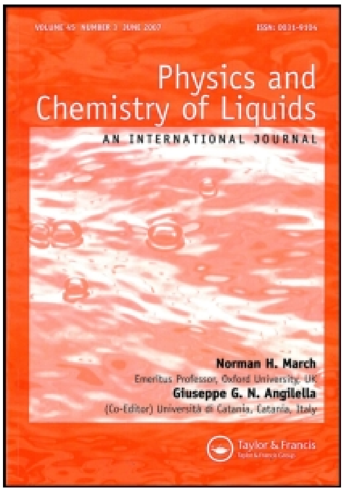

**Physics and Chemistry of Liquids**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

# Thermodynamic Properties of the Systems n-Butyl Acetate-Chloroethanes and Ethenes

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**To cite this Article** Gowrisankar, M. , Rambabu, K. , Venkateswarlu, P. and Raman, G. K.(1994) 'Thermodynamic Properties of the Systems n-Butyl Acetate-Chloroethanes and Ethenes', Physics and Chemistry of Liquids, 28: 1, 29 — 33
**To link to this Article: DOI:** 10.1080/00319109408029537
**URL:** http://dx.doi.org/10.1080/00319109408029537

*Phys. Chem. Liq.*, 1994, Vol. 28, pp. 29–33
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# THERMODYNAMIC PROPERTIES OF THE SYSTEMS n-BUTYL ACETATE-CHLOROETHANES AND ETHENES

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*(Received 13 October 1993)*

Excess volumes of non electrolyte solutions of n-butylacetate with 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloro ethane, 1,1,1-trichloro ethylene and 1,1,2,2-tetrachloro ethylene at 303.15 K by using a dilatometer are reported in this paper. Excess volumes exhibits inversion in sign in all the mixtures.

KEY WORDS: Excess volume, charge transfer.

## INTRODUCTION

A knowledge of excess volumes of mixtures is essential to understand the molecular interactions between unlike molecules, to develop new theoretical models, and also for engineering applications in the processing industry. Molecular interactions in binary mixtures of aceto nitrile with chlorinated aliphatic hydrocarbons have been investigated by a number of workers[1–3]. A literature survey shows that excess volumes for the systems of aromatic hydrocarbons with n-butylacetate have been reported previously[4,5]. However, no systematic attempt has been made to study the interactions in mixtures of n-butyl acetate with chlorinated ethanes and ethenes. That is why, in the present study excess volumes were measured for some industrially important systems (n-Butyl acetate with chlorinated ethanes and ethenes). This investigation is expected to throw light on the effect of successive chlorination and also unsaturation on $V^E$.

## EXPERIMENTAL

Excess volumes were measured directly by using the dilatometer described by Rao and Naidu[6]. The mixing cell contained the bulbs of different capacities which were connected through a $U$ tube with mercury to separate the two components. One end of the bulb was fitted with a capillary (1 mm i.d.), and the other end of the second bulb was fitted with a ground glass stopper. The excess volumes were accurate to

$\pm 0.003\,\text{cm}^3\,\text{mol}^{-1}$. Four dilato meters with different capacities were used to cover the entire molefraction range. The accuracy of the dilatometer was checked using the cyclohexane + benzene system at 298.15 K as a standard. The measured excess volumes for the standard system were in good agreement with values reported earlier in the literature[7].

All chlorinated ethanes and ethenes "proanalysis" grade supplied by Sarabhai Merck, Bombay and n-butylacetate supplied by BDH chemicals, England, were purified by the methods described by Weiss berger[8] and Riddick and Bunger[9]. The purities were checked by comparing measured densities with those reported in the literature[9,10]. Densities were determined using a bicapillary type pycnometer with an accuracy of 2 parts in $10^5$. The data are given in Table 1.

## RESULTS AND DISCUSSION

The experimental excess volumes for the binary mixtures of butyl acetate with chlorinated ethanes and ethenes at 303.15 K are presented in Table 2, and also graphically represented in Figures 1 and 2. The dependence of $V^E$ on composition may be expressed by an empirical equation of the form

$$V^E/Cm^3\,\text{mol}^{-1} = x_1x_2\,[a_0 + a_1(x_1 - x_2) + a_2(x_1 - x_2)^2] \tag{1}$$

Where $a_0, a_1$, and $a_2$ are adjustable parameters and $x_1$ is the molefraction of n-butylacetate. The values of parameters obtained by the least squares method are included in Table 3 along with the standard deviation $\sigma(V^E)$. The values of $\sigma(V^E)$ were obtained using the equation

$$\sigma(V^E) = \left[\frac{(V^E_{\text{exptl}} - V^E_{\text{Calcd}})^2}{n - P}\right]^{1/2} \tag{2}$$

Where '*n*' is the number of experimental data and *P* is the number of parameters. The presence of hydrogen bonding interaction may not be possible between butylacetate and chlorinated ethanes and ethenes as it was provided that the chlorinated ethanes have no active hydrogen. Butyl acetate being highly polar molecule enhanced the

**Table 1** Densities of pure components at 303.15 K.

| *Component* | *Density* ($\rho$)/g cm$^3$ mol$^{-1}$ | |
|---|---|---|
| | *Present work* | *Literature* |
| n-butyl acetate | 0.87132 | 0.87129 |
| 1,2-dichloroethane | 1.23828 | 1.23831 |
| 1,1,1-tri chloro ethane | 1.32092 | 1.32096 |
| 1,1,2,2-tetrachloro ethane | 1.57859 | 1.57860 |
| 1,1,1 trichloro ethylene | 1.45136 | 1.45140 |
| 1,1,2,2 tetra chloro ethylene | 1.60635 | 1.60640 |

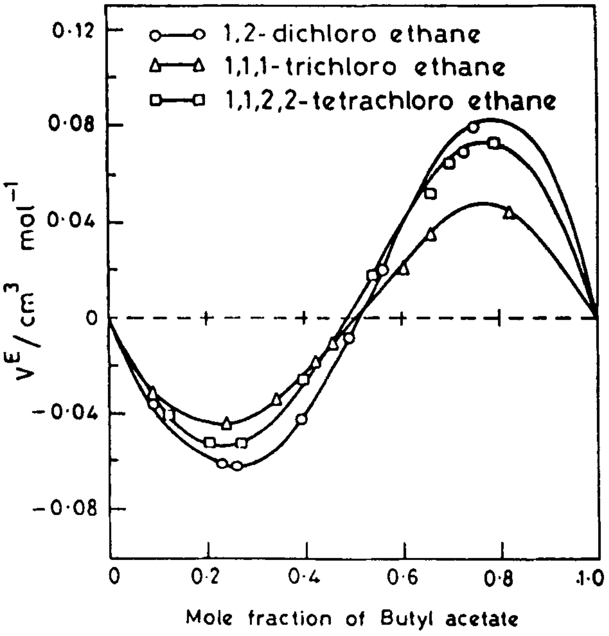

Figure 1

polarity of chlorinated ethanes. So one would expect more dipole–dipole and dipole-induced dipole interactions in the mixtures compared to the pure components. Butyl acetate being an electron donar and chlorinated ethanes being electron acceptors there is a possibility of forming charge transfer complexes between butyl

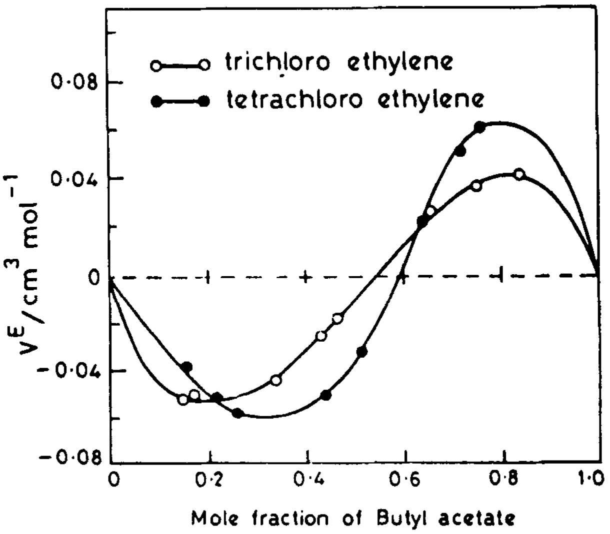

Figure 2

**Table 2** Excess volumes, $V^E$ (cm$^3$ mol$^{-1}$) of n-butyl acetate with chlorinated ethanes and ethenes at 303.15K ($x_1$ is molefraction of n-butyl acetate)

| $x_1$ | $V^E$ | $x_1$ | $V^E$ |
|---|---|---|---|
| n-butyl acetate + 1,2-dichloroethane | | n-butyl acetate + 1,1,2-trichloroethane | |
| 0.0852 | −0.035 | 0.0942 | −0.031 |
| 0.2251 | −0.061 | 0.2428 | −0.044 |
| 0.2563 | −0.063 | 0.3358 | −0.034 |
| 0.3854 | −0.042 | 0.4161 | −0.018 |
| 0.4899 | −0.008 | 0.4615 | −0.010 |
| 0.5589 | 0.020 | 0.5972 | 0.021 |
| 0.7260 | 0.070 | 0.6579 | 0.034 |
| 0.7540 | 0.080 | 0.8201 | 0.044 |
| n-butyl acetate + 1,1,2,2-tetrachloroethane | | n-butyl acetate + 1,1,1 trichloroethylene | |
| 0.1238 | −0.040 | 0.1516 | −0.052 |
| 0.1983 | −0.051 | 0.1682 | −0.050 |
| 0.2654 | −0.052 | 0.3358 | −0.044 |
| 0.3980 | −0.025 | 0.4284 | −0.025 |
| 0.5373 | 0.018 | 0.4575 | −0.018 |
| 0.6556 | 0.053 | 0.6579 | 0.025 |
| 0.7014 | 0.065 | 0.7523 | 0.035 |
| 0.7858 | 0.074 | 0.8421 | 0.041 |
| n-butyl acetate + 1,1,2,2 tetrachloroethylene | | | |
| 0.1550 | −0.037 | | |
| 0.2206 | −0.051 | | |
| 0.2583 | −0.057 | | |
| 0.4365 | −0.050 | | |
| 0.5059 | −0.031 | | |
| 0.6441 | −0.021 | | |
| 0.7167 | 0.051 | | |
| 0.7557 | 0.061 | | |

**Table 3** Values of the parameters $a_0, a_1$ and $a_2$ of the Eq. (1) and the standard deviation of $\sigma(V^E)$ at 303.15 K

| *System n-Butyl acetate +* | $a_0$ | $a_1$ | $a_2$ | $\sigma(V^E)$ |
|---|---|---|---|---|
| | | Cm$^3$ mol$^{-1}$ | | |
| 1,2-dichloro ethane | −0.0129 | 0.7649 | 0.2375 | 0.003 |
| 1,1,1-trichloroethane | 0.0050 | 0.5329 | 0.0162 | 0.006 |
| 1,1,2,2-tetrachloroethane | 0.0221 | 0.7200 | 0.1686 | 0.006 |
| 1,1,1-trichloroethylene | −0.0364 | 0.5191 | −0.011 | 0.004 |
| 1,1,2,2-tetrachloroethylene | −0.1401 | 0.5567 | 0.5907 | 0.006 |

acetate and chlorinated ethanes. These two factors may result in contraction in volume. The factors such as difference in size and shape, loss of dipolar association of Butyl acetate by the addition of chlorinated ethanes and ethenes and vice versa, may lead to expansion in volume. However the actual volume change depends on the relative strengths of two contributions. The experimental negative excess volumes suggest that the dipole–dipole interactions and charge transfer complexation between unlike molecules dominate the volume expansion factors. The existence of dipole–dipole interactions between butyl acetate and chlorinated ethanes and ethenes is further confirmed from the fact that the $V^E$ values becomes increasingly negative from 1,2 dichloro ethane and 1,1,2,2-tetra chloro ethane to tri chloro ethane and chlorinated ethenes. Through the size difference between butyl acetate to tri chloro ethane, chlorinated ethenes.

To discuss the excess volume data for mixtures of butyl acetate with chlorinated ethanes, factors such as (1) presence of double bond, (2) steric hindrance exhibited by chlorine atoms on ethylenic double bond and (3) partial saturation of electron with drawing ability of chlorine atoms due to the presence of $\pi$ electorns in the double bond are to be considered in addition to the contributions discussed earlier. The experimental $V^E$ values which are positive at higher concentrations of butyl acetate indicates that the volume expansion factors dominates in this range. The negative values at lower concentration may be due to the weak charge transfer complexation.

An inversion in sign of $V^E$ is observed in the system Butyl acetate, chlorinated ethane and ethene being positive above 0.6 mole fraction and negative at lower concentrations. The interaction between butyl acetate and chlorinated ethane is stronger compared to that of chlorinated ethene with the same number of chlorine atoms.

The observed excess volume is a resultant contribution of the two effects. The negative $V^E$ values indicate that the latter effect is dominant over the former effect in all the systems having negative excess volume.

## *Acknowledgements*

One of the authors Dr. Kantipudi Rambabu is grateful to the C.S.I.R. for the financial support in the form of Research Associateship.

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