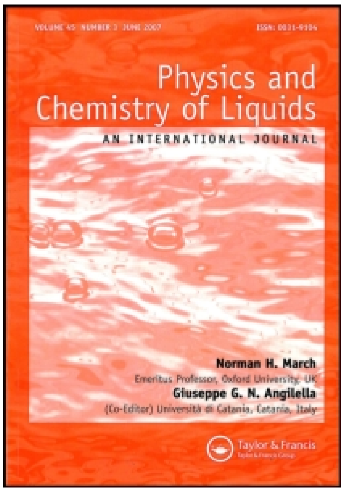

**Physics and Chemistry of Liquids**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

# Excess Volumes of Binary Mixtures of γ-Butyrolactone with Some Aliphatic and Isomeric Alcohols

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**To cite this Article** Rambabu, K. , Udayabhanu, S. , Venkateswarlu, P. and Raman, G. K.(1990) 'Excess Volumes of Binary Mixtures of γ-Butyrolactone with Some Aliphatic and Isomeric Alcohols', Physics and Chemistry of Liquids, 21: 2, 121 — 126

**To link to this Article: DOI:** 10.1080/00319109008028473

**URL:** http://dx.doi.org/10.1080/00319109008028473

*Phys. Chem. Liq.*, 1990, Vol. 21, pp. 121–126
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# EXCESS VOLUMES OF BINARY MIXTURES OF γ-BUTYROLACTONE WITH SOME ALIPHATIC AND ISOMERIC ALCOHOLS

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*(Received 7 July 1989)*

Excess volume data on mixing for binary mixtures of γ-Butyrolactone with propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, propan-2-ol, 2 methyl propan-1-ol, 3 methyl butan-1-ol, have been determined at 303.15 K. The $V^E$ values are negative over the whole range of composition in mixtures containing propan-1-ol, propan-2-ol, butan-1-ol, 2 methyl propan-1-ol, and 3 methyl butan-1-ol. In pentan-1-ol, however, $V^E$ is negative at lower molefractions and positive at higher molefractions, whereas in hexan-1-ol the value of $V^E$ are positive throughout the entire concentration range, which indicates significant interaction between γ-butyrolactone and the aliphatic and isomeric groups. These values are attributed to weak complex formation and predominating de-association of associated liquids by γ-butyrolactone. The results are ascribed to interactions between unlike molecules.

KEY WORDS: Polarizability, dipole interaction.

## 1 INTRODUCTION

In the chemical industry there exists a continuing need for reliable thermodynamic data of binary systems. This is particularly true for systems involved in industrial processes. A survey of the literature reveals that γ-butyrolactone is used in separation processes, yet there have been relatively few measurements on binary mixtures containing γ-butyrolactone. Acree, William *et al.*,[1] (1985) have utilised the thermodynamic data with γ-butyrolactone. Excess thermodynamic properties of liquid mixtures depend on molecular association, de-association, and complex formation. Alcohols are strongly self associated (Franks and Ives,[2] 1966, Battino, R.,[3] 1971), and binary solutions rich in alcohol a three-dimensional network of hydrogen bonded alcohol molecules is believed to be present (Prigogine and Defay,[4] 1953, Rowlinson,[5] 1969) (Dharamaraju, *et al.*,[6] 1983) have reported the excess volumes of acetonitrile with alcohols. However, no attempt has been made to study the interactions between γ-butyrolactone and propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, propan-2-ol, 2 methyl propan-1-ol, and 3 methyl butan-1-ol at 303.15 K. These mixtures have been selected to study the effect of chainlength and branched chains in the alcohols.

## 2 EXPERIMENTAL

The dilatometer used for measuring excess volumes in the present work is similar to that described by Rao and Naidu,[7] (1974). The mixing cell contains two bulbs of different capacities connected through a U-tube containing mercury to separate the two bulbs. One end of the bulb is closed with a ground glass stopper. Five dilatometers with different capacities were used to cover the entire composition range. The composition of each mixture was determined directly by weighing. The dilatometers were kept in a thermostat controlled to ± 0.01 K. The excess volumes were reproducible to $\pm 0.003\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$. The experimental method was previously checked (Stokes *et al.*,[8] 1970) for the test systems cyclohexane + benzene and the results obtained showed a standard deviation of $\pm 0.003\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$.

Analytical grade propan-1-ol, butan-1-ol, pentan-1-ol, hexan-1-ol, propan-2-ol, 2 methyl propan-1-ol, and 3 methyl butan-1-ol, were purified by fractional distillation. γ-butyrolactone, Fluka, AG 99% Gc pure was used without further purification. All the compounds were dried over activated molecular sieves. The purity of the chemicals were checked by comparing the densities and the boiling points of the components with those reported in the literature (Riddick and Bunger,[9] 1970). The densities were measured using a bicapillary Pycknometer which gave an accuracy of five parts in $10^5$. The boiling points were measured using a Swietoslawski-type ebulliometer which gave an accuracy of ± 0.2 K. The measured values are included in Table 1 along with literature values (Timmermans,[10] 1950, Riddick and Bunger,[9] 1970).

## 3 RESULTS AND DISCUSSION

These excess volume data at 303.15 K for the mixtures are listed in Table 2 and also graphically represented. The $V^E$ values are in Figure 1 fitted to an empirical equation of the form

$$V^E = x(1-x)[a_0 + a_1(2x-1) + a_2(2x-1)^2 \qquad (1)$$

**Table 1** Boiling points and densities of pure components at 303.15 K.

| *Compound* | *Boiling point (K)* | | *Density P (g cm$^{-3}$)* | |
|---|---|---|---|---|
| | *Experiment* | *Literature* | *Experiment* | *Literature* |
| γ-butyrolactone | 476.9 | 477.0 | 1.11730 | *1.12600 |
| Propan-1-ol | 370.2 | 370.3 | 0.79600 | 0.79567 |
| butan-1-ol | 390.7 | 390.8 | 0.80201 | 0.80206 |
| Pental-1-ol | 411.1 | 411.2 | 0.80760 | 0.80764 |
| Hexan-1-ol | 430.4 | 430.6 | 0.81204 | 0.80179 |
| Propan-2-ol | 355.5 | 355.6 | 0.76691 | 0.77690 |
| 2 methyl propan-1-ol | 381.1 | 381.1 | 0.79439 | 0.79439 |
| 3 methyl butan-1-ol | 403.7 | 403.6 | 0.80177 | 0.80179 |

*at 293.15 K

**Table 2** Excess volumes $V^E$ of $\gamma$-butyrolactone with some aliphatic and isomeric alcohols at 303.15 K.

| *Molefraction of $\gamma$-butyrolactone* | *($cm^3$ $V^E$ $mol^{-1}$)* | *Molefraction of $\gamma$-butyrolactone* | *($cm^3$ $V^E$ $mol^{-1}$)* |
|---|---|---|---|
| $\gamma$-butyrolactone + Propan-1-ol | | $\gamma$-butyrolactone + butan-1-ol | |
| 0.0991 | −0.070 | 0.1493 | −0.023 |
| 0.2361 | −0.114 | 0.2539 | −0.042 |
| 0.3239 | −0.129 | 0.3516 | −0.052 |
| 0.4916 | −0.120 | 0.4919 | −0.059 |
| 0.5165 | −0.115 | 0.5269 | −0.056 |
| 0.6729 | −0.097 | 0.5865 | −0.054 |
| 0.7532 | −0.080 | 0.7248 | −0.042 |
| 0.8698 | −0.055 | 0.8843 | −0.020 |
| $\gamma$-butyrolactone + Pentan-1-ol | | $\gamma$-butyrolactone + hexan-1-ol | |
| 0.1479 | −0.005 | 0.1987 | 0.070 |
| 0.2245 | −0.006 | 0.2337 | 0.081 |
| 0.3091 | −0.009 | 0.3088 | 0.082 |
| 0.4234 | −0.007 | 0.4439 | 0.086 |
| 0.5234 | 0.002 | 0.5776 | 0.085 |
| 0.6549 | 0.019 | 0.6831 | 0.084 |
| 0.7727 | 0.034 | 0.7847 | 0.078 |
| 0.9134 | 0.031 | 0.8845 | 0.060 |
| $\gamma$-butyrolactone + Propan-2-ol | | $\gamma$-butyrolactone + 2 methyl propan-1-ol | |
| 0.1304 | −0.085 | 0.1404 | −0.054 |
| 0.2194 | −0.134 | 0.2443 | −0.080 |
| 0.3228 | −0.172 | 0.3724 | −0.100 |
| 0.4616 | −0.192 | 0.5671 | −0.096 |
| 0.5845 | −0.174 | 0.6153 | −0.089 |
| 0.6736 | −0.146 | 0.7127 | −0.076 |
| 0.8183 | −0.080 | 0.7940 | −0.056 |
| 0.9176 | −0.033 | 0.9044 | −0.025 |
| $\gamma$-butyrolactone + 3 methyl butan-1-ol | | | |
| 0.2122 | −0.072 | | |
| 0.3398 | −0.097 | | |
| 0.3711 | −0.100 | | |
| 0.4066 | −0.102 | | |
| 0.5954 | −0.093 | | |
| 0.7642 | −0.059 | | |
| 0.8396 | −0.042 | | |
| 0.9156 | −0.020 | | |

where $x$ is the molefraction of $\gamma$-butyrolactone. The values of the coefficients $a_0$, $a_1$, and $a_2$ obtained by the least squares method, are included in Table 3 along with the standard deviation $\sigma$ ($V^E$). The data included in Table 2 show that the $V^E$ values are negative in mixtures of $\gamma$-butyrolactone with propan-1-ol, butan-1-ol over the entire composition range, while in pentan-1-ol it is sigmoid and in hexan-1-ol it is positive over the entire composition range. These results indicate that as the chainlength increases the interaction between aliphatic alcohols and $\gamma$-butyrolactone is showing positive $V^E$ at higher alcohols and while negative at lower alcohols.

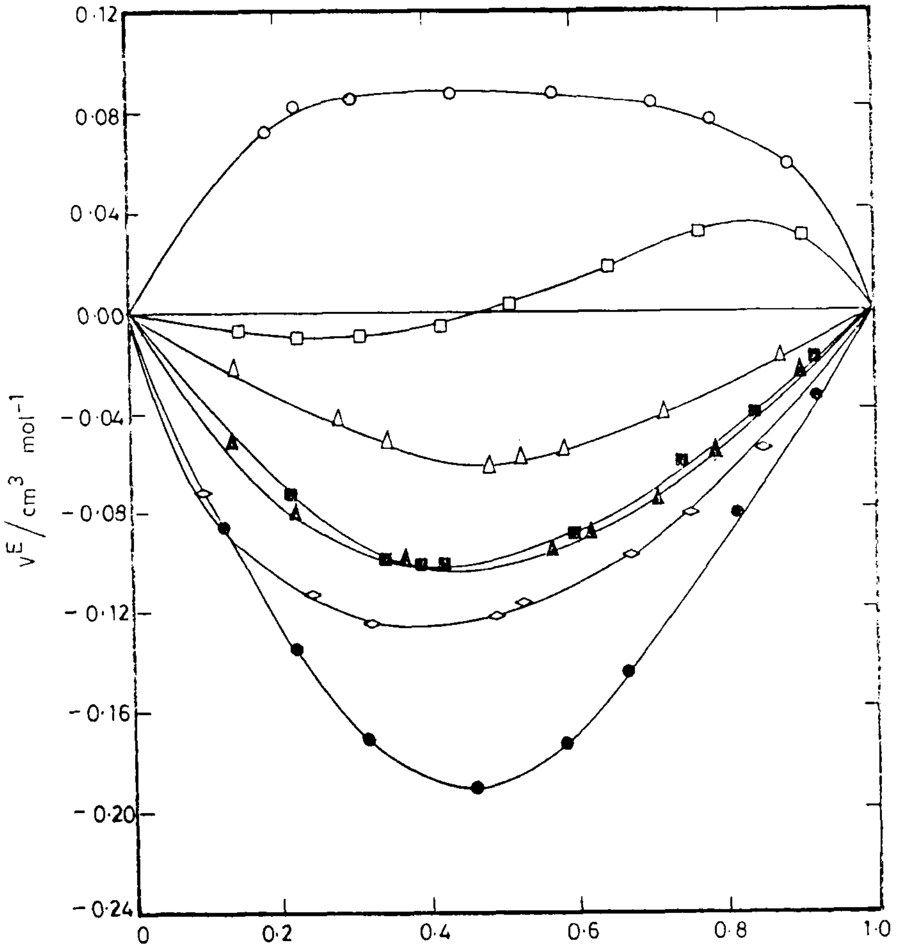

**Figure 1** Mole fraction of γ-butyrolactone ($x_1$); ◇ Propan-1-ol; ● Propan-2-ol; ▲ 2 methyl propan-1-ol; △ butan-1-ol; □ Pentan-1-ol; ■ 3 methyl butan-1-ol; ○ hexan-1-ol.

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

| *System* *γ-butyrolactone* | $a_0$ ($cm^3\ mol^{-1}$) | $a_1$ ($cm^3\ mol^{-1}$) | $a_2$ ($cm^3\ mol^{-1}$) | $\sigma(V^E)$ |
|---|---|---|---|---|
| Propan-1-ol | −0.473 | 0.185 | −0.256 | ±0.003 |
| butan-1-ol | −0.230 | −0.004 | 0.073 | ±0.002 |
| Pentan-1-ol | −0.005 | 0.230 | 0.287 | ±0.002 |
| Hexan-1-ol | 0.337 | 0.022 | 0.377 | ±0.003 |
| Propan-2-ol | −0.756 | 0.179 | 0.249 | ±0.001 |
| 2 methyl propan-1-ol | −0.408 | 0.090 | 0.058 | ±0.002 |
| 2 methyl butan-1-ol | −0.410 | 0.094 | 0.097 | ±0.001 |

But, whereas in Isomeric alcohols it is negative over the entire composition range. The excess volumes are possibly influenced by two effects.

1) Expansion in volume because of the loss of dipolar association, difference in size and shape of the component molecules,

2) Contraction in volume because of dipole-dipole, dipole-induced dipole and electron donar-acceptor interactions. The actual value of $V^E$ would depend upon the relative strength of the two apposing effects. The observed values of $V^E$ may be explained qualitatively by postulating the following factors.

i) deploymerisation of alcohols by the addition of $\gamma$-butyrolactone and

ii) Specific and non specific interactions between monomers of alcohol and $\gamma$-butyrolactone. The first factor produces an increase in volume whereas the second factor contributes to decrease in volume. The observed $V^E$ data suggest that the contributions due to factor (i) as dominant at high molefractions of $\gamma$-butyrolactone and the contributions due to factor (ii) became dominant at low molefractions. The decrease in negative values of $V^E$ (at $x = 0.4$) with increase in chainlength of alcohol (except propan-1-ol, pentan-1-ol) suggest that the effect of interaction decreases with increasing chainlength. The higher negative values of $V^E$ for propan-2-ol, 2 methyl propan-1-ol, and 3 methyl butan-1-ol than propan-1-ol, butan-1-ol and pentan-1-ol may be due to steric hinderance of branching alkyl groups. The compact structures of Isomeric alcohols might be responsible for higher negative values than aliphatic alcohols. Therefore it is concluded that Isomeric alcohols interacts more strongly than Aliphatic alcohols. This is due to basis of steric and Electromeric effects. In the case of the system containing Isomeric alcohols, $V^E$ falls in the order,

Propan-2-ol > 3 methyl butan-1-ol > 2 methyl propan-1-ol

This trend may be explained on the basis of steric and electromeric effects. When the alkyl groups of the alcohols becomes more and more branched, the effect of interaction is more and more sterically tindered and the negative $V^E$ values should be in the order. Propan-2-ol > 2 methyl propan-1-ol > 3 methyl butan-1-ol. But in contrast the observed $V^E$ values suggest the stronger interaction in the system $\gamma$-butyrolactone + 2 methyl propan-1-ol than that containing 3 methyl butan-1-ol. This may be due to the electromeric effect predominating over the steric effect in the system, $\gamma$-butyrolactone + 2 methyl propan-1-ol

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