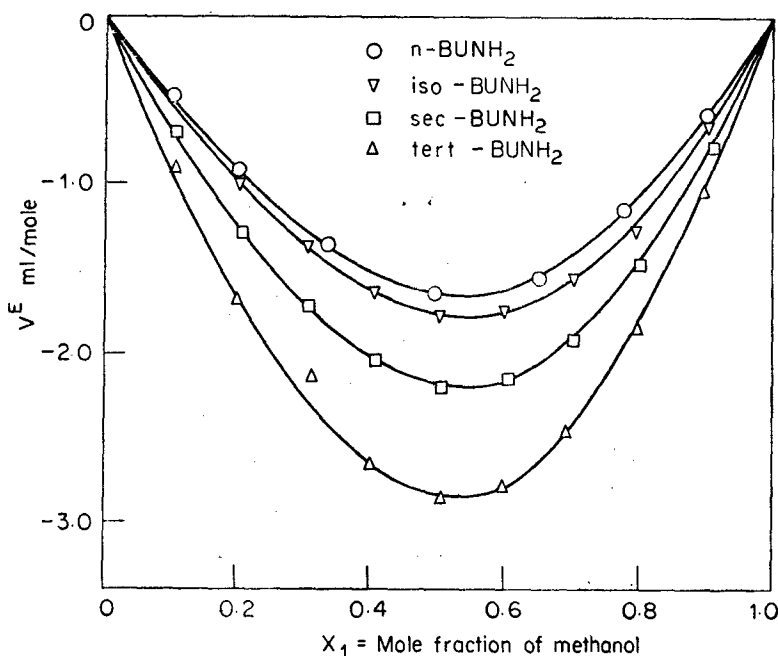
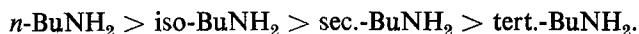


Figure 2. V^E versus x_1 plots for methanol (1)-isomeric butylamine (2) systems at 25° C,

Table 3. The partial molar excess volumes of methanol and butylamine isomers at 25° C.

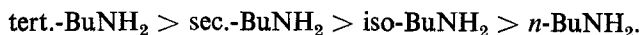
| System | \bar{V}^E ml/mole | |
|---------------------------------|---------------------|------------|
| | Methanol | Butylamine |
| Methanol + <i>n</i> -butylamine | - 4.6 | - 6.2 |
| Methanol + iso-butylamine | - 5.0 | - 6.5 |
| Methanol + sec.-butylamine | - 7.1 | - 8.4 |
| Methanol + tert.-butylamine | - 9.5 | - 10.9 |

formed would depend on the strength of self-association of butylamine as the second complex forming component, *viz.*, methanol is same for all the four systems. The strength of self-association of the four butylamine isomers has the following order (Pradhan and Mathur 1978) :



The magnitude of the volume change on mixing is therefore expected to increase in the reverse order.

The second term contributing the decrease in the volume on mixing is the cooperative accommodation of the molecules (Paraskevopoulos and Missen 1962). The densities of the pure isomers indicate that the cavities in the liquid structure of these isomers increase as



Consequently the geometric fitting of methanol in the liquid structure of amine and the negative volume change on the mixing would increase accordingly.

The values of the partial molar excess volumes of methanol and amine are obtained by extrapolating the V^E/x_1x_2 versus x_1 curves to zero concentrations are given in table 3. The partial molar excess volume of amine in methanol medium decreases from - 6.2 ml/mole to - 10.9 ml/mole as we go from normal to tertiary butylamine. Similarly the partial molar excess volume of methanol also decreases from - 4.6 ml/mole to - 9.5 ml/mole. It therefore seems that both the complex formation and the physical fitting of molecules in the liquid cluster contribute to the increase in the negative volume change on mixing as we go from normal to tertiary butylamine system.

Acknowledgement

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References

- Huyskens Th Zeegers and Huyskens P 1960 *Bull. Soc. Chim. Belg.* **69** 267
Huyskens Th Zeegers and Lambert L 1963 *J. Chem. Phys.* **60** 435
Paraskevopoulos G C and Missen R W 1962 *Trans. Faraday Soc.* **58** 869
Pradhan S D 1978 Ph.D. thesis, University of Bombay (submitted)
Pradhan S D and Mathur H B 1978 *Proc. Indian Acad. Sci.* **A87** 23
Scatchard G, Wood S E and Mochel J H 1939 *J. Am. Chem. Soc.* **61** 3206