

Composition Dependence of Viscosity of *n*-Hexane–Benzene Binary Mixtures at Elevated Temperatures

M. S. Medani* and M. A. Hasan

Department of Chemical Engineering, Faculty of Engineering, Riyadh, Saudi Arabia

Viscosities of *n*-hexane and benzene liquid mixtures of different composition levels at temperatures of 363.15, 383.15, 403.15, 423.15, 443.15, and 463.15 K and the corresponding vapor pressures using a rolling ball viscometer have been measured. Six different equations were tested for the prediction of viscosity at these particular conditions and the McAllister equation was found to fit the experimental data better than the others.

Viscosities of liquid mixtures are not always simple functions of composition. This is because, contrary to the simple gas behavior, they are dependent upon the attractive and repulsive forces of the molecules, together with the ratio of the molecular weights and volumes of the components. Hence, viscosity measurements could be considered as one of the best tools for studying some aspects of the molecular structure, especially at elevated temperatures. Individual differences of structure and force fields are so numerous that the number of possibilities of interlocking among molecules is almost endless. In a system, where the mixture components enter into some chemical bonding, the excess free energy of mixing is unrelated to viscosity and no success was found in inserting it into equations for predicting viscosities of mixtures. In the case of a mixture of *n*-hexoic acid and piperidine, the viscosity of the mixture was reported to be 100 times as high as the viscosity of either component (2). The large excess in viscosity may be attributed to the formation of association polymer. Hence, the viscosities of mixtures in such cases are impossible to predict.

The object of the present work is to measure the viscosity of *n*-hexane–benzene mixtures at temperatures up to 463.15 K and at the corresponding saturation pressures. This includes comparison of experimental viscosity data with those calculated with several different models.

Experimental Section

Materials. Benzene used in this work was "Analar" grade while *n*-hexane was of analytical grade, both supplied by B.D.H. These substances were tested for impurities in a Pye 104 chromatograph using a 1 m by 2.2-mm i.d. column of Poropak Q at 175 °C. It was found that no further purification was needed.

Apparatus. The apparatus used in this work was a rolling ball viscometer. It consisted primarily of a ferromagnetic stainless steel precision bearing ball and had a diameter of 7.958 ± 0.0009 mm, a 0.57-m long nonmagnetic stainless steel barrel of 13.36 mm o.d. and 8.255 \pm 0.038 mm i.d. as well as two sensing coils connected to a timing unit where the roll time of the ball was measured in milliseconds. The viscometer was connected to a liquid reservoir which was made of a 0.48-m long stainless steel tube of 51.76 mm i.d. and 60.3 mm o.d. The viscometer and reservoir should be allowed to tilt 30° either side by mounting it in trunnion. The whole apparatus was housed in a thermostatically controlled oil bath of an internal volume of about 114 L. Details of the apparatus were described elsewhere (8).

Temperature was measured by a platinum-resistance thermometer which was calibrated to an accuracy of ± 0.1 K while

pressure was measured by standard test gauges calibrated to $\pm 0.12\%$ of full scale reading. Repeatability of the roll time measurements ranged from ± 0.045 to $\pm 0.161\%$ with a mean of $\pm 0.123\%$. The viscometer was calibrated using analar benzene as the reference liquid at three angles of inclination of the viscometer tube, i.e., 14° 54', 9° 58', and 5° 56' (measured by Vernier Protractor), and the constants of the viscometer were calculated (θ). For a representative sample, all the liquid present in the sampling line and sample valve should be removed and discarded. For this reason capillary tubing was used for the sampling line so that only a small amount of liquid need be discarded in this operation. Before sampling, the sample bombs were evacuated and sealed off from the vacuum system. Samples were taken after the conditions within the cell had remained steady to within ± 0.1 K, for at least 30 min and at 30-min intervals thereafter.

Compositions of the samples obtained were determined by the refractive index measurement. A high-precision Abbe' refractometer was used in the determination at 293.15 K.

Pure Component Viscosities. Viscosities of pure benzene and *n*-hexane at temperatures up to 493.15 K and under the corresponding vapor pressures were measured and reported elsewhere (8).

Results and Discussions

Values of the coefficients of viscosity, μ , of *n*-hexane–benzene liquid mixtures at 363.15, 383.15, 403.15, 423.15, 443.15, and 463.15 K at the corresponding vapor pressures appear in Table I. These values represent the average of the measured viscosity at the three different angles using the relevant constants of calibration. The error in these values at all temperatures is estimated to be about $\pm 0.22\%$. These data cover the full composition range and it is clear that they do not show points of maximum or minimum.

A number of empirical and semitheoretical equations have been reported in the literature for the prediction of mixture viscosities from those of pure components, only a few of them are described here.

From Eyring's activation energy model (5), the viscosity of a binary mixture could be defined as

$$\ln \mu V = x_1 \ln \mu_1 V_1 + x_2 \ln \mu_2 V_2 \quad (1)$$

where V , V_1 , and V_2 are molal volumes of the mixture, components 1 and 2, respectively.

Bingham (7) employed the equation

$$1/\mu = x_1/\mu_1 + x_2/\mu_2 \quad (2)$$

while Tamura and Kurata (11) assumed that the relaxation time of each collision is proportional to the probability of collision and that the volume change of mixing is small. They derived the equation

$$\mu = x_1 \phi_1 \mu_1 + x_2 \phi_2 \mu_2 + 2(x_1 x_2 \phi_1 \phi_2)^{1/2} \mu_{12} \quad (3)$$

where μ_{12} is an empirical constant, dependent upon the temperature, and ϕ is the volume fraction.

McAllister (7) derived the following equation based upon Eyring's equation (eq 1) and assuming three-body interactions. He assumed that the probability for these interactions to take

Table I. Viscosity Data for Liquid Mixtures of *n*-Hexane-Benzene (in 10³ (N s)/m²)

Mole fraction of <i>n</i> -hexane			Mole fraction of <i>n</i> -hexane			Mole fraction of <i>n</i> -hexane		
Exptl	Predicted from eq 4		Exptl	Predicted from eq 4		Exptl	Predicted from eq 4	
At 363.15 K			At 383.15 K			At 403.15 K		
0.9102	0.1715	0.176	0.9102	0.139	0.144	0.9102	0.110	0.117
0.7772	0.185	0.184	0.7771	0.152	0.149	0.7781	0.123	0.121
0.6880	0.187	0.189	0.6878	0.150	0.154	0.6887	0.126	0.126
0.5829	0.200	0.197	0.5828	0.163	0.161	0.5831	0.136	0.132
0.5035	0.208	0.204	0.505	0.174	0.167	0.5069	0.139	0.138
0.3996	0.211	0.215	0.3998	0.175	0.177	0.3996	0.147	0.148
0.3260	0.225	0.224	0.3264	0.183	0.186	0.3308	0.150	0.155
0.1815	0.243	0.247	0.1765	0.203	0.206	0.1773	0.173	0.173
0.1336	0.259	0.256	0.1315	0.214	0.213	0.1304	0.181	0.179
0.0432	0.274	0.276	0.0421	0.2315	0.236	0.0425	0.193	0.192
At 423.15 K			At 443.15 K			At 463.15 K		
0.9102	0.089	0.097	0.9102	0.070	0.0785	0.9102	0.0524	0.0594
0.7749	0.101	0.102	0.7747	0.083	0.084	0.7745	0.0625	0.063
0.6828	0.108	0.107	0.6824	0.092	0.089	0.6814	0.068	0.068
0.5918	0.113	0.112	0.5897	0.101	0.095	0.5879	0.080	0.075
0.5017	0.119	0.118	0.5019	0.103	0.102	0.5015	0.0865	0.088
0.3936	0.1235	0.126	0.3922	0.109	0.111	0.3922	0.094	0.094
0.3304	0.128	0.131	0.3320	0.114	0.116	0.3307	0.100	0.101
0.1680	0.146	0.147	0.1680	0.128	0.129	0.1682	0.110	0.115
0.1184	0.152	0.153	0.1189	0.132	0.133	0.1192	0.114	0.118
0.0392	0.163	0.168	0.0387	0.135	0.138	0.0390	0.121	0.120

Table II. Absolute Average Percentage Deviations with Various Equations

Temp, K	Eq 1	Eq 2	Eq 3	Eq 4	Eq 5	Eq 7
363.15	4.89	4.16	1.19	1.31	1.61	7.45
383.15	4.78	4.35	2.05	1.84	1.72	7.31
403.15	5.22	4.64	2.14	1.65	1.77	8.02
423.15	5.39	4.60	5.34	2.47	2.86	8.34
443.15	4.22	3.67	3.83	3.33	3.86	7.36
463.15	5.83	6.00	6.43	6.43	3.94	9.13
Av error	5.05	4.57	3.50	2.41	3.02	7.93

place is dependent only on the concentration and not on the free energy of activation. Also, he proposed that the free energies of activation for viscosity of mixtures are additive quantities. Thus

$$\ln \nu = x_1^3 \ln \nu_1 + 3x_1^2 x_2 \ln \nu_{12} + 3x_1 x_2^2 \ln \nu_{21} + x_2^3 \ln \nu_2 - \ln [x_1 + x_2 M_2 / M_1] + 3x_1^2 x_2 \ln [(2 + M_2 / M_1) / 3] + 3x_1 x_2^2 \ln [(1 + 2M_2 / M_1) / 3] + x_2^3 \ln (M_2 / M_1) \quad (4)$$

where ν_{12} and ν_{21} are constants at a corresponding temperature and to be determined from experimental data.

Heric and Brewer (6) analyzed their data for 14 binary non-electrolyte systems at 298.15 K and showed that among eq 1, 4, and 5 the best correlation was McAllister's. However, they applied two more empirical equations, i.e.

$$\nu = x_1 \nu_1 + x_2 \nu_2 + x_1 x_2 [A + B(x_1 - x_2) + C(x_1 - x_2) + D(x_1 - x_2)^3 + \dots] \quad (5)$$

and

$$\ln \nu = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 \ln M_1 + x_2 \ln M_2 - \ln (x_1 M_1 + x_2 M_2) + x_1 x_2 \cdot [A + B(x_1 - x_2) + C(x_1 - x_2)^2 + \dots] \quad (6)$$

They reported that eq 5 and 6 produced the same degree of accuracy and both were better than eq 4. This is not unexpected

as the number of constants in these two equations is more than in the McAllister equation.

It is worth noting that the last terms of the above two equations are identical with Redlich and Kister's presentation of Gibbs excess free energy of mixing ΔG^E (10).

Cullinan (3) developed the following relationship to predict viscosities for regular binary mixtures based upon the statistical mechanical theory of transport in liquid mixtures, i.e.

$$\mu = \mu_1^{x_1} \mu_2^{x_2} (V_A / V_G) \quad (7)$$

where

$$V_A = x_1 \bar{V}_1 + x_2 \bar{V}_2$$

and

$$V_G = \bar{V}_1^{x_1} \bar{V}_2^{x_2}$$

and \bar{V}_1 and \bar{V}_2 are partial molal volumes of components 1 and 2.

Heric and Brewer measured the excess molal volume ΔV^E for *n*-hexane and benzene mixtures at 298.15 K. They found that it showed a maximum value of about 0.4% with an average of 0.25%. Hence, in the calculations involved, the excess molal volume was neglected and the molal volumes of the pure components were used instead of the partial molal volumes.

The fittings of eq 1, 2, 3, 4, 5, and 7 are compared in Table II. The absolute average percentage deviation at different temperature levels is taken as the criterion for the fitting of each equation.

From the analysis of the present data, it could be said that McAllister's equation (4) proved itself to be the best among the proposed equations. This confirms the findings of other workers from their analysis on other systems (4, 5).

The average percentage error of this semitheoretical equation is 2.4 which, considering the inadequacy of the basic equation of Eyring's old model, is remarkably good.

Acknowledgment

The authors wish to express their thanks to Professor G. G. Haselden of the Department of Chemical Engineering, the Uni-

versity of Leeds, for allowing this work to be done in his department.

Glossary

A, B, C	constants
ΔG^F	Gibbs excess free energy of mixing, J/mol
M	molecular weight
\bar{V}	molal volume, L/mol
\bar{V}_i	partial molal volume, L/mol
x_i	mole fraction of (i) in the liquid
μ	viscosity coefficient, (N s)/m ²
ν	kinematic viscosity, m ² /s
μ_{ij}	constant

ν_{ij}, ν_{ji}	constants
ϕ	volume fraction

Literature Cited

- (1) Bingham, E. C., "Fluidity and Plasticity", McGraw-Hill, New York, N.Y., 1922.
- (2) Bretsznader, B., "Prediction of Transport and other Physical Properties of Fluids", Pergamon Press, New York, N.Y., 1971.
- (3) Cullinan, H. T., *Ind. Eng. Chem. Fundam.*, **7**, 177 (1968).
- (4) Ghai, R. K., Dullien, F. A. L., *Can. J. Chem. Eng.*, **49**, 260 (1971).
- (5) Glasstone, S., Laidler, K. J., Eyring, H., "Theory of Rate Processes", McGraw-Hill, New York, N.Y., 1941.
- (6) Heric, E. L., Brewer, J. G., *J. Chem. Eng. Data*, **12**, 574 (1967).
- (7) McAllister, R. A., *AIChE J.*, **6**, 427 (1970).
- (8) Medani, M. S., Hasan, M. A., *Can. J. Chem. Eng.*, **55**, 203 (1977).
- (9) Medani, M. S., Hasan, M. A., *J. Appl. Chem. Biotechnol.*, **27**, 80 (1977).
- (10) Redlich, O., Kister, A. T., *Ind. Eng. Chem.*, **40**, 345 (1948).
- (11) Tamura, M., Kurata, M., *Bull. Chem. Soc. Jpn.*, **25**, 32 (1952).

Received for review November 30, 1976. Accepted July 6, 1977.

Additivity of Volumes in Hydrated Melts: Mixtures of Magnesium Nitrate Hexahydrate with Sodium and Potassium Nitrate

Surender K. Jain,* Harbans L. Jindal, and Niraj P. Kulshreshtha
Hindu College, University of Delhi, Delhi-110007, India

Densities of molten mixtures of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with NaNO_3 and KNO_3 were measured as a function of temperature and univalent nitrate content. The equivalent volume-composition isotherms were linear with respect to equivalent fraction of NaNO_3 or KNO_3 , over the composition range investigated. Partial equivalent volumes (\bar{V}_i) of the constituents were computed by extrapolating these linear isotherms.

The volumes in many binary molten nitrate mixtures (5, 6) and hydrated melts (7, 3) are reported to be additive. The principle of additivity provides a useful basis for estimating the equivalent volumes of mixtures from limited density data. In continuation of the studies (3, 4) regarding physicochemical behavior of hydrated salts, the results of the density measurements for the system $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ -(Na, K) NO_3 are presented in this paper.

Experimental Section

Material. Salts used in this study were AnalaR (BDH) grade. Alkali metal nitrates were dried by heating at about 200–250 °C for several days. Volumetric analysis of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ using EDTA established its water content within ± 0.02 of the stoichiometric value of 6.

Apparatus. A manometric densitometer originally designed by Husband (2) was modified so as to permit a direct measurement of volume of a known amount of the melt. The densitometer, its calibration, and the measuring technique have been described earlier (3). The temperatures of the oil bath (ca. 15 L) were controlled and measured with a precision of ± 0.1 °C. The estimated precision of the reported densities is $\pm 0.1\%$.

Results and Discussion

The density data for the mixtures investigated have been presented in Tables I and II. The coefficients of linear density/equivalent volume-temperature equations, for various com-

Table I. Density Data for $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ - NaNO_3 Mixtures

Temp, °C	Density, g cm ⁻³	Temp, °C	Density, g cm ⁻³
	9.63 ^a		14.9 ^a
94.7	1.5520	93.0	1.5610
100.2	1.5470	95.4	1.5590
107.0	1.5420	100.0	1.5550
117.0	1.5330	105.1	1.5520
120.0	1.5320	109.0	1.5490
128.0	1.5260	115.0	1.5450
		121.0	1.5360
		126.0	1.5320
		132.0	1.5270
	20.5 ^a		25.0 ^a
89.0	1.5860	96.3	1.5940
91.0	1.5830	97.6	1.5930
95.1	1.5800	100.2	1.5900
99.7	1.5770	108.0	1.5790
105.5	1.5720	112.0	1.5760
110.0	1.5670	116.0	1.5720
116.5	1.5640	121.0	1.5690
123.0	1.5590	128.0	1.5630
129.0	1.5520		

^a Mole percent NaNO_3 .

positions, along with the standard deviation of the fit and the maximum departure of any experimental observation from the "best" straight line drawn through the points, are recorded in Table III. Isotherms of equivalent volume (V_e) vs. equivalent fraction (x') of the univalent nitrate in the mixture were linear (Figure 1) within the limits of experimental accuracy, over the composition range studied, and could be described by equations of the type

$$V_e(\text{cm}^3 \text{equiv}^{-1}) = A - Bx'$$