411. *Solid–Liquid Equilibria in Solutions of Non-electrolytes.*

By R. P. Rastogi and K. T. Rama Varma.

A modified thaw-melt method has been used to study solid–liquid equilibria in solutions of non-electrolytes. The experimental and ideal solidus and liquidus curves almost coincide for the anthracene–acenaphthene system, thereby showing that the system is nearly ideal in both the phases. The naphthalene–phenanthrene and –α-naphthylamine systems are approximately regular, but naphthalene–α-naphthol and –acenaphthene are non-regular and non-ideal.

Phase diagrams [1] have recently been used to yield quantities of thermodynamic interest, but so far only eutectic systems have been satisfactorily investigated. Kleppa [2] has described a method for certain types of eutectic system which makes it possible to separate the calculated partial molar free energy into approximate heat and entropy terms. It appears that solid–liquid equilibrium studies might be used to obtain thermodynamic properties of mixtures but the method has received only scant attention in view of the limitations of experimental technique. We now describe a modified form of thaw-melt method, and measurements are recorded and discussed for five systems in order to see whether they are ideal, regular, or non-ideal.

Experimental

The usual method adopted in such studies is the cooling-curve method which involves two main sources of error. First, on account of supercooling the correct liquidus temperature cannot be obtained. Secondly, owing to separation of the solid mass the thaw point cannot be accurately determined. Further, the necessary plotting of cooling curves is time-consuming. Hence, this method was rejected and one based on the procedure adopted by Rheinboldt [3] and

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[1] Chipman, *Discuss. Faraday Soc.*, 1948, **4**, 23.
[2] Kleppa, *J. Phys. Chem.*, 1955, **59**, 175.
[3] Rheinboldt, *J. prakt. Chem.*, 1925, **11**, 242.

Pounder and Masson[4] was employed. This method eliminates the above two sources of error and is both rapid and direct.

Reagents.—" AnalaR " reagents were used without further purification. The purity was checked by determination of m. p.

Preparation of Mixtures.—Mixtures were prepared as described by Pounder and Masson.[4] The temperature of the bath was kept near the f. p.s of the components in order to prevent vaporization.

Determination of Melting Points and Thaw Points.—The bath consisted of a 500-c.c. beaker filled with water, glycerol, or paraffin wax according to the temperature range involved. It was fitted with a wooden cover through which passed a thermometer graduated in 0·1°, the capillary tube of the form employed by Pounder and Masson, and an electrical heater. Heaters of different resistances were employed so as to secure a 1° rise in temperature in about 5 min. The bath was illuminated from behind so that the beginning of melting and solidification could be observed conveniently, and the bath liquid was stirred magnetically so as to minimize temperature gradients. The m. p.s and thaw points were determined according to Pounder and Masson. The thermometers were calibrated against standard thermometers with N.P.L. certificates. Corrections were made for emergent stem. The experimental conditions did not warrant the use of a thermocouple. In almost all cases the thaw points and m. p.s were very sharp, being reproducible to ±0·1°.

The liquidus and solidus temperatures are plotted against molar fractions in Figs. 1—5. The broken curves show the theoretical values for ideal mixtures. The values of thaw points (t.p.) and m. p.s for anthracene–acenaphthene systems are given in the Table, x being the mole-fraction of anthracene.

x	0·0996	0·2409	0·3412	0·5002	0·5140	0·5561	0·5683	0·6326	0·7327	0·7946	0·9694
T.p.	103·3°	109·6°	113·8°	121·9°	121·9°	129·2°	128·1°	137·6°	157·7°	163·0°	180·0°
M. p.	115·8°	146·1°	158·8°	181·8°	181·8°	185·1°	185·1°	189·3°	198·9°	203·4°	212·0°

DISCUSSION

Of the systems studied, naphthalene–α-naphthol, –α-naphthylamine, and –phenanthrene have been previously studied by the cooling-curve method.[5] In the following Table the eutectic composition (in mole-fractions) of naphthalene and the eutectic temperatures are compared.

	Eutectic temp. :		Eutectic comp. :	
Second component	Authors	Others	Authors	Others
α-Naphthylamine *	28·1°	28·0°	0·36	0·295
α-Naphthol †	54·5	61·0	0·487	0·395
Phenanthrene *	48·1	48·5	0·558	0·62

* For other authors, see ref. 5(*b*). † For other authors, see ref. 5(*a*).

For the eutectic systems the ideal curves were plotted by using the following expression,[6] which gives the ideal composition in the liquid phase when $r_1^l = 1$:

$$-\ln x_1^l r_1^l = \frac{\Delta_f h^\circ_1}{\boldsymbol{R}}\left(\frac{1}{T}-\frac{1}{T^\circ_1}\right)+\frac{\Delta_f C^\circ_{p,1}}{\boldsymbol{R}}\left(\ln\frac{T^\circ_1}{T}+1-\frac{T^\circ_1}{T}\right) \quad . \quad . \quad (1)$$

where x_1^l is the mole-fraction of component 1 in the liquid phase, and $\Delta_f h^\circ_1$ is the latent heat of fusion at the m. p., T°_1, $\Delta_f C^\circ_{p,1} = C^\circ_{p,1}{}^l - C^\circ_{p,1}{}^s$ where $C^\circ_{p,1}{}^l$ is the molar heat capacity at constant pressure of component 1 in the liquid state and $C^\circ_{p,1}{}^s$ that for the same component in the crystalline state, and r_1^l is the activity coefficient of component 1 in the liquid state.

It is seen that the ideal curves closely approximate to experimental curves in the naphthalene–phenanthrene and the naphthalene–α-naphthylamine system. The large deviation in mixtures of naphthalene and α-naphthol is due to association of α-naphthol on account of hydrogen bonding. It seems that the hydrogen bond in α-naphthylamine is

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[4] Pounder and Masson, *J.*, 1934, 1357.

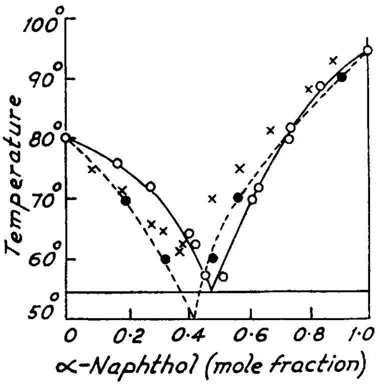
[5] (*a*) Crompton and Whiteley, *J.*, 1895, **67**, 327; (*b*) Rudolfi, *Z. phys. Chem.*, 1909, **66**, 705.

[6] Prigogine and Defay, " Chemical Thermodynamics," Longmans Green and Co., 1954.

comparatively very weak and hence no significant departures from ideality are observed. For comparison, molar volumes of naphthalene and α-naphthylamine are given below :

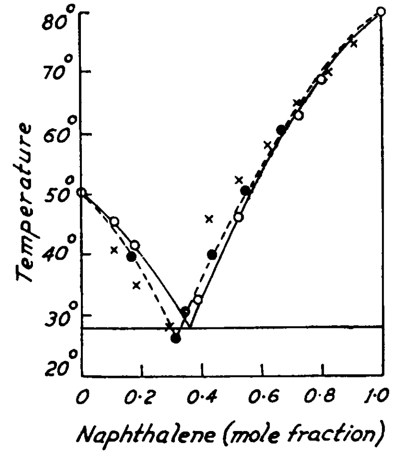
	Molar vol. in solid phase	Molar vol. in liquid phase		Molar vol. in solid phase	Molar vol. in liquid phase
Naphthalene	111·93	132·5 at 95°	α-Naphthylamine ...	122·11	129·87 at 50°

FIG. 1. *Naphthalene–α-naphthol.*



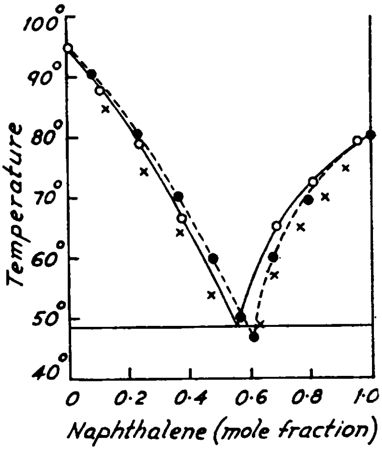
– – – – Ideal curves.
——— Experimental curves.
× Crompton and Whiteley's results.[5a]

FIG. 2. *Naphthlene–α-naphthylamine.*



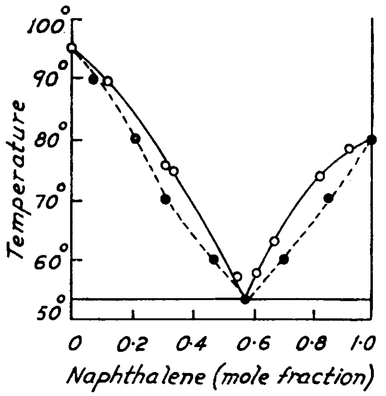
– – – – Ideal curves.
——— Experimental curves.
× Rudolfi's results.[5b]

FIG. 3. *Naphthalene–phenanthrene.*



– – – – Ideal curves.
——— Experimental curves.
× Rudolfi's results.[5b]

FIG. 4. *Naphthalene–acenaphthene.*



– – – – Ideal curves.
——— Experimental curves.

The non-ideality of the naphthalene–acenaphthene system is mainly due to difference in size and shape of the molecules of the two components.

In a regular solution, the activity coefficients are given by

$$\boldsymbol{RT} \ln r_1 = \alpha x_2^2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where α is a constant supposed to be independent of temperature.[7]

According to Guggenheim's theory [8] of strictly regular solutions, α is dependent on temperature. However, in this discussion we shall assume it to be independent of temperature owing to experimental limitations. From equation (2) it follows that if ln r_1 is plotted

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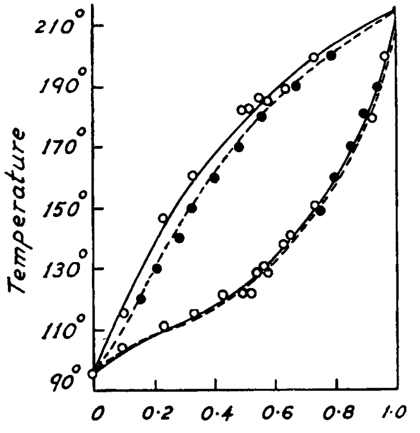
[7] Hildebrand and Scott, " Solubility of Non-electrolytes," Reinhold Publ. Corp., New York, 1950.
[8] Guggenheim, " Mixtures," Oxford, 1952.

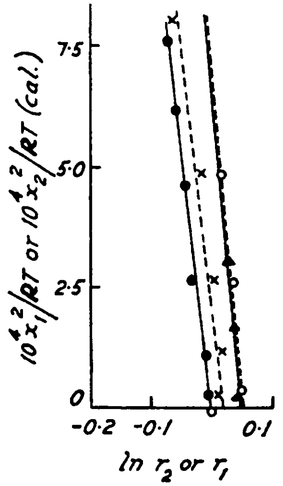
against x_2^2/T, or ln r_2 against x_1^2/T, a straight line should be obtained passing through the origin. In order to test the conformity of the eutectic systems to regular mixtures, ln r_1 and ln r_2 were calculated from equation (1) from the two branches of the liquidus curves, and in Fig. 6 they are plotted against x_2^2/T and x_1^2/T, respectively. For liquid mixtures of naphthalene with phenanthrene and with α-naphthylamine the two curves have practically the same slope and pass close to the origin, indicating slight deviation from regular behaviour especially in the second system. The expression $\boldsymbol{R}T \ln r_1 = k\phi_2^2$, where k is a constant and ϕ_2 is the volume fraction of the second component, could not be used in analysing our data since the values for the densities and the coefficient of volume expansion of the substances in the liquid phase were not available.

FIG. 5. *Anthracene–acenaphthene.*



---- Ideal curves.
——— Experimental curves.

FIG. 6.



—●—●— Naphthalene–phenanthrene, ln r_2 against x_1^2/T.
—○—○— Naphthalene–phenanthrene, ln r_1 against x_2^2/T.
—×—×— Naphthalene–α-naphthylamine, ln r_2 against x_1^2/T.
—▲—▲— Naphthalene–α-naphthylamine, ln r_1 against x_2^2/T.

Anthracene and acenaphthene form complete series of solid solutions. The ideal liquidus and solidus curves have been plotted in Fig. 5 by Seltz's procedure.[9] The following equations were used :

$$x_2^l = (\exp \lambda_1 - 1)/[\exp \lambda_1 - \exp(-\lambda_2)]\,;\quad x_2^s = (\exp \lambda_1 - 1)/[\exp(\lambda_1 + \lambda_2) - 1]. \quad (3)$$

where $\lambda_1 = (\Delta_f h^\circ{}_1/\boldsymbol{R})(1/T - 1/T^\circ{}_1)$

and $\lambda_2 = (\Delta_f h^\circ{}_2/\boldsymbol{R})(1/T - 1/T^\circ{}_2)$

The observed and the calculated solidus curve practically coincide. There is slight departure in the liquidus curves. The behaviour of the system is analogous to that observed in germanium–tin alloys.[10] The ideality of the system was also tested by comparing observed slopes and those calculated by the equations (4) due to Rastogi : [11]

$$\frac{\mathrm{d}x_1^l}{\mathrm{d}T} = \frac{x_1^s\Delta_f h^\circ{}_1 + x_2^s\Delta_f h^\circ{}_2}{\boldsymbol{R}T^2\left(\dfrac{x_1^s}{x_1^l} - \dfrac{x_2^s}{x_2^l}\right)}\,;\quad -\frac{\mathrm{d}x_1^s}{\mathrm{d}T} = \frac{x_1^l\Delta_f h^\circ{}_1 + x_2^l\Delta_f h^\circ{}_2}{\boldsymbol{R}T^2\left(\dfrac{x_1^l}{x_1^s} - \dfrac{x_2^l}{x_2^s}\right)} \quad . \; . \; . \quad (4)$$

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[9] Seltz, *J. Amer. Chem. Soc.*, 1934, **56**, 307.
[10] Thurmond, *J. Phys. Chem.*, 1953, **57**, 827.
[11] Rastogi, *Proc. Nat. Inst. Sci. India*, 1955, **21**, 144.

It is found that the slopes agree to within 10%. It seems therefore that both the solid and the liquid phase are approximately ideal. The conclusion is not surprising in view of the fact that the molar volumes of the two components in the solid phase are very similar (acenaphthene, 149·7 c.c.; anthracene, 155·35 c.c.).

The authors gratefully acknowledge the support of the Indian Council of Scientific and Industrial Research for the present investigation and a maintenance grant to K. T. R. V.

LUCKNOW UNIVERSITY. [*Received, October* 26*th*, 1955.]