

Short Communication

para-Nitrotoluene as a depolarizer for magnesium batteries

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Abstract

Magnesium cells have been fabricated using *p*-nitrotoluene (PNT) as a cathode depolarizer. The performance characteristics of 1V/3 A h cells have been investigated at various current densities and with different electrolytes. The cathodic efficiency of PNT is discussed in terms of the discharge behaviour. Cyclic voltammetry studies have demonstrated the irreversible nature of PNT.

Introduction

Recently, there has been considerable renewed interest in the development of magnesium-based batteries. This has arisen because of the high cost of the lithium-based counterparts [1, 2]. Magnesium batteries exhibit the advantage of providing service over a wide temperature range, i.e., from -40 to +60 °C. This is due to the inherent exothermic nature of magnesium corrosion during controlled rates of discharge.

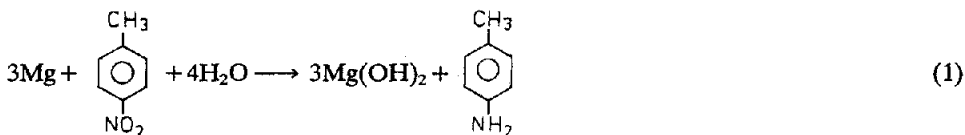
In military applications [3], costly magnesium-mercuric oxide batteries have been used. These have subsequently been replaced by systems that employ conventional inorganic depolarizers such as CuO, MnO₂, Ag₂O₃, etc. Nevertheless, these depolarizers have limited output capacity because, during reduction, they involve the transfer of only one or two electrons.

Several classes of organic compounds [4, 5] exhibit multi-electron transfer per molecule and, hence, are recommended for battery applications. Glicksman and Morehouse [6-8] have undertaken a comprehensive study of the different organic molecules and suggest the use of dinitro compounds for high energy-density batteries. These compounds can involve the transfer of as many as 12 electrons. In a recent study, Sivasamy *et al.* [9] reported a comparative examination of *m*-dinitrobenzene and substituted dinitrobenzenes and concluded that the maximum electron transfer that can be practically realized varies from 6 to 8. Endrey and Reilly [10] have investigated the reduction mechanism of aromatic nitro compounds and observed that *p*-nitrotoluene

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(PNT) exhibited the best performance at high current densities in 'C'-size dry cells using GABOT GP - 1478 black.

In view of the above observations, it is clearly of value to conduct a comprehensive examination of the much cheaper and less toxic PNT (6-electron transfer) compound as a possible depolarizer for magnesium reserve batteries. The basic reaction is:



In this paper, a report is given of the performance of PNT in magnesium batteries at different current densities and with different electrolytes, viz., 2 M solutions of magnesium chloride (MgCl_2), magnesium bromide (MgBr_2) and magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$).

Experimental

Chemicals

p-Nitrotoluene (BDH, UK), MgCl_2 , MgBr_2 (LOBA/Chemie, AR) and $\text{Mg}(\text{ClO}_4)_2$ (Merck, AR, Germany) were used.

Cell fabrication and discharge studies

Rectangular cathodes (6 cm × 4 cm) were employed. Copper mesh grid served as the current collector. The electrodes were prepared by pressing a cathode mix of 3 g PNT, 50% acetylene black and 3–5 ml of 2–3 wt.% binder (e.g., CMC, starch, etc.) on to the copper mesh at an optimized pressure. 2 M solutions of magnesium perchlorate, bromide or chloride were used as the electrolyte. The anodes consisted of magnesium alloy (AZ 31) sheets of dimensions: 6 cm × 4 cm × 1.5 mm.

In each cell, the cathode was coupled with two anodes. The separators were fabricated from cellophane sheet. The cells were discharged at constant current densities of 2.1, 4.2, 6.3 and 10.5 mA cm⁻² at 28 °C. Multiple experiments were performed and the reproducibility was within ±2%.

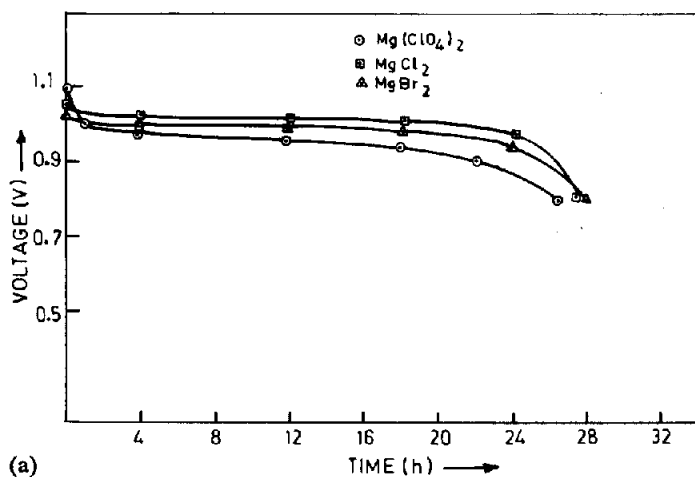
Cyclic voltammetry

Experimental solutions of PNT, prepared in small amounts of pure acetonitrile, were combined with the $\text{Mg}(\text{ClO}_4)_2$ supporting electrolyte to give the desired concentration. The PNT was reduced at a glassy-carbon electrode of area 0.07 cm². Nitrogen gas was bubbled through the solution. The gas was purified by passage through pyrogalol, concentrated sulfuric acid and distilled water. The measurements were made using a thermostat set at 28 °C ± 1 °C.

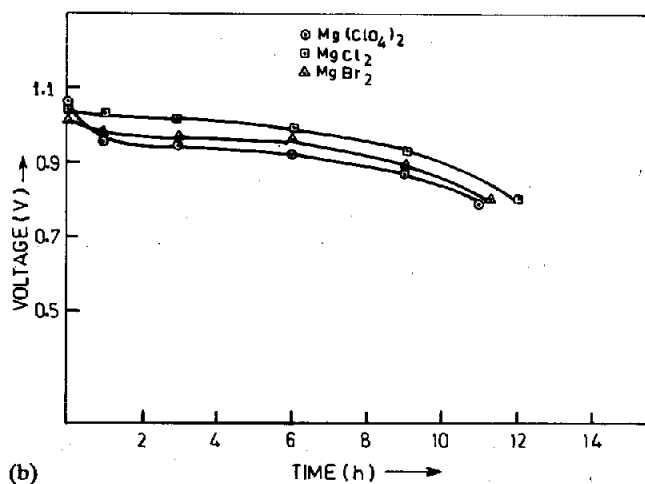
All experiments were performed with a BAS 100A electrochemical analyser (Bio Analytical System, USA) in conjunction with a digital plotter (DMF-40 series Houston Instrument Division). Voltammograms were recorded for the pure solvent, i.e., before the addition of electroactive species. All potentials were measured (and are reported) with respect to a Ag/AgCl reference electrode. A platinum wire served as the counter electrode. Cyclic voltammograms were obtained for concentrations in the range of 5 to 20 mM, sweep rates between 50 and 300 mV s⁻¹, and a potential range of -300 to -900 mV.

Results

Figures 1(a) to (d) show the discharge curves obtained for PNT/magnesium cells at different current densities and 30 °C with $\text{Mg}(\text{ClO}_4)_2$, MgBr_2 and MgCl_2 electrolyte solutions, respectively. The potential is high initially and then rapidly decays to a constant value (i.e., a plateau). The average operating voltages of the cells at various current densities and in different electrolytes are presented in Fig. 2. The internal resistance is highest in cells using MgBr_2 electrolyte, i.e., 0.48 Ω compared with 0.36 and 0.40 Ω for MgCl_2 and $\text{Mg}(\text{ClO}_4)_2$, respectively. This may be attributed to the fact that, in concentrated solutions ($> 1 \text{ M}$), the mobility of ions falls due to increases in the salt concentration and the free ions [11–13].



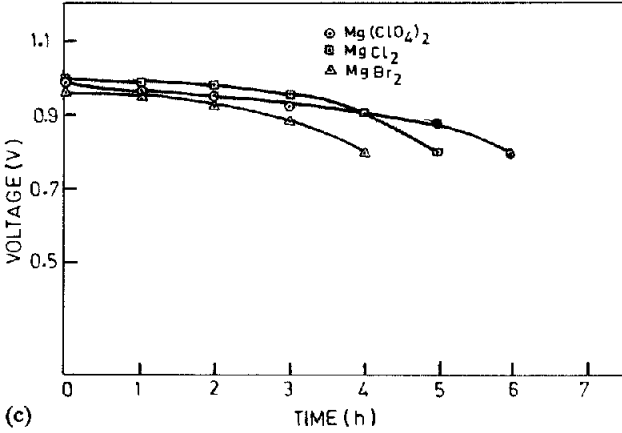
(a)



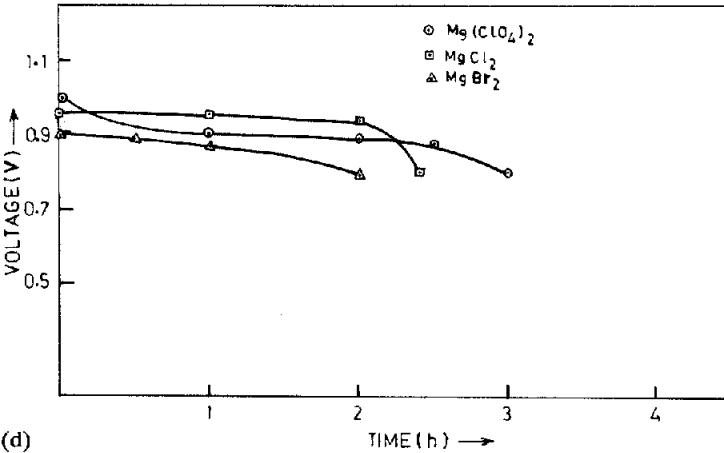
(b)

Fig. 1.

(continued)



(c)



(d)

Fig. 1. Discharge curve of Mg/PNT cells in different electrolytes at: (a) 2.1, (b) 4.2, (c) 6.3 and (d) 0.5 mA cm⁻².

Cyclic voltammetric studies (Table 1) of PNT reduction in Mg(ClO₄)₂ indicate only one wave. This shows that the reaction kinetics are irreversible.

Table 2 presents the capacity of the magnesium/PNT cells obtained at different current densities. At high current densities (>4.2 mA cm⁻²), the best performance is exhibited by cells using a Mg(ClO₄)₂ electrolyte.

Discussion

For discharge rates up to 4.3 mA cm⁻², the magnesium cells exhibited almost the same efficiency, irrespective of the chosen electrolyte. This is despite the fact that magnesium exhibits different corrosion rates in the respective electrolytes. By contrast,

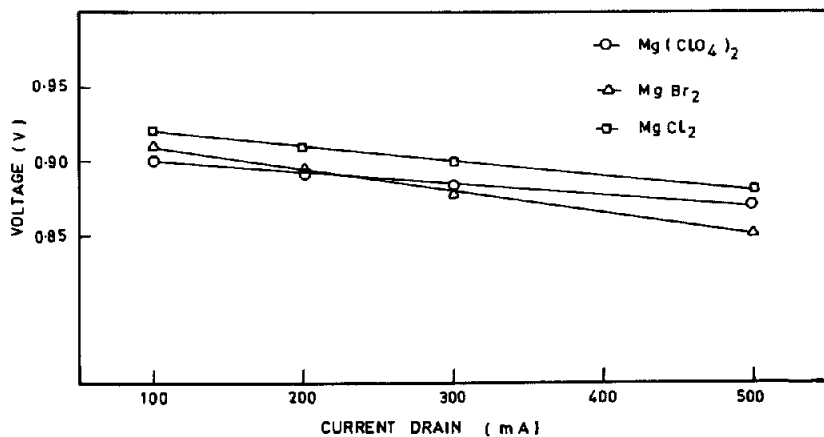


Fig. 2. Operating potentials of Mg/PNT cells at various current densities and electrolytes.

TABLE 1

Cyclic voltammetric data for reduction of PNT

| PNT concentration (mM) | Sweep rate (ν) (mV s ⁻¹) | $i_p \times 10^{-1}$ (mA) | $i_p/\nu^{1/2} \times 10^{-5}$ | $-E_p$ (mV) | $E_{p/2}$ (mV) | $E_p - E_{p/2}$ (mV) | $i_p/AC\nu^{1/2} \times 10^{-5}$ |
|------------------------|--|---------------------------|--------------------------------|-------------|----------------|----------------------|----------------------------------|
| 5 | 50 | 2.16 | 3.05 | 700 | 678 | 26 | 8.71 |
| | 100 | 3.03 | 3.03 | 708 | 680 | 28 | 8.66 |
| | 150 | 3.52 | 2.87 | 714 | 684 | 30 | 8.20 |
| | 200 | 4.13 | 2.92 | 721 | 688 | 33 | 8.34 |
| | 250 | 4.54 | 2.87 | 725 | 690 | 35 | 8.21 |
| | 300 | 4.91 | 2.83 | 730 | 692 | 38 | 8.10 |
| 10 | 50 | 4.64 | 6.56 | 698 | 670 | 28 | 9.37 |
| | 100 | 6.67 | 6.67 | 711 | 678 | 33 | 9.53 |
| | 150 | 8.07 | 6.59 | 720 | 682 | 38 | 9.42 |
| | 200 | 9.28 | 6.56 | 727 | 686 | 41 | 9.38 |
| | 250 | 10.37 | 6.56 | 732 | 688 | 44 | 9.37 |
| | 300 | 11.31 | 6.53 | 737 | 692 | 45 | 9.33 |
| 15 | 50 | 6.98 | 9.86 | 710 | 678 | 32 | 9.40 |
| | 100 | 9.65 | 9.65 | 723 | 682 | 41 | 9.19 |
| | 150 | 11.65 | 9.51 | 732 | 688 | 44 | 9.06 |
| | 200 | 13.35 | 9.44 | 738 | 690 | 48 | 8.99 |
| | 250 | 14.74 | 9.32 | 744 | 692 | 52 | 8.88 |
| | 300 | 16.00 | 9.24 | 749 | 696 | 53 | 8.80 |
| 20 | 50 | 9.36 | 13.23 | 714 | 682 | 32 | 9.45 |
| | 100 | 12.78 | 12.78 | 728 | 688 | 40 | 9.13 |
| | 150 | 15.38 | 12.56 | 738 | 694 | 44 | 8.97 |
| | 200 | 17.48 | 12.36 | 746 | 698 | 48 | 8.83 |
| | 250 | 19.18 | 12.13 | 752 | 700 | 52 | 8.66 |
| | 300 | 20.76 | 11.99 | 758 | 702 | 56 | 8.56 |

TABLE 2

Capacity ($A h g^{-1}$) of magnesium/PNT cells

| Electrolyte | Discharge current density ($mA cm^{-2}$) | | | |
|---------------|--|------|------|------|
| | 2.1 | 4.2 | 6.3 | 10.5 |
| $Mg(ClO_4)_2$ | 0.88 | 0.73 | 0.60 | 0.50 |
| $MgCl_2$ | 0.92 | 0.80 | 0.50 | 0.40 |
| $MgBr_2$ | 0.93 | 0.75 | 0.40 | 0.33 |

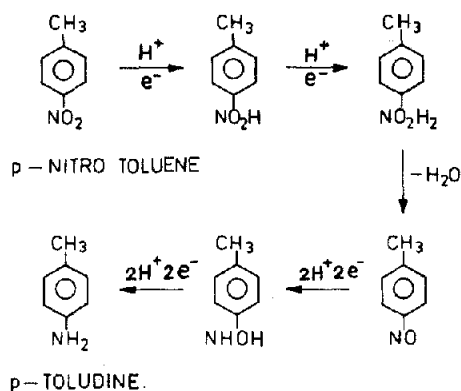


Fig. 3. Reduction mechanism of PNT.

at higher discharge rates, cells with $Mg(ClO_4)_2$ electrolyte exhibit marginally better capacity than those using either $MgCl_2$ or $MgBr_2$.

A comparison of the reduction efficiency of PNT with other nitro compounds suggests that the use of PNT yields similar battery performance and is capable of working even at higher current densities, i.e., up to $10.5 mA cm^{-2}$. Figure 3 illustrates the possible reduction mechanism for the conversion of PNT to *p*-toluidine. The *para*-position of the CH_3 group favours the reduction of the NO_2 group and, hence, enhances the capacity of the cells. Similar results were obtained in the case of 2,6-DNT [9]. The reduction efficiencies and the number of electrons transferred at different discharge rates and electrolytes are presented in Table 3. The complete reduction of nitro to the amino group involves 6 electrons and this, of course, corresponds to 100% efficiency. Hence, the experimental efficiency is proportional to the number of electrons transferred. It is interesting to note that, for current densities up to $4.2 mA cm^{-2}$, the number of electrons transferred is almost same (4 to 5) in the different electrolytes. At higher currents, however, $Mg(ClO_4)_2$ gives superior performance and the number of electrons transferred is much lower (≈ 3) thus indicating a more incomplete reduction of the nitro group. Similar behaviour was also observed in the case of dinitro compounds such as 2,4 DNT and 2,6 DNT [9].

Cyclic voltammetry studies were performed to gain information on the kinetics of the reduction of PNT. $Mg(ClO_4)_2$ was used as the supporting electrolyte because of its superior performance at high current densities. A well-defined cathodic peak is obtained but there is no evidence of an anodic peak. This indicates that the reduction

TABLE 3

Number of electrons transferred (n) and efficiency (%) for reduction of PNT

| Electrolyte | Current density (mA cm^{-2}) | | | | | | | |
|-----------------------------|---|----|-----|----|-----|----|------|----|
| | 2.1 | | 4.2 | | 6.3 | | 10.5 | |
| | n | % | n | % | n | % | n | % |
| $\text{Mg}(\text{ClO}_4)_2$ | 4.5 | 75 | 3.7 | 62 | 3.1 | 52 | 2.6 | 43 |
| MgCl_2 | 4.7 | 78 | 4.1 | 68 | 2.6 | 43 | 2.1 | 35 |
| MgBr_2 | 4.8 | 80 | 3.9 | 65 | 2.1 | 35 | 1.7 | 28 |

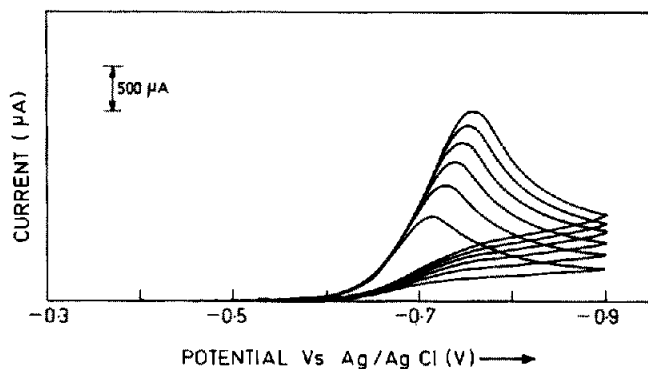


Fig. 4. Cyclic voltammogram of 20 mM PNT in 2 M magnesium perchlorate at various sweep rates.

process has an irreversible nature. A typical voltammogram is presented in Fig. 4. Table 1 summarizes the data obtained on the effect of PNT concentration (C) and sweep rate (ν) on the peak potential (E_p). With increasing sweep rate and concentration, the peak potential shifts to more negative potentials, thereby confirming the irreversible nature of PNT reduction.

A plot (Fig. 5) of peak current, i_p , versus $\nu^{1/2}$ exhibits a linear relationship. This behaviour suggests that the reduction of PNT is diffusion-controlled. Table 1 also presents the effect of PNT concentration (from 2.5 to 20 mM) at various sweep rates (50 to 300 mV s^{-1}). A plot of i_p versus C (Fig. 6) indicates a linear relationship. A constant value is observed for $E_p - E_{p/2}$ and $i_p/AC\nu^{1/2}$, within experimental error (A = area of the working electrode). These factors further confirm that the reduction of PNT proceeds by a diffusion-controlled process.

Conclusions

1. PNT is capable of operating at higher current densities in magnesium perchlorate electrolyte.

2. The cathodic efficiency of PNT is 70% at low current densities (2.1 mA cm^{-2}) and is 43% even when the current density is increased to 10.5 mA cm^{-2} .

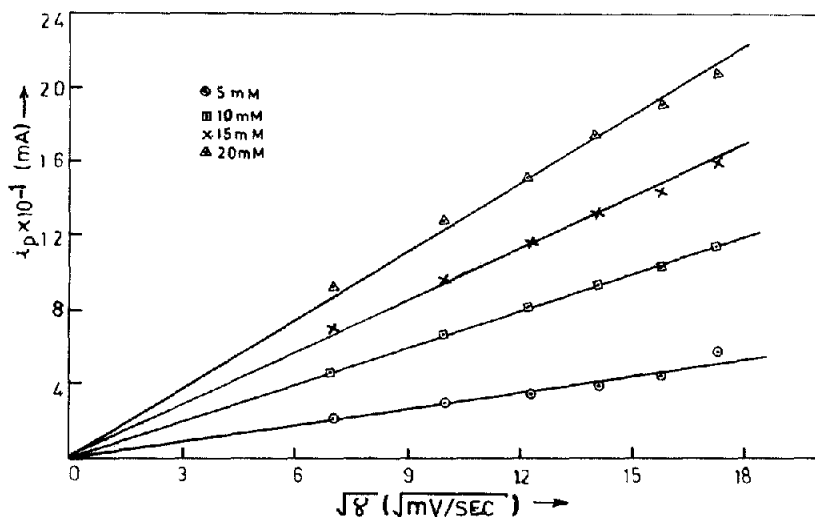


Fig. 5. Variation of peak current (i_p) with sweep rate ($v^{1/2}$).

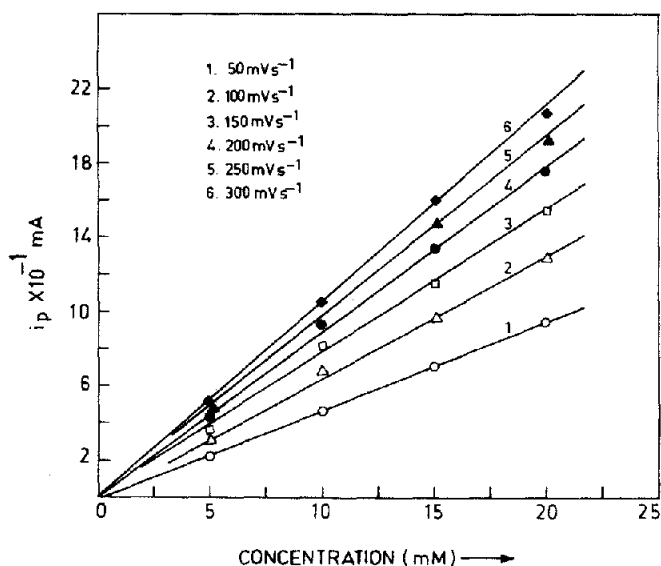


Fig. 6. Variation of peak current (i_p) with concentration of PNT.

3. The electrochemical reduction of PNT is both irreversible and diffusion-controlled.

Acknowledgement

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References

- 1 L. Jarvis, *J. Power Sources*, 32 (1990) 271.
- 2 T. D. Gregory, R. J. Hoffman and R. C. Winterton, *J. Electrochem. Soc.*, 137 (1990) 775.
- 3 A. J. Legath and D. B. Wood, *Proc. 23rd Annual Power Sources Conf., May, 1969*, p. 86.
- 4 R. Udhayan, N. Muniyandi and P. B. Mathur, *J. Power Sources*, 34 (1991) 303.
- 5 C. K. Morehouse and R. Glicksman, *J. Electrochem. Soc.*, 104 (1957) 467.
- 6 R. Glicksman and C. K. Morehouse, *J. Electrochem. Soc.*, 105 (1958) 613.
- 7 C. K. Morehouse and R. Glicksman, *J. Electrochem. Soc.*, 105 (1958) 306.
- 8 R. Glicksman and C. K. Morehouse, *J. Electrochem. Soc.*, 105 (1958) 299.
- 9 K. Sivasamy, S. Rajeswari and K. Dakshinamurthy, *J. Power Sources*, 25 (1989) 295.
- 10 A. L. Endrey and T. A. Reilly, *Proc. 22nd Ann. Power Sources Conf., May, 1968*, p. 91.
- 11 J. Barthel, *J. Pure Appl. Chem.*, 51 (1979) 2093.
- 12 G. Kumar, S. Vasudevan and N. Muniyandi, *J. Power Sources*, in press.
- 13 G. Kumar, Janakiraman, N. Namboodiri, Gangadharan, Saminathan, Kanagaraj and N. Sharief, *J. Chem. Eng. Data*, 36 (1991) 467.