

Densities and Viscosities of Aqueous Maleic Acid Solutions between 25 and 90 °C

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The densities and viscosities of aqueous maleic acid solutions were determined in all the possible ranges of concentrations between 25 and 90 °C. Likewise, empirical correlations were obtained to relate these properties with the concentration and the temperature.

Introduction

Maleic anhydride is obtained industrially by the catalytic oxidation of hydrocarbons. One of the most widely used methods for its recovery from the gaseous flow coming from the reactor is by means of absorption with water. In the next step the resulting aqueous maleic acid solution flows to evaporators. Then the acid solution is concentrated and, afterwards, dehydrated producing maleic anhydride vapors and water. For an adequate design of the absorption tower and the evaporators, it is necessary to know the densities and the viscosities of the maleic acid solutions as a function of concentration and temperature.

It must be added that the maleic acid in concentrated solutions and at high temperatures is isomerized to fumaric acid (in our research unit, a kinetic study on this reaction is being carried out). This, together with the available instrumental techniques, has limited the temperatures at which the densities and the viscosities were measured to less than 90 °C.

In the literature only a correlation between the density of aqueous maleic acid solutions and the concentration at 25 °C has been found (1). This correlation is based on Weiss and Downs (2) experimental data.

Experimental Section

The densities were measured by use of a digital densimeter Anton Paar Model DMA 45. With this instrument the mass of an exactly defined sample volume is determined from the oscillation period of the cell which contains it, when it undergoes an undamped oscillatory movement (3). The thermostatic system incorporated in the densimeter allows the temperature to be maintained within a limit of error of ± 0.05 °C. For each temperature the instrument constants are determined from oscillation period measurements with two samples of known density, air and water (4). The experimental error for these measurements was estimated to be $\pm 10^{-4}$ g/cm³ within the range of 0.5–1.5 g/cm³. The average value was calculated at each temperature from a set of measurements for which the maximum difference among them was less than 0.02%.

The viscosities were measured by use of an automatic equipment, Viscomatic 1 of FICA, with a thermostated glass capillary tube, Ubbelohde-type, 0.4 mm diameter. The experimental techniques of this equipment have been described (5).

Due to the wide interval of temperatures and compositions which had to be covered, low flow times have sometimes been found (<200 s), and therefore in all the cases the kinetic energy corrections had to be considered in order to calculate the viscosities. Besides the circulation of the thermostatic liquid, the viscometer tube was covered with a regulated heating strip of 180 W which minimized heat loss and water vapor condensa-

Table I. Densities (g/cm³) of Aqueous Solutions of Maleic Acid

concn, wt %	temp, °C				
	25	40	60	80	90
0.00	(0.9971)	(0.9922)	(0.9832)	(0.9718)	(0.9653) ^a
10.08	1.0316	1.0253	1.0148	1.0069	1.0002
19.61	1.0648	1.0572	1.0456	1.0364	1.0304
29.98	1.1034	1.0945	1.0814	1.0714	1.0649
40.15	1.1434	1.1333	1.1191	1.1085	1.1000
52.22		1.1811	1.1659	1.1518	1.1446
61.63			1.2028	1.1871	1.1795
72.07					1.2192

^aFrom ref 4.

tion, giving limits of error of 0.05 °C. On the other hand, given the viscosimeter characteristics, a sufficient amount of the sample needed in order to make evaporation negligible was introduced. The maximum difference in the viscosity values determined at each temperature and at each concentration was less than 0.1%. The viscosimeter was calibrated with oils of known viscosity and density (δ).

Maleic acid with an acidity of 99.5 wt % and a content of fumaric acid less than 0.5 wt % was used. The solutions were prepared by weighing, and then the concentration was determined by potentiometric titration with NaOH 0.1 N. The percentage of fumaric acid was determined by chromatographic analysis of the dimethyl esters of maleic and fumaric acids. The maximum error in the determination of the maleic acid concentration by titration is less than 0.3%. In the tables where experimental data are shown, values of percentages with four figures are the average values obtained from several analysis.

Density. Results and Correlation

The densities of the aqueous solutions of maleic acid were measured at temperatures of 25, 40, 60, 80, and 90 °C and at concentrations of 0 to up to 72 wt % of acid, at intervals of 10%, except in those cases where the solubility of the maleic acid was not total.

The experimental average values of the densities, related to the water density at 4 °C (4), are shown in Table I.

The differences between our experimental values of densities at 25 °C and those which are plotted vs. concentration in the paper by Weiss and Downs (2) are less than 0.2%.

Different equations were tested to correlate the density ρ with the concentration c and the temperature t . These equations were of the type

$$\rho(t, c) = \sum_{i=0}^2 \sum_{j=0}^2 a_{ij} t^i c^j \quad (1)$$

Of all the correlations carried out, including the values of the densities of pure water (4), the best one corresponds to the case where the concentration is expressed in mass fraction w_A of maleic acid and the temperature t in °C. The equation obtained by multiple linear regression is

$$\rho = 1.004 - 1.954 \times 10^{-4} t - 2.44 \times 10^{-6} t^2 + (3.606 \times 10^{-1} - 1.752 \times 10^{-3} t + 1.404 \times 10^{-5} t^2) w_A + (8.472 \times 10^{-2} + 7.033 \times 10^{-4} t - 1.262 \times 10^{-5} t^2) w_A^2 \quad (2)$$

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Table II. Viscosities (mPa·s) of Aqueous Solutions of Maleic Acid

concn, wt %	temp, °C				
	25	40	60	80	90
0.00	(0.890)	(0.653)	(0.467)	(0.355)	(0.315) ^a
10.08	1.092	0.792	0.595	0.450	0.408
19.61	1.349	0.968	0.696	0.528	0.477
29.98	1.775	1.255	0.861	0.649	0.584
40.15	2.459	1.702	1.115	0.832	0.741
52.22		2.540	1.571	1.144	1.009
61.00			2.245	1.557	1.357
72.07					2.080

^a From ref 4.

The coefficient of the multiple correlation is 0.99995, and the standard deviation of the experimental points from this equation is 0.00087 g/cm³.

Viscosity. Results and Correlation

The viscosities of the aqueous maleic acid solutions for experimental conditions similar to those in the determination of densities were measured. The experimental results are tabulated in Table II.

Several empirical equations have been tested to correlate viscosity in function with concentration and with temperature. The best obtained equation which relates the viscosity μ to the absolute temperature T and the mole fraction of maleic acid x_A is the following

$$\log \mu = -1.0375 + 2.810 \times 10^7 T^{-3} - 5.284 \times 10^{13} T^{-6} + (3.740 - 1.974 \times 10^7 T^{-3} + 1.534 \times 10^{15} T^{-6}) x_A + (-3.151 \times 10^8 T^{-3} + 4.966 \times 10^{15} T^{-6}) x_A^2 \quad (3)$$

The multiple correlation coefficient is 0.9992, and the standard deviation of the experimental points from this equation is 0.0227 mPa·s.

This equation has been selected because we had observed that the relationship between $\log \mu$ and the composition and the temperature was almost in accordance to the equations proposed by Litovitz (7) and Suryanarayana and Venkatesan (8).

Glossary

t	temperature, °C
T	temperature, K
w_A	mass fraction of maleic acid
x_A	mole fraction of maleic acid

Greek Letters

ρ	density, g/cm ³
μ	absolute viscosity, mPa·s

Registry No. Maleic acid, 110-16-7.

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Determination of Activity Coefficients of Oxygenated Hydrocarbons in Squalane by Gas-Liquid Chromatography

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A study of the thermodynamics of oxygenated hydrocarbons and aromatic solutes in squalane was conducted using gas-liquid chromatography. Solute infinite-dilution activity coefficients were determined at four temperatures in the range of 30-45 °C. The corresponding excess thermodynamic properties were calculated and the results were examined and discussed according to the regular solution theory and the perturbation theory of solutions.

Knowledge of the thermodynamics of nonelectrolytic solutions is of great theoretical and practical importance in physical chemistry and chemical engineering. Static methods are accurate, but in most cases, time consuming. In contrast GLC has been shown to be rapid, efficient, and capable of 1-2% accuracy in the determination of infinite-dilution activity coefficients and related solution thermodynamic properties (1). The accuracy of activity coefficients as measured by GLC depends on the type of systems studied, careful control of the experimental parameters, and the availability of accurate physical data. For systems where the only retention mechanism operative is solute absorption in the bulk of the stationary phase,

the accuracy can be as good as 1% or better.

In this study we sought to apply the GLC method with squalane as stationary phase for the determination of the solution properties of oxygenated aliphatic and aromatic hydrocarbons. The solutes were selected to represent different functional groups. Squalane was chosen because it has been extensively studied by GLC and by static techniques and considerable quantities of thermodynamic properties of a wide range of solutes have been accumulated (2-8). Although most of the studies in the cited literature were conducted at temperatures exceeding those studied here, an attempt was made to compare our results with independent measurements.

Solute activity coefficients were determined at four temperatures. The corresponding thermodynamic properties were calculated and the results were examined and discussed according to the regular solution theory and the perturbation theory of solutions.

Theory

Solute activity coefficients at infinite dilution in the stationary phase are related to GLC measured specific retention volume by the expression (9)