This system was determined to indicate the curvature of the glaserite field.

	Composition of liquid phase, g./100 g. H₂O		
Solid phase	K_2SO_4	Na_2SO_4	$MgSO_4$
K_2SO_4	15.75	2.75	13.10
K_2SO_4	15.95	5.10	13.10
Glaserite	15.45	6.30	13.10
Glaserite	14.10	8.90	13.10
Glaserite	11.90	14.60	13.10
Glaserite	10.55	19.65	13.10
Glaserite	8.70	29.00	13.10
Na_2SO_4	5.90	38.95	13.10
Na_2SO_4	4.05	39.25	13.10
Na_2SO_4	2.20	39.00	13.10

of the boundaries between the glaserite, schoenite and astrakhanite fields. The correctness of our results is supported by (a) the fact that the experimental points on the lines MN, ZN and JN converge accurately to the experimental point N; and (b) that preliminary experiments on systems made up to correspond with equilibrium according to D'Ans showed that these systems were not in equilibrium, since on rotation in the thermostat some or all of the solid phases disappeared. The preliminary experiments confirmed the experience[9] of previous investigators that equilibrium with respect to glaserite and astrakhanite is established very slowly. This was one reason for our experimental expedient of beginning with a solution of approximately the correct composition and adding ample excess of each of the expected solid phases.

The points representing equilibrium with solutions of constant magnesium content (the line bfgc in Fig. 1) serve to indicate the form of the glaserite surface, and should make it possible to estimate, with reasonable accuracy, the composition of all the solutions that can exist in equilibrium with glaserite.

Summary

The system K_2SO_4–Na_2SO_4–$MgSO_4$–H_2O has been completely re-determined at 35°. The boundaries between the glaserite, schoenite and astrakhanite fields have been revised, and the shape of the glaserite surface is described in some detail.

(9) Ref. 3, pp. 131, 109.

NEDLANDS, WESTERN AUSTRALIA
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The Physical and Chemical Properties of Hydrocarbon Solutions of Aluminum Bromide. I. The Solubility of Aluminum Bromide in n-Hexane[1]

BY EDWARD R. BOEDEKER[2] AND ALEX G. OBLAD[2]

During the course of a detailed study of a number of hydrocarbon reactions catalyzed by aluminum bromide it was found necessary to determine the solubility of aluminum bromide in n-hexane. The results of these solubility determinations are here reported. The solubility of aluminum bromide in n-butane has been determined by Heldman and Thurmond.[3] Using their data and those obtained in the present study the solubility of aluminum bromide in normal paraffin hydrocarbons is discussed from a standpoint of an ideal solution and Hildebrand's theory of regular solutions.

Experimental

Because of the ease with which an aluminum bromide–hydrocarbon complex is formed in the presence of water or oxygen,[4] it was necessary to exercise extreme caution so that no water or oxygen was admitted to the ampules while charging them with the aluminum bromide and hydrocarbon.

The hydrocarbon employed was Phillips commercial n-hexane which was freed of aromatics by treatment with fuming sulfuric acid. The resulting product was then distilled through a fractionating column of approximately 55 theoretical plates. The middle fraction of the n-hexane flat was used and had the following physical properties: b. p. 68.2° (750 mm.), $n^{25}D$ 1.3722 (lit.[5] b. p. 68.3° (750 mm.), $n^{25}D$ 1.3722).

The aluminum bromide was prepared by direct combination of the elements and was distilled twice in the presence of metallic aluminum before being introduced into the reservoir of the vacuum system.

The glass ampules which were used in the solubility studies were charged with aluminum bromide and n-hexane in the following manner: The weighed glass ampule was attached to a vacuum system by means of a ground glass joint. The

(1) Presented as part of a paper given at the Southwest Regional Meeting of the American Chemical Society. Dallas, Texas. December 12 and 13, 1946.

(2) Present address: Texas State Research Foundation, Renner, Texas.

(3) Heldman and Thurmond, THIS JOURNAL, **66**, 427 (1944).

(4) Pines and Wackher, ibid., **68**, 595 (1946); Oblad and Gorin, Ind. Eng. Chem., **38**, 822 (1946); Montgomery, McAter and Franke, THIS JOURNAL, **59**, 1768 (1937).

(5) A. P. I. Project No. 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons, June 30, 1945.

system was evacuated and aluminum bromide was distilled into the ampule. The system was brought to atmospheric pressure by admitting nitrogen, which had been freed of oxygen by passing over copper turning at 350° and dried by passing through a column of barium oxide and then through phosphorus pentoxide. n-Hexane from a calibrated and thermostated buret was charged to the ampule, the latter being still attached to the vacuum system. The contents of the ampule were then frozen in liquid nitrogen, the system evacuated, and the ampule sealed off. The two pieces of the ampule were weighed. Since the amount of n-hexane charged to the ampule was known, as was the weight of the ampule itself, the weight of aluminum bromide charged was obtained by weight difference.

The buret containing the n-hexane was thermostated by the circulation of water from a constant temperature bath through a jacket surrounding the buret.

The buret for introducing the n-hexane was calibrated and gave amounts of n-hexane which were reproducible within ±0.05% or less.

The ampules, as first prepared, contained large crystals of aluminum bromide. To ensure equilibrium between the liquid and solid phase during the solubility measurements, the ampules were heated to dissolve completely the aluminum bromide and were then immersed in cold water and shaken vigorously to obtain small crystals. The small crystals so obtained dissolved readily upon subsequent heating.

The method of obtaining the solubility curve was essentially that used by Heldman and Thurmond.[3] The ampules were rotated mechanically in a water-bath, whose temperature was slowly increased. The temperature at which the last crystal of aluminum bromide disappeared was taken as the solution temperature. The rate of heating near the solution temperature was about 0.2° per minute. Temperatures were read on a calibrated (Bureau of Standards) 0.1° thermometer. Solution temperatures were reproducible to 0.2°.

That the conditions under which the ampules were prepared were anhydrous is attested by the fact that only one ampule showed any complex formation. No analyses were made to determine the amount of isomerization which had taken place in the ampules. However, on the basis of experimental work carried out by the authors on the isomerization of n-hexane, it can be concluded that no isomerization occurred between the time the ampules were prepared and the solubility measurements made.

Results

In Table I are given the solution temperatures and compositions of the solutions examined. The moles of aluminum bromide are calculated on the basis of the formula Al_2Br_6. The total moles of

n-hexane in the liquid phase was obtained by subtracting from the total hexane charge the estimated moles of vapor. The moles of vapor was approximated using the vapor pressure of n-hexane[6] at the solution temperature, assuming both the perfect gas equation and Raoult's law to be valid for the system. The vapor volume in all of the ampules was estimated to be about 2 cc.

TABLE I

SOLUTION TEMPERATURES OF ALUMINUM BROMIDE–n-HEXANE MIXTURES

t, °C.	Al₂Br₆ Wt. % liq. phase	Mole fract.	t, °C.	Al₂Br₆ Wt. % liq. phase	Mole fract.
30.6	31.00	0.068	60.3	70.56	0.280
33.1	34.55	.079	60.5	70.73	.281
40.5	41.98	.105	69.8	81.68	.420
44.1	46.47	.123	70.3	82.47	.433
48.5	51.46	.146	70.7	82.18	.428
49.9	53.36	.154	72.6	84.81	.476
50.0	53.95	.156	82.4	92.91	.685
50.6	55.11	.166	86.6	95.00	.757
53.9	58.80	.188	97.5[a]	100.0	.000
55.0	62.1	.209			

[a] Miscible at this point in all proportions with n-hexane.

The consistency of the results points to an accuracy of about 1 or 2% in determining the composition of the mixtures. The maximum deviation from the smoothed curves drawn through the experimentally determined points occurs at 82.4° and is in error by 2.7%.

At the melting point and temperatures above this liquid aluminum bromide and hydrocarbons are miscible in all proportions.

Discussion

The plot of the logarithm of the solubility expressed in mole fraction of aluminum bromide dimer vs. the reciprocal of the absolute temperature is shown in Fig. 1. All of the points fall close to a smooth curve of the inverted S type. This type curve is encountered when the solvent and solute have different internal pressures.[7]

The solubility of aluminum bromide in n-butane is shown in Fig. 1, as is also the ideal solubility. The ideal solubility was calculated from the van't Hoff isochore

$$\log N = \frac{L_f}{4.58}\left(\frac{1}{T} - \frac{1}{T_m}\right) \qquad (1)$$

using the heat of fusion of 5.4 kcal. per mole of dimer[8] and the molar heat capacity data (cal./mole/deg.) for solid and liquid aluminum bromide as given by Kelley[8c]

solid $C_p = 37.48 + 37.32 \times 10^{-3}T$
liquid $C_p = 59.02$

(6) Kay, THIS JOURNAL, **68**, 1336 (1946).

(7) Hildebrand, "Solubility of Non-Electrolytes," Reinhold Publishing Co., New York, N. Y., 1936, p. 170.

(8) (a) Fischer, *Z. anorg. allgem. Chem.*, **200**, 332 (1931); (b) Kabkukoa, *C. A.*, **3**, 970 (1909); (c) Kelley, *Bur. Mines Bull.*, 371 (1934).
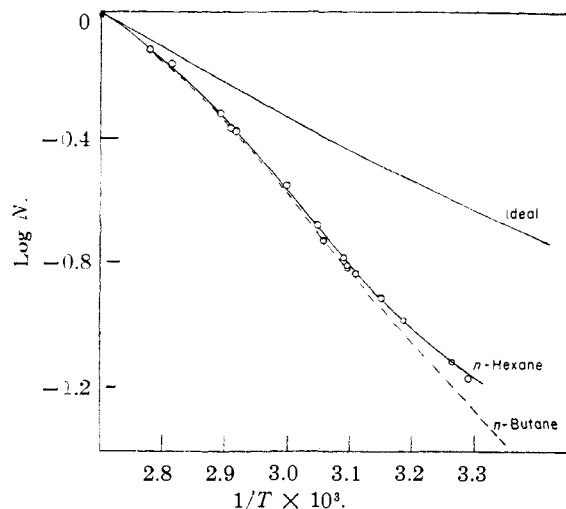
Fig. 1.—Solubility of aluminum bromide in n-hexane and in n-butane (N = mole fraction Al_2Br_6).

Aluminum bromide is somewhat more soluble in n-hexane than in n-butane on a molar basis, but its solubility is still much smaller than the ideal solubility as calculated previously. The increased solubility of aluminum bromide in n-hexane over that in n-butane is to be expected on the basis of the internal pressure characteristics of the two hydrocarbons. From the data given by Hildebrand[9] for the internal pressures of the straight chain paraffins, it can be predicted that the solubility of aluminum bromide would increase in going from one normal paraffin hydrocarbon to the next higher number of the homologous series since there is a regular increase in the internal pressure for each additional $-CH_2$-group.

By referring to Fig. 1 it can be seen that at the lower temperatures the solution of aluminum bromide in n-hexane is more nearly ideal than the corresponding solution of n-butane.

In order to determine how well solutions of aluminum bromide in hydrocarbons behave as regular solutions, $\ln\gamma_1$ for aluminum bromide was calculated at several temperatures for the system n-hexane–aluminum bromide as well as for the system n-butane–aluminum bromide making use of Hildebrand's[10] equation for regular solutions where the components have differing molar volumes

$$RT \ln\gamma_1 = V_1 \left(\frac{N_2 V_2}{N_1 V_1 + N_2 V_2}\right)^2 \left[\left(\frac{\Delta E_1}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2}{V_2}\right)^{1/2}\right]^2 \quad (2)$$

The values of $\ln\gamma$, thus calculated were compared to the observed values. A summary of these calculations is given in Table II. The values of ΔE_1 and V_1 for n-hexane were calculated from the heat of vaporization and the densities given by Lemons and Felsing.[11] The heat of

(9) Ref. 7, p. 104.
(10) Ref. 7, p. 73.
(11) Lemons and Felsing, THIS JOURNAL, **65**, 46 (1943).

vaporization of aluminum bromide at the boiling point is 12.0 kcal. per mole of dimer.[12] Using the value of ΔC_p of vaporization = -18 cal./mole/deg.[12] the heat of vaporization of aluminum bromide was estimated at the several temperatures and the energy of vaporization obtained by subtraction of RT. From the density of solid aluminum bromide at 25°, 3.01 g./cc. and the coefficient of cubical expansion, 2.83 $\times$ 10^{-4} cc./deg.,[13] the molal volume of solid aluminum bromide at 100° was calculated to be 181 cc. At that temperature, the molal volume of the liquid is 203 cc.[14] The molal volume of liquid aluminum bromide was calculated at other temperatures using the percentage increase of volume upon melting at 100° and the data given previously for the solid.

The values of ΔE_2 and V_2 for n-butane were calculated from careful plots of the data of Sage, Webster and Lacey.[15]

The "observed" values for $\ln\gamma_1$ were taken as the logarithm of the ratio of the ideal solubility to the observed solubility.

TABLE II

$\ln\gamma_1$ FOR ALUMINUM BROMIDE IN n-BUTANE AND n-HEXANE SOLUTIONS

| | | $\ln\gamma_1$ | | |
| | n-Butane | | n-Hexane | |
t, °C.	From Equation 2	Observed	From Equation 2	Observed
25	1.31	1.68	0.78	1.63
40	1.20	1.17	.68	1.09
60	0.77	0.56	.56	0.57
80	.21	.11	.10	.10

At the lower temperatures, it can be stated that the calculated and observed values of $\ln\gamma_1$ are in better agreement for the system containing n-butane than for the one containing n-hexane. Thus, the n-hexane aluminum bromide system is less regular in the Hildebrand sense than the corresponding n-butane system. However, as the temperature is increased the agreement between calculated and observed values of $\ln\gamma_1$ for both systems is more satisfactory.

Heldman and Thurmond[3] have calculated the value of $\ln\gamma_1$ at 25° for aluminum bromide for the system n-butane–aluminum bromide making use of equation (2). They estimated values of ΔE_1 and V_1 for aluminum bromide and used values of ΔE_2 and V_2 for n-butane given by Hildebrand.[9] $\ln\gamma_1$ calculated by them was 1.4 and this was compared to the observed value of 1.3 (taken as the logarithm of the ratio of the ideal to the observed solubility at 25°, the ideal solubility was taken by them from equation (1) using the heat of fusion at the melting point of aluminum bromide). In view of the values obtained in Table II, the agreement

(12) Fischer and Rahlfs, Z. anorg. allgem. Chem., **205**, 1 (1932).
(13) Klemm, Tilk and Muellenheim, ibid., **176**, 11 (1928).
(14) Biltz and Voight, ibid., **126**, 39 (1923); Sugden, J. Chem. Soc., 316 (1929).
(15) Sage, and Webster and Lacey, Ind. Eng. Chem., **29**, 1188 (1937).

obtained by Heldman and Thurmond for $\ln \gamma_1$ at 25° is a result of their failing to take into consideration the change of the heat of fusion with temperature.

It can be concluded from the present study that a solution of aluminum bromide in a normal hydrocarbon becomes more ideal as the number of carbon atoms in the hydrocarbon increases.

From the relationship of the experimental solubility curves for aluminum bromide in n-butane and n-hexane, it is further concluded that such systems are quite regular in the Hildebrand sense, i.e., the solubility curves for any one solute in a number of different solvents will form a family of curves.

Summary

The solubility of aluminum bromide in n-hexane has been measured from 30.6° to the melting point of the salt.

The difference between the actual and the ideal solubility of aluminum bromide in n-hexane and n-butane is in approximate conformance with the internal pressure characteristics of these hydrocarbons according to the equation of Hildebrand.

Data are still not sufficient to allow the prediction of the solubility of aluminum bromide in a normal paraffin hydrocarbon.

DALLAS, TEXAS   RECEIVED FEBRUARY 10, 1947

The Electric Moments of Some Aromatic Selenium Compounds

BY MAX T. ROGERS AND TOD W. CAMPBELL

Very few measurements of the dipole moments of organic compounds of selenium have been made. Since information concerning bond angles, bond moments, and resonance in selenium compounds may be derived from such data, the electric moments of a series of aromatic selenides, diselenides and selenocyanates have been measured in benzene solution.

Experimental

Materials

Benzene.—J. T. Baker C. P. benzene was dried over sodium and filtered before use, d^{25}_4 0.87340, n^{25}D 1.4978.

Purification and Analysis of Compounds.—The compounds reported are all solids described in the literature. They were obtained in a high state of purity by repeated fractional crystallization to constant melting point. Most were analyzed for selenium by a flame combustion method.[1]

Dibenzyl diselenide was prepared by allowing benzyl selenocyanate to stand in methanol for ten days. The crude product was purified and analyzed[1]; m. p. 93°.

Diselenides.—Other diselenides were prepared from the corresponding Grignard reagent by addition of purified[2] selenium. The resulting selenophenol was oxidized to the diselenide with a stream of air[2,3]; diphenyl diselenide, m. p. 63°; di-p-tolyl diselenide, m. p. 47°; di-p-bromophenyl diselenide, m. p. 108°.

Selenides.—These were prepared from the corresponding diazotized amine and potassium selenide[4]; di-p-tolyl selenide, m. p. 69.5; di-p-chlorophenyl selenide, m. p. 96°. Benzyl selenocyanate was prepared from benzyl chloride and potassium selenocyanate in alcohol,[5] m. p. 72°.

Selenocyanates.—Other selenocyanates were prepared from the corresponding diazotized amine and potassium

selenocyanate after the method of Behagel and Rollman[6]; p-tolyl selenocyanate, m. p. 70°; p-chlorophenyl selenocyanate, m. p. 55°.

Apparatus and Methods

Electric moments were determined in benzene at 25° by the dilute solution method. Dielectric constants were measured to ± 0.001 with a heterodyne-beat apparatus previously described[7]; densities to ± 0.00005 with a graduated pycnometer[8] of 10-ml. capacity. Refractive indices were determined to ± 0.0001 with a Zeiss Abbe refractometer. The mole refractions of the solids were calculated from the refractive indices n^{25}D of the solutions using the equations

$$R_{12} = \frac{(n^2 - 1)}{(n^2 + 2)} \frac{M_1 f_1 + M_2 f_2}{d}$$

and MR_D (solute) $= R_2 = (R_{12} - R_1)/f_2 + R_1$ where R_1, R_2 and R_{12} are the mole refractions of solvent, solute, and solution, respectively; d the density of a solution containing mole fraction f_2 of solvent of molecular weight M_1. The average of the values of MR_D obtained as above from solutions of different concentration, was used as the sum of the atomic and electronic polarizations in calculating μ.[9] Since the dispersion correction to MR_D and the atomic polarization tend to cancel both have been neglected rather than try to estimate two small uncertain quantities.[10]

The experimental data and molar polarizations are shown in Table I; the derived values of the molar polarization at infinite dilution P_∞, the mole refraction MR_D, and the dipole moment μ,

(1) J. D. McCullough, T. W. Campbell and N. J. Krilanovich, Ind. Eng. Chem. Anal. Ed., **18**, 638 (1946); the analyses of seven of the compounds used here are given in this article.

(2) T. W. Campbell and J. D. McCullough, THIS JOURNAL, **67**, 1965 (1945).

(3) D. G. Foster, "Organic Syntheses," Vol. XXIV, John Wiley and Sons, New York, N. Y., 1944, p. 89.

(4) H. M. Leicester, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, N. Y., 1943, p. 238.

(5) C. L. Jackson, Ann., **179**, 1 (1875).

(6) O. Behagel and M. Rollman, J. prakt. Chem., **123**, 336 (1929).

(7) M. T. Rogers and J. D. Roberts, THIS JOURNAL, **68**, 843 (1946).

(8) G. R. Robertson, Ind. Eng. Chem. Anal. Ed., **11**, 464 (1936).

(9) For method of calculation, see Smyth, "Dielectric Constants and Molecular Structure," Reinhold Publishing Co., New York, N. Y., 1931.

(10) C. P. Smyth, THIS JOURNAL, **51**, 2051 (1929).