Excess Thermodynamic Properties of Binary Liquid Systems: Cyclohexane + Toluene, Amyl Alcohol + Toluene & Ethylene Glycol + Pyridine

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\[ \Delta^*G^E, \Delta^*H^E, \Delta^*S^E \text{ and } *C_p^E \text{ for the systems (a) cyclohexane + toluene, (b) amyl alcohol + toluene and (c) ethylene glycol + pyridine have been evaluated. The negative values of } \Delta^*G^E \text{ together with positive values of } \partial \Delta^*G^E / \partial T \text{ provide evidence for the complex formation in the systems (a) and (b). The positive values of } \Delta^*G^E \text{ only at lower glycol concentration and the negative values of } \partial \Delta^*G^E / \partial T \text{ apparently suggest either the absence or the presence of weak type of complex formation in system (c). The negative values of } \Delta^*H^E \text{ and } \Delta^*S^E \text{ in the systems (a) and (b) and positive in (c) reinforce the above deduction.} \]

In an earlier publication\(^1\) we reported on the excess volumes and excess viscosities of the title binary systems in order to have an insight into the type of interactions in these binaries. The excess thermodynamic functions, namely, the excess Gibb's free energy (\(\Delta^*G^E\)), the excess enthalpy (\(\Delta^*H^E\)), the excess heat capacity (\(*C_p^E\)) and the excess entropy (\(\Delta^*S^E\)) of mixing have now been calculated for these binaries utilizing the data reported earlier\(^1\). These parameters are quite useful in understanding the strength and the nature of interactions among the molecules of the two-component systems\(^2\).

The reagents used and the methods adopted were the same as described earlier\(^1\).

The excess Gibb's free energy of flow (\(\Delta^*G^E\)) has been calculated from the viscosity and density data using expression (1).

\[ \Delta^*G^E = RT[\ln \eta V - (x_1 \ln \eta_1 V_1 + x_2 \ln \eta_2 V_2)] \]

in which the terms have their usual meaning. The excess enthalpy of flow (\(\Delta^*H^E\)), the excess entropy of flow (\(\Delta^*S^E\)) and the excess heat capacity (\(*C_p^E\)) are obtained employing Eq. (3) to (4)

\[ \Delta^*H^E = -T^2 \partial(\Delta^*G^E / T) / \partial T \]

\[ = -RT^2 \left\{ \left[ \frac{\partial \ln \eta}{\partial T} - (x_1 \frac{\partial \ln \eta_1}{\partial T} + x_2 \frac{\partial \ln \eta_2}{\partial T}) \right] + \left\{ \frac{1}{V} \frac{\partial V}{\partial T} - \left( \frac{x_1}{V_1} \frac{\partial V_1}{\partial T} + \frac{x_2}{V_2} \frac{\partial V_2}{\partial T} \right) \right\} \right\} \]

\(\Delta^*S^E = (\Delta^*H^E - \Delta^*G^E) / T \) \quad \ldots (3)

\[*C^E_p = \partial \Delta^*H^E / \partial T \]

\[ = -2RT \left\{ \left[ \frac{\partial \ln \eta}{\partial T} - (x_1 \frac{\partial \ln \eta_1}{\partial T} + x_2 \frac{\partial \ln \eta_2}{\partial T}) \right] \right\} \]

\[ + \left\{ \frac{1}{V} \frac{\partial V}{\partial T} - \left( \frac{x_1}{V_1} \frac{\partial V_1}{\partial T} + \frac{x_2}{V_2} \frac{\partial V_2}{\partial T} \right) \right\} \]

\[ - RT^2 \left\{ \left[ \frac{\partial^2 \ln \eta}{\partial T^2} - \left( \frac{x_1}{\partial T} \frac{\partial^2 \ln \eta_1}{\partial T^2} + \frac{x_2}{\partial T} \frac{\partial^2 \ln \eta_2}{\partial T^2} \right) \right] \right\} \]

\[ + \left\{ \frac{1}{V} \frac{\partial^2 V}{\partial T^2} - \left( \frac{x_1}{V_1} \frac{\partial^2 V_1}{\partial T^2} + \frac{x_2}{V_2} \frac{\partial^2 V_2}{\partial T^2} \right) \right\} \]

\[ - \left\{ \left( \frac{1}{V} \frac{\partial V}{\partial T} \right)^2 - \left( \frac{x_1}{V_1} \frac{\partial V_1}{\partial T} \right)^2 + \frac{x_2}{V_2} \frac{\partial V_2}{\partial T} \right\} \right\} \] \quad \ldots (4)

All the calculations and the least-squares fitting were made over an IBM-1130 computer.

The negative values of excess Gibb's free energy of flow for cyclohexane + toluene system (a) (Fig. 1) over the entire range of temperature and composition indicate the presence of complex formation by an exothermic process by \(n\)-\(\pi\) interactions between the components, as suggested earlier\(^1\). The values of the derivative \(\partial \Delta^*G^E / \partial T \) are positive which is a clear evidence for the presence of specific interactions.

Fig. 1—Plots of \(\Delta^*G^E\) versus mol fraction of (a) cyclohexane and (b) amyl alcohol for cyclohexane + toluene and amyl alcohol + toluene systems, respectively.
For amyl alcohol + toluene system (b) the results are similar to those of binary system (a) (Fig. 1), the only difference being that the magnitude of $\Delta^E$ in this case is much higher than that in system (a). This indicates relatively strong interactions between the unlike molecules forming complexes. The positive values of the derivative, $\partial \Delta^E / \partial T$ further reinforce the above view.

For the glycol + pyridine system (c) the $\Delta^E$ values are negative at low glycol concentrations, but as glycol concentration increases, the $\Delta^E$ values go on increasing and become positive at high glycol concentrations and high temperature. The values are positive even at low glycol concentrations and low temperatures (Fig. 2). An explanation similar to that provided in an earlier investigation for this system based on excess volume and excess viscosity data, also holds good in the present study for this behaviour.

The minimum for the $\Delta^E$ plots for the system cyclohexane + toluene is at $x_1$ (cyclohexane) = 0.57, for amyl alcohol + toluene, $x_1$ (amyl alcohol) = 0.52 (Fig. 1) and for the glycol + pyridine $x_1$ (glycol) = (0.15-0.23) and that maxima for system (c) occurs at $x_1$ (glycol) = (0.71-0.77) (Fig. 2). This shows that maximum complex formation or specific interactions occur at the minimum and the maximum dispersive forces dominate at the maximum of the $\Delta^E$ plots. If we compare the minima observed$^1$ in the viscosity plots, we conclude that the minima or maxima in excess viscosity plots give the composition of the complex formed while the minima or the maxima in $\Delta^E$ plots give the composition at which the maximum interactions are expected.

The plots of $\Delta^E$ for the systems cyclohexane + toluene and amyl alcohol + toluene are similar to those of $\Delta^E$ but are almost independent of temperature, that is, $\partial \Delta^E / \partial T = C^E = 0$ for these systems. It seems that in the binary liquid mixtures, where both the components follow Arrhenius behaviour, the excess enthalpies are affected only by the nature of the components. The minima in the $\Delta^E$ plots of cyclohexane + toluene system is again at $x_1$ (cyclohexane) = 0.57. The molecular sizes of both the components do not differ much but toluene molecules are slightly dipolar due to the presence of conjugating $\pi$-electrons and a $\text{-CH}_3$ group. The shift in maxima towards cyclohexane is, therefore, in agreement with the earlier predictions$^3$.

As $\Delta^E$ is negative and large in magnitude for amyl alcohol + toluene system, the energy liberated, as a result of interaction of $\pi$-electrons of toluene with amyl alcohol molecules, dominates over the energy required to break the self-associated hydrogen bonds in amyl alcohol. The sizes of amyl alcohol and toluene molecules are almost the same and the molecules of amyl alcohol are highly polar, the minima should, therefore, be situated$^3$ towards the non-polar or the less polar component, toluene. As the minima is at $x_1$ (amyl alcohol) = 0.52, or slightly towards amyl alcohol, the molecular mass instead of molecular size should be taken into consideration, so that the heavier molecular mass of toluene and the orientation of amyl alcohol molecules can compensate for each other.

The $\Delta^E$ values for glycol + pyridine are positive throughout the range of composition, suggesting an endothermic interaction. This can be explained by assuming the nature of interaction between glycol and pyridine as shown in Scheme 1.

\[ (\text{C}_2\text{H}_4\text{O}_2)_n \rightarrow \sum (\text{C}_2\text{H}_4\text{O}_2)_m \]

\[ (\text{C}_5\text{H}_5\text{N})_2 \rightarrow 2\text{C}_3\text{H}_3\text{N} \]

\[ -\Delta H_3 \]

\[ \sum (\text{C}_2\text{H}_4\text{O}_2)_r, (\text{C}_5\text{H}_5\text{N})_s \]

Scheme 1

where $n$ is very large, $m$ and $r$ are arbitrary numbers not necessarily in any order, the ratio of $x$ and $y (x:y)$ should generally be $1:1$ as predicted$^1$ by excess viscosity plots but they may have any value particularly when there is a complex formation between the pyridine molecules and any fragment of glycol's network. The overall excess enthalpy may be given as

\[ \Delta^E = \Delta H_1 + \Delta H_2 - \Delta H_3 \]

The values of $\Delta H_1$ are expected to be positive and very large in magnitude, those of $\Delta H_2$ to be positive but small in magnitude as compared to $\Delta H_1$ and those of $\Delta H_3$ to be negative and small. $\Delta^E$ values are, therefore, expected to be large and positive as is
Fig. 3—Plots of $\Delta^*H^E$ versus mol fraction of glycol for glycol + pyridine system
evident from the experimental values. The maxima for
the $\Delta^*H^E$ plots in the temperature range 82° to 32°C,
are obtained at $x_1$ (glycol) = 0.62-0.71. In the lower
temperature range, dissociation of highly self-
associated glycol is suppressed due to the larger mass.
Also the polarity of pyridine molecules seems to shift
the maxima towards the glycol quite appreciably. In
the higher temperature range the dissociation of self-
associated glycol molecules shifts the maxima
relatively towards the pyridine side (Fig. 3). The $\Delta^*H^E$
values for this system are temperature dependent, since
one of the two components, viz. glycol does not follow
the Arrhenius equation for viscosity. The derivative
$\delta \Delta^*H^E/\delta T$ or the $^*C_F^P$ for this system is positive at
lower glycol concentrations and negative at higher
glycol concentrations (Fig. 4). It is, therefore,
concluded that at lower glycol concentrations the
specific interactions are present, as is apparent from
our earlier predictions based on the $\Delta^*G^E$ and $\eta^E$
values. The negative values of $^*C_F^P$ at higher glycol
concentrations suggest little likelihood for the specific
interactions.

The excess entropy of flow $\Delta^*S^E$ follows exactly a
pattern similar to that of $\Delta^*H^E$. As the $\Delta^*S^E$
values like those of $\Delta^*H^E$ do not vary with temperature for
the systems cyclohexane + toluene and amyl alcohol
+ toluene but vary for glycol + pyridine system.

References
2 Henry V Kehaian, Krystne Sosnkswa-Kehaian & Regina