

THERMODYNAMIC MAGNITUDES OF L-MENTHOL /- ACETONITRILE AND L-MENTHOL / CARBON TETRACHLORIDE BINARY MIXTURE BY VPO

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ABSTRACT

In this paper we have studied the thermodynamic behaviour of L-menthol in acetonitrile and carbon tetrachloride by vapour pressure osmometry (VPO) in the temperature range 303–323 K. We have found that L-menthol behaves in a different way in both solvents.

From osmotic coefficients we have calculated the excess functions of the system. In L-menthol/carbon tetrachloride we have found a great deviation from ideal behaviour, on the contrary, the deviation is very slight in the other system. This circumstance hinders the study of this system with VPO.

The behaviour of L-menthol in carbon tetrachloride has been discussed as a function of molecular interactions. Finally, self-association phenomena have been detected. By means of theoretical models the association number has been calculated.

INTRODUCTION

The possibility of using a thermoelectric method to obtain vapour pressure osmometry measurements was first described by Hill [1]. However, this method was not widely used until the development of devices which allowed the detection of very small differences of temperature.

Nowadays, thanks to the development of microelectronics, VPO of high sensibility exists. This offers new possibilities for the thermodynamic study of systems which cannot be studied using other physical methods [2].

The application of VPO to the thermodynamic study of binary solute-solvent systems is nowadays very extensive [3–10]. This method allows us to obtain perfectly reproducible thermodynamic parameters with significant agreement with the literature [3].

In the present work, we have used this experimental method to study two binary systems: L-menthol/carbon tetrachloride and L-menthol/acetonitrile. The analysis of the results obtained indicates a very different behaviour of L-menthol in both solvents as will be shown below.

EXPERIMENTAL

The measurements were carried out using a Knauer vapour pressure osmometer (VPO) model 1974 with a universal probe that was able to operate between 293 and 400 K.

Solvents were used without further purification. The purity of the solids used was checked using differential thermal analysis (DTA).

The measurements were made between 303 and 323 K, in a range of concentration lower than 1 molal.

The temperature of the measuring cell was maintained constant with an error lower than 0.25 K.

Taking into account the different experimental errors we can estimate an absolute range of error lower than 0.005 for the corresponding values of the osmotic coefficients, Φ .

RESULTS

The VPO apparatus has been calibrated as a function of molar concentration of biphenyl in carbon tetrachloride and acetonitrile, respectively, at several temperatures. The experimental data obtained for both systems have been treated by the method of least squares, using a Commodore C-64 computer. To fit the experimental ΔR values we have employed a polynomial equation of fifth degree, following the general form

$$\Delta R = a + bx + cx^2$$

The coefficients obtained are shown in Tables 1 and 2.

Tables 3 and 4 give the coefficients of the polynomial equation for the systems L-menthol/carbon tetrachloride and L-menthol/acetonitrile at different temperatures.

The calculation of the osmotic coefficient, Φ , was carried out using the equation

$$\Phi = \bar{m}/m\nu$$

where m and \bar{m} are the theoretical and experimental molality, respectively,

TABLE 1

Coefficients of the equation $\Delta R(m)$ for the calibration system biphenyl/ CCl_4

| T (K) | a | b | c | d | e | f |
|---------|-----|-------|--------|-------|--------|-------|
| 303 | 0 | 8410 | -4211 | 297 | 4730 | -3547 |
| 313 | 0 | 9549 | -6072 | 5564 | -2480 | |
| 318 | 0 | 10659 | -14665 | 3459 | -35357 | 13989 |
| 323 | 0 | 10855 | -10531 | 19735 | -22795 | 10309 |

TABLE 2

Coefficients of the equation $\Delta R(m)$ for the calibration system biphenyl/acetonitrile

| T (K) | a | b | c | d | e |
|---------|-----|------|-------|------|------|
| 303 | 0 | 2292 | -1468 | 1663 | -863 |
| 313 | 0 | 2532 | -1544 | 1758 | -955 |
| 323 | 0 | 2648 | -780 | 108 | 5 |

TABLE 3

Coefficients of the equation $\Delta R(m)$ for the system L-menthol/ CCl_4

| T (K) | a | b | c | d | e | f |
|---------|-----|-------|--------|-------|--------|-------|
| 303 | 0 | 8503 | -19135 | 37702 | -37356 | 13856 |
| 313 | 0 | 8769 | -8199 | 4812 | -985 | |
| 318 | 0 | 9957 | -15392 | 22072 | -17452 | 5647 |
| 323 | 0 | 10832 | -17252 | 24302 | -16320 | 3773 |

TABLE 4

Coefficients of the equation $\Delta R(m)$ for the system L-menthol/acetonitrile

| T (K) | a | b | c | d | e |
|---------|-----|------|------|-------|-------|
| 303 | 0 | 1924 | 58.5 | -787 | 361 |
| 313 | 0 | 2258 | -459 | -89.5 | 42 |
| 323 | 0 | 2339 | -386 | -0.41 | -34.5 |

and ν is the total number of ions in solution, which is equal to unity in the two systems studied [6].

In Tables 5 and 6 we can see the $\Phi(m)$ values at different temperatures against molality for the L-menthol/carbon tetrachloride and L-menthol/acetonitrile systems.

TABLE 5

Values of the function $\Phi(m)$ at different temperatures for the system L-menthol/ CCl_4

| T (K) | $m = 0.2$ | 0.4 | 0.6 | 0.8 | 1.0 |
|---------|-----------|-------|-------|-------|-------|
| 303 | 0.755 | 0.655 | 0.610 | 0.565 | 0.530 |
| 313 | 0.845 | 0.760 | 0.685 | 0.630 | 0.595 |
| 318 | 0.850 | 0.765 | 0.700 | 0.665 | 0.640 |
| 323 | 0.860 | 0.770 | 0.730 | 0.710 | 0.680 |

TABLE 6

Values of the function $\Phi(m)$ at different temperatures for the system L-menthol/acetonitrile

| T (K) | $m = 0.2$ | 0.4 | 0.6 | 0.8 | 1.0 |
|---------|-----------|-------|-------|-------|-------|
| 303 | 0.920 | 0.958 | 0.955 | 0.938 | 0.931 |
| 313 | 0.942 | 0.962 | 0.959 | 0.949 | 0.960 |
| 323 | 0.901 | 0.918 | 0.935 | 0.949 | 0.957 |

DISCUSSION

For a non-ideal system the chemical potential, μ_i , can be expressed as a function of the composition by

$$\mu_i = \mu_i^*(T, p) + RT \ln \gamma_i x_i \quad (1)$$

where $\mu_i^*(T, p)$ is the standard chemical potential, γ_i the activity coefficient and x_i the mole fraction. We can also express the chemical potential in the following form

$$\mu_i = \mu_i^*(T, p) - RT\Phi_1 m M_1 \times 10^{-3} \quad (2)$$

Relating eqns. (1) and (2) and taking into account the Gibbs–Duhem equation we can obtain

$$\ln \gamma_2 = (\Phi - 1) + \int_0^m \frac{\Phi - 1}{m} dm - \ln x_1 \quad (3)$$

Figures 1 and 2 show the plot of $\ln \gamma_1$ and $\ln \gamma_2$ against molality, m , at the different temperatures measured, for the system L-menthol/carbon tetrachloride. For the other system, since the $\Phi(m)$ values are near to unity (see Table 6) it is impossible to obtain accurate values for the activity coefficient of L-menthol in acetonitrile. For this reason, the thermodynamic study using VPO cannot be carried out in the range of temperature and molality used.

In Fig. 2 we can see that there is an important change in the γ_2 values in the temperature range 303–313 K. This behaviour can be explained taking into account the possible breaking of the self-association of L-menthol molecules. This self-association can be due to the formation of hydrogen bonding between hydroxyl groups. In the literature [11,12], it has been reported that this is the temperature at which the hydrogen bonding is broken. As a consequence of this, the system tends towards a more ideal behaviour.

It is possible to calculate the excess thermodynamic functions, such as Gibbs free energy, entropy and enthalpy, which are given by the following expressions

$$G^E = RT \sum_1^2 x_i \ln \gamma_i$$

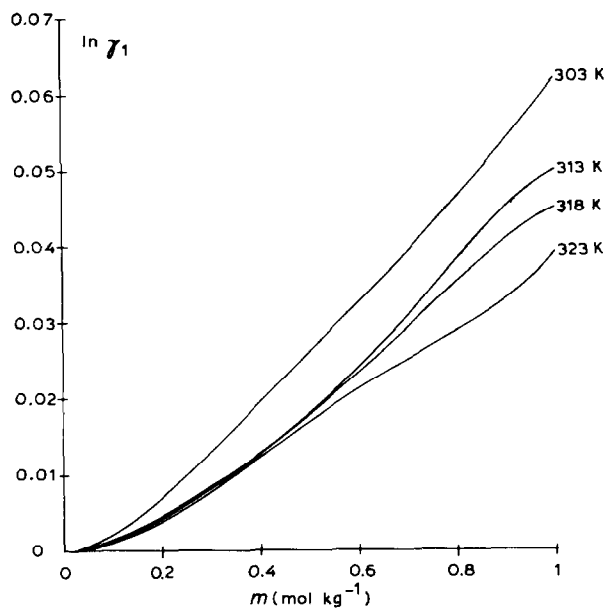


Fig. 1. Plot of $\ln \gamma_1$ against molality at different temperatures for the L-menthol/carbon tetrachloride system.

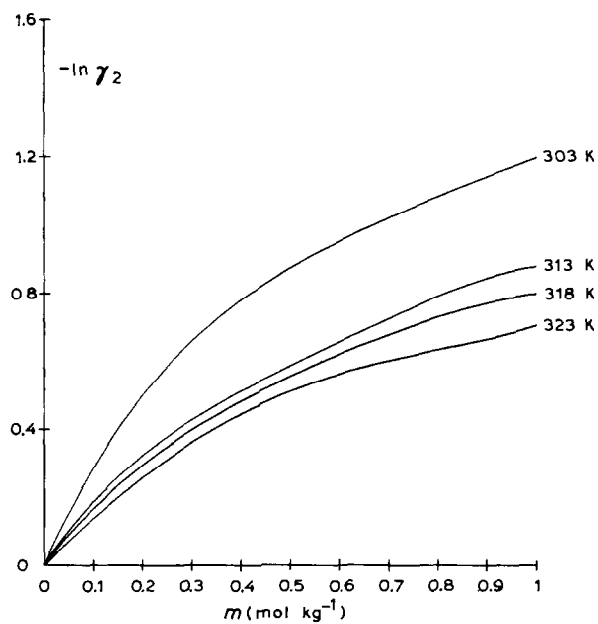


Fig. 2. Plot of $\ln \gamma_2$ against molality at different temperatures for the L-menthol/carbon tetrachloride system.

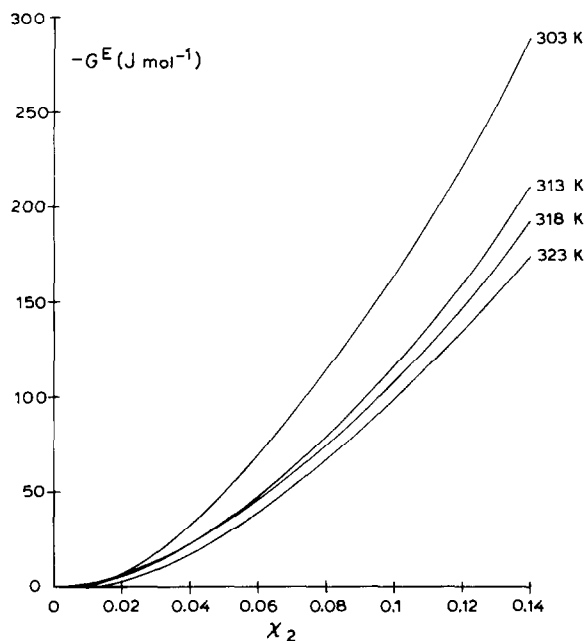


Fig. 3. Plot of Gibbs excess free energy, G^E , against molar fraction, χ_2 , of L-menthol at different temperatures for the L-menthol/carbon tetrachloride system.

$$S^E = - \left(\frac{\partial G^E}{\partial T} \right)_{p,m}$$

$$H^E = G^E + TS^E$$

Figure 3 shows the plot of G^E against the mole fraction of L-menthol, χ_2 , at different temperatures. The G^E values suggest the existence of a great compatibility between both components of the mixture. This in apparent contradiction with the γ_2 - m_2 values, which were discussed above. However, we can explain this behaviour taking into account that carbon tetrachloride can solvate the L-menthol associated species. We think that a plausible mechanism can be the following: polar interactions can be established between chloride atoms of the carbon tetrachloride and methyl groups of L-menthol dimers or tetramer molecules (as will be explained later). This mechanism can explain the high G^E values obtained for this system.

The G^E dependence on temperature, at constant mole fraction, is reasonable if we consider that chloride atom-methyl group interactions are weaker as temperature increases.

If we compare, at any composition, the sharp increase of $\ln \gamma_2$ between 303 and 313 K with the corresponding one for G^E , we note a smaller jump in this case, which can be explained taking into account that the formation of hydrogen bonding is a phenomenon that contributes to an increase of G^E

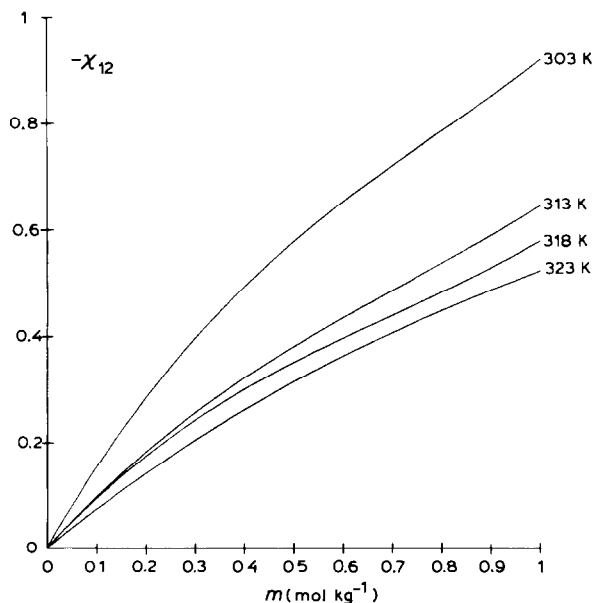


Fig. 4. Plot of interaction parameter, χ_{12} , against molality at different temperatures for the L-menthol/carbon tetrachloride system.

values, while the interaction between the associated L-menthol species with carbon tetrachloride decreases them.

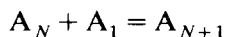
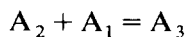
On considering the dependence of G^E on the product of mole fractions $\chi_1\chi_2$, It is possible to evaluate the solute-solvent interaction parameter, χ_{12} , using the Guggenheim-Stokes equation [13]

$$G^E = \chi_{12}RT\chi_1\chi_2$$

Figure 4 shows the plot of the χ_{12} interaction parameter as a function of molality at different temperatures. As can be seen, as molality increases the interaction parameter, χ_{12} , becomes more negative. The same behaviour is observed with decreasing temperature. This indicates an increase in the L-menthol-carbon tetrachloride interactions, as was said above.

It is possible to determine the degree of association in the system from the osmotic pressure coefficient. In a recent paper we developed different association models which allow us to determine approximately the association number of the solute in solution [14,15].

We have found that the model which best reproduces our experimental data is an open association mechanism of the type



where n association processes occur and where the identity of all the partial

association constants of the system is assumed. However, we have found that temperature and molality affect these constants, i.e., at 323 K and low molality values, the dimerization process is more important. If we increase molality and/or decrease temperature we note that the behaviour of L-menthol in carbon tetrachloride becomes more complicated [16].

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