

**EXCESS VOLUME OF MIXTURES OF OXAALKANES AND BRANCHED ALKANES**

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*Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.*

Equimolar values of the excess volume,  $V^E$ , have been obtained at 25 °C for a series of oxaalkanes, 2,5-dioxahexane, 2,5,8-trioxanonane, 2,5,8,11-tetraoxadodecane, and 2,5,8,11,14-pentaoxapentadecane, mixed with a series of highly-branched alkanes: 2,2-dimethylbutane, 2,2,4-trimethylpentane, 2,2,4,6,6-pentamethylheptane, and 2,2,4,4,6,8,8-heptamethylnonane. The Prigogine-Flory thermodynamic theory predicts the large variations of  $V^E$  with the chain-lengths of the molecules in the two series.

Much insight has been gained into the thermodynamics of non-electrolyte mixtures through the study of systems involving homologous series, for instance the normal alkanes. In particular, the excess Gibbs energy,  $G^E$ , excess enthalpy,  $H^E$ , excess volume,  $V^E$ , and excess heat capacity,  $C_P^E$  have been obtained for the normal alkanes mixed with the series of glymes, i.e., 2,5-dioxahexane or monoglyme ( $G_1$ ), 2,5,8-trioxanonane or diglyme ( $G_2$ ), 2,5,8,11-tetraoxadodecane or triglyme ( $G_3$ ) and 2,5,8,11,14-pentaoxapentadecane or tetraglyme ( $G_4$ ). Reference<sup>1</sup> gives references for much of this work and also gives a group contribution interpretation. We present here equimolar  $V^E$  data for the glymes with a series of highly-branched alkane isomers: 2,2-dimethylbutane (br- $C_6$ ), 2,2,4-trimethylpentane (br- $C_8$ ), 2,2,4,6,6-pentamethylheptane (br- $C_{12}$ ), and 2,2,4,4,6,8,8-heptamethylnonane (br- $C_{16}$ ).

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Interpretation is made through the Prigogine–Flory theory<sup>2,3</sup> (PF). This, and similar theories, associate the excess thermodynamic quantities with differences between the component liquids in: first, their molecular “chemical natures” and, second, their free volumes. The first difference expresses itself as an “antipathy” between the components and appears in all excess functions as the  $X_{12}$  contribution. Members of a series have similar chemical nature, as for the glymes where one-third of the chain-atoms are oxygens and for the branched alkanes which are essentially globular molecules covered with methyl groups. Hence the  $X_{12}$  contribution should be roughly equal for all the glyme + alkane systems, except for small changes due to changing molecular size. The free volume of a liquid is expressed by the reduced volume,  $\tilde{V}$ , which is obtained directly from the thermal expansion coefficient,  $\alpha$ , and the temperature. The free volume difference,  $(\tilde{V}_1 - \tilde{V}_2)$ , gives a single contribution in  $H^E$  and the excess entropy,  $S^E$ , but two contributions<sup>4,5</sup> to  $V^E$ . These are the  $\tilde{V}(T)$  curvature term proportional to  $(\tilde{V}_1 - \tilde{V}_2)^2$  and the  $P^*$  term, proportional to  $(P_1^* - P_2^*)(\tilde{V}_1 - \tilde{V}_2)$ . Here the reduction parameter for pressure,  $P^*$ , is the cohesive energy density of the liquid at 0 K. It is obtainable from  $\alpha$ ,  $T$  and the isothermal compressibility,  $\kappa_T$ . Thus,  $V^E$  is more complex than  $H^E$  and  $S^E$ .

## EXPERIMENTAL

The glymes and branched alkanes were obtained at 99% purity from Aldrich Chemical Co. and Wiley Organics. They were used without further purification except for drying. Values of  $V^E$  were obtained at 25 °C using a vibrating densitometer (Sodev, Sherbrooke QC, Canada). Although  $V^E$  was obtained as a function of composition, only equimolar values will be considered here. Accuracy should be to within 0.01 cm<sup>3</sup> mol<sup>-1</sup>. Equimolar  $H^E$  values are required to calculate the  $X_{12}$  parameter of the systems for the PF predictions. These were obtained at 30 °C with the Setaram C-80 Calorimeter. Preliminary measurements indicate that  $C_P^E$  for the  $G_m + \text{br-}C_n$  systems are smaller than for the  $G_m + \text{n-}C_n$  systems. Thus,  $H^E$  data at 30 °C should not differ from the required 25 °C data by more than 1%, which corresponds to the estimated experimental accuracy. The 30 °C data were used for predictions at 25 °C.

## RESULTS AND DISCUSSION

### *Parameters for Theory*

The pure component parameters used in the PF predictions are listed in Table I. The data for the branched-alkane series and for  $G_1$  to  $G_3$  are from literature sources as indicated. For  $G_4$  we have used a recent determination<sup>6</sup> of the isothermal compressibility at 20 °C. The density data of ref.<sup>7</sup> gives  $\alpha$  at 20 °C and hence a value of  $P^*$  at 20 °C, taken to be the same at 25 °C. The present value seems more reasonable than that in ref.<sup>7</sup> which was based on an estimate<sup>8</sup> for the compressibility of  $G_4$ . Newer values of  $\alpha$  and  $P^*$  for the br- $C_n$  are available<sup>9</sup>, but they are very close to those in Table I and they make a negligible difference in the predictions. Values of  $s$ , the molecular surface/volume

TABLE I  
Parameters of the pure components at 25 °C

| Compound                        | $10^3\alpha$ , K <sup>-1</sup> | $P^*$ , J cm <sup>-3</sup> | $\rho$ , g cm <sup>-3</sup> | $s$ , Å <sup>-1</sup> |
|---------------------------------|--------------------------------|----------------------------|-----------------------------|-----------------------|
| G <sub>1</sub>                  | 1.268 <sup>a</sup>             | 573 <sup>a</sup>           | 0.86182 <sup>a</sup>        | 1.132 <sup>b</sup>    |
| G <sub>2</sub>                  | 1.060 <sup>a</sup>             | 611 <sup>a</sup>           | 0.93878 <sup>a</sup>        | 1.063 <sup>b</sup>    |
| G <sub>3</sub>                  | 0.965 <sup>a</sup>             | 626 <sup>a</sup>           | 0.98080 <sup>a</sup>        | 1.023 <sup>b</sup>    |
| G <sub>4</sub>                  | 0.921 <sup>a</sup>             | 641 <sup>c</sup>           | 1.00570 <sup>a</sup>        | 1.000 <sup>b</sup>    |
| br-C <sub>6</sub> <sup>d</sup>  | 1.458                          | 379                        | 0.6446                      | 0.88                  |
| br-C <sub>8</sub> <sup>d</sup>  | 1.21                           | 387 <sup>e</sup>           | 0.6878                      | 0.81                  |
| br-C <sub>12</sub> <sup>d</sup> | 0.969                          | 393                        | 0.7454                      | 0.82                  |
| br-C <sub>16</sub> <sup>d</sup> | 0.855                          | 399                        | 0.7813                      | 0.77                  |

<sup>a</sup> Ref.<sup>7</sup>. <sup>b</sup> Ref.<sup>10</sup>. <sup>c</sup> See text. <sup>d</sup> Ref.<sup>15</sup>. <sup>e</sup> Recalculated from ref.<sup>16</sup>. (Value of 370 J cm<sup>-3</sup> in ref.<sup>15</sup> appears incorrect.)

TABLE II  
Data on the glyme + branched alkane mixtures

| System                             | $H^E(x = 0.5)$ , J mol <sup>-1</sup> | $X_{12}$ , J cm <sup>-3</sup> | $10^8 X_{12}/s_1$ , J cm <sup>-2</sup> | $V^E(\text{exp})$ , cm <sup>3</sup> mol <sup>-1</sup> |
|------------------------------------|--------------------------------------|-------------------------------|--|---|
| G <sub>1</sub> + br-C <sub>6</sub> | 1 110                                | 52.9                          | 46.7                                   | 0.63  |
| + br-C <sub>8</sub>                | 1 240                                | 54.7                          | 48.3                                   | 0.90  |
| + br-C <sub>12</sub>               | 1 320                                | 50.9                          | 45.0                                   | 1.07  |
| + br-C <sub>16</sub>               | 1 330                                | 49.4                          | 43.6                                   | 1.09  |
| G <sub>2</sub> + br-C <sub>6</sub> | 1 320                                | 53.5                          | 50.3                                   | 0.14  |
| + br-C <sub>8</sub>                | 1 500                                | 54.5                          | 51.2                                   | 0.64  |
| + br-C <sub>12</sub>               | 1 770                                | 53.9                          | 50.7                                   | 1.06  |
| + br-C <sub>16</sub>               | 1 810                                | 51.2                          | 48.2                                   | 1.24  |
| G <sub>3</sub> + br-C <sub>6</sub> | 1 570                                | 57.0                          | 55.7                                   | 0.19  |
| + br-C <sub>8</sub>                | 1 750                                | 56.4                          | 55.1                                   | 0.50  |
| + br-C <sub>12</sub>               | 1 990                                | 52.2                          | 51.0                                   | 1.07  |
| + br-C <sub>16</sub>               | 2 100                                | 50.2                          | 49.1                                   | 1.37  |
| G <sub>4</sub> + br-C <sub>6</sub> | 1 720                                | 58.0                          | 58.0                                   | 0.34  |
| + br-C <sub>8</sub>                | 1 950                                | 57.6                          | 57.6                                   | 0.40  |
| + br-C <sub>12</sub>               | 2 380                                | 56.2                          | 56.2                                   | 1.00  |
| + br-C <sub>16</sub>               | –                                    | –                             | 57.3                                   | –   |

ratio, may be obtained from the surface ( $q$ ) and volume ( $r$ ) parameters for the glymes<sup>10</sup>. These are calculated from Bondi group contributions which are convenient but which may overestimate surface area. Different values<sup>11</sup> of the same parameters were obtained using geometric considerations based on crystallographic data and molecular models, which was the method used in the literature for the branched-alkane parameters. These values are listed in Table I. We have, however, used both sets of  $s$  values in order to calculate  $X_{12}$  from the equimolar  $H^E$ . The predicted equimolar  $V^E$  are, in fact, independent of the  $s$  values. This follows from the free volume contributions to  $V^E$  being independent of  $s$ . The equimolar contribution to  $V^E$  is fitted to  $H^E$  and therefore is also independent of  $s$ , which affects only the skewing of the composition dependence of the  $X_{12}$  contribution.

### Excess Enthalpies

Table II shows values of  $H^E$  (equimolar mixture,  $x = 0.5$ ) which are positive and large for all the systems. Table I also shows  $X_{12}$  and  $X_{12}/s_1$  values derived from  $H^E$  using the PF theory and the  $s$  values of Table I. Somewhat different values of  $X_{12}$  and  $X_{12}/s_1$  are found using  $s$  values of ref.<sup>10</sup>. In principle,  $X_{12}/s_1$  is the parameter indicating most closely the difference of chemical natures of the component molecules. Assuming the  $\text{CH}_2$  groups of the  $G_m$  and the  $\text{CH}_3$  groups of the br- $C_n$  to be similar,  $X_{12}/s_1$  should be proportional to  $\alpha_0^2$ , where  $\alpha_0$  is the fraction of the glyme surface which is of oxygen character. Due to the effect of the  $\text{CH}_3$  ends of the  $G_m$  molecules,  $\alpha_0$  increases<sup>10,11</sup> with chain-length. Using  $\alpha_0$  values from ref.<sup>11</sup> gives  $X_{12}/s_1 \alpha_0^2$  decreasing with increasing glyme chain-length.  $\alpha_0$  values from ref.<sup>10</sup> give a much more constant value of  $X_{12}/s_1 \alpha_0^2$ , and hence from this point of view the Bondi parameters are superior.

It also seems that  $X_{12}$  or  $X_{12}/s_1$  decreases as the size of the br- $C_n$  molecule increases within a set of systems for any one glyme, and particularly for  $G_3$  and  $G_4$ . Such an effect is not predicted by the theory, but is consistent with non-random mixing of the component for large  $m$  and  $n$ , as these systems are not far from phase separation. Similar effects at large  $m$  and  $n$  are a feature of glyme + n-alkane systems and have been discussed in ref.<sup>1</sup>. Non-randomness or concentration fluctuations are also the cause of the "W-shape" composition dependence of  $C_P^E$  found<sup>10</sup> in the glyme + n-alkane systems. This effect seems to be a possibility here.

### Excess Volumes

A much larger variation amongst the systems is found for  $V^E$  than for  $H^E$ , as seen in Table II and Fig. 1. For a single glyme,  $V^E$  increases with br- $C_n$  carbon number. Thus,  $V^E$  is negative for  $G_3$  and  $G_4$  + br- $C_6$  but increases to 1.3 for  $G_3$  + br- $C_{16}$  and 1.0  $\text{cm}^3 \text{mol}^{-1}$  for  $G_4$  + br- $C_{12}$ ,  $G_4$  + br- $C_{16}$  being phase-separated at 25 °C. This increase is typical of  $V^E$  for a molecule of high  $P^*$  value mixed with a series of either normal<sup>5</sup> or branched<sup>12</sup>

$C_n$ , and Fig. 1 shows that it is predicted by PF theory. However, with increasing  $n$ , the predicted  $V^E$  rise considerably above the experimental. This is a trend which has been found<sup>12</sup> with cyclohexane + br- $C_n$ . Heintz<sup>13</sup> suggests that it may indicate a packing

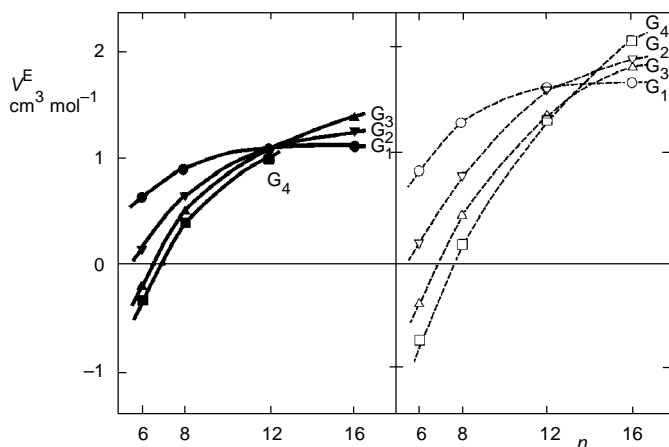


FIG. 1

Experimental (left-hand) and predicted (right-hand)  $V^E$  values for the indicated glymes mixed with branched alkanes, plotted against alkane carbon number. The prediction for  $G_4 + \text{br-}C_{16}$  (which is phase-separated) is made with an average  $X_{12}$  value for  $G_4$  systems

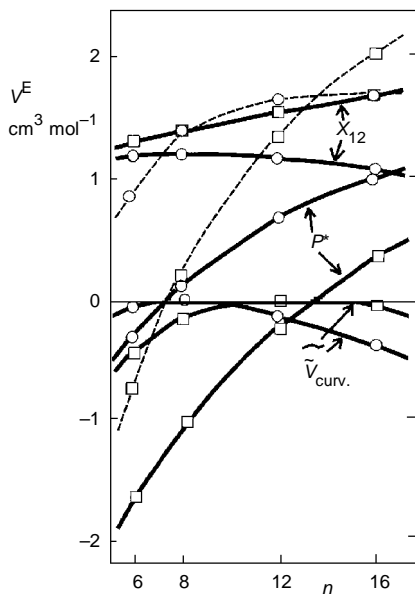


FIG. 2

The  $X_{12}$ ,  $\tilde{V}$  curvature, and  $P^*$  contributions for  $G_1 + \text{br-}C_n$  (O) and  $G_4 + \text{br-}C_n$  (□) plotted as full curves against alkane carbon number. The total  $V^E$  for the two systems indicated as dashed curves

effect where the large globular br-C<sub>n</sub> molecules leave interstitial spaces in the liquid into which the small cyclohexane molecules may enter. Perhaps the same may occur here with the small-diameter glyme chains entering these spaces. Preliminary PF predictions for glyme + n-alkane systems show substantially better agreement with experiment, indicating that the shape of the branched-alkane molecules may have something to do with the poorer predictions.

Figure 1 shows a complex behaviour of  $V^E$  for a single br-C<sub>n</sub> and increasing glyme chain-length. Thus, the  $V^E$  decrease with  $m$  for br-C<sub>6</sub> but increase with  $m$  for br-C<sub>16</sub> with a cross-over at br-C<sub>12</sub>. The order is predicted well for br-C<sub>6</sub> but imperfectly at br-C<sub>16</sub>. Nevertheless, as usual, PF predicts the main trends of the  $V^E$  data.

Figure 2 shows the origin of the  $V^E$  predictions in the three contributions to  $V^E$ . These are plotted against carbon number of the branched alkane for G<sub>1</sub> and G<sub>4</sub> systems, the other systems being intermediate. It is seen that the  $X_{12}$  contribution varies little between G<sub>1</sub> and G<sub>4</sub> or with carbon number, thus directly reflecting the  $H^E$  values where the  $X_{12}$  contribution over-shadows the free volume contribution. The physical origin of the  $X_{12}$  term lies in the "antipathy" between the components which increases the free volume, and hence volume, of the mixture relative to the pure components.

The negative  $\tilde{V}(T)$  curvature term is small for both sets of systems, becoming zero when  $\tilde{V}_1 = \tilde{V}_2$  or  $\alpha_1 = \alpha_2$ , i.e. at  $m \approx 7$  for G<sub>3</sub> systems and  $m \approx 13$  for G<sub>4</sub> systems. Its physical origin is discussed in refs<sup>4,5</sup>.

The remaining  $P^*$  term explains the large variation of  $V^E$  amongst the systems. This term is proportional to  $(P_1^* - P_2^*)(\tilde{V}_1 - \tilde{V}_2)$  with the quantity  $(P_1^* - P_2^*) \approx 200 \text{ J cm}^{-3}$  for the systems. The  $P^*$  term therefore varies as  $\tilde{V}_1 - \tilde{V}_2$ . As seen in Fig. 2 it crosses from negative to positive at  $m \approx 7$  and  $m \approx 13$  for the G<sub>1</sub> and G<sub>4</sub> systems, respectively. Due to the importance of this term in the total,  $V^E$  is smaller for the G<sub>4</sub> systems than for G<sub>1</sub> for almost all br-C<sub>n</sub>. The physical origin of this term lies in the liquid free volume depending on intermolecular cohesion (as well as temperature). In the PF theory, the mixture is equated to a single liquid whose intermolecular cohesion reflects the concentration of each of the components weighted by their cohesions. Since the glymes interact more strongly than the branched alkanes ( $P_1^* > P_2^*$ ), the solution will preferentially reflect the glyme concentration and the glyme free volume. Thus, if  $\tilde{V}_1 > \tilde{V}_2$ , the free volume of the mixture will be greater than the average of the pure components, and  $V^E$  is positive. If  $\tilde{V}_1 < \tilde{V}_2$ ,  $V^E$  will be negative, as observed in the  $P^*$  contribution in Fig. 2, and finally seen in the behaviour of the total  $V^E$ .

In future work we expect to compare experimental and predicted  $V^E$  for the present systems with those for glyme + normal alkane and glyme + cyclic alkane systems. This would complement the already existing interpretation<sup>7,14</sup> of some of those systems.

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