for magnesium chloride except for the 100 wt % solvent. The marked decrease in the conductivity of magnesium sulfate is probably due to the decrease in solubility in higher weight percent solvents.

Inspection of the constants a and b show some of the following tendencies. The viscosity seems to influence the constant a in a reciprocal fashion since, in general, the constant a goes through a minimum at the middle weight percent solvents which is opposite in trend with the viscosity as a function of weight percent ethanol. The constant b tends to become more negative while the dielectric constant decreases, this may imply that there is a reciprocal relationship between b and the dielectric constant of the solvent as a function of temperature.

Figure 5 is an interesting graph of the ratio L/L_m vs. the ratio C/μ for the various solvents and temperatures of magnesium sulfate and magnesium chloride with a total of 345 points. This plot may indicate that the opposing forces acting on the electrolyte at the point on the conductance curve where $L = L_m$ and $C = \mu$ are virtually the same regardless of the temperature, solvent composition, and the nature of the electrolyte. The opposing effects are balanced at L_m and μ, thus giving two experimentally determined parameters which may be used in an empirical equation to represent the specific conductance of electrolytes in solvents that give maxima or for those solvents where the maxima may be found by a reasonable extension of the empirical equation.

In Equation 3, if theoretical significance could be assigned to constants a and b, the equation would become a theoretical one. The authors are working on this problem at present.

ACKNOWLEDGMENT

We thank L. B. Sims for the weighted least-squares program and Alan Baker of the University of Arkansas Computer Center for his assistance with the Calcomp Plotter.

LITERATURE CITED

(1) Akerlof, G. C., *J. Am. Chem. Soc.*, **54**, 4125 (1932).
(2) Amis, E. S., Casteel, J. F., *J. Electrochem. Soc.*, **117**, 213 (1970).
(3) Amis, E. S., Foster, N. G., *Z. Physic. Chem. NF*, **3**, 365 (1955).
(4) Amis, E. S., Goldenberg, N., *ibid.*, **30**, 65 (1961).
(5) Amis, E. S., Than, A., *J. Inorg. Nucl. Chem.*, **31**, 1685 (1969).
(6) Bockris, J. O'M., Kortum, G., "Textbook of Electrochemistry," Vol. I, p. 199, Elesvier, New York, N.Y., 1951.
(7) Bradshaw, B. C., Jones, G., *J. Amer. Chem. Soc.*, **55**, 1780 (1933).
(8) Brasunstein, J., Robbins, C. D., *J. Electrochem. Soc.*, **9**, 1218 (1969).
(9) Smith, E. L., *J. Chem. Soc.*, (1927), **1927**, p 1288.
(10) Wentworth, W. E., *J. Chem. Educ.*, **42**, 96 (1965).
(11) Wentworth, W. E., *ibid.*, p 162.

Received for review March 1, 1971. Accepted September 24, 1971. Work supported by NASA and NDEA. Complete computer versions of the specific conductance of magnesium sulfate and magnesium chloride will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Business Operations Department, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036, by referring to author, title of article, volume, and page number. Remit by check or money order $5.00 for photocopy or $2.00 for microfiche.

Solubility of Propane and Carbon Dioxide in Heptane, Dodecane, and Hexadecane

WALTER HAYDUK,[1] EDGAR B. WALTER, and PHILIP SIMPSON
Department of Chemical Engineering, University of Ottawa, Ottawa, Ont., Canada

New data are reported for the solubilities of propane and carbon dioxide gases in normal heptane, dodecane, and hexadecane over the temperature range from 10–50°C.

The solubility devices used in these experiments were of the type described previously (*5*). The measurements entailed a small flow of deaerated solvent, continuously in contact with gas in a spiral tube, while the rate of gas absorption was measured volumetrically by observing the volumetric rate of shrinkage of gas confined at constant pressure in a buret over mercury. The mercury leveling bottle was raised by a rotating threaded shaft, chain-driven by a variable-speed motor of about 10–100 rpm. A spring-loaded half nut supporting the leveling table could be engaged into the rotating shaft at any desired elevation. The mechanical leveling device accurately controlled the gas volume and hence gas pressure. A U-tube in each of the solubility devices served to keep the volume of the absorbing system constant while solution was being accumulated. A difference in levels in the U-tube represented essentially the deviation in pressure from atmospheric pressure which could always be kept to less than 1 cm of liquid, and when the gas volume was read, to less than 0.1 cm, by suitable adjustment of the motor speed. The solubility measurements, therefore, were always performed at essentially atmospheric pressure.

The design of the solubility apparatus permitted the measurement of the residual volume of vapor-free gas. In this design the problem of incomplete saturation of the gas with solvent vapor was entirely avoided. Care had to be taken, however, to maintain at least a small flow of gas from the gas buret into the absorption spiral at all times during the experiment to prevent any diffusion of solvent vapor back into the gas buret.

Two different solubility devices were used, one for high solubility (propane) and the other for moderate solubility (carbon dioxide) as shown in Figure 1. The first used a solution microburet and gas buret, of 5.0 ml (graduated to 0.01 ml), and 50-ml capacity, respectively. Deaerated liquid was charged into the apparatus by means of a Harvard Apparatus syringe pump using a 0.25-rpm motor along with a 10-ml gas-tight Hamilton syringe. The solvent infusion rate was 0.04402 ml per min. The volumetric infusion rate was determined accurately by weighing the quantity of distilled water delivered in a given period of time. The very low infusion rate for deaerated solvent was consistent with the very high propane solubility. The end of the syringe needle touched the wall of the spiral to ensure that an uninterrupted film of solvent flowed

---

[1] To whom correspondence should be addressed.

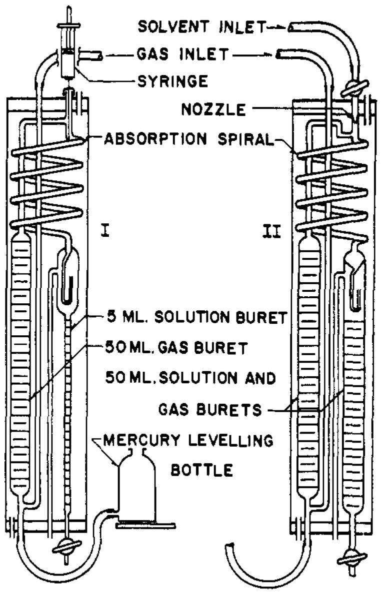

Figure 1. Apparatus for highly soluble gases (I) and moderately soluble gases (II)

down the tube to keep the pressure in the gas buret constant. If the solvent entered dropwise, the gas pressure tended to vary in a cycle equivalent in frequency to that for drop formation.

The second solubility apparatus utilized solution and gas burets both of 50-ml capacity because the Ostwald coefficients of carbon dioxide were of the order of 1 (ml gas/ml solvent). This apparatus was connected directly to the deaerating device while the solvent flow rate was controlled by means of a stopcock to give an approximate flow of 0.2 ml/min. In this case the volume of solution accumulated was used as a basis for calculating the solubility, whereas in the formerly described apparatus the elapsed time for a particular measurement was taken to represent a specific solvent volume.

The degassing apparatus consisted of a leveling bottle used for the first stage of deaeration and a glass tube about 1 cm in diameter and 100 cm in length for the second stage. A 1-mm capillary was sealed into the side of the tube, the lower end of which was either closed with a septum stopper for withdrawal of solvent by syringe, or connected directly to the solubility apparatus. After initial deaeration under vacuum for about 30 min the solvent was permitted to flow from the bottle through the capillary nozzle and to spray into the tube where it was accumulated. A heater was provided for heating the less volatile solvents in the first stage of deaeration.

The procedure for measuring the solubilities with either solubility apparatus was essentially the same. Constant temperature (±0.05°C) water was circulated through the jacket. The temperature drop of the heating water for the measurements at 40°, 45°, and 50°C was less than 0.2°C so that the temperature at the inlet was increased slightly to yield the desired average temperature in the jacket. While the solvent was being deaerated, dry gas was slowly purged through the apparatus. During the latter operation the mercury level was lowered below the gas inlet tee. While the gas was flowing, a flow of deaerated solvent was started into the apparatus either by syringe or directly through the stopcock, and both streams were purged through the apparatus for about 30 min. Solution accumulated in the solution buret was then drained, the solvent rate was adjusted if necessary, and a quantity of solution was accumulated in the solution buret until the volume could be easily read. The mercury-raising device was started confining a volume of gas in the gas buret. The gas flow was stopped and the inlet tube, now effectively becoming one leg of a manometer, was opened to the atmosphere. The pressure in the absorption spiral was regulated by adjusting the motor speed. Successive pairs of readings of residual dry gas volume and solution volume (or time) were obtained at suitable time intervals. A linear plot of gas volume and solution volume (or solvent volume) was made in each case and an average slope obtained. One solubility determination took from 2 to 4 hr.

Tests were performed to ensure that the solution leaving the absorption spiral was fully saturated with gas. The solvent flow was reduced to about half the normal rate and the solubility determined. Because the solubility at the reduced solvent rate was invariably identical within experimental error to that performed at the normal rate, it was assumed that with the flow rates and length of absorption spiral used, the solution was indeed saturated.

The solubilities were expressed as the Ostwald coefficient, L, and the mole fraction dissolved gas at a gas partial pressure of 1 atm was named x. The Ostwald coefficient has been defined (*1*) as the volume of gas which will dissolve in a unit volume of solvent at the particular temperature. Further, to the limit that Henry's law applied, the Ostwald coefficient is independent of pressure. The experiments were all performed at a total pressure equivalent to the prevailing barometric pressure. The volume of vapor-free gas that dissolved in the solvent was measured at a condition different from that existing near the gas-liquid interface within the absorption spiral where the gas was considered to be saturated. An adjustment was required to determine the volume that the gas would occupy if saturated with solvent vapor:

$$v_G = v_G' \frac{P_t}{p_G} \tag{1}$$

With apparatus I, the volumetric rate at which solvent was charged into the apparatus was directly available by considering the total elapsed time during the solubility determination:

$$v_L = \theta S \tag{2}$$

The volume of solution rather than volume of solvent, was obtained with apparatus II. The volume of solvent contained in a given volume of solution involved a knowledge of the partial molal volume of the dissolved gas:

$$v_L = v_S - \frac{v_G p_G V_L}{V_G} \tag{3}$$

The second term of the above equation represents the volume of solution occupied by the dissolved gas and although small, was calculated. The Ostwald coefficient is then given by:

$$L = \frac{v_G}{v_L} \tag{4}$$

The solubility was also expressed as a mole fraction in solution, x, for a gas partial pressure of 1 atm. Henry's law was used in converting the solubility at a gas partial pressure p_G, of slightly less than atmospheric pressure, to that at exactly 1 atm.

The gases used in these experiments were obtained from the Matheson Co. The propane was of the Instrument grade having a specified minimum purity of 99.5% and the carbon dioxide was of the Coleman Instrument grade having a specified minimum purity of 99.99%. The gas molar volumes at 25°C and 1 atm pressure were taken as 24, 342 cc/g mol (*2*), and 24, 111 cc/g mol (*3*) for carbon dioxide, and propane, respectively. Gas molar volumes were interpolated from the compilations of Din.

The solvents were supplied by Canadian Laboratory Supplies (Canlab). The hexane and heptane were of the Chromatoquality grade with a specified minimum purity of 99.0 mol % and had lot analyses well above the minimum specification. The dodecane and hexadecane were specified olefin-free with minimum purities of 99.0%. Refractive indices of the paraffin solvents of similar grade had formerly (*5*) checked those of

Table I. Solubilities of Propane and Carbon Dioxide in Hexane, Heptane, Dodecane, and Hexadecane

Gas	Solvent	Temp, °C			
		25	35	45	
Propane	Hexane L	23.75			
	x	0.115			
	x	0.116 (7)			
	Heptane L	21.65	17.30	14.60	
	x	0.117	0.0942	0.0798	
	Dodecane L	14.95	12.24	10.21	
	x	0.123	0.101	0.0831	
	Hexadecane L	12.65	10.25	8.58	
	x	0.133	0.109	0.0896	
		10	25	40	50
Carbon dioxide	Heptane L	2.24	1.95	1.71	
	$(10^4)\,x$	139	117	99.5	
	$(10^4)\,x$		121 (4)		
	Dodecane L	1.55	1.37	1.22	
	$(10^4)\,x$	149	127	109	
	Hexadecane L		1.16	1.05	1.00
	$(10^4)\,x$		138	121	113

L = Ostwald coefficient; x = mole fraction.

other workers. The densities and vapor pressures (calculated from Antoine constants) were obtained from Rossini (*6*).

RESULTS

The solubilities of propane at 25°, 35°, and 45°C in heptane, dodecane, and hexadecane and of carbon dioxide at 10°, 25°, and 40°C in heptane and dodecane, and at 25°, 40°, and 50°C in hexadecane are reported in Table I both as Ostwald coefficients and mole fractions. The solubility of propane in hexane at 25°C was measured and compared with that of Thomsen and Gjaldbaek (*7*). A similar comparison was made for the solubility of carbon dioxide in heptane at 25°C with that of Gjaldbaek (*4*). Whereas the former comparison was very favorable (within 1%), the latter comparison was not (about 3% difference). Because Gjaldbaek described corrections for contamination of air in the carbon dioxide for his measurements, we considered the possibility for error in his reported results. Repeated attempts failed to reproduce the somewhat higher value.

ACKNOWLEDGMENT

The authors acknowledge with appreciation use of the University of Ottawa Computing Centre.

NOMENCLATURE

L = Ostwald coefficient
p_G = gas partial pressure, atm
P_t = total pressure, atm
S = solvent infusion rate, ml/min
v_G' = volume of dry gas absorbed, ml
v_G = equivalent volume of vapor saturated gas absorbed, ml
v_L = volume solvent, ml
v_S = volume solution, ml
V_G = gas molar volume at atmospheric pressure and temperature of experiment, ml/g mol
V_L = partial molal volume of dissolved gas in solntion, ml/g mol
x = mole fraction dissolved gas at partial pressure of 1 atm
θ = elapsed time of solubility experiment, min

LITERATURE CITED

(1) Battino, R., Clever, H. L., *Chem. Rev.*, **66**, 395 (1966).
(2) Din, F., "Thermodynamic Functions of Gases," Vol. 1, p 124, Butterworths, London, 1956.
(3) Din, F., *ibid.*, Vol. 2, p 136, 1962.
(4) Gjaldbaek, J. C., *Acta. Chem. Scand.*, **7**, 537 (1953).
(5) Hayduk, W., Cheng, S. C., *Can. J. Chem. Eng.*, **48**, 93 (1970).
(6) Rossini, F. D., et al., Am. Petroleum Inst. Res. Project 44, *Circ.*, Natl. Bur. Stand., 1947.
(7) Thomsen, E. S., Gjaldbaek, J. C., *Acta Chem. Scand.*, **17**, 134 (1963).

Received for review March 10, 1971. Accepted September 7, 1971. Work supported by an operating grant from the National Research Council of Canada.

Liquid-Solid Equilibria in the Na^+—$HCOO^-$, —CNS^-, —NO_3^- Ternary System

MARIA A. BERCHIESI, AUGUSTO CINGOLANI, and GIANFRANCESCO BERCHIESI[1]
Istituto Chimico, Università degli Studi, 62032 Camerino, Italy

Thermal analysis and differential scanning calorimetry were used to study solid-liquid equilibria in order to draw the polythermal projection of the ternary system Na^+—$HCOO^-$, —CNS^-, —NO_3^-. Five crystallization regions and three invariant points were identified.

Research on the molten salts systems showed the connections between polythermal projections of the systems and the thermodynamic or structural properties of the components. Outline of the K^+—$HCOO^-$, —CNS^-, —NO_3^- system was discussed previously (*1*). The present paper deals with the crystallization temperatures in the Na^+—$HCOO^-$, —CNS^-, —NO_3^- ternary system.

EXPERIMENTAL

The first crystallization temperatures of the melted mixtures were determined by a Chromel-Alumel thermocouple, checked by comparison with an NBS-certified Pt resistance thermometer, and connected with a Leeds & Northrup type K-5 potentiometer. The pyrex container of the melted mixtures was put in a furnace whose temperature was controlled by a second thermocouple, connected with a Leeds & Northrup

[1] To whom correspondence should be addressed.