Solubility of Gaseous Paraffins in Methanol and Isopropyl Alcohol

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The solubilities of propane, n-butane and isobutane in methanol and isopropyl alcohol have been measured at pressures up to one atmosphere and at temperatures between 0 and 50°. Results are reported as mole fraction of hydrocarbon at a given total pressure and are also presented in the form of an empirical equation. Measurements of the vapor pressure of isopropyl alcohol are included. The partial molal excess free energy, enthalpy and entropy of the hydrocarbons at infinite dilution have been calculated from the results and are discussed in terms of extended association of the alcohols.

Measurements of the solubility of propane, n-butane and isobutane in ethanol have been reported in a previous article.[2] The measurements have now been extended to methanol and isopropyl alcohol and the results are reported in this paper.

Experimental

The apparatus, procedure, purification of the hydrocarbons and method of calculation were the same as before.[2]

Synthetic methanol was treated by the method of Morton and Mark,[3] fractionated through a 50-plate column, dried with magnesium,[4] and stored in a sealed flask. The density was $d^{25.00}_4$ 0.78653 ± 0.00002, in exact agreement with the value given by Jones and Fornwalt.[5] Young's values[6] were used for the densities at other temperatures. A measurement of the vapor pressure at 0.00° gave the value 30.41 ± 0.05 mm. Vapor pressures at higher temperatures were calculated from the equation published by Scatchard, Wood and Mochel.[7]

Isopropyl alcohol was fractionated through a 50-plate column, dried with magnesium[4] and stored in a sealed flask. A small quantity of 2,4-dinitrophenylhydrazine was added to keep possible traces of acetone from coming over when the samples were distilled off. The density was $d^{25.00}_4$ 0.78081 ± 0.00002, $d^{50.00}_4$ 0.7587 ± 0.0001. Brunel[8] gives d^{25}_4 0.78084. Densities at other temperatures were calculated from the equation $d^t_4 = 0.80122 - 7.826 \times 10^{-4}t - 1.36 \times 10^{-6}t^2$, which reproduces our measurements at 25° and 50°, that of Young and Fortey[9] at 0° and that of Langdon and Keyes[10] at 35°. We measured the vapor pressure of our sample of isopropyl alcohol from 0° to 50°, and the values fitted the following equation closely

$$\log_{10} P_{mm} = 8.39400 - 1702.47/(t + 227)$$

This equation is believed to be reliable to 0.1 mm. It is in poor agreement with the vapor pressures of Parks and Barton.[11]

Second virial coefficients of the two alcohols were taken to be 1.5 times the values calculated from the equation of Keyes, Smith and Gerry.[12]

Results

Compositions and vapor pressures of the solutions measured are given in Tables I and II. It was previously found[2] that the vapor pressures of solutions of these gases in ethanol could be represented by the equation

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

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(3) A. A. Morton and J. G. Mark, Ind. Eng. Chem., Anal. Ed., **6**, 151 (1934).

(4) H. Lund and J. Bjerrum, Ber., **64**, 210 (1931).

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(10) W. M. Langdon and D. B. Keyes, Ind. Eng. Chem., **35**, 459 (1943).

(11) G. S. Parks and B. Barton, THIS JOURNAL, **50**, 24 (1928).

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$$\log [(p - p_1^0)/x_2] + p(\beta_2 - v_2/RT)$$
$$= A - B/(t + C) - rx_2 \qquad (1)$$

where p is the vapor pressure, p_1^0 is the vapor

TABLE I

VAPOR PRESSURE OF SOLUTIONS OF HYDROCARBONS IN METHANOL

Solute	Temp., °C.	$x_2{}^a$	$p{}^b$
Propane	0.00	0	30.4
		0.02039	756.4
	25.00	0	126.9
		0.004988	464.0
		.007040	598.1
		.009569	759.6
	50.00	0	416.1
		0.003232	758.4
n-Butane	25.00	.01651	494.6
		.02410	635.6
		.03171	762.0
	35.00	0	209.6
		0.01920	750.6
	50.00	.008075	756.8
Isobutane	25.00	.007100	364.0
		.01316	548.2
		.02103	764.3
	35.00	.01370	757.7
	50.00	.006002	758.1

a Mole fraction of hydrocarbon. b Total pressure in mm. Probable error 0.4 mm.

TABLE II

VAPOR PRESSURE OF SOLUTIONS OF HYDROCARBONS IN ISOPROPYL ALCOHOL

Solute	Temp., °C.	$x_2{}^a$	$p{}^b$
Propane	0.00	0	7.8
		0.05804	754.9
	25.00	0	43.5
		0.01830	507.9
		.02317	626.7
		.02783	760.5
	50.00	0	177.0
		0.01423	754.7
n-Butane	25.00	.05285	430.2
		.07755	579.5
		.11056	752.7
	35.00	0	78.7
		0.07531	760.3
	50.00	.04149	752.1
Isobutane	25.00	.02758	355.0
		.04441	525.6
		.06930	753.1
	35.00	.04984	761.0
	50.00	.02977	762.0

a Mole fraction of hydrocarbon. b Total pressure in mm. Probable error 0.4 mm.

pressure of pure alcohol, and x_2, β_2, v_2 are the mole fraction, second virial coefficient (in mm.$^{-1}$ if p is in mm.), and liquid molal volume of the hydrocarbon. It was assumed that this equation would also be true for solutions in methanol and isopropyl alcohol. Therefore, the variation of solubility with pressure was studied at 25° only and single determinations were made at the other temperatures. Table III gives the values found for the constants in equation 1. This equation with the listed values of the constants reproduces the experimental vapor pressures to within a few tenths of a millimeter. However, it should not be used for extrapolations much beyond 0.1 mole fraction of hydrocarbon or to temperatures much higher or lower than the experimental range.

TABLE III

CONSTANTS IN VAPOR PRESSURE EQUATION FOR SOLUTIONS
OF HYDROCARBONS IN ALCOHOLS

System	A	B	C	r
Propane in:				
Methanol	6.57864	358.48	181	2.820
Isopropyl alcohol	6.09520	312.26	161	0.979
n-Butane in:				
Methanol	6.20283	285.90	133	3.400
Isopropyl alcohol	6.34472	503.19	182	1.109
Isobutane in:				
Methanol	6.49704	377.30	168	3.540
Isopropyl alcohol	5.81733	272.84	132	1.195

Discussion

The excess partial molal free energy, enthalpy and entropy of the hydrocarbons at infinite dilution at 25°, calculated from the data as described before,[2] are given in Table IV, with the values for ethanol solutions included for comparison. All three functions, $\overline{F}_2^E$, $\overline{H}_2^M$ and $-T\overline{S}_2^E$, decrease on going from methanol to ethanol to isopropyl alcohol for all hydrocarbons studied. The excess free energy also increases uniformly on going from propane to n-butane to isobutane.

The behavior of alcohol–hydrocarbon systems has been discussed with considerable success by Redlich and Kister[13] on the basis of extended association; the alcohol is assumed to form linear polymers of all orders, and the equilibrium constant K

(13) O. Redlich and A. T. Kister, *J. Chem. Phys.*, **15**, 849 (1947).

TABLE IV

EXCESS PARTIAL MOLAL THERMODYNAMIC FUNCTIONS AT
INFINITE DILUTIONS OF HYDROCARBONS IN ALCOHOLS AT
25°, CAL./MOLE

System	$\overline{F}_2^E$	$\overline{H}_2^M$	$-T\overline{S}_2^E$
Propane in:			
Methanol	1455	478	977
Ethanol	1096	244	851
Isopropyl alcohol	879	227	652
n-Butane in:			
Methanol	1597	527	1070
Ethanol	1187	395	792
Isopropyl alcohol	943	393	550
Isobutane in:			
Methanol	1603	701	902
Ethanol	1205	362	843
Isopropyl alcohol	972	332	640

for the reaction

$$A_{i-1} + A = A_i \qquad (2)$$

is taken to be independent of the order i of the polymer. This treatment gives for the partial molal excess free energy of the hydrocarbon at infinite dilution the value

$$\overline{F}_2^E(0) = B'v_2 + RT \ln (K + 1) \qquad (3)$$

where B' is a constant and $K + 1$ is the average number of alcohol units per polymeric molecule in the pure alcohol. The term $RT \ln (K + 1)$ would be equal to $-T\overline{S}_2^E(0)$ if it were not for the fact that addition of hydrocarbon causes some of the alcohol polymers to dissociate. This effect can be shown to increase the value of $T\overline{S}_2^E(0)$ by about $0.2\Delta H$, where $-\Delta H$ is the enthalpy change for reaction 2. Then we have

$$RT \ln (K + 1) = -T\overline{S}_2^E(0) + 0.2\Delta H \qquad (4)$$

$$\overline{H}_2^M(0) = B'v_2 + 0.2\Delta H \qquad (5)$$

The excess entropy can be either positive or negative, depending on the relative magnitudes of $RT \ln (1 + K)$ and $0.2\Delta H$.

Examination of the values listed in Table IV shows that ΔH cannot be larger than about 2000 cal. unless B has unreasonably large negative values. For $\Delta H = 2000$ cal., the degree of polymerization $K + 1$ ranges from 5 for isopropyl alcohol to 10 for methanol.

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