

Densities and Viscosities of Methanol-Water Mixtures

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HYDROGEN ION MOBILITY in aqueous alcoholic mixtures was investigated. Its contribution to abnormal ion mobility requires accurate values of the densities and viscosities of these media at different temperatures between 25° and 50° C. For methanol-water mixtures, accurate density values have been determined by Clifford and Campbell (3) at 25° C. only. Subnis, Bhagwat, and Kanugo (14) determined the densities at 30°, 40°, and 50° C., but their values were always very high—e.g., their densities at 30° C. were even higher than either Clifford and Campbell's or ours at 25° C. Our data agreed with those obtained by Clifford and Campbell at 25° C., which experimental data at 25° C. are plotted on our density-mole per cent curve in Figure 2. Density values, corresponding to their mole percentages, calculated from our empirical Equation 3 agree, within the errors shown in Table III, with their reported experimental values.

Viscosities of only a few of these mixtures are available from the International Critical Tables. The results for the densities and viscosities of these mixtures at 25°, 30°, 40°, and 50° C. are reported here; also, our data are reported empirically with a power series equation of the form

$$y = \sum_{i=0}^n a_i x^i \quad (1)$$

In Equation 1, y denotes the density d , viscosity η , or molal volume V ; and x , the independent variable, denotes alcohol weight percentage W , alcohol mole percentage N , or temperature t° C. The constants, a_i , were determined by the least squares procedure using the IBM 650 digital computer, except a_0 which was, in some cases, chosen to agree with accepted values of density and viscosity of water.

Using Equation 1 and the computed constants included in the tables, the experimenter can calculate tables of values for density and/or viscosity for any value of the independent variable.

The maximum deviation of the calculated values from Equation 1 as compared with the experimental values was always less than 0.1 and 0.6% for density and viscosity data, respectively. This deviation can be further reduced to any reasonable arbitrary minimum by adding more terms to Equation 1.

EXPERIMENTAL

Chemically pure methanol was further purified from acetone traces, using the method recommended by Bates, Mullaly, and Hartley (1). It was then fractionated to constant boiling point through an efficient column, dried with aluminum amalgam by the McKelvey (12) method, and then boiled for 6 hours with freshly dehydrated copper sulfate while passing a current of pure air following Hartley and Raikes' method (6). The resulting absolute methanol was odorless, free of any detectable ketone, and had a density d_4^{25} of 0.7869 gram per ml. compared to the International Critical Tables value of 0.78683 gram per ml., and to Clifford and Campbell's value of 0.78687 gram per ml. (3). The water used was triply distilled from acid, alkaline, and neutral permanganate solutions and had a specific conductance of 0.8×10^{-6} .

Results of a literature survey by Manufacturing Chemists Association (13) reveal that a majority of such measurements gave $d_4^{25} = 0.7865$ gram per ml. However, the literature is not unanimously definite on this point. Densities obtained at higher temperatures for the same methanol sample (Table I) agree within ± 0.0001 with all the corresponding literature values available.

Solutions were prepared by adding the calculated amount of absolute alcohol by weight to a preweighed amount of water. Correction for buoyancy was evaluated and taken into account. The set of weights used was certified by the National Bureau of Standards. Density determinations were made at each composition and at each temperature with two pycnometers calibrated with water as a standard. Values obtained by the two pycnometers always agreed to within ± 0.0001 .

Viscosities were determined by a modified Ostwald viscometer of the type described by Cannon and Fenske (2). The viscometer dimensions were carefully selected to give a maximum calculated kinetic energy correction of about 0.2% for the range of viscosities encountered in this work. Among several advantages of this viscometer is that it is free from surface tension corrections because practically all the efflux time is measured when the menisci of both the upper and lower levels are in tubes of equal diameter. This is very advantageous, for in the case considered, a change of over 300% in surface tension takes place between pure water and pure methanol. Loading errors never exceeded 0.002%. Errors resulting from failing to align the viscometer in the constant temperature bath in an exact vertical position were avoided by the aid of a small plumb bob made of silk and a small piece of lead, and placed in the open arm of the viscometer. The viscometer was calibrated by measuring the efflux time of pure water at 20° C. The value of 10.02 millipoises was used for the viscosity of water at 20° C. as recommended by the Bureau of Standards (15). Correction of the viscometer constants for change in temperature was eliminated entirely by preheating the samples and the viscometer to test temperature before loading (2).

Both density and viscosity measurements were carried out in a constant temperature bath controlled by an electronic unit capable of keeping the temperature constant to within $\pm 0.005^\circ$ C. Temperature measurements were made by very sensitive Bureau of Standards calibrated thermometers.

RESULTS

Tables I and II summarize the experimental results obtained. Empirical equations relating the different parameters follow.

Density of the mixtures, d_4^t , as a function of weight percentage methanol, W .

$$d_4^t \text{ (g./ml. in vacuo)} = \sum_{i=0}^5 a_i W^i \quad (2)$$

In this equation, a_0 was chosen to agree with the density values of water given in the International Critical Tables (8). Values of a_0 through a_5 evaluated at the five different

Table I. Densities, d_4^t , and Molal Volumes, V , of Methanol-Water Mixtures at Different Temperatures

Wt. % Methanol	Mole % ^a Methanol	25° C.		30° C.		35° C.		40° C.		50° C.	
		d, g./ml.	Vol., ml.	d, g./ml.	Vol., ml.	d, g./ml.	Vol., ml.	d, g./ml.	Vol., ml.	d, g./ml.	Vol., ml.
0 ^b	0	0.9971	18.068	0.9957	18.094	0.9941	18.123	0.9923	18.156	0.9881	18.233
10	5.88	0.9802	19.221	0.9786	19.253	0.9768	19.288	0.9747	19.330	0.9700	19.424
20	12.33	0.9647	20.468	0.9628	20.508	0.9606	20.555	0.9582	20.607	0.9526	20.728
30	19.43	0.9492	21.852	0.9467	21.909	0.9440	21.972	0.9410	22.042	0.9354	22.174
40	27.27	0.9315	23.447	0.9285	23.523	0.9254	23.602	0.9220	23.689	0.9148	23.876
50	35.99	0.9119	25.293	0.9096	25.357	0.9060	25.457	0.9022	25.565	0.8944	25.787
60	45.76	0.8904	27.442	0.8870	27.548	0.8835	27.657	0.8795	27.783	0.8709	28.057
70	56.75	0.8673	29.951	0.8637	30.076	0.8595	30.223	0.8553	30.371	0.8465	30.687
80	69.22	0.8426	32.905	0.8381	33.081	0.8333	33.272	0.8291	33.440	0.8204	33.795
90	83.50	0.8152	36.468	0.8110	36.657	0.8057	36.898	0.8014	37.096	0.7928	37.498
95	91.44	0.8006	38.524	0.7962	38.737	0.7911	38.987	0.7864	39.220	0.7775	39.669
100	100	0.7869	40.720	0.7819	40.981	0.7771	41.234	0.7723	41.490	0.7627	42.013

^a Molecular weight = 32.043. ^b Reference (8).

working temperatures are recorded in Table III. The maximum percentage error given in column 8 is: max. $(d_{obsd} - d_{calcd}) / 100 / d_{obsd}$. The mean percentage error given in column 9 is:

$$1/m \sum_{i=1}^m |d_{i,obsd} - d_{i,calcd}| / 100 / d_{i,obsd}$$

where m denotes the number of experimental values obtained between pure alcohol and pure water at one and the same temperature.

Figure 1 graphically illustrates the closeness of fit between Equation 2 and typical experimental density data. A smaller number of terms in Equation 2 was inadequate for precise data representation.

Density of mixtures, d_4^t , as a function of mole percentage methanol, N .

$$d_4^t \text{ (g./ml. in vacuo)} = \sum_{i=0}^5 a_i N^i \quad (3)$$

In this equation a_0 is the same as a_0 of Equation 2. Constants a_0 through a_5 are given in Table III.

Figure 2 graphically illustrates the closeness of fit between Equation 3 and typical experimental density data.

Molal volumes of mixtures, V , as functions of mole fraction methanol, N .

$$V \text{ (ml.)} = \sum_{i=0}^5 a_i N^i \quad (4)$$

In this equation a_0 was chosen to agree with the molal volumes of water computed from density values of water given above. Equation 4 can also be used to derive the expressions of the partial molal volumes (11) as follows:

$$\text{Methyl partial molal volume } v_m = V + (1 - N) dV/dN \quad (5)$$

$$\text{Water partial volume } v_w = V - N dV/dN \quad (6)$$

Temperature dependence of density, d_4^t , for mixtures, between $t = 25^\circ$ and 50° C.

$$d_4^t = \sum_{i=0}^4 a_i t^i \quad (7)$$

An equation of the fourth degree was found to give the same order of accuracy as Equations 2, 3, and 4 in this particular case. Constants a_0 through a_4 were determined for different methanol percentages by weight and recorded in Table IV.

Absolute viscosity of mixtures, η , as a function of weight percentage methanol, W .

$$\eta \text{ (Millipoise)} = \sum_{i=0}^5 a_i W^i \quad (8)$$

In this equation, a_0 was chosen to agree with the values

Table II. Viscosities of Methanol-Water Mixtures at Different Temperatures

Wt. % Methanol	Mole % Methanol ^a	Viscosity, Millipoises				
		25° C.	30° C.	35° C.	40° C.	50° C.
0 ^b	0	8.95	8.00	7.21	6.54	5.49
10	5.88	11.55	10.15	8.94	8.00	6.56
20	12.33	13.92	12.06	10.62	9.41	7.59
30	19.43	15.40	13.36	11.72	10.34	8.23
40	27.27	15.95	13.81	12.13	10.74	8.54
50	35.99	15.34	13.37	11.80	10.46	8.41
60	45.76	14.01	12.39	10.98	9.81	7.95
70	56.75	12.18	10.85	9.74	8.76	7.22
80	69.22	10.05	9.07	8.29	7.52	6.30
90	83.50	7.82	7.14	6.67	6.12	5.22
95	91.44	6.59	6.12	5.66	5.32	4.58
100	100.00	5.41	5.07	4.74	4.50	3.96

^a Molecular weight = 32.043.

^b Values of water viscosity are reported by Dorsey (4). Since Dorsey's value for viscosity of water at 20° C. is 10.09 millipoises, correction of all his values to the new National Bureau of Standards basis of 10.02 millipoises was given some consideration. The following are pertinent points:

Dorsey's values were obtained "from a consideration of all pertinent data available" (4, p. 182). He adds, "They are the results of an entirely independent study of the recorded data, and involve many complete recomputations." This led us to believe that his values for 30°, 35°, 40°, and 50° C. are not necessarily based on his 10.09-millipoise value for 20° C.

Comparison between Dorsey's values and those of Bingham and Jackson (4, p. 184) reveals that Dorsey's values at 30°, 35°, 40°, and 50° C. are lower than the corresponding Bingham and Jackson's values, although the latter values are based on 10.05 millipoises for water at 20° C.

Hardy and Cottington [*J. Research Natl. Bur. Standards* 42, 573 (1949)] reported a value of 6.551 millipoises for water at 40° C. based on 10.05 millipoises for water at 20° C. Correction of this value to 10.02 basis gives 6.531 millipoises compared to Dorsey's value of 6.536 millipoises without correction.

In view of this lack of agreement, it was decided to keep Dorsey's values as they are. Whether Dorsey's values will, in the light of future investigations, need to be corrected or not, the viscosity values recorded in Table II will not be affected because those are based on 10.02 millipoises for water at 20° C.

Table III. Computed Constants of Various Equations at Different Temperatures

Temp., ° C.	a_0	a_1	a_2	a_3	a_4	a_5	Max. % Error	Mean. % Error
Equation 2: Density, d_4^t in G./Ml., vs. Weight % Methanol, W								
25	0.9971	-1.8527×10^{-3}	2.2013×10^{-5}	-6.0418×10^{-7}	$+5.3912 \times 10^{-9}$	-1.8012×10^{-11}	-0.05	0.02
30	0.9957	-1.8577×10^{-3}	$+1.9615 \times 10^{-5}$	-5.3092×10^{-7}	4.4949×10^{-9}	-1.4274×10^{-11}	+0.05	0.01
35	0.9941	-1.8278×10^{-3}	1.3727×10^{-5}	-3.5368×10^{-7}	2.3168×10^{-9}	-4.9507×10^{-12}	-0.04	0.01
40	0.9923	-1.8409×10^{-3}	1.2424×10^{-5}	-3.4028×10^{-7}	2.4143×10^{-9}	-6.1299×10^{-12}	-0.03	0.01
50	0.9881	-1.9417×10^{-3}	1.7956×10^{-5}	-5.5712×10^{-7}	5.4346×10^{-9}	-1.9714×10^{-11}	-0.06	0.02
Equation 3: Density, d_4^t in G./Ml., vs. Mole % Methanol, N								
25	0.9971	-2.8930×10^{-3}	2.9907×10^{-5}	-6.0876×10^{-7}	5.9438×10^{-9}	-2.0581×10^{-11}	-0.08	0.04
30	0.9957	-2.9883×10^{-3}	3.4526×10^{-5}	-7.4395×10^{-7}	7.5625×10^{-9}	-2.7269×10^{-11}	-0.07	0.03
35	0.9941	-3.0331×10^{-3}	3.3232×10^{-5}	-6.8854×10^{-7}	6.7625×10^{-9}	-2.3385×10^{-11}	-0.05	0.02
40	0.9923	-3.0601×10^{-3}	2.9977×10^{-5}	-5.8571×10^{-7}	5.6578×10^{-9}	-1.9397×10^{-11}	-0.06	0.03
50	0.9881	-3.1257×10^{-3}	2.7332×10^{-5}	-5.3337×10^{-7}	5.5450×10^{-9}	-2.0748×10^{-11}	+0.09	0.04
Equation 4: Molal Volumes, in Ml., vs. Mole Fraction of Methanol, N								
25	18.068	19.324	-0.39832	9.3660	-7.6821	2.0494	+0.08	0.04
30	18.094	19.623	-2.1367	15.192	-14.873	5.0875	+0.05	0.03
35	18.123	19.756	-1.7467	13.767	-12.394	3.7326	-0.04	0.02
40	18.156	19.791	-0.40699	10.244	-8.7175	2.4280	+0.05	0.02
50	18.233	19.951	0.81614	8.8399	-9.1047	3.2833	-0.08	0.04
Equation 8: Viscosity, η in Millipoises, vs. Weight % Methanol, W								
25	8.95	0.24099	3.8479×10^{-3}	-2.1872×10^{-4}	2.3409×10^{-6}	-8.1493×10^{-9}	+0.27	0.10
30	8.00	0.20233	2.6359×10^{-3}	-1.5929×10^{-4}	1.6602×10^{-6}	-5.6258×10^{-9}	-0.33	0.10
35	7.21	0.15417	3.4838×10^{-3}	-1.6859×10^{-4}	1.8071×10^{-6}	-6.4851×10^{-9}	-0.19	0.08
40	6.54	0.13139	2.7079×10^{-3}	-1.3226×10^{-4}	1.3872×10^{-6}	-4.8712×10^{-9}	-0.32	0.11
50	5.49	0.10196	1.3259×10^{-3}	-7.6409×10^{-5}	7.8579×10^{-7}	-2.7156×10^{-9}	+0.33	0.10
Equation 9: Viscosity, η , in Millipoises, vs. Mole % Methanol, N								
25	8.95	0.54929	-1.2468×10^{-3}	4.0795×10^{-5}	7.2924×10^{-7}	-4.7553×10^{-9}	+1.80	0.72
30	8.00	0.44634	-9.7573×10^{-3}	2.5606×10^{-5}	6.3434×10^{-7}	-3.9059×10^{-9}	+1.41	0.56
35	7.21	0.36936	-7.7954×10^{-3}	1.4103×10^{-5}	5.9862×10^{-7}	-3.5458×10^{-9}	+1.96	0.78
40	6.54	0.30680	-6.1310×10^{-3}	1.4968×10^{-6}	6.0250×10^{-7}	-3.3182×10^{-9}	+1.66	0.61
50	5.49	0.22387	-4.6508×10^{-3}	1.1518×10^{-5}	2.8063×10^{-7}	-1.7008×10^{-9}	+1.34	0.47

^c Molecular weight = 32.043.

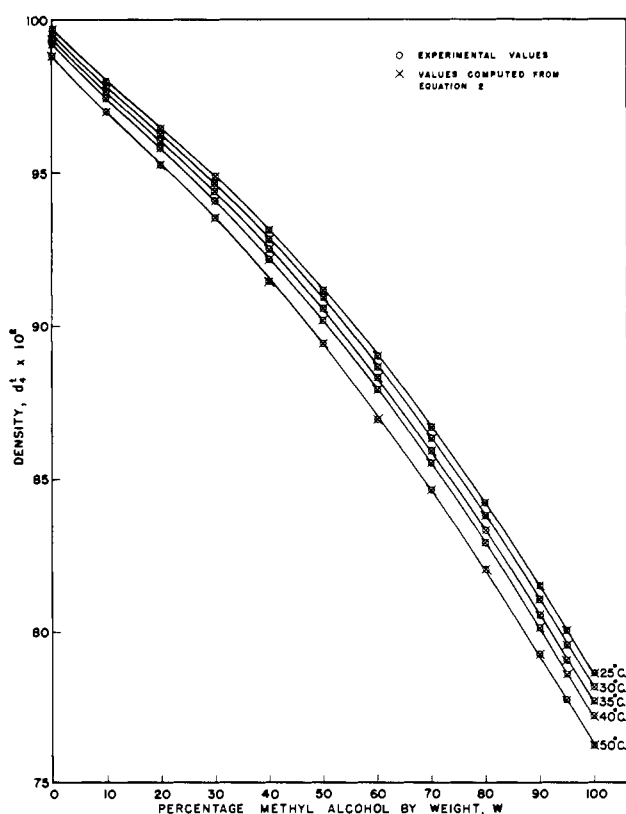


Figure 1. Comparison of experimental and computed data for density, d_4^t , vs. percentage methanol by weight, W

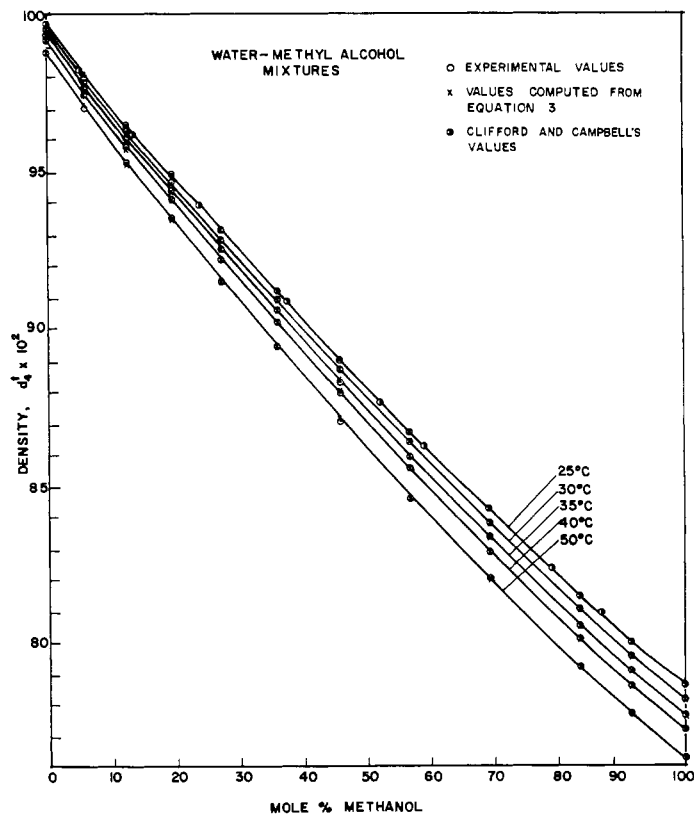


Figure 2. Comparison of experimental and computed data for density, d_4^t , vs. mole per cent methanol

Table IV. Computed Constants for Different Weight Percentages of Methanol

Wt. % Methanol	a_0	a_1	a_2	a_3	a_4	Max. % Error	Mean % Error
Equation 7: Density, d_4 in G./Ml., vs. Temperature, t° C.							
0	1.1648	-1.9364×10^{-2}	8.2879×10^{-4}	-1.5558×10^{-5}	1.0631×10^{-7}	-0.05	0.02
10	1.1117	-1.4933×10^{-2}	6.3450×10^{-4}	-1.1955×10^{-5}	8.2093×10^{-8}	-0.01	0.01
20	8.8852×10^{-1}	9.7838×10^{-3}	-4.3998×10^{-4}	8.2770×10^{-6}	-5.7565×10^{-8}	+0.01	0.01
30	8.5160×10^{-1}	1.2585×10^{-2}	-5.6522×10^{-4}	1.0555×10^{-5}	-7.2290×10^{-8}	+0.02	0.01
40	9.6817×10^{-1}	-3.4993×10^{-3}	1.3800×10^{-4}	-2.7738×10^{-6}	1.9733×10^{-8}	0.00	0.00
50	9.6206×10^{-1}	-4.5013×10^{-3}	1.6846×10^{-4}	-3.2283×10^{-6}	2.2369×10^{-8}	0.00	0.00
60	9.9612×10^{-1}	-1.0699×10^{-2}	4.1849×10^{-4}	-7.6195×10^{-6}	5.0549×10^{-8}	0.00	0.00
70	9.3393×10^{-1}	-6.1523×10^{-3}	2.2865×10^{-4}	-4.2553×10^{-6}	2.8876×10^{-8}	-0.01	0.00
80	8.9900×10^{-1}	-4.7077×10^{-3}	1.5801×10^{-4}	-2.8846×10^{-6}	1.9575×10^{-8}	-0.02	0.01
90	9.9865×10^{-1}	-1.9995×10^{-2}	8.3439×10^{-4}	-1.5900×10^{-5}	1.1127×10^{-7}	-0.07	0.03
100	8.6237×10^{-1}	-7.1042×10^{-3}	2.6727×10^{-4}	-5.0440×10^{-6}	3.4857×10^{-8}	-0.01	0.00
Equation 10: Viscosity, η , in Millipoises, vs. Temperature, t° C.							
0	25.503	-1.4464	4.8228×10^{-2}	-8.0351×10^{-4}	5.1496×10^{-6}	+0.25	0.14
10	29.880	-1.4226	4.1265×10^{-2}	-6.5175×10^{-4}	4.1783×10^{-6}	-0.30	0.15
20	19.832	3.0041×10^{-1}	-4.1435×10^{-2}	9.8528×10^{-4}	-7.4939×10^{-6}	+0.31	0.15
30	24.914	-5.5901×10^{-2}	-2.7324×10^{-2}	7.1099×10^{-4}	-5.5129×10^{-6}	+0.19	0.09
40	27.385	-1.8143×10^{-1}	-2.5714×10^{-2}	7.3737×10^{-4}	-6.0257×10^{-6}	+0.19	0.09
50	23.126	1.0769×10^{-1}	-3.3298×10^{-2}	8.1673×10^{-4}	-6.2318×10^{-6}	+0.25	0.12
60	30.371	-1.1161	2.6533×10^{-2}	-3.8134×10^{-4}	2.3553×10^{-6}	-0.13	0.06
70	16.780	1.0788×10^{-1}	-2.2029×10^{-2}	5.0683×10^{-4}	-3.7180×10^{-6}	+0.18	0.09
80	41.483×10^{-1}	1.1447	-6.1256×10^{-2}	1.2072×10^{-3}	-8.4552×10^{-6}	+0.54	0.27
90	55.288×10^{-1}	1.8792	-8.9590×10^{-2}	1.7346×10^{-3}	-1.2170×10^{-5}	-0.54	0.50
100	16.429	-1.0987	4.1657×10^{-2}	-7.3310×10^{-4}	4.7938×10^{-6}	-0.57	0.28

of the viscosity of water from Dorsey's selection (4). Constants a_0 through a_5 are given in Table III. Figure 3 illustrates the closeness of fit between Equation 8 and typical experimental viscosity data.

Absolute viscosity of mixtures, η , as a function of mole percentage methanol, N .

$$\eta \text{ (Millipoises)} = \sum_{i=0}^5 a_i N^i \quad (9)$$

In this equation, a_0 is the same as a_0 of Equation 8.

Viscosity values computed from this equation had a maximum error of 1.96% and a maximum mean error of 0.78% compared to the corresponding values of 0.3 and 0.11% obtained from Equation 8 using the constants given in Table III. The difference in maximum error in these two cases is a natural result of the least squares

analysis, since the data in the two cases are different and the number of parameters is identical. The closeness of fit in such analyses of experimental data, with a given number of parameters generally becomes better as the number of inflection points in the data decreases. Inspection of Figure 4 reveals one additional inflection point compared with Figure 2; therefore, for our six parameter least squares fits, the closeness of fit is expected to be better in the relation represented by Equation 8 than that represented by Equation 9. Readers interested in computing viscosity values for solution mixtures of known mole percentages are therefore advised to calculate the corresponding weight percentages and use Equation 8, rather than using Equation 9 directly unless $\pm 1.96\%$ maximum error is tolerable.

Temperature dependence of viscosity, η , for mixtures, between $t = 25^\circ$ and 50° C.

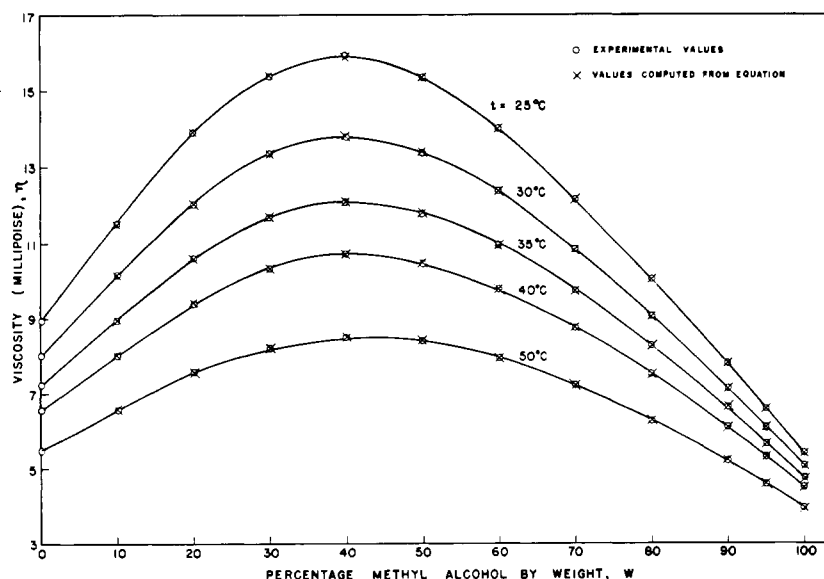


Figure 3. Comparison of experimental and computed data for viscosity, η , vs. percentage methanol by weight, W

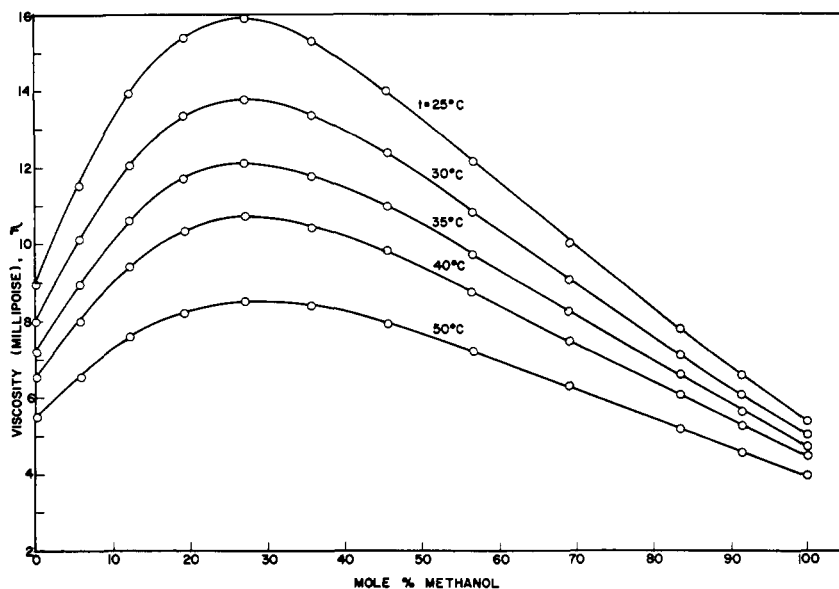


Figure 4. Viscosities of water-methanol mixtures, η , vs. mole per cent methanol

$$\eta \text{ (Millipoise)} = \sum_{i=0}^4 a_i t^i \quad (10)$$

This empirical representation by a power series is more precise, within this range of temperature, than that predicted by the theoretically based equations suggested by Gutmann and Simmons (5) for viscosity of liquids in general or by Kampmeyer (10) and by Innes (7) for water and mercury. It is also more precise than that predicted by the equation:

$$\eta = a/(b + t)^n \quad (11)$$

used in the International Critical Tables (9) for methanol. A simple theoretical temperature dependence equation for viscosity of mixtures of liquids has not yet been derived.

LITERATURE CITED

- (1) Bates, H.H., Mullaly, J.M., Hartley, H., *J. Chem. Soc.* **123**, 401 (1923).
- (2) Cannon, M.R., Fenske, M.R., *Ind. Eng. Chem., Anal. Ed.* **10**, 297 (1938).
- (3) Clifford, G., Campell, J.A., *J. Am. Chem. Soc.* **73**, 5449 (1951).
- (4) Dorsey, E.N., "Properties of Ordinary Water Substances," pp. 183-5, Reinhold, New York, 1940.
- (5) Gutmann, R., Simmons, L.M., *J. Appl. Phys.* **23**, 977 (1952).
- (6) Hartley, H., Raikes, H.R., *J. Chem. Soc.* **127**, 525 (1925).
- (7) Innes, K.K., *J. Phys. Chem.* **60**, 817 (1956).
- (8) International Critical Tables, vol. **III**, p. 25, McGraw-Hill, New York, 1928.
- (9) *Ibid.*, vol. **V**, p. 11, 1929.
- (10) Kampmeyer, P.M., *J. Appl. Phys.* **23**, 99 (1952).
- (11) Lewis, G.N., Randall, M., "Thermodynamics and the Free Energy of Chemical Substances," p. 33, McGraw-Hill, New York, 1923.
- (12) McKelvey, E.C., *Natl. Bur. Standards, Bull.* **9**, 364 (1913).
- (13) Manufacturing Chemists Association. Selected Values of Properties of Chemical Compounds, MCA Research Project. Washington, D. C., 1960.
- (14) Subnis, S.W., Bhagwat, W.V., Kanugo, R.B., *J. Indian Chem. Soc.* **25**, 575 (1948).
- (15) Swindells, J.F., Coe, J.R., Jr., Godfrey, T.B., *J. Research Natl. Bur. Standards* **48**, 1 (1952).

RECEIVED for review November 10, 1960. Accepted June 13, 1961.

CORRECTION

In "Critical Properties of Mixtures of Normal Paraffin Hydrocarbons" [Doyle O. Etter and W.B. Kay, *J. CHEM. ENG. DATA* **6**, 409 (1961)], the legends for Figures 2 and 3 should be reversed.

Equation 5 should read:

$$P_c = P_{cL} + \left[9400M_L^{-1.71}x_L^{2.06}M_L^{-0.115} - 557M_L^{-1.265} \right] (M_{av} - M_L)$$

Equation 31 should read:

$$\phi_4(P_{c4}, x_4) = a_4 \left(\frac{x_4}{1 - x_1 - x_2 - x_3} \right)^{b_4} \left[\frac{M_{av} - M_1W_1 - M_2W_2 - M_3W_3}{1 - W_1 - W_2 - W_3} - M_4 \right] (1 - x_1 - x_2 - x_3)$$