Bull. Chem. Soc. Jpn., 63, 265—266 (1990)

The Headspace Gas Chromatographic Study on (Biphenyl, Naphthalene)-(Benzene, Cyclohexane, 1-Octanol) Binary Mixtures at 298.15 K

Isao Sanemasa
Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami 2-39-1, Kumamoto 860
(Received August 12, 1989)

Synopsis. The vapor pressure of each constituent of the title binary mixtures, except for 1-octanol, was measured by the headspace gas chromatography as a function of biphenyl or naphthalene mole fraction in a relative scale taking the vapor pressure of the pure component as unity.

We recently reported the solubility in water of biphenyl and naphthalene in the binary mixtures with benzene, cyclohexane, or 1-octanol as a function of biphenyl or naphthalene mole fraction.[1)] In the present study, the same binary mixtures are examined by the headspace gas chromatographic method to see whether or not the aqueous solubility and the vapor pressure of the constituent correlate with each other. The headspace gas chromatography has been reported to be suitable for the thermodynamic study of binary mixtures.[2)]

Experimental

Materials. The materials used here are the same as those described in the previous paper.[1)]

Apparatus and Procedures. A required amount of biphenyl or naphthalene was weighed out and transferred into a vial bottle of 20 cm³ capacity in which a 5 or 2 cm³ portion of benzene, cyclohexane, or 1-octanol had been placed. A Teflon-coated magnet of 2 mm $\phi \times 5$ mm was put into the vial. After being sealed with a Teflon-lined septum stopper covered with an aluminum cap having a hole of 5 mm diameter in its center, the vial was immersed completely in a water-bath thermostated at 25.0±0.1 °C and the content was stirred for at least 24 h by a magnetic stirrer under the bath. Then, the vapor in the vial was analyzed by a Shimadzu GC-14A gas chromatograph equipped with a Shimadzu HSS-2B headspace gas sampler; the volume of the gas injected was 0.4 cm³. A Tenax GC (60—80 mesh) column of 3.4 mm $\phi \times 2$ m was used at 240 °C and a flame ionization detector was used. A Shimadzu Chromatopac C-R6A determined peak areas.

The peak area obtained for each constituent was compared with that for the corresponding pure component; the peak area of pure component was taken as unity. Thus, the vapor pressure of the constituent of the binary mixtures was expressed in a relative scale.

In the case that 1-octanol is the constituent component, no significant change in the peak area as a function of the composition was observed.

Results and Discussion

In Figs. 1 and 2 is shown the relative vapor pressure of the constituent of the binary mixtures, r, as a function of biphenyl or naphthalene mole fraction, X. Each solid line refers to the relative solubility of the corresponding component in water, which is taken from our previous paper.[1)] The two plots for each constituent, both in relative scales, are in a reasonable agreement with each other. This means that Henry's law holds for the solubility of the constituent component of the binary mixtures in water.

In the case of naphthalene–benzene system, a slight positive deviation was observed for naphthalene by aqueous solubility measurements,[1)] while, in the present vapor pressure measurements, naphthalene appears to form an almost ideal solution with benzene. Since there have been sufficient reported data supporting this binary system being not ideal,[3,4)] the aqueous solubility method seems to give more reliable results.

The present date have been treated by the curve-fitting method to relate r to X as follows:
biphenyl (a)–benzene (b) system;

$$r_a = 2.75\,X_a$$

and

$$r_b = 1.00 - 0.781\,X_a,$$

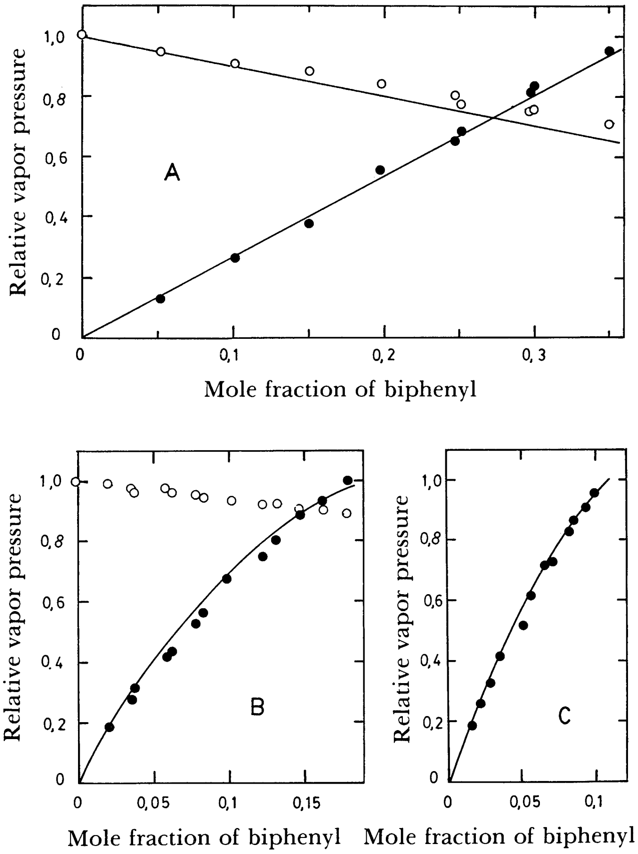

Fig. 1. Relative vapor pressure of the constituent as a function of biphenyl mole fraction. Biphenyl–benzene (A), –cyclohexane (B), –1-octanol (C). Biphenyl (●). The solid line indicates the relative aqueous solubility of the corresponding constituent taken from Ref. 1.

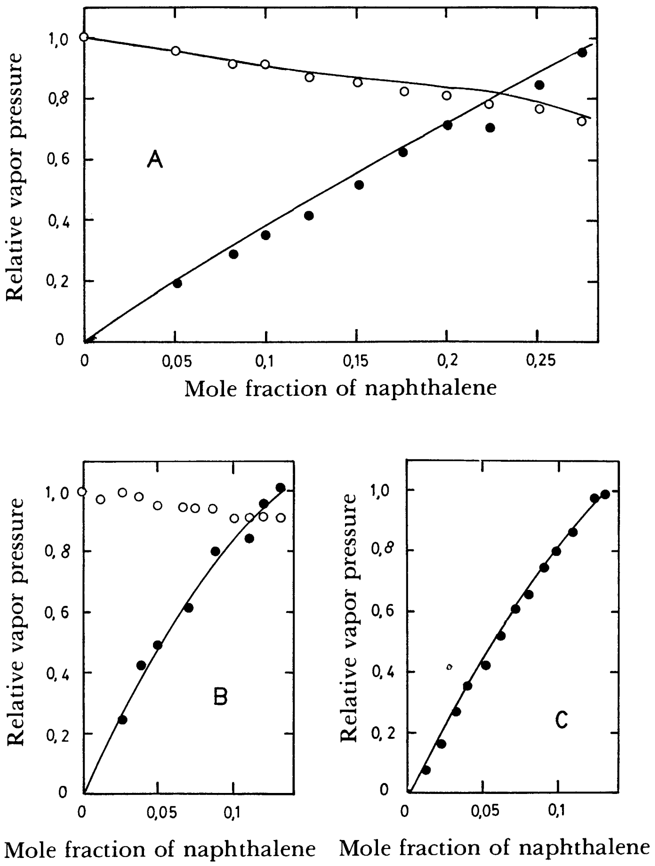

Fig. 2. Relative vapor pressure of the constituent as a function of naphthalene mole fraction. Naphthalene-benzene (A), -cyclohexane (B), -1-octanol (C). Naphthalene (●). The meaning of the solid line is the same as that of Fig. 1.

biphenyl (a)-cyclohexane (b) system;

$$r_a = -9.73 X_a^2 + 7.30 X_a + 2.57\times10^{-2}$$

and

$$r_b = 1.00 - 0.581 X_a,$$

biphenyl (a)-1-octanol (b) system;

$$r_a = -31.3 X_a^2 + 12.9 X_a - 7.34\times10^{-3}$$

naphthalene (a)-benzene (b) system;

$$r_a = 3.45 X_a$$

and

$$r_b = 1.00 - 0.967 X_a,$$

naphthalene (a)-cyclohexane (b) system;

$$r_a = -26.1 X_a^2 + 11.0 X_a + 2.16\times10^{-3}$$

and

$$r_b = 1.00 - 0.697 X_a,$$

naphthalene (a)-1-octanol (b) system;

$$r_a = -13.7 X_a^2 + 9.65 X_a - 1.78\times10^{-2}.$$

If we postulate that both biphenyl and naphthalene form ideal solutions with benzene, the fugacity ratio, f_s/f_l, can be estimated from the above r–X equations: 0.364 for biphenyl and 0.290 for naphthalene. The vapor pressure of biphenyl and that of naphthalene are sufficiently low, then, the fugacity of the pure solid hydrocarbon, f_s, and that of the supercooled liquid hydrocarbon, f_l, can be made equal to the pure solid vapor pressure and to the supercooled liquid vapor pressure, respectively. The supercooled liquid hydrocarbon being taken as the standard state of the solid hydrocarbon, the activity coefficients, γ, of biphenyl (a) and naphthalene (b) can be expressed as follows:

$$\gamma_a = 0.364\, r_a/X_a$$

and

$$\gamma_b = 0.290\, r_b/X_b.$$

References

1) I. Sanemasa, M. Kumamaru, K. Ishibashi, and T. Deguchi, *Bull. Chem. Soc. Jpn.*, **62**, 1061 (1989).

2) A. Hussam and P. W. Carr, *Anal. Chem.*, **57**, 793 (1985).

3) E. L. Heric and C. D. Posey, *J. Chem. Eng. Data*, **9**, 35 (1964).

4) P. B. Choi, C. P. Williams, K. G. Buehring, and E. McLaughlin, *J. Chem. Eng. Data*, **30**, 403 (1985).