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Solid–liquid equilibrium in a binary system with incongruent melting complex compound

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Abstract

Solidus and liquidus equilibrium lines in binary phenol–bisphenol A system were determined with use of a DSC-1B calorimeter Experimental equilibrium data were correlated by means of liquid phase activity coefficient equations (Redlich–Kister, Van Laar, NRTL) with one constraint based on the condition of solid–liquid equilibrium (Schroeder equation)

INTRODUCTION

Although the synthesis and properties of other bisphenols have widely been reported in the literature [1,2], only bisphenol A (4,4′-isopropylidinebisphenol) has achieved extensive industrial use. Growing interest in and demand for purest bisphenol A, mainly for epoxy resins [1–6], made a study of some of its thermochemical and thermodynamic properties desirable. This work comprises experimental results on solid–liquid equilibrium in the binary phenol–bisphenol A system, needed for purification of bisphenol A by melt crystallization, which produces exceptionally high purity bisphenol A.

EXPERIMENTAL

Materials

Bisphenol A was prepared by the boron trifluoride etherate-catalysed condensation of phenol with acetone under acidic conditions, and was thoroughly purified. Polarographically the bisphenol A was found to contain 0.01 wt% of 2,4′-isopropylidenebisphenol. Thin layer chromatography revealed only very faint spots attributable to phenol and to the *ortho–para* isomer. Differential scanning calorimetry, on a DSC-1B instrument (Perkin–Elmer), gave a purity value of 99.98 mol%. This was obtained at a scanning rate of 0.5 °C min^{-1}, maximum (“range 1”) sensitivity, under a nitrogen atmosphere in volatile sample pans with fitted aluminium discs

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placed over the samples before sealing of the pans. Samples were weighed on a Cahn model G electrobalance. Chart area was evaluated with the aid of a General Radio electronic counter. The melting point of bisphenol A obtained on the DSC-1B and extrapolated to the 100% pure material was $T_f° = 431.10$ K (157.95 °C).

Phenol, obtained directly from an industrial column (Mazovian Petrochemical Works, Płock) and chromatographically 99.9% pure, was thoroughly dehydrated over molecular sieves type 4Å and distilled off through a 3-TP column to remove sieve particles. Its melting temperature obtained directly on the DSC-1B calorimeter was 314.00 K (40.85 °C).

Method

Melting temperatures and enthalpies and heat capacities in the solid and liquid phases for pure phenol, bisphenol A and their molecular compound have been determined with the use of the DSC-1B calorimeter with respect to 99.9999 mol% pure gal (International Enzymes Limited, UK), indium and synthetic sapphire [7].

Experimental heat capacity data were correlated with quadratic or linear equations by means of non-linear or linear regression analysis values of ΔC_p, which is the difference between the heat capacities of liquid and solid substances at the melting point, calculated for phenol, bisphenol A and their molecular compound were 15.043, 19.94 and 22.0 cal mol^{-1} K^{-1}, respectively (Table 1).

TABLE 1

Equations correlating heat capacities of phenol, bisphenol A and their molecular compound and ΔC_p calculated from them

Phenol, solid	$\Delta C_p = 15.043$ cal mol^{-1} K^{-1}
$C_p(T) = -4879.95 + 49.6816\,T$ $-0.1675\,T^2 + 1.8957\times10^{-4}\,T^3$	
Phenol, liquid	
$C_p(T) = 24.312 + 0.07592\,T$	
Bisphenol A, solid	$\Delta C_p = 19.94$ cal mol^{-1} K^{-1}
$C_p(T) = 335.272 - 1.5092\,T$ $+2.2456\times10^{-3}\,T^2$	
Bisphenol A, liquid	
$C_p(T) = 254.798 - 0.8047\,T$ $+1.1517\times10^{-3}\,T^2$	
Phenol–Bisphenol A compound, solid	$\Delta C_p = 22.0$ cal mol^{-1} K^{-1}
$C_p(T) = 34.4734 + 0.04237\,T$	
Phenol–Bisphenol A compound, liquid	
$C_p(T) = 22.4659 + 0.1340\,T$	

The solid–liquid phase diagram for the binary phenol–bisphenol A system was determined in the DSC-1B differential scanning calorimeter. Liquidus lines were tested additionally by the Alekseev method.

The incongruent melting phenol–bisphenol A molecular compound in the solid phase was found in the system; the composition of the compound was found to be 70.81 mol% of bisphenol A.

The enthalpy of the incongruent melting compound was measured in the DSC-1B by the extrapolation method in the range of composition from the eutectic to the invariant point, where the pure molecular compound crystallizes.

RESULTS AND CORRELATION

The experimental solid–liquid equilibrium data were correlated by means of liquid phase activity coefficient equations with one constraint and assumption of ideal behaviour of the solid phase. For the sake of correlation the phenol–bisphenol A system was divided into two subsystems: (1) beginning from pure phenol through the eutectic point to the invariant point (371.15 K) on the liquidus line; (2) from pure phenol to the eutectic point and from pure bisphenol A to the same invariant point (371.15 K) on the liquidus line. The following models were tried.

(i) Redlich–Kister polynomial expansions RK-1 (equivalent to Regular) to RK-4 involving 1–4 adjustable parameters

$$\begin{aligned} RT \ln \gamma_1 &= x_2^2\big[A + B(1-4x_1) + C(1-2x_1)(1-6x_1) \\ &\qquad + D(1-2x_1)^2(1-8x_1)\big] \\ RT \ln \gamma_2 &= x_1^2\big[A + B(3-4x_1) + C(1-2x_1)(5-6x_1) \\ &\qquad + D(1-2x_1)^2(7-8x_1)\big] \end{aligned} \tag{1}$$

(ii) Van Laar

$$\begin{aligned} RT \ln \gamma_1 &= Ax_2^2/[x_2 + (A/B)x_1]^2 \\ RT \ln \gamma_2 &= Bx_1^2/[x_1 + (B/A)x_2]^2 \end{aligned} \tag{2}$$

(iii) Renon–Prausnitz (NRTL-2, i.e. with preset $\alpha = 0.3$)

$$\begin{aligned} \ln \gamma_1 &= x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + G_{21}x_2}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + G_{12}x_1)^2}\right] \\ \ln \gamma_2 &= x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + G_{12}x_1}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + G_{21}x_2)^2}\right] \end{aligned} \tag{3}$$

where $\tau_{21} = C_{21}/RT$; $\tau_{12} = C_{12}/RT$; $G_{21} = \exp(-\alpha_{12}\tau_{21})$; $G_{12} = \exp(-\alpha_{21}\tau_{12})$; $\alpha_{21} = \alpha_{12}$. The adopted maximum-likelihood (ML) method [8] leads to minimization of the objective function as

$$Q = \Sigma_{i=1}^{n}\left[\left(\frac{\Delta x_i}{\sigma_x}\right)^2 + \left(\frac{\Delta T_i}{\sigma_T}\right)^2\right] \tag{4}$$

where Δx_i and ΔT_i are differences between the calculated and experimental values of x and T at the i-th experimental point, respectively, and σ_x and σ_T are the standard deviations in temperature and composition, 0.1 K and 0.001 mole fraction, respectively.

Conditions describing the solid–liquid equilibrium (Schroeder equation) were introduced as a constraint

$$\frac{\gamma_i^{\mathrm{s}} y_i}{\gamma_i^{1} x_i} = \exp\left[\left(\frac{\Delta H_{fi}}{T_{fi}} - \Delta C_{pi}\right)\frac{(T_{fi} - T)}{RT} - \Delta C_{pi}\ln\left(\frac{T}{T_{fi}}\right)\Big/ R\right] \tag{5}$$

On the assumption of ideal behaviour of the solid phase (no solubility of the solid in solid) the above equation reduces for the first component to

$$\frac{1}{\gamma_1^{1} x_1} = \exp\left[\left(\frac{\Delta H_{f1}}{T_{f1}} - \Delta C_{p1}\right)\frac{(T_{f1} - T)}{RT} - \Delta C_{p1}\ln\left(\frac{T}{T_{f1}}\right)\Big/ R\right] \tag{6}$$

and the same for the second component with $i = 2$. The symbols denote γ_i^{s}, γ_i^{1}, activity coefficients of solid (s) and liquid (l) phases; x_i, y_i mole fraction of i-th constituent in liquid (x) and solid (y) phases; ΔH_{fi}, heat of melting of i-th constituent; T_{fi}, melting temperature of i-th constituent; T, equilibrium temperature; ΔC_{pi}, difference in heat content between liquid

TABLE 2

Model parameters and values of σ, $\overline{\Delta x_i}$ and $\overline{\Delta T_i}$ for subsystem (1)

Model	Parameters (cal mol^{-1})		σ	$\overline{\Delta x_i}$	$\overline{\Delta T_i}$	$\lvert\kappa_i^{\mathrm{s}}\rvert > 1$
Regular	1061 20		22.501	0.0084	1 12	5
Redlich–Kister 2	1060 27	439 28	4 356	0.0022	0 24	4
Redlich–Kister 3	1080 37	524.97				
	201.60		2 109	0.0010	0 11	4
Redlich–Kister 4	1078.13	544 05				
	320 41	131 35	2.056	0.0009	0.11	3
Van Laar	2145 71	718 84	2.024	0.0009	0 11	4
NRTL-2 ($\alpha = 0\ 3$)	1947 02	−106 08	3.234	0.0017	0.34	5

TABLE 3

Solid–liquid equilibrium for phenol (C_6H_6O)(1)–(Phenol–Bisphenol A) ($C_6H_6O \cdot C_{15}H_{22}O_3$)(2)

Exptl and calcd values of meas. var.						Activity coefficients				
T_e	T_c	X_e	X_c	Y_e	Y_c	GMS1C	GMS2C	GML1C	GML2C	κ
96.45	96.49	0.5311	0.5312	0.00	0.00	1.00	1.00	1.17	1.79	0.18
94.65	94.52	0.5876	0.5871	0.00	0.00	1.00	1.00	1.11	1.91	−0.67
90.00	89.98	0.6751	0.6750	0.00	0.00	1.00	1.00	1.06	2.09	0.09
88.00	88.04	0.7034	0.7037	0.00	0.00	1.00	1.00	1.05	2.16	−0.25
83.45	83.71	0.7542	0.7566	0.00	0.00	1.00	1.00	1.03	2.28	1.71
80.15	80.06	0.7938	0.7927	0.00	0.00	1.00	1.00	1.02	2.37	−0.65
70.25	70.12	0.8672	0.8649	0.00	0.00	1.00	1.00	1.01	2.59	1.24
65.00	64.96	0.8927	0.8917	0.00	0.00	1.00	1.00	1.01	2.70	−0.50
52.50	52.54	0.9350	0.9365	0.00	0.00	1.00	1.00	1.00	2.95	0.76
44.10	44.12	0.9548	0.9560	0.00	0.00	1.00	1.00	1.00	3.11	0.59
37.80	38.13	0.9633	0.9610	1.00	1.00	1.00	1.00	1.00	3.20	1.93
38.50	38.76	0.9718	0.9699	1.00	1.00	1.00	1.00	1.00	3.24	1.53
38.95	38.94	0.9723	0.9724	1.00	1.00	1.00	1.00	1.00	3.25	−0.08
39.10	39.23	0.9774	0.9765	1.00	1.00	1.00	1.00	1.00	3.26	−0.73
39.55	39.64	0.9831	0.9824	1.00	1.00	1.00	1.00	1.00	3.29	−0.54
39.95	39.84	0.9845	0.9853	1.00	1.00	1.00	1.00	1.00	3.30	−0.62
40.00	40.06	0.9887	0.9883	1.00	1.00	1.00	1.00	1.00	3.31	0.33

Standard deviations in observables. No. 1 etc.: $\sigma(T) = 0.1000$, $\sigma(x) = 0.0010$, Goodness-of-fit, $\sigma = 2.109$. Two-variable fit: 17 data points, one constraint(s), three parameters; melting points (°C) = 40.89, 102.00; heats of fusion (cal mol^{-1}) = 2745.00, 8800.00, specific heat differences at m.p. (cal mol^{-1} K^{-1}) = 15.043 22.000 Solid phase model = Ideal, liquid phase model = Redlich–Kister (A, B, C (cal mol^{-1})). Parameter estimates = 1080.37, 524.97, 201.604

and solid phases at melting point of i-th pure component; and R, the gas constant

Application of the maximum-likelihood method, with the errors inherent in the x_i, T_i and y_i observations, assumes to follow a normal distribution pattern and to be mutually independent. An overall measure of the goodness of fit of the model to the experimental data is then

$$\hat{\sigma} = \left[Q_{\min}/(n-m) \right]^{1/2} \tag{7}$$

where the subscript min denotes the value of Q at its minimum, n the number of experimental points, and m is number of model parameters. The distance κ_i between an experimental individual i-th data point (x_i^{E}, T_i^{E}) and the estimate (x_i^{c}, T_i^{c}) of its true value is

$$\kappa_i = \left[\left(\frac{\Delta x_i}{\sigma_x} \right)^2 + \left(\frac{\Delta T_i}{\sigma_T} \right)^2 \right]^{1/2}$$

Recently [8] we have suggested that

$$\kappa_i^{\mathrm{s}} = \left[\mathrm{sign}\ (\Delta x_i) \right] \kappa_i / \hat{\sigma}$$

The sign of Δx_i is attributed to κ_i^{s} in order to have the experimental point located "below" or "above" the response curve. If systematic errors are absent, κ_i^{s} should be randomly distributed about zero. The biggest excursions ($|\kappa_i^{\mathrm{s}}| > 1$) may indicate outliers.

Sybsystem (1)

The composition in subsystem (1), for the sake of avoiding a shift during data reduction, was recalculated to match the proper experimental points in the overall composition. The results of solid–liquid equilibrium data reduction in subsystem (1) are presented in Tables 2 and 3.

TABLE 4

Model parameters and values of σ, $\overline{\Delta x_i}$ and $\overline{\Delta T_i}$ for subsystem (2)

Model	Parameters (cal mol^{-1})		σ	$\overline{\Delta x_i}$	$\overline{\Delta T_i}$	$\lvert\kappa_i^{\mathrm{s}}\rvert > 1$
Regular	−330 48		9.896	0.0058	0.61	6
Redlich–Kister 2	−668.04	397.72	2.147	0.0012	0.12	4
Redlich–Kister 3	−995.87	761.82				
	−313 41		2.876	0.0007	0.07	4
Redlich–Kister 4	−806.51	557.74				
	−130 66	−45.18	1.471	0.0007	0.06	5
Van Laar	−484.66	−2112.01	5.534	0.0032	0.30	6
NRTL-2 ($\alpha = 0.3$)	2222.44	−1365.34	3.591	0.0021	0.20	6

TABLE 5

Solid–liquid equilibrium for phenol (C_6H_6O)(1)–Bisphenol A ($C_{15}H_{22}O_3$)(2)

Exptl and calcd values of meas. var.						Activity coefficients				
T_e	T_c	X_e	X_c	Y_e	Y_c	GMS1C	GMS2C	GML1C	GML2C	κ
150.00	149.80	0.1502	0.1491	0.00	0.00	1.00	1.00	0.54	1.00	−0.79
145.50	145.32	0.2245	0.2233	0.00	0.00	1.00	1.00	0.54	1.00	0.75
140.00	140.08	0.3010	0.3015	0.00	0.00	1.00	1.00	0.54	1.00	−0.33
134.00	134.01	0.3780	0.3781	0.00	0.00	1.00	1.00	0.54	0.99	−0.05
130.00	130.04	0.4200	0.4204	0.00	0.00	1.00	1.00	0.55	0.97	0.19
122.50	122.56	0.4854	0.4862	0.00	0.00	1.00	1.00	0.57	0.94	−0.37
118.00	118.10	0.5175	0.5189	0.00	0.00	1.00	1.00	0.58	0.91	−0.59
111.00	110.86	0.5664	0.5640	0.00	0.00	1.00	1.00	0.60	0.86	0.95
108.00	108.07	0.5780	0.5794	0.00	0.00	1.00	1.00	0.61	0.84	−0.54
100.00	99.93	0.6205	0.6190	0.00	0.00	1.00	1.00	0.63	0.77	0.56
37.80	38.18	0.9735	0.9695	1.00	1.00	1.00	1.00	0.99	0.06	−1.94
38.27	38.45	0.9738	0.9720	1.00	1.00	1.00	1.00	0.99	0.05	0.88
38.50	38.85	0.9794	0.9760	1.00	1.00	1.00	1.00	1.00	0.05	1.69
38.95	39.10	0.9800	0.9786	1.00	1.00	1.00	1.00	1.00	0.05	0.71
39.10	39.39	0.9844	0.9817	1.00	1.00	1.00	1.00	1.00	0.05	1.38
39.55	39.78	0.9880	0.9860	1.00	1.00	1.00	1.00	1.00	0.04	1.05
39.95	39.97	0.9884	0.9882	1.00	1.00	1.00	1.00	1.00	0.04	0.09
40.00	40.19	0.9925	0.9909	1.00	1.00	1.00	1.00	1.00	0.04	0.87

Standard deviations in observables: No. 1 etc. $\sigma(T) = 0.1000$, $\sigma(x) = 0.0010$, Goodness-of-fit $\sigma = 2.876$. Two-variable fit: 18 data points; one constraint(s); three parameters; melting points (°C) = 40.89, 157.94, heats of fusion (cal mol^{-1}) = 2745.00, 7350.00; specific heat differences at m.p. (cal mol^{-1} K^{-1}) = 15.043, 19.940 Solid phase model = Ideal, liquid phase model = Redlich–Kister (A, B, C (cal/mol^{-1})). Parameter estimates = −995 873, 761 816, −313.406

Table 2 summarizes, for all models used, the model parameters, an overall measure σ of the goodness of fit of the model, the mean value of $\overline{\Delta x_i}$, $\overline{\Delta T_i}$ (calculated minus measured) and the last criterion of the goodness of fit: that is, the number of outliers. Table 3 presents a full set of data for the "best" three-parameter Redlich–Kister equation: experimental, "e", and calculated, "c", values of x_1 and T_1, model parameters σ, κ_i^s showing the reproduction of an individual experimental data point and its being "below" or "above" the response curve, and calculated activity coefficients for solid (ideal) and liquid phases.

Subsystem (2)

The results of experimental solid–liquid equilibrium data reduction in subsystem (2) are presented in Tables 4 and 5. Table 4 summarizes for all models the model parameters, an overall measure, σ, of the goodness of fit of the model, the mean value of $\overline{\Delta x_i}$, $\overline{\Delta T_i}$ (calculated minus measured) and the number of outliers. Table 5 presents a full set of data for the "best" Redlich–Kister equation.

When evaluating the goodness of fit of the mathematical model to the experimental data, one should bear in mind the thermodynamic sense of the system.

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