Boiling Points and Surface Tensions of Mixtures

of Benzyl Acetate with Dioxane, Aniline, and *Meta*-Cresol

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Accurate measurements of boiling points and surface tensions of mixtures of benzyl acetate with dioxane, aniline, and *meta*-cresol over the entire range of concentration are reported. Results have been analyzed in terms of the quasi-crystalline model. It is possible to represent composition dependence of heats of mixing, boiling points, and surface tensions by means of equations obtained from this model using different parameter values for each property. The quasi-crystalline model to these systems is empirically applied.

BOILING POINT and surface tension (5) measurements of binary liquid mixtures reported earlier revealed that a number of such mixtures behave like regular solutions. Even in such a mixture as acetone and isopropanol where both acetone and isopropanol are polar molecules, the measurements of heats of mixing (11), boiling points, and surface tensions (6) showed the regular solution behavior. This led to an investigation of some of the more complex binary mixtures such as benzyl acetate with dioxane, aniline, and *m*-cresol. Moore, Russel, and Styan (8, 9) had reported measurements of dielectric constant, volume, and heats of mixing, and had indicated that the different groups of the two components interact. We thought it desirable to supplement the previous studies by further ones involving boiling points and surface tensions.

EXPERIMENTAL

Purification of the material. The best available grades of benzyl acetate and *m*-cresol were dried over anhydrous sodium sulphate for long periods and fractionally distilled. Aniline (A.R.) was dried over caustic potash and fractionally distilled. Dioxane (A.R.) was refluxed with HCl treated with caustic potash, allowed to stand over sodium, and fractionally distilled. The densities at 30° C. were: benzyl acetate, 1.0482; dioxane, 1.0232; aniline, 1.0151; and *m*-cresol, 1.0275. These values agreed with published values.

Equipment. The experimental arrangement used for the determination of boiling points was similar to Smith's (10), except for a few modifications necessary because of the relatively higher temperatures. The Beckman thermometer was replaced by a four-junction copper-constantan thermocouple previously calibrated between 0° to 250° C. The final boiling points are accurate within 0.1° C. For surface tensions, the capillary tube method described by the authors earlier was employed. The accuracy obtained for surface tension was within 0.2%. Density measurements of the pure components as well as the mixtures were made by using a pyknometer described by Mathot and Desmyter (7) and agreed with those quoted by Moore and Styan (9).

Results on boiling points are recorded in Tables I and II, and Figure 1. In Tables I and II, column 3 shows the boiling points T_q of different composition x, calculated (5)
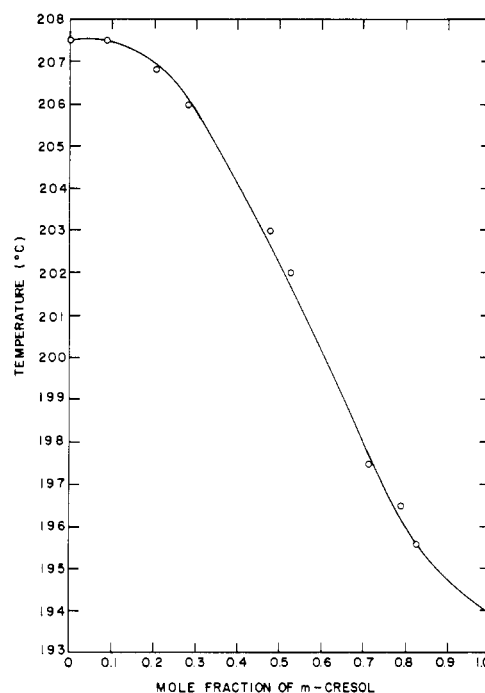
Figure 1. Boiling point of benzyl acetate and *m*-cresol at 600 mm. of Hg pressure

from the Guggenheim (4) quasi-crystalline relation for the saturated vapor pressure P over the mixture, *viz.*,

$$P = P_1 x \exp\left[(1-x)^2 \frac{\omega_T}{RT} \right] + P_2 (1-x) \exp\left[\frac{x^2 \omega_T}{RT} \right] \quad (1)$$

where P_1 and P_2 are the saturated vapor pressures of the pure components 1 and 2 at the absolute temperature T given by the relations of the type:

$$\log_{10} P = (-0.05223 \, \alpha/T) + \beta \quad (2)$$

ω_T is the interaction constant at T, and R is the gas constant. Column 2 shows the boiling points T_i for the corresponding ideal mixture (for which $\omega_T = 0$). The observed boiling points are shown in column 4. Boiling points in the system benzyl acetate–*m*-cresol could not be represented by Equation 1; data for this system are presented graphically in Figure 1, and represented by an empirical equation:

$$T_b = 207.5 - 13.5x + 19.672x (1-x) (1 - 1.456x) \quad (3)$$

Surface tension measurements of the three systems at 30° C. are shown in Figure 2, 3, and 4. The full line curve has been computed by using the quasi-crystalline relation:

$$\exp\left[-\gamma a/kT\right] = x \exp\left[\frac{-\gamma_2{}^a}{kT}\right]\exp\left[\frac{(1-x)^2\,\omega}{4kT}\right]$$
$$+ (1-x)\,\exp\left[\frac{-\gamma_1{}^a}{kT}\right]\exp\left[\frac{x^2\,\omega}{4kT}\right] \quad (4)$$

where γ, γ_1, and γ_2 are the surface tensions of the mixture and the pure molecule in the surface, and k the Boltzmann constant.

Table I. Boiling Points of Benzyl Acetate with Dioxane at 600 mm. of Hg Pressure

$\alpha_1^a = 52329$; $\alpha_2^b = \omega = 878$ cal. mole^{-1} (25° C.)

$\beta_1 = 8.4758$; $\beta_2 = 8.0043$; $(d\omega/dT) = 3.31$ cal. mole^{-1} deg.$^{-1}$

Mole Fraction of Benzyl Acetate	Boiling Points, ° C.		
	T	T_q	T_o
0.00	95.0	95.0	95.0
0.20	100.7	98.5	96.8
0.30	105.0	100.4	98.6
0.40	110.0	102.0	100.5
0.50	116.0	103.0	103.0
0.60	123.4	105.0	106.5
0.70	132.5	107.7	114.2
0.80	145.7	117.5	127.4
0.90	171.5	137.5	150.0
1.00	207.5	207.5	207.5

^{a}Subscript 1 = benzyl acetate. ^{b}Subscript 2 = dioxane.

Table II. Boiling Points of Benzyl Acetate and Aniline at 760 mm. of Hg pressure

$\alpha_1^a = 51058$; $\alpha_2^b = 45952$; $\omega = 24$ cal. mole^1

$\beta_1 = 8.3568$; $\beta_2 = 8.1278$; $(d\omega/dT) = 0$ over the temp. range

Mole Fraction of Benzyl Acetate	Boiling Point, ° C.		
	T_i	T_q	T_o
0.00	184.5	184.5	184.5
0.10	186.6	186.5	186.3
0.30	191.3	191.2	189.9
0.50	196.7	196.5	196.5
0.70	202.8	202.5	203.2
0.90	210.0	209.9	209.9
1.00	214.0	214.0	214.0

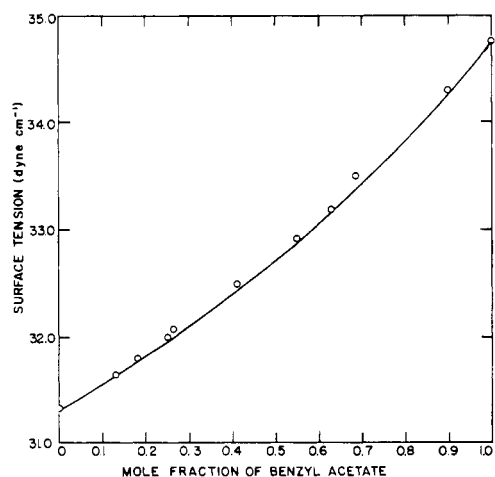^{a}Subscript 1 = benzyl acetate. ^{b}Subscript 2 = aniline.

Figure 2. Surface tension of benzyl acetate and dioxane at 30° C.

The value of a was calculated from the molecular volume of benzyl acetate which was as a spherical molecule. That $a = 46$ A^2 was taken as constant for the three systems under investigation because of the similarity in the sizes of these molecules. The values of ω for the three systems were then calculated from Equation 5 for an equimolecular mixture:

$$\omega = 16kT\log_e \frac{2\exp\left[(\gamma_1 - \gamma)\,a/kT\right]}{1 + \exp\left[(\gamma_1 - \gamma_2)\,a/kT\right]} \quad (5)$$
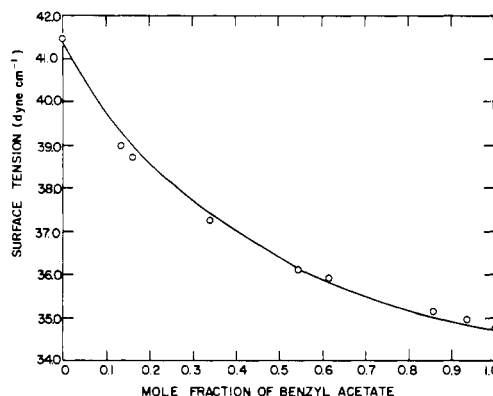

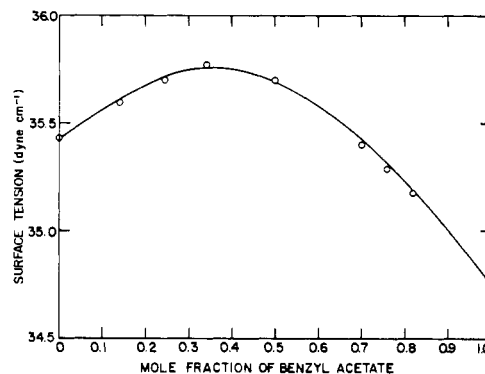Figure 3. Surface tension of benzyl acetate and aniline at 30° C.

Figure 4. Surface tension of benzyl acetate and m-cresol at 30° C.

DISCUSSION

Equations derived from the quasi-crystalline model were reasonably successful in representing composition dependence of heat of mixing, boiling point, and surface tension in these three systems except for the composition dependence of boiling point in the system benzyl acetate-m-cresol. Table III shows, however, that the interaction parameters required for representation differ markedly from property to property, and in fact those representing heats of mixing differ in sign from those representing boiling points and surface tensions. This is in contrast to the six systems reported earlier (1, 5, 6), where a single interaction parameter sufficed for the representation of all three properties for a system. Therefore, the quasi-crystalline model cannot explain the properties of the system of benzyl acetate-dioxane, benzyl acetate-aniline, and benzyl acetate-m-cresol without modification.

Evidence for specific interaction between the two components for these systems has already been advanced from the infrared absorption work (2, 3) which appears to be the reason for this limited agreement between the experiment and the theory.

Table III. Comparison of the Value of "ω" the Interaction
Constant Parameter Obtained from Different Measurements
at 30° C.

	"ω" Cal. Mole^{-1}		
Systems	Heats of mixing	Boiling points	Surface tension
Benzyl acetate and dioxane	−118	894	104
Benzyl acetate and aniline	−64	24	924
Benzyl acetate and m-cresol	−1064		463

ACKNOWLEDGMENT

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Densities of Binary Mercury-Rich Amalgams
of Cadmium and Zinc

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Densities have been measured in binary mercury-rich amalgams containing 0 to 10
atomic per cent cadmium and 0 to 5.6 atomic per cent zinc. Measurements were
obtained over a temperature range from 50° to 150°C. Using the method of least
squares, the density values were used to determine a linear expression for zinc
amalgam densities and a quadratic expression for cadmium amalgam densities as a
function of the atomic fraction of the solute.

Densities FOR MERCURY-RICH AMALGAMS of
cadmium and of zinc at temperatures from 50° to 150° C.
have been measured as part of an investigation of liquid
diffusion behavior in these systems. The density data
previously available for these systems consisted of measure-
ments at 25° C. by Hulett and De Lury (2) for cadmium
amalgams and by Crenshaw (1) for zinc amalgams.

EXPERIMENTAL

Materials and Apparatus. The materials and chemicals
used in this work were ACS Reagent Grade except for the
cadmium which was obtained from the Consolidated Mining
and Smelting Co. of Canada, Ltd., and contained
99.999% Cd.

Dilute amalgams were prepared by dissolving the solute

zinc or cadmium directly in the mercury. The technique
of Hulett and De Lury (2) was used in the production
of the more concentrated amalgams. In this technique,
mercury is made the cathode of a cell, and a platinum
anode is placed in distilled water over the mercury; the
solute material is placed on the mercury surface, and a
12-volt potential applied to the cell in order to enhance
the amalgam formation. This type of cell also provided
a convenient method for storing the prepared amalgams
to avoid the preferential oxidation of the solute. Amalgams
were in some instances stored under a deoxygenated
glycerol layer.

The pycnometers used in the density measurements were
made using a T/S No. 19/38 borosilicate glass ground
joint as shown in Figure 1. The capillary section of the
pycnometer was approximately 0.5 mm. inside diameter.
The pycnometer volumes were approximately 14.5 cc. and
the weight of the pycnometer and amalgam charge was
approximately 190 grams. The apparatus shown at the
right in Figure 1 was used in the preparation of some